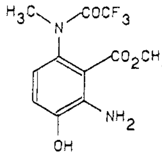
by using standard methods (three steps, 62% overall from alcohol **10**).

We were then in a position to begin assembly of spirocyclic system. Regeneration of **3b** from **8** with 1 equiv of *n*-BuLi at −78 °C,[17] followed by addition of a solution of bromide **4** (1.5 equiv) in HMPA to the anion **3b** at 0 °C, provided the key alkylated vinyl ether **11** in 70% yield from **3a** (Scheme IV). Subsequent cyclopropanation of **11** using Et_2Zn/CH_2I_2 gave cleanly a mixture of diasteromeric cyclopropanes **12**.[21] The required substrate for the crucial closure to the spiroketal nucleus was now complete. Most pleasingly, direct treatment of the mixture of cyclopropanes **12** with *p*-TsOH–H_2O in benzene at 55 °C for 5 h gave the monoprotected spiroketal **2a** as a *single diastereomer* in 55% overall yield (from **11**).[22] Furthermore, **2b** (required for X-14885A (vide supra)) was obtained in comparable yield from **11** under the same conditions (unoptimized).

With the central spiroketal intermediate **2a** in hand, incorporation of the pyrrole unit was effected by using a variant of the Nicolaou procedure (Scheme IV).[23] Oxidation of **2a** gave the expected carboxylic acid which was converted to the desired α-keto pyrrole **13** in 80% overall yield (from **2a**) via treatment of the 2-thiopyridyl ester with a solution of pyrrole magnesium chloride in toluene. Desilylation of **13** with TBAF in THF followed by oxidation gave the pyrrole acid **14** ($[\alpha]^{23}{}_D$ +116° (*c* 0.15, $CHCl_3$) lit.[7] $[\alpha]^{25}{}_D$ +121° (*c* 0.01 $CHCl_3$)) which was identical in all respects (TLC, NMR, HRMS, $[\alpha]_D$) with material obtained by degradation of natural material.[24]

Treatment of acid **14** with aminophenol **15** (prepared by a modification of Evans' protocol[6,25]), benzotriazolyloxy-*tris*-(dimethylamino)phosphonium hexafluorophosphate (BOP),[26] and Et_3N in DMF gave the intermediate amide, which was directly closed to benzoxazole **16** by exposure of the crude amide to pyridinium *p*-toluene sulfonate (PPTS) in $ClCH_2CH_2Cl$ (73% overall from **14**).[27] Benzoxazole **16** was identical with authentic material in all respects.[27] Cleavage of the trifluoroacetyl group with TBAF in THF afforded (−)-A-23187 methyl ester **17** identical in all respects with authentic material.[28] Dealkylation to (−)-A-23187 (**1a**) with LiSPr in HMPA proceeded as previously described.[6] More efficiently, treatment of **16** with excess LiSPr in HMPA directly afforded **1a** (98%).



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Supplementary Material Available: NMR and analytical data (including spectra) for compounds **2a**, **2b**, **3a**, **4**, **6**, **8**, **10–14**, and **16** (14 pages). Ordering information is given on any current masthead page.

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(22) Both diastereomeric cyclopropanes **12** were transformed to **2a** by equilibration of the methyl group adjacent to the spiro ring junction,[6] presumably via the intermediate oxonium ion. The major byproduct was the spirocyclic diol arising from loss of the TBDPS group (30%), whose formation can presumably be avoided by modification of the TBDMS protecting group.

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(25) Aminophenol **15** was prepared in four steps from methyl 2-trifluoroacetamido-5-hydroxybenzoate: (1) TBDMSCl (1.1 (equiv), imidazole (2 equiv), DMF (70%); (2) CH_3I (20 equiv), K_2CO_3, acetone, Δ, 5 h (98%); (3) HNO_3, HF, CH_3NO_2 (70%); (4) H_2, 10% Pd–C, CH_3OH (90%).

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(28) Synthetic (−)-A-23187 (**1a**) (mp 185–187 °C, $[\alpha]^{25}{}_D$ −48.4° (*c* 0.3, $CHCl_3$)) and synthetic (−)-A-23187 methyl ester (**17**) were identical (TLC, mmp (free acids), IR, NMR (300 MHz), and MS) with authentic samples of natural (−)-A-23187 (mp 186–187 °C, $[\alpha]^{23}{}_D$ −45.1° (*c* 0.3, $CHCl_3$) and (−)-A-23187 methyl ester (prepared by methylation (CH_2N_2) of natural A-23187).[24]

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Discovery of a New, Metallic (but Not Superconducting) Compound in the La–Sr–Cu–O System: $La_5SrCu_6O_{15}$

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The discovery of high-temperature superconductivity, first[1] near 40 K and later[2] near 90 K, has generated enormous interest in copper oxide compounds. From a materials perspective, the 90 K system $RBa_2Cu_3O_{7-\delta}$ (R = rare earth, Y), represented a new compound.[3,4] The superconductors with $T_c \sim 40$ K turned out[5,6] to be one of the phases studied earlier by Raveau and co-workers:[7,8] $La_{2-x}Sr_xCuO_4$ ($x \sim 0.15$) and the Ba analogue. As shown schematically in Figure 1, the stable compounds in the La-Sr-Cu-O system include: (1) the superconducting phase[7,8] (noted above) which has the K_2NiF_4-type structure of single sheets of corner sharing CuO_6 octahedra; (2) the $La_{2-x}Sr_{1+x}Cu_2O_{7-\delta}$ phase[9] having the $Sr_3Ti_2O_7$-type structure with double sheets of octahedra; and (3) two linear CuO chain compounds[10] $SrCuO_2$ and Sr_2CuO_3. We report here the discovery of a new highly conducting phase: $La_5Sr_1Cu_6O_{15}$. It is the first compound related to the cubic perovskite in this system and has metallic conductivity but does not become superconducting down to 5 K.

The samples were prepared by solid-state reaction in alumina crucibles from appropriate mixtures of La_2O_3, $SrCO_3$, and CuO. The powders were mixed and ground in an alumina mortar and pestle, fired in flowing oxygen at 900 °C for 6 h; followed by 3 cycles of regrinding, firing in flowing oxygen at 1025 °C for 16 h, and cooling slowly to room temperature (over 6 h).

The new phase is identified by its X-ray powder diffraction pattern, shown in Figure 2 together with the pattern of the related compound[11,12] $La_4BaCu_5O_{13}$. The composition $La_5SrCu_6O_y$ was

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[†] Permanent address: Department of Physics, University of Tokyo, Tokyo, Japan.

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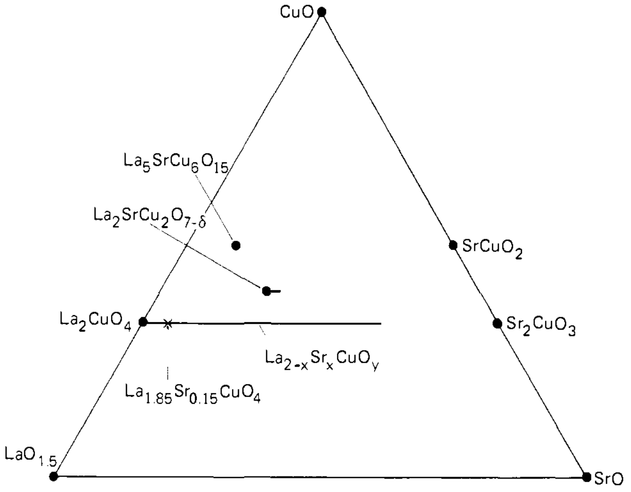

Figure 1. Diagram showing the compositions of the stable compounds formed in the La-Sr-Cu-O system.

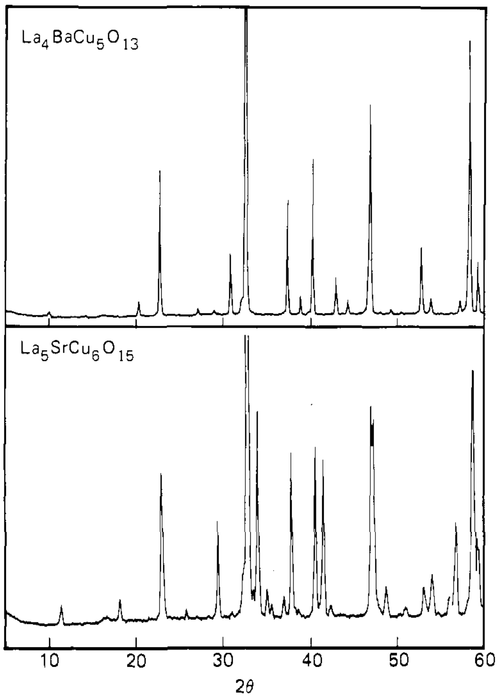

Figure 2. X-ray powder diffraction spectrum for $La_5SrCu_6O_{15}$ compared with that of $La_4BaCu_5O_{13}$.

initially determined by varying the Sr/La ratio and minimizing the amount of second phase in the X-ray powder pattern. For this composition there is very little second phase evident in the powder pattern, although small (<1%) amounts of the $La_{2-x}Sr_xCuO_4$ phase can be detected by weak anomalies near 40 K in the conductivity and magnetic susceptibility. Microprobe analysis was performed on four different areas on a pellet. In addition, a number of platelike single crystals of this phase were individually analyzed by energy dispersive X-ray analysis in a TEM. Both techniques confirmed the above composition. Iodometric titration analysis determined the oxygen content as $y = 14.9 \pm 0.1$.

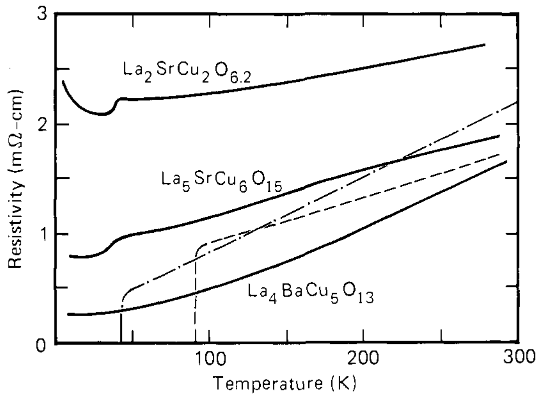

Figure 3. The electrical conductivity of $La_5SrCu_6O_{15}$, compared with two nonsuperconductors and two superconductors: $YBa_2Cu_3O_7$ (dashed) and $La_{1.85}Sr_{0.15}CuO_4$ (dashed-dot).

Table I. Effective Copper Valence (V) and T_c

	V	T_c (K)	Cu-O network
$La_4BaCu_5O_{13}$	2.4	<5	anisotropic 3-D
$YBa_2Cu_3O_{7.0}$	2.33	93	sheets and chains
$La_2SrCu_2O_{6.2}$	2.2	<5	sheets
$La_5SrCu_6O_{15}$	2.17	<5	sheets and ??
$La_{1.85}Sr_{0.15}CuO_4$	2.15	40	sheets
$YBa_2Cu_3O_{6.7}$	2.13	60	sheets and ??

As in the $La_4BaCu_5O_{13}$ compound,[11] TGA measurements indicate that the oxygen content is quite stable, at least when compared with the large variations observed[13,14] in $YBa_2Cu_3O_y$. Materials made and annealed under different oxygen partial pressures showed the same properties, including the absence of superconductivity.

The X-ray powder pattern (Figure 2) can be indexed with a unit cell 15.37 × 15.43 × 3.86 Å or approximately 4 × 4 × 1 of the cubic perovskite cell with $c = 3.86$ Å. Preliminary analysis[15] indicates that the structure may be viewed as a cubic perovskite with channels (rather than sheets) of oxygen vacancies, similar to those found[12] in $La_4BaCu_5O_{13}$ and a number of CaMn oxides.[16] The copper oxygen electronic overlap in the c direction is excellent and unimpeded, although along the a and b directions the channels of oxygen vacancies interrupt the overlap somewhat. Thus, this is an anisotropic three-dimensional material, similar to $La_4BaCu_5O_{13}$ but in contrast to the strongly two-dimensional overlap in the two superconducting systems.

The resistivity of $La_5SrCu_6O_{15}$ is shown[17] in Figure 3, together with that of the following: (1) the related Ba compound: (2) $La_2SrCu_2O_{6.2}$ whose layers each contain two sheets of CuO_5 pyramids; (3) and (4) the two superconducting compounds: $La_{1.85}Sr_{0.15}CuO_4$ (dashed-dot) and $YBa_2Cu_3O_7$ (dashed). Clearly, the conductivity of the newly discovered compound is metallic and comparable in magnitude with that of the other copper oxide metals and superconductors. Measurements down to 5 K show[17] no evidence of bulk superconductivity in this new compound. (The anomaly near 40 K is associated with a small (<1%) amount of second phase of the 40 K superconducting phase.) In addition to being the first metallic copper oxide phase discovered since $YBa_2Cu_3O_7$, the significance of $La_5SrCu_6O_{15}$ is illustrated in Figure 3: it is one of three examples of copper oxide metals that are chemically similar to and have common structural features with the high T_c superconductors but do *not* become superconducting above 5 K.

A further comparison of these five compounds is shown in Table I, where we have also included the somewhat reduced[18] $YBa_2Cu_3O_{6.7}$ which has $T_c = 60$ K. There is no clear correlation in

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Table I between superconductivity and the effective copper valence (calculated from the nominal stoichiometry). Thus, all five compounds have the features believed necessary for high T_c superconductivity: they are copper oxides that have metallic conductivity, effective copper valence between 2+ and 3+, and structures with Cu–O networks, separated by ordered oxygen vacancies. From the data in Figure 3 and Table I, these features may be *necessary* for superconductivity, but they are clearly not sufficient. We conclude that the phenomenon of high T_c superconductivity is a subtle one.

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Note Added in Proof. The title compound has been independently observed by the groups at Caen[19] and Northwestern[20] and its structure solved.[19] We thank B. Raveau and K. Poeppelmeier for communicating their results prior to publication.

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Sequential Insertion by an Extraordinarily Reactive (Cyclopentadienyl)cobalt Anion Complex

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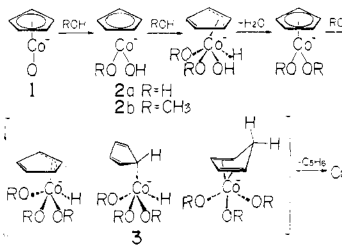
We recently described the formation of several novel examples of transition-metal oxide and polyoxide negative ions as products of gas-phase reactions between dioxygen and the 17-electron metal carbonylates $Fe(CO)_4^-$, $Cr(CO)_5^-$, and $Mo(CO)_5^-$.[1] In exploring the scope of this oxidation reaction with metal ion complexes possessing larger, polydentate organic ligands, we discovered that certain of the organometallic oxide product ions exhibit an enhanced gas-phase reactivity that is usually found only with highly coordinatively unsaturated species such as atomic ions or small metal ion fragments.[2] We describe here the gas-phase ion-molecule reactions of $CpCoO^-$ (**1**, Cp = η-C_5H_5), formed from oxidation of $CpCo(CO)_2^-$ by O_2, and show how this ion undergoes facile addition and sequential oxidative insertion reactions that are promoted by haptotropic rearrangement ("slippage") of the cyclopentadienyl ligand.

Our experiments were carried out at 298 K in a flowing afterglow apparatus that was recently mated to a triple quadrupole tandem mass spectrometer.[3] Collision-induced dissociation (CID) experiments with negative metal ions generated in the flow reactor (P(He) = 0.40 Torr; $\bar{v}$ = 9400 cm/s; F(He) = 190 STP cm^3/s) were performed in the triple quadrupole analyzer under single-collision conditions with argon target gas ($P(Ar) = 10^{-5}$ Torr). Bimolecular and termolecular reactions of mass-selected ions with neutral reagents in the central quadrupole were carried out under multiple-collision conditions ($P \simeq 10^{-4}$ Torr), with the axial kinetic energy of the reactant ion minimized (KE (c.m.) $\leq$ 0.1 eV).[4]

Scheme I



The $CpCo(CO)_2$ complex forms an abundant molecular anion in the flowing afterglow by thermal electron capture.[5] This ion undergoes a relatively slow reaction with O_2 ($k_{obsd} = 5.7 \pm 0.5 \times 10^{-11}$ cm^3/s; k_{obsd}/k_{coll} = 0.1) to yield $CpCoO^-$ (48%), $CpCo^-$ (30%), $CpCo(CO)O^-$ (12%), and $CpCo(CO)O_2^-$ (8%) as the major primary product ions. At higher O_2 flow rates, CoO_n^- and CoO_nH^- (n = 2, 3, 4) ions emerge as secondary and tertiary oxidation products.

The $CpCoO^-$ ion displays extraordinary reactivity for a (formally) 17-electron metal anion complex that distinguishes it from simple metal carbonylates[2b] and the other cyclopentadienylcobalt ions listed above, including $CpCo^-$. While **1** does not react with methane or other alkanes, it does react in a general way with Bronsted acids (HA) such as water, amines, alcohols, thiols, and certain unsaturated hydrocarbons by the stepwise addition–dehydration sequence shown in eq 1. In many cases the $CpCoA_2^-$ product reacts further with HA to yield an adduct and the CoA_3^- ion by displacement of 1,3-cyclopentadiene.

$$\mathrm{CpCoO^-} \xrightarrow{\mathrm{HA}} \mathrm{CpCo(OH)A^-} \xrightarrow[-\mathrm{H_2O}]{\mathrm{HA}} \mathrm{CpCoA_2^-} \xrightarrow[-\mathrm{C_5H_6}]{\mathrm{HA}} \mathrm{CoA_3^-} \tag{1}$$

$$\mathrm{HA = NH_3, H_2O, ROH, RCO_2H, H_2S, RSH}$$

Isotope-labeling and CID experiments show that reactions of **1** with H_2O and alcohols occur by the sequential O–H insertion mechanism outlined in Scheme I. Addition of H_2O to **1** produces a bishydroxide complex ($CpCo(OH)_2^-$, **2a**), as evidenced by the occurrence of two *sequential* H/D exchanges when this ion reacts with D_2O in the middle quadrupole,[6] and by the identical yields for H_2O loss and $H_2{}^{18}O$ loss from CID of the $CpCo^{18}O^-/H_2O$ adduct formed in the flow tube. Interestingly, the reactions of $CpCo^{18}O^-$ with H_2O or $CpCoO^-$ with $H_2{}^{18}O$ do not produce an observable $^{18}O/^{16}O$ exchange.[7] This indicates that once addition of water across the cobalt–oxygen bond occurs, collisional stabilization takes place faster than redissociation of H_2O.

The H/D exchanges described above are actually a result of reversible *hydroxyl* exchange on the metal, rather than protonic exchange on oxygen. Thus, the $CpCo(OH)(^{18}OH)^-$ ion, formed by H_2O addition to $CpCo^{18}O^-$, reacts further with H_2O to yield $CpCo(OH)_2^-$, while the doubly labeled ion $CpCo(OD)(^{18}OD)^-$ (m/z 162) reacts with H_2O to produce $CpCo(OH)(^{18}OD)^-$ (m/z 161) and $CpCo(OD)(OH)^-$ (m/z 159), but *no* $CpCo(OH)(^{18}OH)^-$ (m/z 160) (eq 2).

$$\mathrm{CpCo^{18}O^-} \xrightarrow{\mathrm{D_2O}} \underset{m/z\ 162}{\mathrm{CpCo(^{18}OD)(OD)^-}} \xrightarrow{\mathrm{H_2O}} \underset{m/z\ 161}{\mathrm{CpCo(^{18}OD)(OH)^-}} + \underset{m/z\ 159}{\mathrm{CpCo(OH)(OD)^-}} \tag{2}$$

Reversible OH/OCH_3 exchanges are evident in the methanol reactions which also demonstrate that metal insertion into the C–O bond of methanol does *not* occur in this system.[8] For example,

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