where $\hat{a}_j = 4\hat{s}_j - (\hat{l}\cdot\hat{s})\hat{l}_j - \hat{l}_j(\hat{l}\cdot\hat{s})$, where $j = x, y,$ or z and $|\overset{\pm}{\bar{\mathrm{A}}}_1\rangle$ is the ground state modified by spin–orbit mixing, we have

$$g_{zz} = 2.0023 - \frac{8\alpha_2\alpha_1c_1}{\Delta a_2} \times [\alpha_2\alpha_1c_1\zeta_{\mathrm{m}} - 2\alpha_2'\alpha_1'c_{\mathrm{n}}'c_\sigma'\zeta_{\mathrm{L}}(\cos(\theta - 90))] \quad \text{(A11)}$$

$$g_{xx} = 2.0023 - \frac{2}{\Delta b_2}[\alpha_1\beta_2\zeta_{\mathrm{m}}(c_1 + 3^{1/2}c_2) + 4\beta_2''\alpha_1'c_{\Pi_2}'c_{\mathrm{n}}'\zeta_{\mathrm{L}}(\cos(\theta - 90))(\cos\phi)][\alpha_1\beta_2(c_1 + 3^{1/2}c_2) + 4\beta_2''\alpha_1'c_{\Pi_2}'c_{\mathrm{n}}'(\cos(\theta - 90))(\cos\phi)] \quad \text{(A12)}$$

$$g_{yy} = 2.0023 - \frac{2}{\Delta b_1}[\alpha_1\beta_1\zeta_{\mathrm{m}}(c_1 - 3^{1/2}c_2) + 4\beta_1''\alpha_1'c_{\Pi_1}'c_{\mathrm{n}}'\zeta_{\mathrm{L}}(\cos(\theta - 90))(\sin\phi)][\alpha_1\beta_1(c_1 - 3^{1/2}c_2) + 4\beta_1''\alpha_1'c_{\Pi_1}'c_{\mathrm{n}}'(\cos(\theta - 90))(\sin\phi)] \quad \text{(A13)}$$

$$A_{zz} = \bar{A} + P\left[\frac{2}{3}\Delta g_{zz} - \frac{1}{3}(\Delta g_{xx} + \Delta g_{yy}) - \frac{4\alpha_1^2}{7}(c_1^2 - c_2^2) + \frac{3c_1 + 3^{1/2}c_2}{14(c_1 - 3^{1/2}c_2)}\Delta g_{yy} + \frac{3c_1 - 3^{1/2}c_2}{14(c_1 + 3^{1/2}c_2)}\Delta g_{xx}\right] \quad \text{(A14)}$$

$$A_{xx} = \bar{A} + P\left[\frac{2}{3}\Delta g_{xx} - \frac{1}{3}(\Delta g_{yy} + \Delta g_{zz}) + \frac{2\alpha_1^2}{7}(c_1^2 - c_2^2 - 2(3^{1/2})c_1c_2) + \frac{3^{1/2}c_2}{14c_1}\Delta g_{zz} - \frac{3c_1 + 3^{1/2}c_2}{14(c_1 - 3^{1/2}c_2)}\Delta g_{yy}\right] \quad \text{(A15)}$$

$$A_{yy} = \bar{A} + P\left[\frac{2}{3}\Delta g_{yy} - \frac{1}{3}(\Delta g_{xx} + \Delta g_{zz}) + \frac{2\alpha_1^2}{7}(c_1^2 - c_2^2 + 2(3^{1/2})c_1c_2) - \frac{3^{1/2}c_2}{14c_1}\Delta g_{zz} - \frac{3c_1 - 3^{1/2}c_2}{14(c_1 + 3^{1/2}c_2)}\Delta g_{xx}\right] \quad \text{(A16)}$$

$$\bar{A} = P\left[-\kappa + \frac{1}{3}(\Delta g_{zz} + \Delta g_{xx} + \Delta g_{yy})\right] + A_{4\mathrm{s}}\alpha_1^2c_{\mathrm{s}}^2 \quad \text{(A17)}$$

$$\Delta g_{ii} = g_{ii} - 2.0023$$

$P = gg_{\mathrm{N}}\beta_{\mathrm{N}}\beta\langle r^{-3}\rangle$ where r is the radial extension of the 3d orbitals. $A_{4\mathrm{s}}$ = the hyperfine splitting constant for an electron in the metal 4s orbital. κ = isotropic Fermi contact contribution.

Registry No. $(PPh_4)Na(\mathbf{1})$, 97689-50-4; $(PPh_4)Na(\mathbf{2})$, 97689-52-6; $(PPh_4)(\mathbf{3})$, 104834-06-2; $NaSSiMe_3$, 87495-22-5; $Na_4(acac)_2[VO(pdt)_2]$, 104834-08-4; $VO(acac)_2$, 3153-26-2; $(NMe_4)Na[VO(pdt)_2]$, 104834-09-5; $(Me_4N)Na[VO(edt)_2]$, 89061-83-6; $(PPh_4)Na[VO(pdt)_2]$, 104834-10-8; hexamethyldisilathiane, 3385-94-2.

Supplementary Material Available: Complete listings of atomic coordinates, isotropic and anisotropic thermal parameters, and interatomic distances and angles (8 pages); listings of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page. A complete crystallographic structure report (MSC Report 84105) is available on request from the Indiana University Chemistry Library.

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How a Bifunctional Complex Drives Reactivity of CO_2-like Molecules: Sodium [*N*,*N'*-Ethylenebis(salicylaldiminato)]cobaltate(I) Promotion of the Reductive Coupling of Molecules Resembling CO_2

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The bifunctional complex [Co(salen)Na(THF)] (**1**, salen = *N*,*N'*-ethylenebis(salicylaldiminato) dianion) promotes the reductive coupling of methyl pyruvate, diethyl ketomalonate, and *p*-tolylcarbodiimide via a C–C bond formation. Methyl pyruvate is transformed in diastereomeric dimethyl dimethyltartrates and *p*-tolylcarbodiimide into tetra-*p*-tolyloxalamidine, while **1** is oxidized to [Co(salen)]. A free-radical pathway involving the homolytic cleavage of a Co–Co σ bond is suggested. Reaction of **1** with diphenylketene, DPK, suggests an alternative pathway for the reductive coupling of CO_2-like molecules. The reaction occurs in a 1:1 DPK/Co molar ratio and gives $\{[Co(salen)]_2Na_2[Co(salen(DPK)_2)]\}\cdot 3THF$ (**8**), which is a trinuclear cobalt(II) complex containing two intact [Co(salen)] units bridged by two Na^+ ions to a third cobalt(II) unit, where the metal is surrounded by a hexadentate ligand resulting from the addition of two DPK molecules to the same imino group of the salen ligand. The X-ray analysis shows a rather close proximity between the carbon atoms belonging to the two DPK molecules as in a precoupling stage. Any C–C bond formation between those carbon atoms will restore the original imino functionality in the salen ligand. This may be another plausible pathway leading to a C–C bond between CO_2-like molecules. Processes involving reactive sites and electron transfers from an aromatic polydentate ligand surrounding a metal are very important in compounds driving reactions of small molecules. Complex **1** promotes the usual reductive disproportionation of aryl isocyanates, RNCO (R = phenyl, 1-naphthyl). Crystallographic details for complex **8**: space group $P\bar{1}$ (triclinic); a = 16.313 (2) Å; b = 19.164 (3) Å; c = 15.020 Å; α = 107.16 (2)°; β = 113.23 (2)°; γ = 102.06 (2)°; Z = 2; D_{calcd} = 1.410 g cm^{-3}. The final R factor was 0.085 for 2742 observed reflections.

Introduction

General objectives in the activation of carbon dioxide by transition-metal complexes are the formation of M–C and C–C bonds. The latter bond can be achieved either by a reductive coupling or by the incorporation of CO_2 into an organic substrate.[1-4] It must be pointed out, however, that the majority of

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metal-promoted transformations of carbon dioxide lead to the preferential formation of metal–oxygen and carbon–oxygen bonds.[1–4] There are a number of rather unusual characteristics that compounds should possess in order to manage this chemistry. Such compounds must contain, preferably, acidic and basic sites in their structure, and so be "bifunctional";[5] they have to be able to control the transfer of either one or two electrons to the substrate[6–9] and to contain ligands that can impart not only special properties to the metal but can provide actual reactive sites for the substrate. With use of the bifunctional complex sodium [*N*,*N'*-ethylenebis(salicylaldiminato)]cobaltate(I), [Co(salen)Na(THF)],[10] in combination with CO_2-like molecules, all the above-mentioned factors have been brought into play.

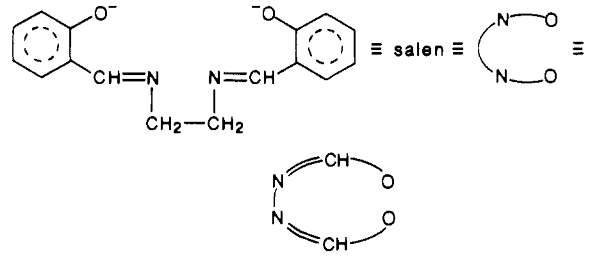
Significant knowledge of the factors controlling the transformations of CO_2 can be gained by using molecules that resemble CO_2, rather than CO_2 itself.[11] The major difference between CO_2 and CO_2-like molecules resides, in many cases, in their electron-acceptor properties.[12] From those studies we have found that the formation of a free-radical-type fragment by the transfer of a single electron favors the C–C bond formation, while a two-electron-transfer process seems a prerequisite for the fixation of CO_2 or its reductive disproportionation.[7,8]

This paper describes the reaction of [Co(salen)Na(THF)][10] with different CO_2-like molecules, which undergo reductive coupling, reductive disproportionation, or addition to the salen ligand. Such results emphasize the role of various reactive sites in the complex, the importance of the electron-transfer degree to the CO_2-like molecule, and the role of the polydentate ligand. The reaction of **1** with diphenylketene was communicated.[13]

Experimental Section

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods. [Co(salen)Na(THF)][10] and diphenylketene[14] were prepared as previously reported. Diethyl ketomalonate, methyl pyruvate, phenyl isocyanate, 1-naphthyl isocyanate, and *p*-tolylcarbodiimide are commercially available compounds, which have been recrystallized or distilled before use. Infrared spectra were recorded with a Perkin-Elmer Model 983 spectrophotometer. ^{1}H NMR spectra were taken with a 360-MHz Bruker apparatus. Magnetic susceptibility was determined by the Faraday method.

Abbreviations:



$[Co(salen)Na(THF)]_n$,[10] will be abbreviated throughout the paper as [Co(salen)Na(THF)].

Reaction of [Co(salen)Na(THF)] with DEKM. Diethyl ketomalonate (DEKM; 1.50 g, 8.61 mmol) was added to a THF solution (50 mL) of **1** (3.50 g, 8.33 mmol). The solution color changed from deep green to red, and then a red solid crystallized. This solid was in many cases [Co(salen)]; in a few other cases the solid was an adduct between [Co(salen)] and the sodium salt of an organic residue having a characteristic IR band at 1710 cm^{-1}. When this labile adduct was recrystallized from DMF, [Co(salen)] was released. A further amount of [Co(salen)] was recovered from the THF solution by adding NaI, which forms a very insoluble adduct, [Co(salen)NaI] (**4**). DEMK was found to react with **1** in a 1:1 molar ratio, by following the loss of the CO band in the IR spectrum. The total yield of [Co(salen)] was always greater than 80%. The isolation of the organic compound was not attempted.

Synthesis of [Co(salen)NaI] (4). A THF suspension of [Co(salen)] (0.76 g, 2.34 mmol) and NaI (0.35 g, 2.33 mmol) was stirred for a few hours. The color of the suspension changed from deep red to orange, and a microcrystalline solid was obtained (ca. 95%). Anal. Calcd for [Co(salen)NaI], $C_{16}H_{14}CoIN_2NaO_2$: C, 40.43; H, 2.95; N, 5.89; I, 26.73. Found: C, 40.65; H, 2.72; N, 5.65; I, 28.05.

Reaction of [Co(salen)Na(THF)] with Methyl Pyruvate. A THF solution (10 mL) of methyl pyruvate (0.22 g, 2.15 mmol) was added to a THF solution (25 mL) of **1** (1.01 g, 2.40 mmol). The deep green color of the solution smoothly changed to red. The solution was warmed to 40 °C for 4 h and then cooled to room temperature overnight. A red crystalline solid formed that has a carbonylic band at 1700 cm^{-1} (vs. 1735 cm^{-1} in methyl pyruvate). Its recrystallization from DMF gave [Co(salen)]. When a THF solution of NaI was added to the mother solution, [Co(salen)NaI] was recovered. The overall yield of [Co(salen)] was ca. 83%. The IR spectrum showed that methyl pyruvate reacted in a 1:1 molar ratio with complex **1**. A similar reaction was carried out with the purpose of identifying the organic product of the reaction as follows. Methyl pyruvate (2.05 mL, 22.69 mmol) was added to a THF solution (150 mL) of **1** (7.85 g, 18.68 mmol). The solution was kept standing for 2 days. Then NaI (3.0 g, 20.0 mmol) was added and the suspension stirred overnight. The [Co(salen)NaI] adduct was removed by filtration, leaving a light red solution, which was evaporated to dryness. The residue was treated with 2 mL of concentrated HCl (37%), diluted with 40 mL of water. Then the suspension was saturated with NaCl and extracted with $CHCl_3$. The chloroform solution dried over Na_2SO_4 and evaporated to dryness gave an oil that was identified as pure diastereomeric dimethyl dimethyltartrates (yield ca. 25%). The IR spectrum in CCl_4 solution showed a band centered at 3490 cm^{-1} (OH) and a C=O band at 1737 cm^{-1}. The ^{1}H NMR spectrum (CCl_4, Me_4Si) showed four peaks at τ 6.20 (s), 6.33, 8.55, and 8.65 and a broad peak due to the OH protons centered at τ 6.20, in agreement with a mixture of diastereoisomers as reported in the literature.[15]

Reaction of [Co(salen)Na(THF)] with RNCO (R = 1-Naphthyl, Phenyl). A THF solution (20 mL) of 1-naphthyl isocyanate (0.30 mL, 1.91 mmol) was slowly added to a THF solution (25 mL) of **1** (0.86 g, 2.05 mmol). The IR spectrum of the solution showed the appearance of two bands at 1880 and 1670 cm^{-1}, while the band of the isocyanate (2260 cm^{-1}) almost completely disappeared. Complex **1** reacted in a 1:1 molar ratio with RNCO, and the stoichiometry was established by following the loss of the band at 2260 cm^{-1} as a function of the amount of isocyanate added. The red solution was evaporated to half of the original volume, and then Et_2O (50 mL) was added. A microcrystalline red-orange solid precipitated (0.97 g), having an IR spectrum with a significant band at 1715 cm^{-1}. [Co(salen)] was obtained by crystallization of the solid from DMF. When the solid was added to a THF solution (25 mL) of NaI (0.61 g, 4.0 mmol), [Co(salen)]NaI precipitated quantitatively.

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Table I. Summary of Crystal Data and Intensity Data Collection

formula	$C_{76}H_{62}Co_3N_6Na_2O_8 \cdot 3C_4H_8O$
a, Å	16.313 (2)
b, Å	19.164 (3)
c, Å	15.020 (2)
α, deg	107.16 (2)
β, deg	113.23 (2)
γ, deg	102.06 (2)
Z	2
M_r	1626.5
calcd density, g/cm^3	1.410
space group	$P\bar{1}$
radiation	niobium-filtered Mo Kα (λ = 0.71069 Å)
μ, mm^{-1}	0.72
scan type	θ–2θ
scan range, deg	±0.5 from peak center
scan speeds, deg/min	2.5–10
bkgds	stationary cryst at ±0.5°
2θ limits, deg	5–46
criterion for observn	$I > 2\sigma(I)$
unique obsd data	2742
unique total data	9674
cryst dimens, mm	0.30 × 0.16 × 0.48

The resulting solution was almost completely evaporated, and then by addition of diluted HCl a white crystalline solid formed (mp 284 °C), which was found to be 1,3-bis(1-naphthyl)urea (yield ca. 71%). Similar results have been obtained with PhNCO. When the reaction was carried out in a gas-volumetric apparatus, no carbon monoxide evolution was observed.

Reaction of [Co(salen)Na(THF)] with *p*-Tolylcarbodiimide. Complex **1** (0.92 g, 2.19 mmol) was added to a THF (100 mL) solution of *p*-tolylcarbodiimide (1.0 g, 4.50 mmol). A day later a green solid crystallized from the solution (yield ca. 60%). The solid was identified as $[Co(salen)]_2Na(THF)_2$. Anal. Calcd for $C_{40}H_{44}Co_2N_4NaO_6$: C, 58.76; H, 5.42; N, 6.85. Found: C, 58.18; H, 5.87; N, 6.72. *p*-Tolylcarbodiimide reacted with complex **1** in a 1:2 molar ratio, as proven in a reaction followed by IR. Some experiments have been carried out with the purpose to identify the transformation undergone by *p*-tolylcarbodiimide. *p*-Tolylcarbodiimide (3.20 g, 14.4 mmol) was added to a THF solution (200 mL) of **1** (12.1 g, 28.7 mmol). The IR spectrum of the solution showed the C=N band of free *p*-tolylcarbodiimide at 2100 cm^{-1}. Then the solution was refluxed for 3 days until the C=N band completely disappeared. EtOH (95%, 70 mL) was added to the suspension, which was then exposed to the air. The inorganic residue, which did not contain organic derivatives of *p*-tolylcarbodiimide, as determined by an IR spectrum, was recovered by filtration. The mother liquor was evaporated to dryness and the residue extracted with boiling benzene. The benzene suspension was filtered over Al_2O_3 and eluted with Et_2O. Thin-layer chromatography on silica gel using Et_2O/*n*-hexane (1:1) resulted in the separation of two fractions. The major one is a red oil, which was further purified by chromatography on silica gel with use of $CHCl_3$. A yellow fraction was obtained, from which pale yellow crystals of tetra-*p*-tolyloxalamidine crystallized (mp 184–185 °C).[16]

Reaction of [Co(salen)Na(THF)] with Diphenylketene, Complex 6. A THF solution (20 mL) of DPK (0.44 mL, 2.49 mmol) was added to a THF solution (10 mL) of **1** (1.07 g, 2.54 mmol). The IR spectrum of the solution showed the disappearance of the C=O band of DPK, which was revealed only when the DPK/Co ratio was higher than 1:1. The solution changed color from deep green to red and gave on standing for 3 days at room temperature red crystals of $[Co(salen)]_2Na_2[Co(salen\text{-}(DPK)_2)] \cdot 3THF$ (**6**, yield ca. 60%). Anal. Calcd for $C_{88}H_{86}Co_3N_6Na_2O_{11}$: C, 64.99; H, 5.33; N, 5.17; Na, 2.82. Found: C, 64.70; H, 5.64; N, 5.20; Na, 2.60. The IR spectrum of the solid did not show any band above 1635 cm^{-1} (ν(C=N)). $\mu_{eff} = 5.53\ \mu_B$/trimetallic unit.

X-ray Data Collection and Structure Refinement. The crystal was wedged into a thin glass capillary. Preliminary cell dimensions determined from rotation and Weissenberg photographs were subsequently refined by applying a least-squares procedure to the 2θ setting of 28 reflections in the range $20 < 2\theta < 34°$. The refinement yielded the lattice parameters listed in Table I together with details on intensity data collection. The space group $P\bar{1}$, assumed on the basis of intensity distribution statistics, was confirmed by structure analysis.

Intensities were measured at room temperature by a single-crystal Siemens AED diffractometer using niobium-filtered Mo Kα radiation. The intensity of a standard reflection was monitored after every 20 reflections as a check on crystal and instrument stability. No signficant or systematic change in the measured intensity of this reflection was observed during data collection. For intensity and background the "five-point technique"[17] was used. Data were collected in the usual way for Lorentz and polarization effects, but not for absorption ($\mu\bar{r}$ = ca. 0.1).

Initial coordinates for the three Co atoms present in the asymmetric unit were obtained from an *E* map produced by the program MULTAN.[18] Two subsequent Fourier syntheses revealed all non-hydrogen atoms except those of the solvent molecules. After two cycles of isotropic full-matrix refinement[19] the *R* index was 16%. A difference Fourier map computed at this stage showed two THF solvent molecules and a set of nine diffuse peaks, indicating the presence of a third, disordered, solvent molecule (C(100)...C(108)). All the peaks were taken into account to resolve the disorder. Site occupation factors, initially assigned on the basis of the electron density on each peak, were adjusted by refining isotropically different models. The model quoted in Table II was considered the most reliable since it gave the best fit between observed and calculated distributions in the final difference synthesis and the most acceptable values for thermal parameters. Various attempts to improve it gave unsatisfactory results without any significant changes in the structural parameters of the complex molecule.

The complete refinement of the structure, performed isotropically for the atoms in the phenyl rings and solvent molecules and anisotropically for the remaining non-hydrogen atoms, led to a final *R* factor of 0.085. Owing to the low data:parameter ratio, all phenyl rings were refined with "rigid body" constraint (C–C = 1.395 Å, C–C–C = 120°). No attempts were made to locate hydrogen atoms. A final difference Fourier map showed some peaks of height 0.5 e Å^{-3} in the regions of the phenyl rings: no other peak had electron densities greater than 0.3 e Å^{-3}.

The function minimized was $\sum w|\Delta F|^2$ first with unit weights and then with $w^{-1} = \sigma^2(F_0) + 0.002F_0^2$. No evidence for secondary extinction was found. Scattering factors of neutral atoms were taken from standard sources.[20] The effects of anomalous dispersion were included in all structure factor calculations.

The final positional parameters are listed in Table II. Listings of isotropic and anisotropic thermal parameters, a list of structure factors, and equations of least-squares planes are available as supplementary material.

Results and Discussion

Reactions of different CO_2-like molecules have been carried out with the "bifunctional" complex $[Co(salen)Na(THF)]_n$[10] (**1**), which is able to perform the fixation of CO_2 on both metal sites.[5a]

We reacted complex **1** with molecules having electron-withdrawing substituents at the CO functionality, like diethyl ketomalonate, $((EtO_2C)_2CO$, DEKM) and methyl pyruvate $((Me)(MeO_2C)CO$, MP). Diethyl ketomalonate has been used in organic synthesis as the equivalent of carbon dioxide.[21] Although these molecules maintain a high electrophilicity of the >C=O functionality, which is one of the major characteristics of CO_2, their electron-acceptor properties must be significantly different from CO_2.[12]

The reaction of [Co(salen)Na(THF)] (**1**) with diethyl ketomalonate and methyl pyruvate was carried out in THF solution at room temperature. Both reagents were found to react in a 1:1 molar ratio with the cobalt complex. The product of both reactions is a rather labile adduct, complex **2**, between the sodium salt of an organic residue and [Co(salen)].[22,23] Complex **2** can be

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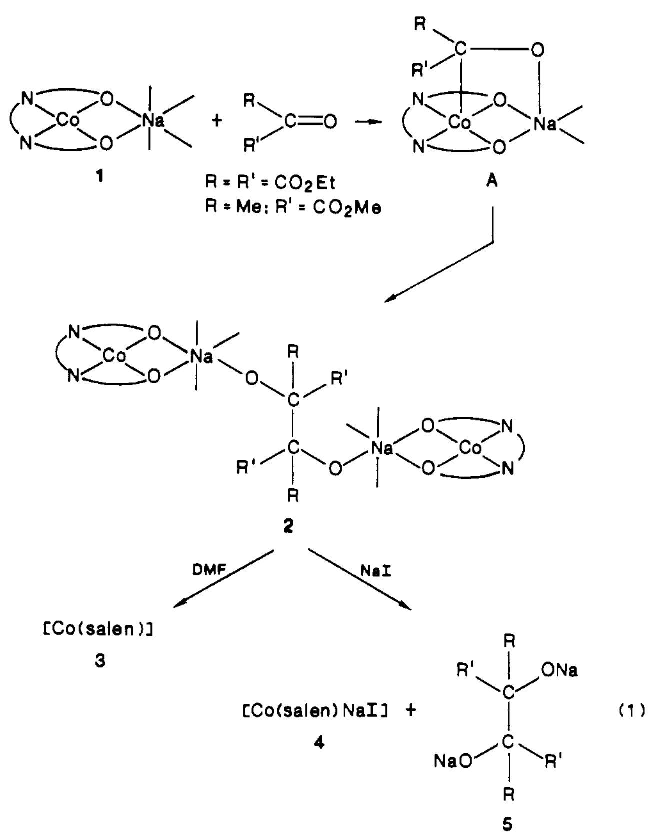
Scheme I



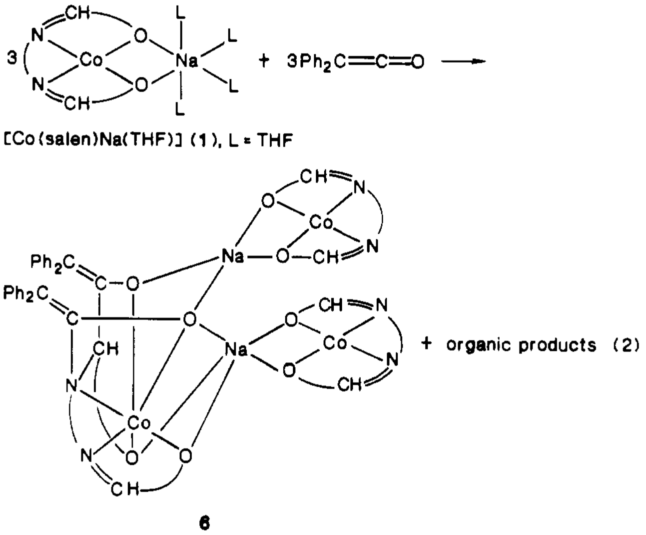
solvent molecules around Na^+ omitted

separated into the two components as reported in the Experimental Section.

The intrinsic lability of **2** is proven by the fact that **3** sometimes crystallizes from the solution, instead of **2**. The formulation we propose for **2** is based on the almost quantitative isolation of [Co(salen)] and the diastereomeric dimethyl dimethyltartrates,[15] when the reaction was carried out with methyl pyruvate. Complexation of sodium salts of different anions by [M(salen)]-type complexes acting as bidentate ligands is a well-established reaction.[22,23] The structure of those compounds in the solid state was proven by X-ray crystallography[22,23] and their lability in solution studied.[24] In this context it has to be mentioned that the reaction of **2** with NaI is a very useful method for freeing the organic salt and for recovering quantitatively [Co(salen)] since [Co(salen)NaI] is very insoluble in THF.[25] A significant question concerns how reaction 1 can proceed. The overall reaction requires the oxidation of cobalt(I) to cobalt(II), one electron being transferred from cobalt to the organic substrate giving, formally, a free radical, which, assisted by the metal, dimerizes to the organic molecule shown in **2** and **5**. The preliminary stage of the reaction of **1** with CO_2, diethyl ketomalonate, and methyl pyruvate should not be so much different, and this is the reason why we propose the intermediate A. Fixation of CO_2, however, requires a net transfer of two electrons, and the cobalt becomes a formal cobalt(III) in the final complex while CO_2 is in the form of a dianion.[5a] In contrast, by a change in the electron-acceptor properties of the substrate, a free radical at the carbon can form with Co–C bond homolytic cleavage[26] or without any intervention of Co–C bond formation. The electron-transfer degree from the metal to CO_2 can be the crucial factor affecting the nature of CO_2 transformations.

As suggested from related work, it seems likely that a two-electron transfer from a metal site to CO_2 determines either its fixation[5,27] or reductive disproportionation,[1-4,7,8,28] while a one-electron transfer is a prerequisite, though not sufficient, for having a reductive coupling.[6,7] In this context, Saveant reports that the free-radical anion CO_2^- formed from the electrochemical reduction of CO_2 may undergo either the dimerization to oxalato anion or to form a head-to-tail dimer that is the precursor of CO_3^{2-} and CO.[6]

The next step in this study was the extension of the reaction in Scheme I to a molecule that has in common with CO_2 the cumulene structure, and we explored the reaction with diphenylketene, DPK. It is known that diphenylketene reacts with electron-rich oxophilic metals at the >C=O functionality, adding to the metal site in a η^2-C,O form and being formally reduced by two electrons.[9,29] The metal-bonded DPK molecule reacted further with an excess of DPK, forming a metallacycle[29] that contains the head-to-tail dimer of the >CO functionality. Such a dimer has been proposed as an intermediate leading to the reductive disproportionation of CO_2 and CO_2-like molecules.[29] Complex **1** reacted with DPK in a 1:1 molar ratio, forming **6** in very good yield:



6

The organic product corresponding to one-third of the DPK transformed in reaction 2 has not been identified, though on the basis of results of reaction 2 and other reactions (vide infra), we

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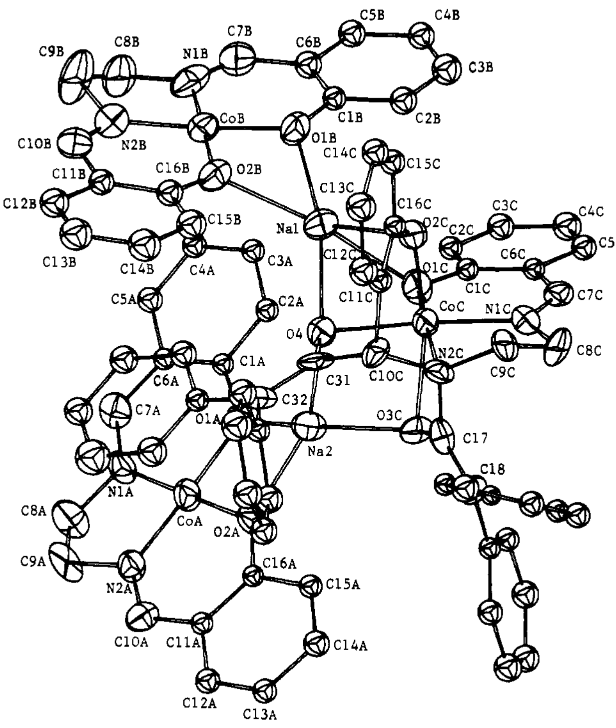


Figure 1. ORTEP view of complex **6**.

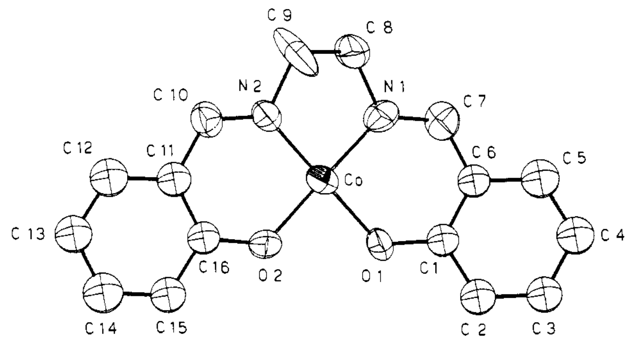


Figure 2. ORTEP view and atomic numbering scheme for the two [Co(salen)] units in complex **6**.

believe that DPK underwent a reductive coupling. The closest relationship of reaction 2 with reaction 1 is that all starting cobalt(I) has been oxidized to cobalt(II), two of them maintaining their structure in the form of [Co(salen)] (CoA and CoB in Figure 1), while the third one is surrounded by a hexadentate ligand resulting from the addition of two molecules of DPK to one of the imino groups of the salen ligand. The trimetallic complex has five unpaired electrons in agreement with the presence of two low-spin cobalt(II) atoms in a square-planar geometry and a cobalt(II) in an octahedral coordination with a high spin state. The electrophilic carbon of the two DPK molecules adds to the imino group rather than to the nucleophilic cobalt(I), and this is the genesis of the hexadentate ligand for CoC (Figure 1). The set of oxygen atoms are acting as chelating ligands for two sodium cations, each one being coordinated to the oxygen of an intact [Co(salen)] unit. An overall view of the structure is reported in Figure 1, while the coordination sphere and numbering scheme for CoA and CoB are in Figure 2 and for CoC in Figure 3. Figure 4 shows a simplified picture of coordination polyhedra around cobalt and sodium ions. The most significant bond distances and angles are listed in Table III. The structural parameters for the two [Co(salen)] units, CoA and CoB, are in the usual range.[27,30] One of the imino groups of the salen around CoC remains intact

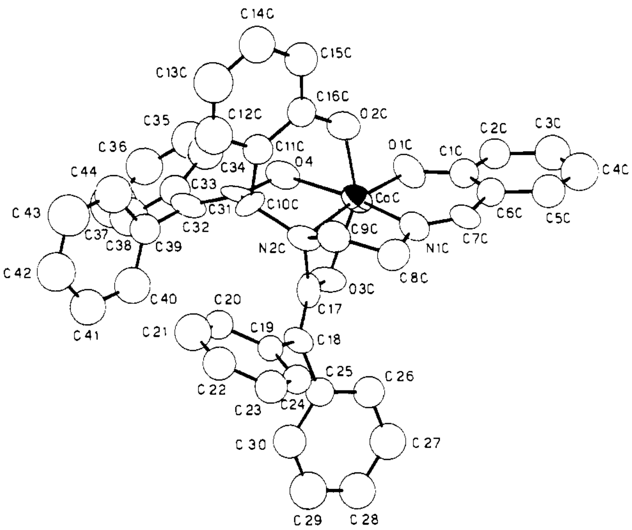
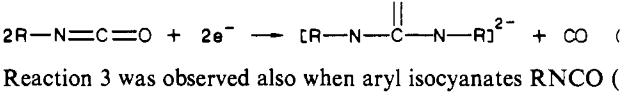


Figure 3. ORTEP view and atomic numbering scheme for the [Co(salen)(DPK)$_2$)] fragment in complex **6**.

(C(7)-N(1) = 1.26 (4) Å) while the other one becomes a C-N single bond (C(10)-N(2) = 1.54 (3) Å) and allows the ligand to adapt to a rather constrained geometry. The C—O bonds from DPK maintain some double-bond character (C(17)-O(3) = 1.28 (4) Å; C(31)-O(4) = 1.33 (4) Å), while a significant lengthening is observed for the C=C double bond (C(17)-C(18) = 1.34 (3) Å; C(31)-C(32) = 1.39 (4) Å).[29] The cobalt-donor atom bond distances are in the usual range for salen derivatives,[30] but for the oxygen atoms from the DPK residue having rather long Co-O bond distances (Co-O(3) = 2.16 (1) Å; Co-O(4) = 2.13 (2) Å). The two DPK moieties are arranged such that C(17) and C(31) form a gauche 1,4 contact; the proximity of these two atoms (C(17)···C(31) = 2.98 (4) Å) can suggest how C-C bonds may be formed in the reductive coupling of CO_2-like molecules. If this happens, the C-C formation of the bond between C(17) and C(31) will restore the original salen structure around CoC. Results from reaction 2 are suggestive on how the polydentate ligand around the metal can drive reactions on CO_2-like molecules or on CO_2 itself, providing not only the assistance to the metal but also reactive sites on which the reaction can actually occur.

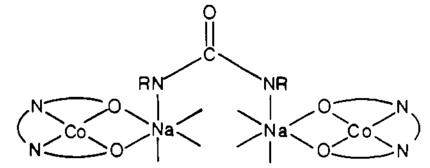
Organic isocyanates are among the most common cumulene structures used for miming CO_2, though they easily undergo, under various conditions, the reductive disproportionation (3).[8a,31]



$$2R{-}N{=}C{=}O + 2e^- \longrightarrow [R{-}N{-}\overset{\overset{O}{\|}}{C}{-}N{-}R]^{2-} + CO \quad (3)$$

Reaction 3 was observed also when aryl isocyanates RNCO (R = 1-naphthyl, phenyl) were reacted with complex **1**:

$$\underset{\mathbf{1}}{2[Co(salen)Na(THF)]} + 2Ar{-}N{=}C{=}O \xrightarrow{-CO}$$



(4)

7

Significant information regarding reaction 4 comes from the IR spectrum of the reaction solution with the two bands at 1670 and 1880 cm^{-1}. Release of CO, which is expected from the reductive disproportionation of isocyanates, was not observed in experiments carried out in gas-volumetric apparatus, since carbon monoxide reacted with the starting material very fast to form [Co(CO)$_4^-$] having a CO broad absorption centered at 1880 cm^{-1}.[32] Therefore,

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Table II. Final Atomic Parameters ($\times 10^4$)

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Molecule A							
Co	999 (2)	88 (2)	−66 (2)	C7	1750 (16)	256 (14)	2067 (19)
O1	859 (10)	967 (8)	694 (9)	C8	1568 (19)	−931 (15)	789 (19)
O2	544 (9)	357 (7)	−1181 (9)	C9	1694 (21)	−1120 (13)	−133 (19)
N1	1479 (12)	−157 (11)	1079 (15)	C10	991 (15)	−1051 (12)	−1781 (18)
N2	1203 (12)	−756 (10)	−795 (14)	C11	585 (9)	−707 (8)	−2486 (11)
C1	1261 (10)	1342 (6)	1739 (13)	C12	378 (9)	−1083 (8)	−3541 (11)
C2	1206 (10)	2073 (6)	2158 (13)	C13	−31 (9)	−785 (8)	−4277 (11)
C3	1544 (10)	2457 (6)	3252 (13)	C14	−233 (9)	−111 (8)	−3959 (11)
C4	1937 (10)	2110 (6)	3926 (13)	C15	−27 (9)	265 (8)	−2904 (11)
C5	1992 (10)	1378 (6)	3507 (13)	C16	382 (9)	−33 (8)	−2168 (11)
C6	1655 (10)	994 (6)	2413 (13)				
Molecule B							
Co	3830 (3)	4131 (2)	4289 (2)	C7	3143 (20)	4391 (14)	5767 (21)
O1	2808 (10)	4438 (8)	3776 (10)	C8	4404 (25)	3868 (16)	6118 (21)
O2	3884 (10)	4039 (8)	3085 (10)	C9	5244 (23)	3963 (21)	5971 (24)
N1	3767 (16)	4181 (12)	5492 (16)	C10	5441 (21)	3741 (15)	4479 (25)
N2	4902 (17)	3897 (14)	4855 (21)	C11	5260 (15)	3702 (10)	3444 (11)
C1	2309 (10)	4678 (9)	4233 (13)	C12	5921 (15)	3528 (10)	3136 (11)
C2	1642 (10)	4969 (9)	3714 (13)	C13	5868 (15)	3558 (10)	2198 (11)
C3	1096 (10)	5233 (9)	4157 (13)	C14	5152 (15)	3761 (10)	1569 (11)
C4	1218 (10)	5207 (9)	5117 (13)	C15	4490 (15)	3935 (10)	1878 (11)
C5	1886 (10)	4916 (9)	5636 (13)	C16	4544 (15)	3905 (10)	2816 (11)
C6	2431 (10)	4652 (9)	5194 (13)				
Molecule C							
Co	565 (2)	3311 (2)	−48 (2)	C20	583 (12)	2695 (7)	−3655 (10)
O1	306 (10)	3226 (8)	1062 (10)	C21	789 (12)	3038 (7)	−4279 (10)
O2	1656 (9)	4376 (7)	852 (9)	C22	88 (12)	3209 (7)	−4984 (10)
O3	−121 (9)	2178 (7)	−1394 (10)	C23	−820 (12)	3037 (7)	−5065 (10)
O4	1737 (10)	2921 (8)	302 (11)	C24	−1026 (12)	2693 (7)	−4441 (10)
N1	−462 (13)	3727 (10)	−636 (15)	C25	−1459 (9)	1457 (7)	−3661 (13)
N2	680 (15)	3282 (10)	−1373 (13)	C26	−2033 (9)	1307 (7)	−3202 (13)
C1	−363 (11)	3414 (8)	1257 (10)	C27	−2876 (9)	640 (7)	−3774 (13)
C2	−473 (11)	3268 (8)	2068 (10)	C28	−3146 (9)	123 (7)	−4805 (13)
C3	−1140 (11)	3477 (8)	2340 (10)	C29	−2572 (9)	274 (7)	−5264 (13)
C4	−1696 (11)	3832 (8)	1801 (10)	C30	−1729 (9)	940 (7)	−4692 (13)
C5	−1586 (11)	3978 (8)	991 (10)	C31	1989 (17)	2873 (13)	−448 (16)
C6	−919 (11)	3769 (8)	719 (10)	C32	2450 (16)	2378 (12)	−710 (16)
C7	−939 (16)	3901 (12)	−172 (15)	C33	2802 (10)	1926 (9)	−95 (13)
C8	−580 (16)	3857 (13)	−1580 (16)	C34	2935 (10)	2102 (9)	933 (13)
C9	353 (17)	3924 (11)	−1607 (15)	C35	3266 (10)	1648 (9)	1462 (13)
C10	1746 (15)	3412 (12)	−1011 (16)	C36	3465 (10)	1018 (9)	961 (13)
C11	2359 (11)	4254 (7)	−245 (21)	C37	3332 (10)	842 (9)	−68 (13)
C12	3057 (11)	4597 (7)	−464 (12)	C38	3001 (10)	1296 (9)	−596 (13)
C13	3717 (11)	5363 (7)	222 (12)	C39	2658 (13)	2343 (11)	−1569 (13)
C14	3678 (11)	5787 (7)	1126 (12)	C40	2089 (13)	1713 (11)	−2573 (13)
C15	2979 (11)	5445 (7)	1345 (12)	C41	2337 (13)	1656 (11)	−3373 (13)
C16	2320 (11)	4678 (7)	659 (12)	C42	3155 (13)	2230 (11)	−3169 (13)
C17	−39 (17)	2487 (15)	−2021 (21)	C43	3724 (13)	2860 (11)	−2165 (13)
C18	−556 (15)	2187 (12)	−3091 (16)	C44	3476 (13)	2917 (11)	−1364 (13)
C19	−325 (12)	2522 (7)	−3736 (10)				
Sodium and Solvent Atoms[a]							
Na1	2235 (7)	3817 (5)	1992 (6)	C94	5550 (56)	939 (38)	8115 (50)
Na2	753 (6)	1618 (5)	−419 (6)	C100	5955 (60)	707 (49)	1877 (74)
O80	6065 (40)	1991 (32)	4823 (50)	C101	6120 (49)	1135 (34)	1183 (45)
C81	4964 (60)	1411 (46)	4097 (63)	C102	6905 (128)	1310 (83)	1566 (125)
C82	4773 (63)	1688 (58)	4835 (92)	C103	7443 (128)	1512 (131)	2243 (167)
C83	5425 (67)	2267 (42)	5873 (64)	O104	7057 (55)	1123 (49)	2653 (63)
C84	6354 (50)	2376 (36)	5930 (57)	C105	6137 (92)	1782 (73)	2032 (96)
O90	6304 (33)	1321 (31)	8127 (32)	C106	6456 (78)	1496 (63)	2821 (76)
C91	6608 (48)	2099 (43)	8748 (55)	C107	6860 (66)	588 (56)	2106 (72)
C92	5857 (55)	2080 (39)	9114 (49)	C108	7097 (118)	2083 (57)	2396 (85)
C93	4980 (53)	1386 (54)	8361 (63)				

[a] The site occupation factors for the atoms in the disordered THF molecule are as follows: 1.0 for C101; 0.75 for C100 and C106; 0.50 for C102, O104, C105, and C108; 0.25 for C103 and C107.

the Co:isocyanate ratio is slightly different from 1:1 because of the reaction of **1** with carbon monoxide. The CO band centered at 1670 cm^{-1} is due to the diphenylurea anion residue.

Characteristization of **7** is particularly intriguing as for all the labile adducts formed from [Co(salen)] and sodium salts.[22,29] Recrystallization of **7** from DMF released [Co(salen)], while its reaction with NaI formed the insoluble [Co(salen)NaI] adduct and released the organic part, which after a mild hydrolysis was recognized as ArNHCONHAr (see Experimental Section). Reaction 4 accounts for the stoichiometry, more than for a

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(32) Fachinetti, G.; Floriani, C.; Zanazzi, P. F.; Zanzari, A. R. *Inorg. Chem.* **1978**, *17*, 3002–3007.

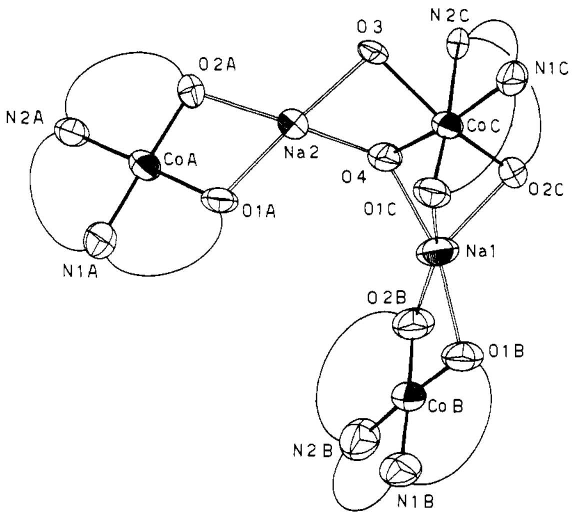


Figure 4. ORTEP view of coordination polyhedra around cobalt and sodium ions.

Table III. Selected Interatomic Distances (Å)

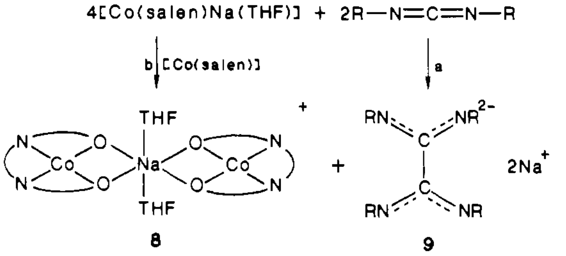
	Molecules A–C		
	molecule A	molecule B	molecule C
Co–O1	1.85 (2)	1.84 (2)	1.92 (2)
Co–O2	1.82 (2)	1.80 (2)	2.03 (1)
Co–N1	1.83 (2)	1.83 (3)	2.01 (1)
Co–N2	1.84 (2)	1.83 (3)	2.06 (2)
Co–O3			2.16 (1)
Co–O4			2.13 (2)
O1–C1	1.32 (2)	1.33 (3)	1.33 (3)
O2–C16	1.33 (2)	1.34 (3)	1.30 (3)
N1–C7	1.29 (3)	1.33 (5)	1.26 (4)
N1–C8	1.47 (4)	1.47 (4)	1.46 (4)
N2–C10	1.29 (3)	1.26 (5)	1.54 (3)
N2–C9	1.46 (4)	1.50 (5)	1.52 (3)
C6–C7	1.42 (3)	1.43 (3)	1.42 (3)
C10–C11	1.43 (3)	1.44 (4)	1.50 (2)
C8–C9	1.43 (5)	1.46 (6)	1.52 (4)
	Molecule C		
N2–C17	1.46 (3)	C10–C31	1.54 (4)
O3–C17	1.28 (4)	O4–C31	1.33 (4)
C17–C18	1.34 (3)	C31–C32	1.39 (4)
C18–C19	1.43 (3)	C32–C33	1.48 (3)
C18–C25	1.52 (2)	C32–C39	1.45 (4)
	Sodium and Solvent Atoms		
Na1–O2C	2.28 (2)	Na2–O3	2.29 (2)
Na1–O1B	2.27 (2)	Na2–O4	2.31 (2)
Na1–O2B	2.40 (2)	Na2–O1A	2.34 (2)
Na1–O4	2.30 (2)	Na2–O2A	2.23 (2)
Na1–O1C	2.69 (2)		

Table IV. Selected Interatomic Angles (deg)

	Molecules A–C		
	molecule A	molecule B	molecule C
O1–Co–O2	85.7 (6)	86.9 (6)	97.0 (6)
O1–Co–N2	177.1 (8)	176.0 (9)	172.7 (7)
O1–Co–N1	93.4 (7)	94.3 (9)	95.4 (8)
O2–Co–N2	94.6 (7)	93.6 (9)	90.2 (7)
O2–Co–N1	178.5 (8)	177.6 (9)	95.7 (7)
N1–Co–N2	86.3 (9)	85.3 (9)	82.3 (8)
Co–O1–C1	127 (1)	129 (1)	126 (1)
O1–C1–C6	121 (1)	123 (2)	123 (1)
C1–C6–C7	124 (2)	121 (2)	126 (2)
C6–C7–N1	122 (2)	126 (3)	128 (2)
N1–C8–C9	110 (2)	110 (3)	106 (2)
C8–C9–N2	109 (3)	105 (3)	110 (2)
C9–N2–C10	117 (2)	114 (3)	117 (2)
N2–C10–C11	122 (2)	122 (3)	110 (2)
C10–C11–C16	123 (2)	124 (2)	126 (2)
C11–C16–O2	124 (1)	120 (2)	121 (1)
C16–O2–Co	127 (1)	130 (1)	128 (1)
	Molecule C		
O1–Co–O3	109.8 (6)	C9–N2–C17	115 (2)
O1–Co–O4	98.3 (7)	N2–C17–C18	123 (3)
O2–Co–O3	149.4 (6)	N2–C17–O3	108 (2)
O2–Co–O4	81.4 (6)	O3–C17–C18	128 (3)
N1–Co–O3	96.1 (7)	C17–C18–C19	124 (2)
N1–Co–O4	166.3 (7)	C17–C18–C25	118 (2)
N2–Co–O3	63.7 (6)	C11–C10–C31	110 (2)
N2–Co–O4	84.3 (8)	C10–C31–O4	116 (2)
O3–Co–O4	80.5 (6)	C10–C31–C32	121 (2)
Co–N2–C9	105 (1)	O4–C31–C32	123 (2)
Co–N2–C10	103 (1)	C31–C32–C33	123 (2)
Co–N2–C17	92 (1)	C31–C32–C39	119 (2)
C10–N2–C17	119 (2)		
	Sodium and Solvent Atoms		
O1C–Na1–O2C	72.4 (6)	O2B–Na1–O1B	64.9 (6)
O1C–Na1–O4	75.3 (6)	O1A–Na2–O2A	66.1 (5)
O1C–Na1–O2B	160.6 (7)	O1A–Na2–O3	146.6 (8)
O1C–Na1–O1B	107.2 (7)	O1A–Na2–O4	119.5 (6)
O2C–Na1–O4	72.7 (6)	O2A–Na2–O3	120.5 (6)
O2C–Na1–O2B	127.1 (7)	O2A–Na2–O4	147.4 (8)
O2C–Na1–O1B	122.6 (7)	O3–Na2–O4	74.0 (6)
O4–Na1–O2B	107.8 (7)	Na1–O4–Na2	124.0 (7)
O4–Na1–O1B	164.7 (8)		

plausible pathway. The proposed structure for the labile adduct **7** is based mainly on the nature of its constituents along with the usual binding of sodium salts by the [Co(salen)] ligand.[22,29]

Carbodiimides have a symmetric cumulene structure without oxygen atoms and very probably with different electron-acceptor properties.[12] It was reported that carbodiimides undergo either the reductive disproportionation to dihydroguanidinium dianion and isocyanide in a process that seems to require the head-to-tail dimerization of the >C=NR functionality[33] or the reductive coupling to tetraalkyloxalamidinyl ligand.[7] Reaction of **1** with *p*-tolylcarbodiimide, *p*-TCD, was significantly slower than that with the other CO_2-like molecules. Reaction was carried out in refluxing THF and found to proceed with a 2:1 Co:*p*-TCD ratio. A green crystalline solid formed, **8**, which did not contain any organic residue, and the tetra-*p*-tolyloxalamidinyl dianion was produced, which was identified by the procedure given in the Experimental Section.



(5)

The same dianion formed from the reductive coupling of *p*-TCD was structurally characterized as a ligand bridging two titanium(III) centers.[7] The reductive coupling of *p*-TCD (pathway a in reaction 5) was promoted by cobalt(I) being oxidized to cobalt(II). [Co(salen)] was recovered, however, in the form of a mixed-valence Co(II)–Co(I) complex, **8**, having the structure shown. Pathway b (reaction 5) leading to **8** was proven by reacting an equimolar solution of **1** and [Co(salen)].[34] The isolation of **8**, instead of **3**, from reaction a is the consequence of its slowness compared with reaction b. Formation of such a mixed-valence complex has never been observed in the reaction of **1** with the other CO_2-like molecules. **8** is a neutral complex, in which the sodium cation is in a pseudooctahedral coordination provided by two [Co(salen)] units and two THF molecules, trans to each other.

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Complex **8** did not react, even under rather drastic conditions, with *p*-TCD, and we found that **8** cannot be considered as a source of **1**. Its synthesis, structure, and chemical behavior will be reported in a forthcoming paper.[34]

Conclusions

Complex **1** exemplifies the two main characteristics that have to be considered in studying the interaction of CO_2 with transition-metal complexes, namely the presence of acidic–basic sites in the structure and the possibility for the metal to transfer either one or two electrons. The assistance of the polydentate ligand is not only that of providing the correct electronic balance at the metal and having oxygen donor atoms for binding a second reactive site. In addition, it can provide reactive sites on which the reaction can actually occur. All these aspects have been emphasized by the results obtained in the reaction of the bifunctional complex **1** with different CO_2-like molecules, which maintain at least one of the main features of carbon dioxide.

Registry No. **1**, 71369-90-9; **4**, 67530-50-1; **6**, 104265-15-8; **8**, 104114-53-6; Co(salen), 14167-18-1; RNCO (R = 1-naphthyl), 86-84-0; PhNCO, 103-71-9; H_2salen, 94-93-9; DEKM, 609-09-6; methyl pyruvate, 600-22-6; dimethyl dimethyltartrate, 74956-34-6; 1,3-bis(1-naphthyl)urea, 607-56-7; 1,3-diphenylurea, 102-07-8; *p*-tolylcarbodiimide, 726-42-1; tetra-*p*-tolyloxalamidine, 75390-40-8; diphenylketene, 525-06-4.

Supplementary Material Available: Isotropic and anisotropic thermal parameters (Tables SI and SII) and equations of least-squares planes (Table SIII) for complex **8** (4 pages); tables of calculated and observed structure factors (11 pages). Ordering information is given on any current masthead page.

Notes

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Use of Bromine(I) Fluorosulfate for the Preparation of New *N*-Bromo Sulfonimides

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Bromine(I) fluorosulfate has been known for more than 2 decades.[1] The compound is a potent oxidizer with the bromine atom being one of the most electrophilic halogens available in a neutral compound. The high thermal stability of $BrOSO_2F$ (up to 150 °C) is rather unexpected in view of the low stability of BrCl and $BrONO_2$.[2] Addition reactions with olefins occur readily,[3,4] and a large number of covalent chlorides[5–7] are found to react with $BrOSO_2F$ in the following way:

$$MCl_n + n\mathrm{BrOSO_2F} \rightarrow M(OSO_2F)_n + n\mathrm{BrCl}$$

Direct reaction of $BrOSO_2F$ with metals has proved very useful for the preparation of fluorosulfates of the 4d and 5d transition series.[8–10]

With appropriate electron-withdrawing groups on nitrogen, *N*-halogen derivatives can approach the reactivity of some *O*-halogen compounds for chlorine and bromine as illustrated by the compounds $(CF_3SO_2)_2NCl$[11,12] and $(FSO_2)_2NCl$.[13] In the course of research with $(CF_3SO_2)_2NCl$,[12] we became increasingly interested in preparing the *N*-bromo analogue. It was obvious that the N–Br bond would be highly reactive and the compound would represent an extremely useful synthon. However, all attempts to prepare it by methods analogous to the preparation of $(CF_3SO_2)_2NCl$ failed. The reaction of Cl_2 on $(CF_3SO_2)_2NAg$ or $[(CF_3SO_2)_2N]_2Hg$ had produced the *N*-chloro derivative in very high yield.[12] However, Br_2 failed to react with either the silver(I) or mercury(II) derivatives. Reaction of Br_2 with $AgN(SO_2CF_3)_2$ in diethyl ether resulted in the immediate precipitation of AgBr but no *N*-bromo derivative could be isolated. Use of other solvents failed to provide a route to $(CF_3SO_2)_2NBr$.

Halogen fluorosulfates have been used effectively to generate other *O*-halogen derivatives by metathesis reactions with oxo salts, e.g.[14]

$$\mathrm{XOSO_2F + CsOClO_3 \rightarrow XOClO_3 + CsSO_3F}$$

$$\mathrm{X = Cl, Br}$$

To our knowledge, related reactions with imides had not been attempted, and we speculated that $BrOSO_2F$ might be an effective route to the desired *N*-bromo compound by reaction with $AgN(SO_2CF_3)_2$. This reaction was indeed successful but was complicated by side reactions.

$$\mathrm{AgN(SO_2CF_3)_2 \xrightarrow[22\ ^\circ C]{BrOSO_2F} \underset{42\%}{(CF_3SO_2)_2NBr} + AgSO_3F + Ag_3(SO_3F)_4 + Br_2}$$

The $AgSO_3F$ formed initially was further oxidized by $BrOSO_2F$ under the reaction conditions,[10] and the Br_2 formed was difficult to remove from the desired product. The use of alkali-metal salts was not attempted because of the possible complications due to complex formation between $BrOSO_2F$ and MSO_3F.[15,16] However, the reaction between $Hg[N(SO_2CF_3)_2]_2$ and $BrOSO_2F$ yielded the desired product in a very clean fashion according to

$$\mathrm{Hg[N(SO_2CF_3)_2]_2 + 2BrOSO_2F \xrightarrow[\sim 12\ h]{22\ ^\circ C,\ dark} \underset{92\%}{2(CF_3SO_2)_2NBr} + Hg(SO_3F)_2}$$

A slight excess of $Hg[N(SO_2CF_3)_2]_2$ over $BrOSO_2F$ is preferable so that no $BrOSO_2F$ is left unreacted; the latter cannot be readily separated from $(CF_3SO_2)_2NBr$.

To check the generality of the reaction as a new method for the preparation of electropositive *N*-bromo compounds, the previously unknown $Hg[N(SO_2F)_2]_2$ was prepared and found to be equally effective in forming the new compound $(FSO_2)_2NBr$.

$$\mathrm{Hg[N(SO_2F)_2]_2 + 2BrOSO_2F \xrightarrow[10\ h]{22\ ^\circ C,\ dark} \underset{92\%}{2(FSO_2)_2NBr} + Hg(SO_3F)_2}$$

These new *N*-bromo sulfonimides are pale yellow liquids at 22 °C, thermally stable in the dark. On exposure to room light at 22 °C in a Pyrex container, the liquids became orange, indicating the formation of bromine. Photolysis under these conditions is slow, resulting in only an ~5% loss of the samples after 3 days.

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