Organometallic Chemistry

Synthesis and some properties of lanthanum, neodymium, and samarium *tert*-butoxycuprates $[(Bu^tO)_5Cu_2Ln]_2$

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Lanthanum, neodymium, and samarium *tert*-butoxycuprates $[(Bu^tO)_5Cu_2Ln]_2$ were synthesized in high yields by reactions of Bu^tOCu with lanthanide metals, the halides SmI_2 and LnX_3 (Ln = La, Nd; X = Cl, I) and by the reaction of Bu^tOLi with a mixture of $LnCl_3$ and CuCl. X-Ray diffraction analysis showed that the structure of $[(Bu^tO)_5Cu_2Sm]_2$ is based on octahedra formed by four copper atoms in equatorial positions and two samarium atoms in axial positions; the copper and samarium atoms are linked by μ_3-bridging Bu^tO groups. The reactions of lanthanum *tert*-butoxycuprate with H_2O, HCl, CpH, PhC≡CH, and CO_2 were studied.

Key words: lanthanides, alkoxycuprates, synthetic methods, structure, reactivity.

Heterobimetal lanthanide alkoxides present interest as reagents and potential catalysts for organic synthesis and as starting compounds for the synthesis of high-temperature superconducting ceramics. Among the large number of known heterobimetal alkoxy derivatives of lanthanides,[1] copper complexes are the least studied. Previously we have shown that[2] *tert*-butoxycuprates $[(Bu^tO)_5Cu_2Ln]_2$ are formed in the reactions of Bu^tOCu with praseodymium and lutetium. In this work, we found that this method can be used to prepare *tert*-butoxycuprates of other lanthanides.

Lanthanum, neodymium, and samarium metals enter into redox transmetallation with Bu^tOCu to give the alkoxycuprates $[(Bu^tO)_5Cu_2Ln]_2$ in high yields. The reaction proceeds in THF or DME at room temperature and is completed over 35—40 h.

$$10\ Bu^tOCu + Ln \xrightarrow[20\ ^\circ C,\ 35-40\ h]{THF\ or\ DME} \underset{73-76\%}{[(Bu^tO)_5Cu_2Ln]_2} + \underset{84-96\%}{6\ Cu}$$

Ln = La, Nd, Sm

An increase in the reaction duration to 60 h does not result in further reduction of the lanthanide alkoxycuprates formed; complete transmetallation does not occur under these conditions. Since the alkoxycuprates $[(Bu^tO)_5Cu_2Ln]_2$ were isolated as the final stable lanthanide-containing products, we attempted to prepare these complexes by other methods. Unexpectedly, it

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turned out that one of the most important methods of the synthesis of heterobimetal lanthanide alkoxides, namely, the reaction of a lanthanide alkoxide with an alkoxide of another metal is inapplicable in this case. It was found that $(Bu^tO)_3La$ does not react with Bu^tOCu in THF or DME in the 20—60 °C temperature range.

Unlike $(Bu^tO)_3Ln$, lanthanide iodides readily react with copper *tert*-butoxide; at appropriate reactant ratios, the target products are formed in high yields.

$$10\ Bu^tOCu + 2\ LnI_3(THF)_3 \xrightarrow[20\ ^\circ C,\ 2-3\ h]{THF}$$

$$\longrightarrow \underset{90-95\%}{[(Bu^tO)_5Cu_2Ln]_2} + \underset{87-90\%}{6\ CuI}$$

Ln = La, Nd

$$10\ Bu^tOCu + 2\ SmI_2(THF)_4 \xrightarrow[20\ ^\circ C,\ 2-3\ h]{THF}$$

$$\longrightarrow \underset{98\%}{[(Bu^tO)_5Cu_2Sm]_2} + \underset{100\%}{4\ CuI} + \underset{92\%}{2\ Cu}$$

The reaction of Bu^tOCu with $LaCl_3$ also gives $[(Bu^tO)_5Cu_2La]_2$ in 97% yield; however, in this case, heating of the reaction mixture to 60—65 °C is required and the reaction time is 20 h.

The reaction of Bu^tOLi with a stoichiometric mixture of $LnCl_3$ and CuCl was found to be the most convenient method for the synthesis of lanthanide *tert*-butoxycuprates

$$10\ Bu^tOLi + 2\ LnCl_3 + 4\ CuCl \xrightarrow[60\ ^\circ C,\ 3-4\ h]{THF}$$

$$\longrightarrow \underset{82-88\%}{[(Bu^tO)_5Cu_2Ln]_2} + \underset{97-100\%}{10\ LiCl}$$

Ln = La, Nd

The lanthanide *tert*-butoxycuprates are crystalline, pale-colored compounds unstable in air. The compounds are readily soluble in common organic solvents; they decompose in an evacuated capillary in the 210—230 °C temperature range and are sublimed *in vacuo* (10^{-2} Torr) at 210—215 °C. The IR spectra of lanthanide *tert*-butoxycuprates are identical and contain a set of absorption bands typical of Bu^tO groups attached to a metal atom (1240, 1220, 1180, 1010, 970, and 920 cm^{-1}). The diamagnetism of the lanthanum complex and the effective magnetic moments of the neodymium (3.96 μB) and samarium (1.51 μB) complexes comply with the trivalent state of the lanthanide atoms and the monovalent state of copper atoms in the compounds. An X-ray diffraction experiment was carried out for the samarium complex $[(Bu^tO)_5Cu_2Sm]_2$.* Unfortunately, due to the poor quality of the crystals, no refined data were obtained. Only a general molecular geometry can be represented with certain confidence; it is based on an octahedron based on four Cu atoms located in the equatorial positions and two Sm atoms located in the axial positions. The Cu and Sm atoms are linked by μ_3-bridging Bu^tO groups and, in addition, each Sm atom carries a terminal *tert*-butoxy group (Fig. 1).

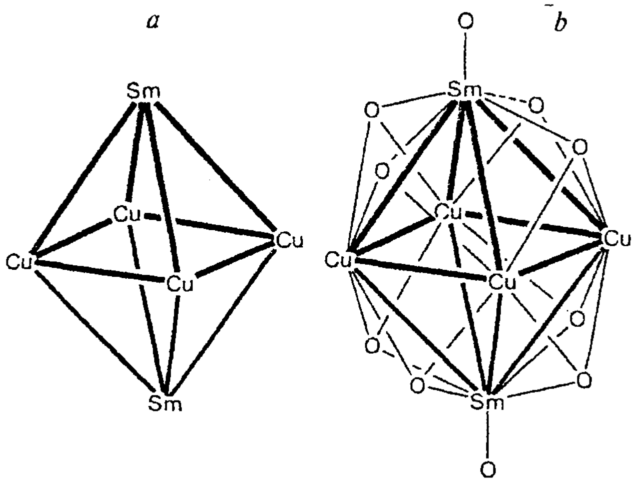

Fig. 1. Metallic core (*a*) and general view (*b*) of the $[(Bu^tO)_5Cu_2Sm]_2$ molecule (the *tert*-butyl groups are omitted).

The assumption that the other $[(Bu^tO)_5Cu_2Ln]_2$ complexes have a similar structure is confirmed by the ^1H NMR spectrum (benzene-d_6) of the lanthanum complex, which exhibits two signals at δ 1.45 and 1.68 with an intensity ratio of 1 : 4; they can be assigned to the protons of the terminal and bridging Bu^tO groups, respectively.

The reactivity of the lanthanide *tert*-butoxycuprates with respect to H_2O, HCl, CpH, PhC≡CH, and CO_2 was studied for the lanthanum complex. It was found that $[(Bu^tO)_5Cu_2La]_2$ is readily hydrolyzed at room temperature in a THF solution to give Bu^tOH (95%), Cu_2O (100%), and $La(OH)_3$ (98%). Under similar conditions, the reaction with excess HCl affords Bu^tOH (96%), CuCl (99%), and $LnCl_3$ (97%). The reaction with PhC≡CH results in the formation of phenylethynylcopper and $(Bu^tO)_3La$.

$$[(Bu^tO)_5Cu_2La]_2 + 4\,PhC{\equiv}CH \xrightarrow[70\ ^\circ C,\ 8\ h]{THF}$$

$$\longrightarrow \underset{55\%}{4\ Bu^tOH} + \underset{100\%}{4\ PhC{\equiv}CCu} + \underset{98\%}{2\ (Bu^tO)_3La}$$

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* The X-ray diffraction analysis of the complex $[(Bu^tO)_5Cu_2Sm]_2$ was carried out by F. Girgdis (Technical University of Berlin).

At 70 °C, the reaction is completed over a period of 7.5—8 h. It should be noted that the resulting $(\mathrm{Bu^tO})_3\mathrm{La}$ does not react with $\mathrm{PhC{\equiv}CH}$ under these conditions.

The reaction of $[(\mathrm{Bu^tO})_5\mathrm{Cu_2La}]_2$ with cyclopentadiene (CpH) is accompanied by the formation of $\mathrm{Cp_3La}$, copper metal, and unidentified organic products. Apparently, at initial reaction steps, cyclopentadienylcopper is formed among other products. In the absence of stabilizing ligands, this compound rapidly decomposes, giving rise to copper metal. This is confirmed by the fact that the reaction carried out in the presence of $\mathrm{PPh_3}$ afforded the stable complex $\mathrm{CpCuPPh_3}$ in a high yield, in addition to tricyclopentadienyllanthanum.[3]

$$[(\mathrm{Bu^tO})_5\mathrm{Cu_2La}]_2 + 10\ \mathrm{CpH} + 4\ \mathrm{PPh_3} \xrightarrow[20\ ^\circ\mathrm{C},\ 20\ \mathrm{h}]{\mathrm{THF}}$$

$$\longrightarrow \underset{82\%}{2\ \mathrm{Cp_3La}} + \underset{86\%}{4\ \mathrm{CpCuPPh_3}} + \underset{98\%}{10\ \mathrm{Bu^tOH}}$$

It has been reported previously that lanthanide alkoxides react with $\mathrm{CO_2}$ to give alkyl carbonates $(\mathrm{ROCO_2})_3\mathrm{Ln}$ insoluble in conventional organic solvents.[4] Therefore, it has been of interest to find out how lanthanide *tert*-butoxycuprates would react with carbon dioxide. It was found that $[(\mathrm{Bu^tO})_5\mathrm{Cu_2La}]_2$ adds $\mathrm{CO_2}$ in a toluene solution at room temperature. Five moles of carbon dioxide per mole of the starting lanthanum complex are absorbed over a period of 6 h; during this period, the initially colorless reaction solution acquires an intense dark-green color. Removal of the solvent gives rise to a solid dark-green compound unstable in air and having a decomposition point of 185—190 °C; unlike the carbonates $(\mathrm{ROCO_2})_3\mathrm{Ln}$, this product is readily soluble in benzene and toluene. The contents of Cu and La found correspond to the formula $(\mathrm{Bu^tOCO_2})_5\mathrm{Cu_2La}$. The IR spectrum contains a set of absorption bands typical of the —O—C(O)—O— (1580, 1360, 1250, and 1070 $\mathrm{cm^{-1}}$) and $\mathrm{Bu^tO}$ groups (1235, 1170, 1015, and 920 $\mathrm{cm^{-1}}$). The structure of the compound is currently being studied.

Thus, we synthesized La, Nd, and Sm *tert*-butoxycuprates, studied some of their reactions taking the lanthanum complex as an example, and established the general features of the structure of the $[(\mathrm{Bu^tO})_5\mathrm{Cu_2Sm}]_2$ molecule.

Experimental

All operations were carried out in sealed evacuated tubes using thoroughly dried and degassed solvents. IR spectra were obtained on a Perkin—Elmer-577 spectrometer; the samples were prepared under argon as mineral oil mulls. ^{1}H NMR spectra were recorded on a DPX-200 spectrometer operating at 200 MHz. Magnetochemical measurements were performed by a previously described procedure.[5] GLC analysis of easily volatile products was carried out on a Tsvet-129 chromatograph with a katharometer as the detector; 300×0.3 cm columns packed with Apiezon (20%) on Chromosorb W and with SE-30 (5%) on Inerton AW were used. The carrier gas employed was helium. Lanthanide preparations produced in Russia and containing no more than 0.1% total impurities were used. The initial compounds, $\mathrm{Bu^tOCu}$,[6] $\mathrm{SmI_2(THF)_4}$,[7] $\mathrm{LnI_3(THF)_3}$,[8] and $\mathrm{LnCl_3}$ [9] were synthesized by known procedures.

Reaction of La with $\mathrm{Bu^tOCu}$. A lanthanum cutting (1.54 g, 11.08 mmol) and $\mathrm{Bu^tOCu}$ (0.85 g, 6.21 mmol) in 20 mL of DME were stirred at ~20 °C for 35 h. Excess lanthanum and the finely dispersed precipitate of copper metal formed were separated from the solution by centrifugation. The excess of lanthanum was dissolved in dilute (10%) hydrochloric acid. The insoluble precipitate was found to contain 0.22 g (95.6%) of copper. The reaction solution was concentrated to 5 mL and kept at 80 °C until the finely crystalline colorless precipitate entirely dissolved. Slow cooling of the solution to ~20 °C gave large crystals shaped like tetragonal bipyramids, which were separated from the solution and dried *in vacuo* at ~20 °C to give 0.59 g (75.6%) of the complex $[(\mathrm{Bu^tO})_5\mathrm{Cu_2La}]_2$, dec.p. 222—226 °C. Found (%): C, 37.41; H, 6.82; Cu, 20.01; La, 21.35. $\mathrm{C_{40}Cu_4H_{90}La_2O_{10}}$. Calculated (%): C, 38.04; H, 7.18; Cu, 20.12; La, 21.99.

Neodymium and samarium *tert*-butoxycuprates were synthesized in a similar way. The reaction of Nd (1.60 g, 11.09 mmol) with $\mathrm{Bu^tOCu}$ (1.07 g, 7.82 mmol) in 20 mL of DME afforded 0.74 g (74.7%) of $[(\mathrm{Bu^tO})_5\mathrm{Cu_2Nd}]_2$ as pale blue coarse crystals shaped like tetragonal bipyramids, dec.p. 207—212 °C. Found (%): C, 36.73; H, 6.86; Cu, 18.66; Nd, 22.65. $\mathrm{C_{40}Cu_4H_{90}Nd_2O_{10}}$. Calculated (%): C, 37.72; H, 7.12; Cu, 19.95; Nd, 22.65.

The reaction of Sm (1.21 g, 8.04 mmol) and $\mathrm{Bu^tOCu}$ (0.79 g, 5.78 mmol) in 20 mL of DME gave 0.54 g (72.9%) of $[(\mathrm{Bu^tO})_5\mathrm{Cu_2Sm}]_2$ as pale-yellow large crystals shaped like tetragonal bipyramids, dec.p. 225—233 °C. Found (%): C, 36.41; H, 6.20; Cu, 19.22; Sm, 23.60. $\mathrm{C_{40}Cu_4H_{90}O_{10}Sm_2}$. Calculated (%): C, 37.36; H, 7.05; Cu, 19.76; Sm, 23.38.

Reaction of $\mathrm{Bu^tOCu}$ with $\mathrm{LaI_3(THF)_3}$. A solution of $\mathrm{Bu^tOCu}$ (1.97 g, 14.41 mmol) in 15 mL of THF was added to a suspension of $\mathrm{LaI_3(THF)_3}$ (2.12 g, 2.88 mmol) in 10 mL of THF. When the reactants were mixed, dissolution of lanthanum iodide and precipitation of copper iodide was observed. The reaction mixture was stirred for 0.5 h at ~20 °C and for 2 h at 60 °C. The precipitate was separated by centrifugation and dried *in vacuo* to give 1.48 g (90.2%) of CuI. Found (%): Cu, 32.80; I, 65.30. CuI. Calculated (%): Cu, 33.15; I, 66.63. The resulting lanthanum *tert*-butoxycuprate was isolated from the reaction solution as described above to give 1.73 g (95.0%) of $[(\mathrm{Bu^tO})_5\mathrm{Cu_2La}]_2$, dec. p. at 220—225 °C. Found (%): Cu, 19.85; La, 21.65. $\mathrm{C_{40}Cu_4H_{90}La_2O_{10}}$. Calculated (%): Cu, 20.12; La, 21.99. The IR spectrum of the product was identical to that of lanthanum *tert*-butoxycuprate synthesized by the reaction of $\mathrm{Bu^tOCu}$ with La metal.

The reaction of $\mathrm{Bu^tOCu}$ with $\mathrm{NdI_3(THF)_3}$ was carried out in a similar way. The yield of $[(\mathrm{Bu^tO})_5\mathrm{Cu_2Nd}]_2$ was 90.3%, dec.p. at 206—212 °C. Found (%): Cu, 18.76; Nd, 22.32. $\mathrm{C_{40}Cu_4H_{90}Nd_2O_{10}}$. Calculated (%): Cu, 19.95; Nd, 22.65. The IR spectrum of the product was identical to that of the neodymium *tert*-butoxycuprate synthesized by the reaction of $\mathrm{Bu^tOCu}$ with Nd metal.

Reaction of $\mathrm{Bu^tOCu}$ with $\mathrm{SmI_2(THF)_4}$. A solution of $\mathrm{Bu^tOCu}$ (1.43 g, 10.46 mmol) in 15 mL of THF was added to a blue-green solution of $\mathrm{SmI_2(THF)_4}$ (1.44 g, 2.07 mmol) in 20 mL of THF. The solution developed a pale-yellow color and a dark-gray precipitate formed. The precipitate was separated by centrifugation and washed with 10% nitric acid. According to iodometric titration, the portion of the precipitate that dissolved in nitric acid was pure copper (0.12 g, 92.3%). The precipitate insoluble in nitric acid was washed with water and acetone and dried *in vacuo* to give 0.75 g (100%) of CuI. Found (%): Cu, 32.55; I, 65.60. CuI. Calculated (%): Cu, 33.15; I, 66.63. Samarium *tert*-butoxycuprate was isolated from the reaction solution as described above to give 1.31 g (97.7%) of $[(Bu^tO)_5Cu_2Sm]_2$, dec. p. at 225—230 °C. Found (%): Cu, 19.15; Sm, 22.85. $C_{40}Cu_4H_{90}O_{10}Sm_2$. Calculated (%): Cu, 19.76; Sm, 23.38. The IR spectrum of the product was identical to that of samarium *tert*-butoxycuprate synthesized by the reaction of Bu^tOCu with Sm metal.

Reaction of Bu^tOCu with $LaCl_3$. A mixture of Bu^tOCu (1.05 g, 7.68 mmol) and $LaCl_3$ (0.38 g, 1.54 mmol) in 20 mL of THF was stirred at 60 °C for 20 h. The precipitate was separated from the solution by centrifugation and dried *in vacuo* to give 0.41 g (89.1%) of CuCl. Found (%): Cu, 35.35; Cl, 63.85. CuCl. Calculated (%): Cu, 35.81; Cl, 64.19. Removal of the solvent from the reaction solution by evaporation *in vacuo* gave 0.94 g (96.9%) of the complex $[(Bu^tO)_5Cu_2La]_2$, dec.p. 222—226 °C. Found (%): Cu, 19.75; La, 21.42. $C_{40}Cu_4H_{90}La_2O_{10}$. Calculated (%): Cu, 20.12; La, 21.99. The IR spectrum of the product was identical to that of lanthanum *tert*-butoxycuprate synthesized by the reaction of Bu^tOCu with La metal.

Reaction of Bu^tOLi with $LaCl_3$ and CuCl. A mixture of Bu^tOLi (0.57 g, 7.11 mmol), $LaCl_3$ (0.34 g, 1.38 mmol), and CuCl (0.28 g, 2.80 mmol) in 20 mL of THF was stirred for 3.5 h at 60 °C. The solvent was evaporated *in vacuo* and the solid residue was extracted with hexane (4×20 mL). The hexane extracts were combined. Evaporation of hexane *in vacuo* gave 0.73 g (82.0%) of $[(Bu^tO)_5Cu_2La]_2$, dec.p. 221—225 °C. Found (%): Cu, 19.98; La, 21.49. $C_{40}Cu_4H_{90}La_2O_{10}$. Calculated (%): Cu, 20.12; La, 21.99. The IR spectrum of the product was identical to that of lanthanum *tert*-butoxycuprate synthesized by the reaction of Bu^tOCu with La metal. The precipitate insoluble in hexane was found to contain 0.29 g (96.6%) of LiCl. Found (%): Cl, 82.65. ClLi. Calculated (%): Cl, 83.63.

Reaction of Bu^tOLi with $NdCl_3$ and CuCl was carried out in a similar way. The reaction of Bu^tOLi (1.02 g, 12.74 mmol), $NdCl_3$ (0.62 g, 2.47 mmol), and CuCl (0.57 g, 5.71 mmol) gave 1.41 g (87.5%) of $[(Bu^tO)_5Cu_2Nd]_2$, dec.p. 205—211 °C. Found (%): Cu, 19.05; Nd, 22.50. $C_{40}Cu_4H_{90}Nd_2O_{10}$. Calculated (%): Cu, 19.95; Nd, 22.65. The IR spectrum of the product was identical to that of neodymium *tert*-butoxycuprate synthesized by the reaction of Bu^tOCu with Nd metal. The yield of LiCl was 0.54 g (100.0%). Found (%): Cl, 82.70. ClLi. Calculated (%): Cl, 83.63.

Reaction of $[(Bu^tO)_5Cu_2La]_2$ with water. A solution of H_2O (0.10 g, 5.54 mmol) in 5 mL of THF was added at –20 °C to a solution of $[(Bu^tO)_5Cu_2La]_2$ (0.37 g, 0.29 mmol) in 15 mL of THF. The resulting finely dispersed brick-red precipitate, which was a mixture of Cu_2O and $La(OH)_3$, was separated from the solution by centrifugation. Extraction with a concentrated solution of ammonia to separate Cu_2O from $La(OH)_3$ gave 0.08 g (100.0%) of Cu_2O and 0.11 g (98.0%) of $La(OH)_3$. (1) Cu_2O. Found (%): Cu, 87.50. Cu_2O. Calculated (%): Cu, 88.82. (2) $La(OH)_3$. Found (%): La, 72.54. H_3LaO_3. Calculated (%): La, 73.14). The reaction solution contained 0.21 g (95.4%) of Bu^tOH (GLC data).

Reaction of $[(Bu^tO)_5Cu_2La]_2$ with HCl. Gaseous HCl (0.14 g, 3.83 mmol) was condensed into a solution of $[(Bu^tO)_5Cu_2La]_2$ (0.48 g, 0.38 mmol) in 15 mL of THF. The resulting finely dispersed white precipitate was separated from the solution by centrifugation, washed with water (3×10 mL) under argon, and dried *in vacuo* at 50 °C to give 0.15 g (99.0%) of CuCl. Found (%): Cu, 35.53. CuCl. Calculated (%): Cu, 35.81. The aqueous solution was evaporated and the solid residue was dried *in vacuo*, the temperature being gradually raised from –20 to 200 °C, to give 0.18 g (96.8%) of $LaCl_3$. Found (%): La, 56.30; Cl, 42.85. Cl_3La. Calculated (%): La, 56.63; Cl, 43.37. The reaction solution contained 0.27 g (96.4%) of Bu^tOH (GLC data).

Reaction of $[(Bu^tO)_5Cu_2La]_2$ with PhC≡CH. A solution of PhC≡CH (0.30 g, 2.93 mmol) in 3 mL of THF was added at –20 °C to a solution of $[(Bu^tO)_5Cu_2La]_2$ (0.85 g, 0.67 mmol) in 15 mL of THF. An amorphous yellow precipitate of phenylethynylcopper gradually formed. The mixture was heated for 8 h at 70 °C. The precipitate was separated by centrifugation, washed with hexane (2×15 mL), and dried *in vacuo* to give 0.44 g (100.0%) of PhC≡CCu. Found (%): Cu, 37.91. C_8H_5Cu. Calculated (%): Cu, 38.59. The IR spectrum of the product was identical to that of an authentic sample.[10] The solvent and volatile products were removed from the reaction solution by vacuum condensation. The residue was dried *in vacuo* at 100 °C for 2 h to give 0.47 g (98.0%) $(Bu^tO)_3La$. Found (%): La, 38.23. $C_{12}H_{27}LaO_3$. Calculated (%): La, 38.77. The IR spectrum of the product was identical to that of an authentic sample.[11] The volatile products contained 0.11 g (55.0%) of Bu^tOH (GLC data).

Reaction of $[(Bu^tO)_5Cu_2La]_2$ with CpH. A solution of CpH (0.20 g, 3.02 mmol) in 3 mL of THF was added at –20 °C to a solution of $[(Bu^tO)_5Cu_2La]_2$ (0.38 g, 0.30 mmol) in 15 mL of THF. The solution gradually developed a dark-brown color and copper metal precipitated. The reaction mixture was kept for 20 h at –20 °C. The precipitate was separated by centrifugation and dried *in vacuo* to give 0.06 g (81.0%) of copper (according to iodometric titration, the precipitate contained 98.8% copper). The solvent and volatile products were removed by condensation *in vacuo* and the residue was washed with hexane (2×10 mL) and sublimed *in vacuo* at 260 °C to give 0.19 g (95.0%) of Cp_3La. Found (%): La, 41.38. $C_{15}H_{15}La$. Calculated (%): La, 41.57. The IR spectrum of the product was identical to that of an authentic sample.[12] The volatile products contained 0.18 g (81.8%) of Bu^tOH (GLC data).

Reaction of $[(Bu^tO)_5Cu_2La]_2$ with CpH in the presence of PPh_3. A mixture of $[(Bu^tO)_5Cu_2La]_2$ (0.51 g, 0.40 mmol), CpH (0.28 g, 4.23 mmol), and PPh_3 (0.42 g, 1.60 mmol) in 15 mL of THF was kept for 20 h at –20 °C. The reaction solution remained colorless and no metallic copper precipiated. The solvent and volatile products were removed by vacuum condensation and the residue was washed with hexane (10×20 mL) and sublimed *in vacuo* at 260 °C to give 0.21 g (82.0%) of Cp_3La. Found (%): La, 41.21. $C_{15}H_{15}La$. Calculated (%): La, 41.57. The IR spectrum of the product was identical to that of an authentic sample.[12] The hexane solutions were combined and the hexane was evaporated *in vacuo* to give 0.54 g (86.5%) of $CpCuPPh_3$. Found (%): Cu, 15.80. $C_{23}H_{20}CuP$. Calculated (%): Cu, 16.25. The IR spectrum of the product was identical to that of an authentic sample.[3] The volatile products contained 0.28 g (98.0%) of Bu^tOH (GLC data).

The X-ray diffraction experiment for $[(Bu^tO)_5Cu_2Sm]_2$ was carried out on a Siemens SMART CCD diffractometer (ω-scan mode, Mo-Kα-radiation, graphite monochromator) at 173 K. The crystals are tetragonal. At 173 K, $a = b = 12.8570$, $c = 16.7593$ Å, $\alpha = \beta = \gamma = 90°$, space group $P4(2)/n$; 4241 independent reflections were measured.

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