Organometallics 1991, 10, 3053–3062

# Substitution Reactions of Sodium Tetracarbonylcobaltate(1−) with Activated Alkenes. Synthesis, Characterization, and Reactions of Alkene Carbonyl Complexes, $Na[Co(CO)_{4-x}(alkene)_x]$ ($x$ = 1 and 2)†

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*Received December 18, 1990*

Reactions of $Na[Co(CO)_4]$ with the activated alkenes maleic anhydride (MA), dimethyl maleate (DM), and fumaronitrile (FN) in THF solution under photochemical conditions afford the monosubstituted products $Na[Co(CO)_3(alkene)]$. Under thermal conditions, in THF at reflux, reactions of $Na[Co(CO)_4]$ with MA, FN, and dimethyl fumarate (DF) each afford the disubstituted complexes $Na[Co(CO)_2(alkene)_2]$. In the corresponding reaction of $Na[Co(CO)_4]$ with DM, the alkene undergoes isomerization to give $Na[Co(CO)_2(DF)_2]$. Tetracyanoethylene (TCNE) and $Na[Co(CO)_4]$ react even at −60 to 0 °C to furnish $Na[Co(CO)_3(TCNE)]$. All of the aforementioned complexes were isolated as different THF solvates and characterized by a combination of elemental analysis and IR and $^1H$ and $^{13}C\{^1H\}$ NMR spectroscopies. They react with CO to yield one or both of $Na[Co(CO)_3(alkene)]$ and $Na[Co(CO)_4]$ and with other activated alkenes (alkene$_2$) to afford one or both of $Na[Co(CO)_2(alkene_1)(alkene_2)]$ and $Na[Co(CO)_{4-x}(alkene_2)_x]$ ($x$ = 1 or 2). The reactivities of the various alkenes toward $Na[Co(CO)_4]$ and of $Na[Co(CO)_3(alkene)]$ and $Na[Co(CO)_2(alkene)_2]$ toward CO and alkene$_2$ are compared. The structure of $Na[Co(CO)_2(DF)_2]\cdot THF$ was elucidated by a single-crystal X-ray diffraction analysis: space group $P\bar{1}$, with $a$ = 13.096 (2) Å, $b$ = 18.287 (2) Å, $c$ = 10.195 (2) Å, $\alpha$ = 90.49 (1)°, $\beta$ = 91.16 (1)°, $\gamma$ = 107.24 (1)°, and $Z$ = 4. The structure was solved and refined to $R$ = 0.102 and $R_w$ = 0.069. The compound is a dimer of $Na[Co(CO)_2(DF)_2]\cdot THF$, formed by interaction of each $Na^+$ ion with the oxygen atoms of two fumarate C=O groups from each $[Co(CO)_2(DF)_2]^-$ anion and with the oxygen atom of a THF molecule. The arrangement of these five oxygen donors around the $Na^+$ ion is trigonal bipyramidal, whereas the geometry of the two CO carbons and the midpoints of the two C=C bonds about the Co atom is approximately tetrahedral.

## Introduction

Salts of $[Co(CO)_4]^-$ had been regarded as inert to substitution of the carbonyl groups under thermal conditions.[1] We found, however, that in the presence of a proper counterion (e.g., $Li^+$, $Na^+$, or $K^+$) facile substitution reactions take place according to eqs 1–4 where R = Ph, $n$-Bu, OPh, and O-$n$-Bu; alkene$_1$ = maleic anhydride (MA) and dimethyl maleate (DM); and alkene$_2$ = maleic anhydride and dimethyl fumarate (DF).[2]

$$M[Co(CO)_4] + x\,^{13}CO \rightleftharpoons M[Co(^{13}CO)_x(CO)_{4-x}] + xCO \quad (1)$$

$$M[Co(CO)_4] + PR_3 \rightleftharpoons M[Co(CO)_3(PR_3)] + CO \quad (2)$$

$$M[Co(CO)_4] + alkene_1 \rightleftharpoons M[Co(CO)_3(alkene_1)] + CO \quad (3)$$

$$M[Co(CO)_4] + 2(alkene_2) \rightleftharpoons M[Co(CO)_2(alkene_2)_2] + 2CO \quad (4)$$

Ion-pairing phenomena[3] play an important role in these ligand replacement reactions of $[Co(CO)_4]^-$ because complexation of $M^+$ by crown ethers dramatically slows down the exchange with $^{13}CO$ and use of $PPN^+$ (PPN = bis(triphenylphosphine)nitrogen) or $[(n\text{-}Bu)_4N]^+$ as the counterion affords no observable reaction.

The complexes with alkene$_1$ and alkene$_2$ (eqs 3 and 4) are the first two members of a series of mixed alkenecarbonylcobaltate(1−) anions. By contrast, examples of analogous mixed $PMe_3$–[4] and $N_2$–alkenecobaltates(1−),[5] as well as tetraalkenecobaltates(1−),[5] are known. Moreover, $M[Co(CO)_3(alkene_1)]$ and $M[Co(CO)_2(alkene_2)_2]$ may be regarded as special cases of complexes $M[Co(CO)_3(X)(Y)]$ and $M[Co(CO)_2(X)_2(Y)_2]$, respectively, where X = Y = alkyl, if one adopts the cobaltacyclopropane formalism for the cobalt–alkene bonds. There are a number of anionic complexes of the type $[Co(CO)_3(X)(Y)]^-$, viz., those with X = alkyl and Y = alkoxycarbonyl,[6] X = acetyl or alkoxycarbonyl and Y = I,[7,8] X = Y = alkoxycarbonyl,[8] X = Y = trialkylsilyl,[9] X = Y = $Ph_3E$ (E = Ge, Sn, Pb),[10] and X = NO and Y = Br or I.[11] Such complexes may be involved as intermediates in stoichiometric and catalytic

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† A major part of this investigation was carried out at The Ohio State University during Ungváry's leave from the University of Veszprém.

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0276-7333/91/2310-3053$02.50/0

**Table I. Selected Spectroscopic Data for Complexes $Na[Co(CO)_3(alkene)]$, $Na[Co(CO)_2(alkene)_2]$, and $Na[Co(CO)_2(alkene_1)(alkene_2)]$**

| complex | IR,[a] $cm^{-1}$ | | $^1H$ NMR,[b] δ | $^{13}C\{^1H\}$ NMR,[b] δ |
|---|---|---|---|---|
| | ν(CN) | ν(CO) | *HC*=*CH* | C=C |
| $Na[Co(CO)_3(MA)]$ | | 2011 (s), 1927 (vs), 1795 (s), 1719 (s) | 3.94 | 41.2 |
| $Na[Co(CO)_3(DM)]$ | | 1997 (s), 1918 (vs), 1904 (vs), 1706 (s) | 3.20 | |
| $Na[Co(CO)_3(DF)]$ | | 1992 (m), 1910 (s), 1896 (s), 1662 (m) | | |
| $Na[Co(CO)_3(FN)]$ | 2206 (s) | 2004 (s), 1923 (vs) | 2.73 | 16.9 |
| $Na[Co(CO)_3(TCNE)]$ | 2220 (m) | 2043 (s), 1971 (vs) | | 14.0 |
| $Na[Co(CO)_2(MA)_2]$ | | 2021 (s), 1969 (s), 1799 (s), 1739 (s br) | 3.59 | 45.9 |
| $Na[Co(CO)_2(DF)_2]$ | | 1998 (s), 1946 (s), 1692 (s), 1657 (w) | 3.26 | 46.5 |
| $Na[Co(CO)_2(FN)_2]$ | 2208 (s) | 2021 (s), 1970 (s) | 2.50 | 22.5 |
| $Na[Co(CO)_2(MA)(FN)]$ | 2207 (m) | 2021 (s), 1969 (s), 1802 (m), 1731 (m br) | 3.52, 2.53 | |
| $Na[Co(CO)_2(MA)(TCNE)]$ | 2221 (m) | 2052 (s), 2010 (s), 1816 (m), 1744 (m br) | | |
| $Na[Co(CO)_2(FN)(TCNE)]$ | 2220 (s br) | 2056 (s), 2018 (s) | | |
| $Na[Co(CO)_4]$ | | 2003 (vw), 1899 (vs), 1886 (vs), 1855 (s)[c] | | |
| MA | | 1846 (w), 1794 (m), 1782 (s) | 6.41[d] | 137.0[e] |
| DM | | 1740 (m), 1733 (m) | 5.98[f] | 130.1[g] |
| DF | | 1731 (m), 1641 (vw) | 6.80[f] | 133.5[h] |
| FN | 2237 (m) | | 6.59 | 119.8[i] |
| TCNE | 2330 (vw), 2253 (m), 2245 (w sh), 2216 (w) | | | |

[a] In THF unless otherwise indicated. [b] In $CD_3OD$ at room temperature unless otherwise indicated. [c] Reference 25. [d] Sadtler standard NMR spectra, no. 10268, in $D_2O$. [e] Sadtler standard carbon-13 NMR spectra, no. 4427, in polysol. [f] In $C_6D_6$. [g] Sadtler standard carbon-13 NMR spectra, no. 164, in $CDCl_3$. [h] Sadtler standard carbon-13 NMR spectra, no. 229, in $CDCl_3$. [i] Sadtler standard carbon-13 NMR spectra, no. 4055, in polysol.

carbonylation reactions.[12] Recently, the possibility of the formation of $[Co(CO)_3(alkene)]^-$ was proposed based on the observation that alcoholic solutions of $[Co(CO)_4]^-$ catalyze the hydroformylation of alkenes under photochemical conditions.[13]

Herein we report in detail the chemistry represented by the reactions in eqs 3 and 4.

## Experimental Section

**General Procedures and Measurements.** All manipulations were performed under an atmosphere of Ar by using standard Schlenk techniques.[14] Reactions at CO pressures > 1 atm were conducted with ca. 5-mL samples in glass pressure vessels. Photochemical experiments were carried out in quartz tubes either with 16 254- or 350-nm lamps in a Rayonet Model RPR-100 reactor or with a 125-W medium-pressure mercury lamp. Gas chromatography of volatile compounds was performed on a Hewlett-Packard Model 5830A analytical instrument using a 30-m glass capillary column with 0.20-μm SP 2330 stationary phase. Elemental analyses for C and H were done by Galbraith Laboratories, Inc., Knoxville, TN. Cobalt was analyzed[15] after oxidation with a mixture of $H_2O_2$ and $HNO_3$. Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 283B or a Carl Zeiss Jena IR 75 spectrophotometer in 0.05-mm solution cells with $CaF_2$ windows and were calibrated with polystyrene. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker AM-250 or a Varian CFT 20 spectrometer, and the chemical shifts are given in ppm downfield from the internal standard $Me_4Si$.

**Materials.** Diethyl ether, pentane, and THF were freshly distilled from Na and benzophenone. Solvents for NMR experiments were distilled under an atmosphere of Ar. $Co_2(CO)_8$ was recrystallized first from $CH_2Cl_2$ and then from heptane under an atmosphere of CO. From it, $Na[Co(CO)_4]$ was prepared by using 1.5% Na/Hg in diethyl ether, and the resulting 0.07 M solution was evaporated to dryness under vacuum. Maleic anhydride (MA), fumaronitrile (FN), and tetracyanoethylene (TCNE) were purchased from Fluka AG and used after sublimation. Dimethyl maleate (DM) was prepared from maleic anhydride and methanol and distilled twice under reduced pressure. Dimethyl fumarate (DF) was synthesized from fumaric acid and methanol and recrystallized twice, first from methanol and then from heptane. Solutions of $K[Co(CO)_4]$ and $Li[Co(CO)_4]$ were prepared from $Co_2(CO)_8$ and potassium and lithium, respectively, in THF at 0 °C. A solution of $HCo(CO)_4$ in octane was obtained by treatment of $Co_2(CO)_8$ with dimethylformamide and concentrated hydrochloric acid according to a literature procedure.[16]

**Preparation of $Na[Co(CO)_3(MA)]$. Method A.** To a solution of $Na[Co(CO)_4]$, prepared from 920 mg (4.74 mmol) of $Na[Co(CO)_4]$ and 30 mL of THF, a solution of maleic anhydride (465 mg, 4.74 mmol) in 30 mL of THF was added at −10 °C, and the mixture was irradiated for 6 h at room temperature with 254-nm lamps in a Rayonet reactor. (With a 125-W medium-pressure mercury lamp, a 36-h irradiation period was necessary to achieve a complete conversion.) Concentration under vacuum of the clear reddish yellow solution gave a dark oil. After trituration with 10 mL of 9:1 pentane–THF at 0 °C, the oil afforded 1.84 g (94% yield) of an orange-brown crystalline solid, $Na[Co(CO)_3(MA)]\cdot 2THF$: $^1H$ NMR ($CD_3OD$) δ 3.94 (s, 2 H, CH), 3.63 (m, 8 H, $OCH_2$), 1.77 (m, 8 H, $CH_2$); $^{13}C\{^1H\}$ NMR ($CD_3OD$) δ 177.27 (COO), 68.78 ($OCH_2$), 41.22 (CH), 26.38 ($CH_2$). IR data for this and other new cobaltate(1−) complexes are presented in Table I.

**Method B.** To a solution of $Na[Co(CO)_4]$ (625 mg, 3.22 mmol) in THF (30 mL), a solution of $Na[Co(CO)_2(MA)_2]\cdot THF$ (1.309 g, 3.22 mmol) in THF (30 mL) was added, and the mixture was irradiated with a 125-W medium-pressure mercury lamp at 12 °C until complete conversion to $Na[Co(CO)_3(MA)]$ was noted by IR spectroscopy (ca. 4 days). The same isolation procedure as above gave 1.20 g (91% yield) of $Na[Co(CO)_3(MA)]\cdot 2THF$.

**Preparation of $Na[Co(CO)_2(MA)_2]$.** A solution of maleic anhydride (1.51 g, 15.4 mmol) in THF (30 mL) was added to $Na[Co(CO)_4]$ (1.36 g, 7.0 mmol) in THF (40 mL) at room temperature. Gas evolution commenced immediately, and the color of the resulting solution became cherry red. Upon refluxing the reaction mixture for 30 min, gas evolution ceased. Heating was continued for an additional 30 min as a slow stream of Ar was passed through the mixture. Filtration at room temperature gave 0.26 g of a brick-red THF-insoluble powder. The filtrate was evaporated to dryness under reduced pressure, and the resulting

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red solid was washed with 10 mL of 9:1 pentane–THF. The yield of $Na[Co(CO)_2(MA)_2]\cdot THF$ was 2.47 g (87%): $^1H$ NMR ($CD_3OD$) $\delta$ 3.63 (m, 4 H, $OCH_2$), 3.59 (s, 4 H, CH), 1.77 (m, 4 H, $CH_2$); $^{13}C\{^1H\}$ NMR ($CD_3OD$) $\delta$ 176.01 (COO), 68.95 ($OCH_2$), 45.87 (CH), 26.69 ($CH_2$). Anal. Calcd for $C_{14}H_{12}CoNaO_9$: C, 41.38; H, 2.95; Co, 14.53. Found: C, 41.72; H, 3.03; Co, 14.27.

**Reaction of $Na[Co(CO)_2(MA)_2]$ with CO.** A stirred 0.1 M solution of $Na[Co(CO)_2(MA)_2]\cdot THF$ in THF was maintained under 1 atm of CO at room temperature, and the change in its composition was followed by IR spectroscopy. A slow formation of $Na[Co(CO)_3(MA)]$ and free maleic anhydride was observed by their characteristic absorptions of 1927 and 1782 $cm^{-1}$, respectively. The conversion was incomplete after 1 day.

When the foregoing reaction was carried out at 15 atm of CO, a 1:2:1:4 mixture of $Na[Co(CO)_2(MA)_2]$, $Na[Co(CO)_3(MA)]$, $Na[Co(CO)_4]$, and free maleic anhydride was observed after 40 min by IR spectroscopy.

**Reaction of $Na[Co(CO)_3(MA)]$ with Fumaronitrile.** To a solution of $Na[Co(CO)_3(MA)]\cdot 2THF$ (41 mg, 0.1 mmol) in THF (1 mL), solid fumaronitrile (7.8 mg, 0.1 mmol) was added and dissolved at room temperature under Ar. In 12 h, quantitative formation of a new complex was noted by IR spectroscopy ($\nu$(CO) 2207 (m), 2021 (s), 1969 (s), 1802 (m), 1731 (m br) $cm^{-1}$). The solvent was then removed under reduced pressure, and the residue was dissolved in $CD_3OD$. The $^1H$ NMR spectrum of this solution showed broad signals of the olefinic protons of coordinated maleic anhydride and fumaronitrile at $\delta$ 3.52 and 2.53, respectively, in a 1:1 ratio. The same spectroscopic results were obtained when $Na[Co(CO)_3(FN)]$ reacted with maleic anhydride under comparable conditions.

**Reaction of $Na[Co(CO)_3(MA)]$ with Tetracyanoethylene.** To a solution of $Na[Co(CO)_3(MA)]\cdot 2THF$ (82 mg, 0.2 mmol) in THF (2 mL), a solution of tetracyanoethylene (19.2 mg, 0.15 mmol) in THF (0.4 mL) was added at –40 °C. After the mixture had been stirred with warming to 0 °C for 10 min, the IR spectrum (0 °C) showed the presence of a new dicarbonyl complex ($\nu$(CO) 2052 (s), 2010 (s), 1816 (s), 1742 (s br) $cm^{-1}$), $Na[Co(CO)_3(TCNE)]$, and unreacted $Na[Co(CO)_3(MA)]$ in a roughly 1:1:1 ratio. The spectrum revealed also the presence of free maleic anhydride (1846 (w), 1794 (m), 1782 (s) $cm^{-1}$).

**Preparation of $Na[Co(CO)_3(DM)]$.** A solution of $Na[Co(CO)_4]$ (590 mg, 3.0 mmol) and dimethyl maleate (0.36 mL, 2.9 mmol) in freshly distilled THF (60 mL) was irradiated with a 125-W medium-pressure mercury lamp for 12 h. During the irradiation, Ar was passed through the reaction mixture, which was maintained at ca. 12 °C by cooling with tap water. The IR spectrum of the resulting red-orange solution showed an essentially complete conversion of the reactants to $Na[Co(CO)_3(DM)]$. Concentration of the solution to ca. 4 mL under reduced pressure at 0 °C afforded a slurry of crystals, which were filtered off, washed with 1:5 THF–pentane, and dried under vacuum below 0 °C. The yield of orange crystals of $Na[Co(CO)_3(DM)]\cdot 3THF$ was 930 mg (59%): mp ~ 25 °C; $^1H$ NMR ($CD_3OD$) $\delta$ 3.63 (m, 12 H, $OCH_2$), 3.48 (s, 6 H, Me), 3.20 (s, 2 H, CH), 1.77 (m, 12 H, $CH_2$); $^1H$ NMR ($CD_2Cl_2$) $\delta$ 3.92 (d, $J$ = 15 Hz, 1 H, CH), 3.68 (m, 12 H, $CH_2$), 3.60 (s, 3 H, Me), 3.35 (s, 3 H, Me), 2.77 (d, $J$ = 15 Hz, 1 H, CH), 1.82 (m, 12 H, $CH_2$); $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) $\delta$ 177.1 (COO), 176.2 (COO), 67.7 ($CH_2$), 51.0 (Me), 50.2 (Me), 48.8 (CH), 41.5 (CH), 25.4 ($CH_2$). Anal. Calcd for $C_{21}H_{32}CoNaO_4$: Co, 11.20. Found: Co, 11.51.

**Reaction of $Na[Co(CO)_3(DM)]$ with CO.** A stirred 0.05 M red-orange solution of $Na[Co(CO)_3(DM)]\cdot 3THF$ in THF was maintained under 1 atm of CO at room temperature. After 5 min, the solution became colorless, and the IR spectrum showed a complete conversion to $Na[Co(CO)_4]$ and free dimethyl maleate.

**Attempted Preparation of $Na[Co(CO)_2(DM)_2]$.** A THF solution (16 mL) of $Na[Co(CO)_4]$ (1.24 g, 6.4 mmol) and dimethyl maleate (2.30 g, 16 mmol) was heated at reflux under Ar for 8 h. The resulting slurry of orange crystals was filtered, and the collected solid was washed with THF (2 × 3 mL) and dried under vacuum. The product (2.3 g, 72% yield) is identical with $Na[Co(CO)_2(DF)_2]\cdot THF$ by IR and $^1H$ NMR spectroscopies. The mother liquor was reacted first with CO and then with air to remove all cobalt from the solution. A gas chromatographic analysis of this solution showed the presence of dimethyl fumarate and dimethyl maleate in a 2:1 molar ratio. A similar treatment of a THF solution of the crystalline orange product revealed by gas chromatography the presence of only dimethyl fumarate.

**Reaction of $Na[Co(CO)_4]$ with Dimethyl Fumarate.** The volume of CO evolved in the title reaction was measured in a thermostated gasometric apparatus[17] under Ar. Thus, a 0.06 M $Na[Co(CO)_4]$ and 0.24 M dimethyl fumarate solution in THF (5 mL) gave off 0.54 mmol of gas in 24 h at 65 °C, corresponding to 1.8 $CO/Na[Co(CO)_4]$. The IR spectrum of the reaction mixture showed the presence of $Na[Co(CO)_2(DF)_2]$ as the only complex, in addition to a small amount of unreacted $Na[Co(CO)_4]$.

**Preparation of $Na[Co(CO)_2(DF)_2]$.** A THF solution (30 mL) of $Na[Co(CO)_4]$ (1.65 g, 8.5 mmol) and dimethyl fumarate (2.55 g, 17.7 mmol) was heated at reflux under Ar for 24 h. Concentration of the resulting mixture to 15 mL and collection of the precipitate by filtration at 25 °C afforded 3.98 g (94% yield) of orange crystals of $Na[Co(CO)_2(DF)_2]\cdot THF$: $^1H$ NMR ($CD_3OD$, 30 °C) $\delta$ 3.63 (m, 4 H, $OCH_2$), 3.46 (s, 12 H, Me), 3.26 (s, 4 H, CH), 1.77 (m, 4 H, $CH_2$); $^1H$ NMR ($CDCl_3$) $\delta$ 3.93 (d, $J$ = 9.4 Hz, 2 H, CH), 3.76 (t, 4 H, $CH_2$), 3.59 (s, 6 H, Me), 3.47 (s, 6 H, Me), 2.73 (d, $J$ = 9.7 Hz, 2 H, CH), 1.84 (q, 4 H, $CH_2$); $^{13}C\{^1H\}$ NMR ($CD_3OD$, 36 °C) $\delta$ 178.6 (COO), 68.8 ($OCH_2$), 50.1 (Me), 46.5 (CH), 26.7 ($CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 210.1 (CO), 177.9 (COO), 177.5 (COO), 67.9 ($CH_2$), 50.9 (Me), 50.3 (Me), 48.6 (CH), 41.5 (CH), 25.6 ($CH_2$). Anal. Calcd for $C_{18}H_{24}CoNaO_{11}$: C, 43.38; H, 4.85; Co, 11.82. Found: C, 42.91; H, 4.83; Co, 11.60.

**Reaction of $Na[Co(CO)_2(DF)_2]$ with CO.** A stirred THF solution (5 mL) of $Na[Co(CO)_2(DF)_2]\cdot THF$ (0.05 M, 0.25 mmol) in a thermostated (25 °C) reaction flask was connected to a gas buret filled with CO-saturated THF and maintained at 25 °C. Absorption of CO commenced immediately and practically ceased after the uptake of 0.47 mmol in 4 h to give an almost colorless solution. The IR spectrum of this solution showed the presence of $Na[Co(CO)_4]$ ($\nu$(CO) 1890 (vs br), 1859 (s) $cm^{-1}$) and free dimethyl fumarate (1731 (s), 1641 (w) $cm^{-1}$). The concentration of CO in solution was calculated from $P_{CO}$ and the solubility of CO in THF.[18] The initial rate of CO uptake was calculated from the change of gas volume with time by using points below 10% conversion.

**Attempted Preparation of $Li[Co(CO)_3(DM)]$.** A THF solution (40 mL) of $Li[Co(CO)_4]$ (ca. 2.1 mmol) and dimethyl maleate (0.26 mL, 2.1 mmol) was irradiated with 254-nm lamps in a Rayonet reactor for 41 h under a continuous purge of Ar. The IR spectrum of the resulting dark orange solution showed a virtually complete conversion of the reactants to $Li[Co(CO)_3(DM)]$ ($\nu$(CO) 2002 (s), 1920 (vs br), 1693 (s br) $cm^{-1}$). Concentration of the solution to 5 mL and crystallization at –78 °C afforded 453 mg of a pale red solid, which turned into a brown–orange, sparingly soluble (in THF) material at room temperature. The IR spectrum of the latter (in THF) showed $\nu$(CO) bands of $Li[Co(CO)_2(DM)_2]$ at 2006 (s), 1957 (s), and 1680 (s) $cm^{-1}$ and of $Li[Co(CO)_4]$ at 1890 (vs) $cm^{-1}$.

**Preparation of $Li[Co(CO)_2(DF)_2]$.** A solution of $Li[Co(CO)_4]$ (748 mg, 4.2 mmol) and dimethyl fumarate (1.22 g, 8.5 mmol) in THF (37 mL) was heated at reflux under Ar for 24 h. The resulting mixture was concentrated to ca. 8 mL, and the precipitate was filtered off at room temperature to yield 1.12 g (65%) of $Li[Co(CO)_2(DF)_2]$ as a light orange, air-sensitive powder sparingly soluble in THF but very soluble in $H_2O$: IR (THF) $\nu$(CO) 2006 (s br), 1957 (s br), 1680 (s br) $cm^{-1}$; $^1H$ NMR ($D_2O$) $\delta$ 3.52 (s, 12 H, Me), 3.30 (s, 4 H, CH); $^{13}C\{^1H\}$ NMR ($D_2O$) $\delta$ 178.5 (COO), 51.5 (Me), 45.1 (CH). Anal. Calcd for $C_{14}H_{16}CoLiO_{10}$: Co, 14.38. Found: Co, 14.05.

**Reaction of $Na[Co(CO)_2(DF)_2]$ with $HCo(CO)_4$.** To a solution of $Na[Co(CO)_2(DF)_2]\cdot THF$ (42 mg, 0.08 mmol) in THF (2 mL), a solution of $HCo(CO)_4$ (0.3 mL, 0.53 M, 0.16 mmol) in octane was added at –20 °C under Ar. In 10 min, the orange color of the reaction mixture changed to wine red. The IR spectrum showed the presence of $[Co_3(CO)_{10}]^-$,[19] dimethyl succinate, and dimethyl fumarate by their characteristic bands at 2001, 1742, and 1731 $cm^{-1}$, respectively. (When the reaction was conducted

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(17) Ungváry, F.; Sisak, A. *Transition Met. Chem.* **1984**, *9*, 265.

(18) Payne, M. W.; Leussing, D. L.; Shore, S. G. *J. Am. Chem. Soc.* **1987**, *109*, 617.

(19) Fieldhouse, S. A.; Freeland, B. H.; Mann, C. D. M.; O'Brien, R. J. *Chem. Commun.* **1970**, 181.

under CO, $Co_2(CO)_8$ and $[Co(CO)_4]^-$ were formed instead of $[Co_3(CO)_{10}]^-$.) The composition of the organic products was determined by quantitative gas chromatography on a sample evaporated to dryness in air and dissolved in octane containing pentadecane internal standard. This analysis showed the formation of 0.065 mmol of dimethyl fumarate and 0.072 mmol of dimethyl succinate.

**Preparation of Na[Co(CO)$_3$(FN)].** A solution of Na[Co(CO)$_4$] (1.26 g, 6.5 mmol) and fumaronitrile (510 mg, 6.5 mmol) in THF (60 mL) was irradiated with a 125-W medium-pressure mercury lamp at 10 °C for 50 h under a continuous purge of Ar. The resulting light yellow solution showed (IR spectroscopy) an essentially complete conversion to Na[Co(CO)$_3$(FN)], with trace amounts of Na[Co(CO)$_4$] and Na[Co(CO)$_2$(FN)$_2$] also present. Concentration of this solution under reduced pressure afforded a yellow oil (2.5 g), which solidified upon storage for ca. 12 h at room temperature: $^1$H NMR ($CD_3OD$) $\delta$ 3.63 (m, $OCH_2$), 2.73 (s, CH), 1.77 (m, $CH_2$); $^{13}C\{^1H\}$ NMR ($CD_3OD$) $\delta$ 125.0 (CN), 68.7 ($OCH_2$), 26.3 ($CH_2$), 16.9 (CH).

**Preparation of Na[Co(CO)$_2$(FN)$_2$].** A solution of fumaronitrile (944 mg, 12.1 mmol) in THF (10 mL) was added to Na[Co(CO)$_4$] (970 mg, 5.0 mmol) in THF (10 mL), and the mixture was heated at reflux for 2 h under a slow stream of Ar. Filtration of the resulting yellow solution and concentration of the filtrate to ca. 2 mL afforded a yellow oil, which solidified upon trituration with 10 mL of pentane at −20 °C. The yield of Na[Co(CO)$_2$(FN)$_2$]·THF, a dark yellow powder, was 1.53 g (84%): $^1$H NMR ($CD_3OD$) $\delta$ 3.63 (m, 4 H, $OCH_2$), 2.50 (s, 4 H, CH), 1.77 (m, 4 H, $CH_2$); $^{13}C\{^1H\}$ NMR ($CD_3OD$) $\delta$ 126.0 (CN), 69.6 ($OCH_2$), 27.3 ($CH_2$), 22.5 (CH). Anal. Calcd for $C_{14}H_{12}CoNaO_3N_4$: Co, 16.12. Found: Co, 16.05.

**Reaction of Na[Co(CO)$_3$(FN)] with Tetracyanoethylene.** To a solution of Na[Co(CO)$_3$(FN)] (49 mg, 0.2 mmol) in THF (2 mL), a solution of tetracyanoethylene (12.8 mg, 0.1 mmol) in THF (0.25 mL) was added at −40 °C. After the mixture had been stirred with warming to 0 °C for 10 min, the IR spectrum (0 °C) showed the presence of a new complex ($\nu$(CO) 2056 (s), 2018 (s) cm$^{-1}$), which decomposed in solution at room temperature to Na[Co(CO)$_3$(TCNE)] and an unidentified precipitate.

**Prepartion of Na[Co(CO)$_3$(TCNE)].** To a cold (−60 °C) stirred solution of Na[Co(CO)$_4$] (970 mg, 5 mmol) in THF (20 mL), a solution of tetracyanoethylene (640 mg, 5 mmol) in THF (40 mL) was added, and the resulting dark yellow mixture was allowed to warm to 0 °C in 2 h. The reaction solution at 0 °C was then concentrated to ca. 20 mL, and the precipitate was filtered off to give 220 mg of a brown powder insoluble in methanol: IR (KBr) 2970 (w), 2870 (w), 2225 (m), 2150 (sh), 2100 (vs), 2020 (m), 1600 (s br) cm$^{-1}$. The solvent was removed from the filtrate at <0 °C, and the resulting dark yellow oil was triturated at −20 °C with 10 mL of 9:1 pentane–THF to yield 1.42 g (55%) of brown microcrystalline Na[Co(CO)$_3$(TCNE)]·3THF: $^1$H NMR ($CD_3OD$) $\delta$ 3.63 (m, $OCH_2$), 1.77 (m, $CH_2$); $^{13}C\{^1H\}$ NMR ($CD_3OD$) $\delta$ 118.4 (CN), 68.8 ($OCH_2$), 26.4 ($CH_2$), 14.0 (C=). Anal. Calcd for $C_{29}H_{24}CoNaO_6N_4$: Co, 11.57. Found: Co, 11.87.

**Crystallographic Analysis of Na[Co(CO)$_2$(DF)$_2$]·THF.** Recrystallization of the title complex from THF gave orange rectangular rods that were suitable for X-ray diffraction. The crystal used for data collection was mounted inside a glass capillary filled with argon. Preliminary examination of the diffraction pattern on a Syntex (Nicolet) P$\bar{1}$ diffractometer indicated a Laue symmetry of $\bar{1}$, which restricts the choice of space group to P1 or P$\bar{1}$. Unit cell constants were determined at ambient temperature by the least-squares fit of the diffractometer setting angles for 25 reflections in the 2$\theta$ range 17–26° with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$(K$\bar{\alpha}$) = 0.71069 Å).

Intensities were measured by the $\theta$–2$\theta$ scan method out to a maximum 2$\theta$ value of 43°. A total of 5379 unique intensities was measured, with 2313 of these satisfying the condition $F_o^2 > 3\sigma(F_o^2)$. Corrections for Lorentz and polarization effects were made in the usual manner and the data put onto an approximately absolute scale by means of a Wilson plot.[20] No correction for absorption was made since the long dimension of the crystal was roughly parallel with the $\phi$ axis of the goniometer, and the cross section of the crystal perpendicular to this long dimension is approximately square. Six standard reflections were measured after every 100 reflections during data collection and indicated a small amount of crystal decomposition during data collection. This decomposition was judged to be so small, from 2 to 4%, as to be negligible. Further crystallographic details are given in Table II.

**Table II. Crystal Data and Data Collection and Refinement Details for Na[Co(CO)$_2$(DF)$_2$]•THF**

| | |
|---|---|
| Crystal Data | |
| formula | $C_{36}H_{48}Co_2Na_2O_{22}$ |
| fw | 996.6 |
| space group | P$\bar{1}$ |
| *a*, Å | 13.096 (2) |
| *b*, Å | 18.287 (2) |
| *c*, Å | 10.195 (2) |
| $\alpha$, deg | 90.49 (1) |
| $\beta$, deg | 91.16 (1) |
| $\gamma$, deg | 107.24 (1) |
| *V*, Å$^3$ | 2331 |
| *Z* | 2 |
| $D_{calcd}$, g cm$^{-3}$ | 1.42 |
| cryst size, mm | 0.16 × 0.19 × 0.34 |
| linear abs coeff, cm$^{-1}$ | 8.01 |
| Data Collection and Refinement | |
| temp, °C | 19 |
| radiatn | Mo K$\alpha$, graphite monochromated |
| 2$\theta$ limits, deg | 4–43 |
| scan speed, deg min$^{-1}$ in 2$\theta$ | 2.0–24.0 |
| background time/scan time | 0.5 |
| scan range, deg | (K$\alpha_1$ −1.0) to (K$\alpha_2$ +1.0) |
| data collected | $+h,\pm k,\pm l$ |
| no. of unique data | 5379 |
| no. of unique data ($F_o^2 > \sigma(F_o^2)$) | 3515 |
| no. of variables | 488 |
| $R(F)^a$ | 0.102 |
| $R_w(F)^b$ | 0.069 |
| error in obsn of unit wt, *e* | 1.93 |
| *R* (on *F* for $F_o^2 > 3\sigma(F_o^2)$) | 0.064 |

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, with $w = 1/\sigma^2(F_o)$.

In space group P$\bar{1}$, the positions of the two independent Co atoms in the asymmetric unit were located by the Patterson method. These two atoms were then used for phasing the data in DIRDIF[21] with the result that both cobalt complexes, the two Na$^+$ ions, and the two THF molecules were clearly evident in the resulting electron density map. The SHELX-76 package was used for all full-matrix least-squares refinements.[22] The asymmetric unit consists of two cobalt complexes, designated as A and B, and two Na$^+$ ions with two THF molecules, also designated as A and B. During the course of least-squares refinement, it was necessary to restrict the C14B atom of one of the fumarate ligands of complex B to an isotropic temperature factor. Several attempts were made to refine this atom anisotropically; each time a set of nonpositive definite thermal parameters was obtained. The atoms of the THF molecules were also refined with isotropic thermal parameters in order to keep the number of variables used in the least-squares refinement at a manageable level. Reasonable positions for the hydrogen atoms bonded to the C=C portions of the DF ligands were located on a difference electron density map. These eight hydrogen atoms were included in the model and their positional parameters were allowed to refine, but their

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(20) Data reduction was performed with the CRYM crystallographic computing package: Duchamp, D. J.; Trus, B. L.; Westphal, B. J. California Institute of Technology, Pasadena, 1964; modified by G. G. Christoph at The Ohio State University, Columbus.

(21) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; Van den Hark, T. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V.; Bruins Slot, H. J.; Haltiwanger, R. C. *DIRDIF: Direct Methods for Difference Structures*; Crystallography Laboratory, University of Nijmegen: The Netherlands, 1983.

(22) Sheldrick, G. M. *SHELX-76. Program for Crystal Structure Determination*; University Chemical Laboratory: Cambridge, England, 1976. A modified version of SHELX-76, redimensioned for a maximum number of 500 variables, was used for the final least-squares cycles: Rabinovich, D.; Reich, K. Department of Structural Chemistry, Weizmann Institute of Science, Rehovot, Israel, 1979.

**Table III. Positional and Equivalent Isotropic Thermal Parameters for $Na[Co(CO)_2(DF)_2]\bullet THF$**

| atom | $x^a$ | $y$ | $z$ | $B_{eq}{}^b$ or $B$, Å$^2$ |
|---|---|---|---|---|
| Co1A | 0.9455 (1) | 0.2409 (1) | 0.8550 (2) | 4.33 (9) |
| C1A | 0.858 (1) | 0.2909 (8) | 0.913 (1) | 5.1 (7) |
| O1A | 0.8010 (8) | 0.3243 (6) | 0.948 (1) | 8.1 (7) |
| C2A | 0.862 (1) | 0.1920 (9) | 0.726 (2) | 6.2 (9) |
| O2A | 0.8007 (9) | 0.1610 (7) | 0.644 (1) | 9.6 (7) |
| C3A | 1.029 (1) | 0.1712 (8) | 0.431 (1) | 7.2 (8) |
| O3A | 1.0382 (7) | 0.2255 (5) | 0.543 (1) | 6.9 (6) |
| C4A | 1.090 (1) | 0.2121 (8) | 0.650 (2) | 4.9 (8) |
| O4A | 1.1358 (7) | 0.1624 (5) | 0.6489 (8) | 5.8 (5) |
| C5A | 1.093 (1) | 0.2592 (8) | 0.768 (1) | 4.5 (7) |
| C6A | 1.061 (1) | 0.3254 (9) | 0.769 (2) | 5.5 (8) |
| C7A | 1.112 (1) | 0.3893 (9) | 0.864 (2) | 5.1 (8) |
| O5A | 1.1704 (7) | 0.3858 (5) | 0.953 (1) | 6.2 (5) |
| O6A | 1.0835 (8) | 0.4511 (7) | 0.833 (1) | 7.8 (6) |
| C8A | 1.130 (1) | 0.5198 (9) | 0.920 (2) | 9.4 (10) |
| C9A | 0.939 (1) | –0.0210 (8) | 0.779 (1) | 7.9 (9) |
| O7A | 0.9008 (7) | 0.0374 (6) | 0.853 (1) | 6.5 (5) |
| C10A | 0.977 (1) | 0.095 (1) | 0.915 (2) | 5.5 (8) |
| O8A | 1.0719 (8) | 0.1002 (5) | 0.9169 (8) | 5.7 (5) |
| C11A | 0.932 (1) | 0.1526 (8) | 0.979 (1) | 4.3 (6) |
| C12A | 0.999 (1) | 0.2184 (9) | 1.036 (2) | 4.5 (7) |
| C13A | 0.969 (1) | 0.2611 (9) | 1.145 (1) | 4.5 (8) |
| O9A | 1.0294 (7) | 0.3193 (6) | 1.1955 (9) | 6.1 (5) |
| O10A | 0.8690 (7) | 0.2320 (5) | 1.1848 (9) | 5.6 (5) |
| C14A | 0.831 (1) | 0.2746 (8) | 1.283 (1) | 7.1 (8) |
| Na1A | 1.2090 (4) | 0.3809 (3) | 1.1758 (5) | 5.6 (3) |
| Co1B | 1.4849 (1) | 0.2534 (1) | 1.1386 (2) | 4.31 (9) |
| C1B | 1.561 (1) | 0.1932 (9) | 1.103 (1) | 5.7 (8) |
| O1B | 1.6151 (8) | 0.1562 (6) | 1.072 (1) | 8.0 (6) |
| C2B | 1.570 (1) | 0.3118 (8) | 1.258 (2) | 6.1 (8) |
| O2B | 1.6235 (9) | 0.3486 (6) | 1.340 (1) | 9.7 (7) |
| C3B | 1.519 (1) | 0.1954 (9) | 0.671 (1) | 8.8 (9) |
| O3B | 1.5496 (7) | 0.2499 (6) | 0.785 (1) | 7.0 (6) |
| C4B | 1.467 (1) | 0.2599 (7) | 0.853 (1) | 4.4 (7) |
| O4B | 1.3746 (7) | 0.2274 (5) | 0.8221 (8) | 5.9 (5) |
| C5B | 1.505 (1) | 0.3113 (8) | 0.965 (1) | 4.9 (7) |
| C6B | 1.432 (1) | 0.3344 (7) | 1.041 (1) | 4.6 (7) |
| C7B | 1.459 (1) | 0.4097 (9) | 1.112 (1) | 5.0 (8) |
| O5B | 1.3912 (7) | 0.4332 (5) | 1.1636 (9) | 6.1 (5) |
| O6B | 1.5626 (7) | 0.4506 (5) | 1.1190 (9) | 6.2 (5) |
| C8B | 1.592 (1) | 0.5209 (7) | 1.204 (1) | 7.5 (8) |
| C9B | 1.381 (1) | –0.0210 (7) | 1.129 (1) | 6.2 (8) |
| O7B | 1.3764 (7) | 0.0545 (5) | 1.1758 (8) | 5.5 (5) |
| C10B | 1.340 (1) | 0.0965 (8) | 1.088 (2) | 4.6 (7) |
| O8B | 1.3105 (7) | 0.0707 (5) | 0.9759 (9) | 5.9 (5) |
| C11B | 1.337 (1) | 0.1712 (9) | 1.136 (2) | 5.1 (8) |
| C12B | 1.367 (1) | 0.1976 (8) | 1.261 (1) | 5.1 (7) |
| C13B | 1.323 (1) | 0.2562 (9) | 1.320 (2) | 5.4 (8) |
| O9B | 1.2562 (7) | 0.2819 (5) | 1.2722 (9) | 6.2 (5) |
| O10B | 1.3615 (8) | 0.2732 (5) | 1.443 (1) | 7.1 (6) |
| C14B | 1.327 (1) | 0.3346 (8) | 1.514 (1) | 7.6 (4)$^c$ |
| Na1B | 1.2297 (4) | 0.1184 (3) | 0.8099 (5) | 5.3 (3) |
| O11A | 1.2055 (9) | 0.4814 (6) | 1.312 (1) | 10.2 (3)$^c$ |
| C15A | 1.281 (2) | 0.556 (1) | 1.317 (2) | 14.2 (7)$^c$ |
| C16A | 1.226 (2) | 0.604 (1) | 1.378 (2) | 12.6 (6)$^c$ |
| C17A | 1.146 (2) | 0.554 (1) | 1.450 (2) | 16.1 (8)$^c$ |
| C18A | 1.133 (2) | 0.474 (1) | 1.414 (2) | 18.0 (9)$^c$ |
| O11B | 1.2419 (7) | 0.0203 (5) | 0.6730 (9) | 8.0 (2)$^c$ |
| C15B | 1.280 (1) | –0.0418 (8) | 0.715 (2) | 8.9 (4)$^c$ |
| C16B | 1.352 (1) | –0.0541 (9) | 0.617 (2) | 11.0 (5)$^c$ |
| C17B | 1.352 (1) | 0.002 (1) | 0.515 (2) | 10.5 (5)$^c$ |
| C18B | 1.259 (1) | 0.0296 (8) | 0.533 (1) | 8.9 (4)$^c$ |

$^a$ Estimated standard deviations in the least significant figure(s) are given in parentheses. $^b$ The form of the equivalent isotropic thermal parameter is $B_{eq} = (8/3)\pi^2\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$. $^c$ Atom refined isotropically.

thermal parameters were each fixed at a value 1.0 Å$^2$ greater than the equivalent isotropic thermal parameter of the attached carbon atom. The methyl hydrogen atoms could not be reasonably located and so were left out of the model. The least-squares refinement was blocked in such a manner that the Co complexes A and B were refined in alternate cycles, with refinement of the $Na^+$ ions and the THF molecules common to all cycles. The final cycle consisted of refinement of the Co complexes and the $Na^+$ ions together in one cycle with two THF molecules fixed. (This was done in order to meet the 500 variable limit in least squares imposed by the modified version of SHELX-76.[22]) The final cycle resulted in agreement indices of $R = 0.102$ and $R_w = 0.069$ for the 3515 intensities with $F_o{}^2 > 1.0\sigma(F_o{}^2)$ and the 488 variables. A structure factor calculation based on the 2313 intensities with $F_o{}^2 > 3\sigma(F_o{}^2)$ gives an $R$ value of 0.064. A final difference electron density map contains maximum and minimum peak heights of 0.31 and –0.26 e/Å$^3$, respectively. Scattering factors used are from the usual sources,[23] with the sodium treated as $Na^+$. Anomalous dispersion terms were included for the Co atom and the $Na^+$ ion. Final positional and equivalent isotropic thermal parameters are given in Table III. Lists of anisotropic thermal parameters, hydrogen atom coordinates, and structure factors are available as supplementary material.[24]

## Results and Discussion

**General Aspects of Reactions.** The formation of mono- and disubstituted alkene complexes of $Na[Co(CO)_4]$ can be visually observed by the appearance of bright yellow, orange, or red colors following the mixing of the colorless THF solutions of the reactants. The IR spectra of these solutions also show characteristic changes compared to the spectra of $Na[Co(CO)_4]$ and free alkene. Thus, the $\nu$(CO) bands of $Na[Co(CO)_4]$ of a rather complex pattern[25] decrease in intensity and then disappear, while new $\nu$(CO) bands of the product grow in at higher wavenumbers. The direction of the shift of $\nu$(CO) indicates substantial cobalt-to-alkene $\pi$ back-donation. Consistently, the $\nu$(CO) or $\nu$(CN) absorptions of the alkene ligands shift in the opposite direction, to lower wavenumbers (cf. Table I). As expected,[26] the monosubstituted complexes show a strong $\nu$(CO) band at 2043–1992 cm$^{-1}$ and a very strong one at 1971–1903 cm$^{-1}$, which is split in some cases. The disubstituted complexes display two $\nu$(CO) absorptions of approximately equal intensity in the range 2056–1946 cm$^{-1}$. The effect of coordination of the alkenes is also apparent in the characteristic shifts to higher fields of the $^1$H and $^{13}$C NMR signals of these ligands (cf. Table I). Significantly, in the less polar solvents $CD_2Cl_2$, $CDCl_3$, and THF-$d_8$, the DM and DF complexes $Na[Co(CO)_3(DM)]$ and $Na[Co(CO)_2(DF)_2]$, respectively, show a doubling (with equal intensity) of signals for each of the otherwise equivalent H and C nuclei (cf. Experimental Section). These observations cannot be explained by the solid-state structure of $Na[Co(CO)_2(DF)_2]\cdot THF$ (cf. Figure 1). However, they are consistent with the coordination of the counterion to only one side of each alkene ligand in forming a tight ion pair in these media. By contrast, in highly polar solvents such as $D_2O$, $CD_3OD$, and $C_2D_5OD$, this splitting could not be observed at room temperature for any of the complexes, including the disubstituted ones, where inequivalent H and C nuclei may still be expected for the solvent-separated ion pairs. Instead, somewhat broadened signals were noted at approximately average chemical shift positions to suggest rapid cation exchange under these conditions.

The alkene-substituted carbonylcobaltate(1–) complexes are formed in equilibrium reactions. Under thermal conditions, the equilibrium can be completely driven to the side of the disubstituted complex by bubbling Ar through

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[23] Scattering factors for the O, C, and H atoms were supplied by SHELX-76. Scattering factors for the Co atom and $Na^+$ ion were obtained from: *International Tables for X-ray Crystallography*; The Kynoch Press: Brimingham, England, 1974; Vol. IV, pp 99 and 149.

[24] See paragraph at end of paper regarding supplementary material.

[25] (a) Edgell, W. F.; Lyford, J., IV; Barbetta, A.; Jose, C. J. *J. Am. Chem. Soc.* **1971**, *93*, 6403. (b) Edgell, W. F.; Lyford, J., IV. *Ibid.* **1971**, *93*, 6407.

[26] See, e.g.: Pruchnik, F. P. *Organometallic Chemistry of the Transition Metals*; Plenum: New York, 1990; Chapter II.

the reaction solution. Selective formation of the monosubstituted complexes can be achieved by UV photolysis of a 1:1 molar mixture of $Na[Co(CO)_4]$ and alkene or of $Na[Co(CO)_4]$ and $Na[Co(CO)_2(alkene)_2]$. The coordinated alkene can be replaced not only by CO but by other alkenes as well. Moreover, by starting with the monoalkene complexes, disubstituted complexes containing different alkenes can be prepared.

Details of the reactions of the various activated alkenes with $Na[Co(CO)_4]$ are presented next.

**Reactions with Maleic Anhydride.** Mixing equimolar amounts of $Na[Co(CO)_4]$ and MA in THF solution under Ar at room temperature results in a slow evolution of gas as the reaction mixture turns cherry red. After 1 equiv of gas has been released, the IR spectrum of the solution shows the presence of not only $Na[Co(CO)_3(MA)]$ but also $Na[Co(CO)_2(MA)_2]$, $Na[Co(CO)_4]$, and free Ma. UV photolysis of this mixture, or of a freshly prepared mixture of equimolar amounts of $Na[Co(CO)_4]$ and MA, both at ca. 25 °C, affords complete conversion to $Na[Co(CO)_3(MA)]$ (eqs 5 and 6), which was isolated in high yield (>90%) as $Na[Co(CO)_3(MA)]\cdot 2THF$.

$$Na[Co(CO)_4] + Na[Co(CO)_2(MA)_2] \xrightarrow{h\nu} 2Na[Co(CO)_3(MA)] \quad (5)$$

$$Na[Co(CO)_4] + MA \xrightarrow{h\nu} Na[Co(CO)_3(MA)] + CO \quad (6)$$

When heated at reflux, a THF solution of a 2:1 molar mixture of MA and $Na[Co(CO)_4]$ gives off 2 equiv of gas to yield the disubstituted complex (eq 7), isolated in 94%

$$Na[Co(CO)_4] + 2MA \xrightarrow{\Delta} Na[Co(CO)_2(MA)_2] + 2CO \quad (7)$$

yield as $Na[Co(CO)_2(MA)_2]\cdot THF$. In addition, a THF-insoluble but water-soluble brick-red solid was obtained in low yield; it shows IR absorptions (in Nujol mull) at 2028 (m), 1974 (m), 1778 (s), 1721 (s br), and 1579 (vs br) cm$^{-1}$. The band at 1579 cm$^{-1}$ suggests the presence of a carboxylate anion or bridging ligand[27] in this byproduct. The solid was not further characterized.

Solutions of $Na[Co(CO)_2(MA)_2]$ in THF at room temperature slowly react with CO at 1 atm to form $Na[Co(CO)_3(MA)]$ and free MA. Under 15 atm of CO, the substitution proceeds further to give $Na[Co(CO)_4]$ but does not reach completion.

The complex $Na[Co(CO)_3(MA)]$ reacts with fumaronitrile (FN) at ca. 25 °C by replacement of CO according to eq 8 and with tetracyanoethylene (TCNE) at −40 °C by replacement of either MA or CO according to eqs 9 and 10, respectively.

$$Na[Co(CO)_3(MA)] + FN \rightarrow Na[Co(CO)_2(MA)(FN)] + CO \quad (8)$$

$$Na[Co(CO)_3(MA)] + TCNE \rightarrow Na[Co(CO)_3(TCNE)] + MA \quad (9)$$

$$Na[Co(CO)_3(MA)] + TCNE \rightarrow Na[Co(CO)_2(MA)(TCNE)] + CO \quad (10)$$

**Reactions with Dimethyl Maleate and Dimethyl Fumarate.** As with MA, a complete monosubstitution of DM in $Na[Co(CO)_4]$ was effected by UV irradiation of an equimolar mixture of the two reactants in THF solution at room temperature (eq 11). The orange crystalline

$$Na[Co(CO)_4] + DM \xrightarrow{h\nu} Na[Co(CO)_3(DM)] + CO \quad (11)$$

product was isolated as $Na[Co(CO)_3(DM)]\cdot 3THF$ in good yield. However, unlike its MA counterpart, $Na[Co(CO)_3(DM)]$ reacts readily and completely with CO at 1 atm in THF solution at ca. 25 °C to regenerate $Na[Co(CO)_4]$ and DM (eq 12).

$$Na[Co(CO)_3(DM)] + CO \rightarrow Na[Co(CO)_4] + DM \quad (12)$$

Thermal reaction between DM and $Na[Co(CO)_4]$ (2.5:1 molar ratio) in THF at reflux leads to the evolution of 2 equiv of CO and, surprisingly, formation of the dimethyl fumarate complex $Na[Co(CO)_2(DF)_2]$ as suggested by the IR absorptions at 1999 (s), 1947 (s), 1701 (sh), 1692 (s), and 1657 (w) cm$^{-1}$ (eq 13). This unexpected product was

$$Na[Co(CO)_4] + 2DM \xrightarrow{\Delta} Na[Co(CO)_2(DF)_2] + 2CO \quad (13)$$

isolated as the orange $Na[Co(CO)_2(DF)_2]\cdot THF$; the same complex was obtained from $Na[Co(CO)_4]$ and DF under comparable conditions (eq 14). The identity of $Na[Co(CO)_2(DF)_2]\cdot THF$ was unequivocally established by an X-ray crystallographic analysis (vide infra). Gas chromatographic analyses of the crude product solution from the former reaction (eq 13) revealed that isomerization of DM to DF occurred not only for the coordinated alkene but also, substantially, for the free, excess alkene. A similar isomerization of DM to DF was observed in analogous carbonylmanganate(1−) complexes; however, it requires more forcing experimental conditions.[28]

$$Na[Co(CO)_4] + 2DF \xrightarrow{\Delta} Na[Co(CO)_2(DF)_2] + 2CO \quad (14)$$

A THF solution of $Na[Co(CO)_2(DF)_2]$ at room temperature absorbs 2 equiv of CO at 1 atm to yield $Na[Co(CO)_4]$ and free DF (eq 15), which was identified by gas chromatography. Thus, displacement of alkene by CO proceeds much more readily in $Na[Co(CO)_2(DF)_2]$ than in $Na[Co(CO)_2(MA)_2]$.

$$Na[Co(CO)_2(DF)_2] + 2CO \rightarrow Na[Co(CO)_4] + 2DF \quad (15)$$

Isolable complexes of $[Co(CO)_2(DF)_2]^-$ also can be obtained from $Co_2(CO)_8$ and DF in saturated hydrocarbons. Accordingly, heating a dilute pentane solution of $Co_2(CO)_8$ and DF (or DM) at reflux results in the evolution of CO and formation of a light brown precipitate. The IR spectrum of this product in THF solution shows metal $\nu$(CO) absorptions at 2009 (s) and 1959 (s) cm$^{-1}$ as well as ligand $\nu$(CO) absorptions at 1732 (s), 1704 (s), and 1660 (s br) cm$^{-1}$. The position and relative intensity of these bands are similar to those reported earlier for an unidentified yellow powder obtained from reaction of $Co_2(CO)_8$ with DF in heptane at room temperature.[29] The stoichiometry of the foregoing conversions accords with eq 16.

$$3Co_2(CO)_8 + 14DF \rightarrow 2[Co(DF)_3][Co(CO)_2(DF)_2]_2 + 16CO \quad (16)$$

Unlike MA or DM, DF shows little propensity to form a stable monosubstituted product. Monitoring by IR spectroscopy the formation (eq 14) or the reaction with CO (eq 15) of $Na[Co(CO)_2(DF)_2]$ under thermal conditions revealed the absence of absorptions of an intermediate complex, $Na[Co(CO)_3(DF)]$. Moreover, after irradiation

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**Table IV. Initial Rates ($r$) of CO Uptake in the Reaction of $Na[Co(CO)_2(DF)_2]$ with CO in THF Solution at 25 °C**[a]

| $[Na[Co(CO)_2(DF)_2]]$ | [CO] | [DF] | $[PPh_3]$ | $10^6 r^b$ |
|---|---|---|---|---|
| 0.017 | 0.0082 | 0.00 | 0.00 | 5.0 |
| 0.038 | 0.0083 | 0.00 | 0.00 | 10.8 |
| 0.017 | 0.0036 | 0.00 | 0.00 | 2.1 |
| 0.017 | 0.0168 | 0.00 | 0.00 | 8.7[c] |
| 0.017 | 0.0084 | 0.10 | 0.00 | 3.5 |
| 0.017 | 0.0083 | 0.00 | 0.080 | 1.9 |

[a] All concentrations in M, rates in M $s^{-1}$. [b] To ±5% except as noted. [c] To ±10%.

of an equimolar mixture of $Na[Co(CO)_4]$ and DF in THF solution at 10 °C with 254- and 350-nm lamps in a Rayonet reactor, only traces of the monosubstituted product could be detected by IR spectroscopy ($\nu$(CO) 1992, 1910, 1896 $cm^{-1}$). This complex rapidly disappears at room temperature, undergoing disproportionation to $Na[Co(CO)_4]$ and $Na[Co(CO)_2(DF)_2]$. Relevant reactions are given in eqs 17–19.

$$Na[Co(CO)_4] + DF \xrightarrow{h\nu} Na[Co(CO)_3(DF)] + CO \quad (17)$$

$$Na[Co(CO)_2(DF)_2] + Na[Co(CO)_4] \xrightarrow{h\nu} 2Na[Co(CO)_3(DF)] \quad (18)$$

$$2Na[Co(CO)_3(DF)] \rightarrow Na[Co(CO)_4] + Na[Co(CO)_2(DF)_2] \quad (19)$$

To learn more about the substitution reaction in eq 15, the initial rate of CO uptake by $Na[Co(CO)_2(DF)_2]$ in THF solution was measured and found to be first order in each of the reactants. Added DF or $PPh_3$ decrease the rate as shown in Table IV. In the presence of $PPh_3$, new IR $\nu$(CO) bands grow in at 2002 and 1956 $cm^{-1}$ and then disappear; they may belong to a mixed DF–$PPh_3$ complex, $Na[Co(CO)_2(DF)(PPh_3)]$.

The foregoing observations are compatible with the dissociation of a DF ligand to furnish a 16-electron intermediate, $Na[Co(CO)_2(DF)]$ (eq 20). This species is then

$$Na[Co(CO)_2(DF)_2] \rightarrow Na[Co(CO)_2(DF)] + DF \quad (20)$$

captured by CO, DF, or $PPh_3$ in competition. Assuming that the reaction with CO is appreciably slower than that with DF or $PPh_3$ and applying the steady-state approximation for the concentration of $Na[Co(CO)_2(DF)]$ lead to the observed rate dependence on the concentrations of $Na[Co(CO)_2(DF)_2]$ and CO. Moreover, the rate expression predicts inhibition of CO uptake by added DF or $PPh_3$. A tricarbonyl complex, $Na[Co(CO)_3(DF)]$, generated in this manner would be required rapidly to convert to $Na[Co(CO)_4]$ and DF, as observed experimentally.

The coordinated DF ligand in $Na[Co(CO)_2(DF)_2]$ can be replaced at room temperature not only with CO but also with MA, FN, or TCNE in reactions that were conveniently studied by IR spectroscopy. With MA and FN, the disubstituted products were obtained as shown in eqs 21 and 22. Interestingly, the reaction with MA yields $Na[Co(CO)_2(MA)_2]$ irrespective of the amount of MA employed, and $\nu$(CO) absorptions of a mixed-ligand complex, $Na[Co(CO)_2(MA)(DF)]$, could not be observed. By contrast, with TCNE, the only carbonylcobaltate(1−) product detected in solution was $Na[Co(CO)_3(TCNE)]$ (eq 23).

$$Na[Co(CO)_2(DF)_2] + 2MA \rightarrow Na[Co(CO)_2(MA)_2] + 2DF \quad (21)$$

$$Na[Co(CO)_2(DF)_2] + 2FN \rightarrow Na[Co(CO)_2(FN)_2] + 2DF \quad (22)$$

$$2Na[Co(CO)_2(DF)_2] + TCNE \rightarrow Na[Co(CO)_3(TCNE)] + CO + ? \quad (23)$$

Its formation was accompanied by decomposition to an insoluble non-carbonyl material. A product containing two TCNE ligands, $Na[Co(CO)_2(TCNE)_2]$, could not be obtained in any of the reactions conducted. In this context, it is worthy of note that the monosubstituted complex $Na[Co(CO)_3(TCNE)]$ shows by far the highest energy $\nu$(CO) bands in the series of $Na[Co(CO)_3(alkene)]$ complexes reported (cf. Table I). This indicates that TCNE is an excellent $\pi$-acceptor ligand, which, as such, decreases the degree of Co=CO $\pi$ bonding. A corresponding disubstituted complex would be expected to show even less Co=CO $\pi$ bonding—it would be essentially a bis(metallacyclopropane)cobalt(III) complex—and therefore exhibit low stability.

To see whether the behavior of these complexes would be affected by the presence of a different counterion, reactions were conducted between $M[Co(CO)_4]$ (M = Li, K) and an excess of DF in THF at reflux. However, each reaction afforded the disubstituted product, isolated as the sparingly THF-soluble $Li[Co(CO)_2(DF)_2]$ and the highly THF-soluble $K[Co(CO)_2(DF)_2]\cdot 2THF$.

UV irradiation of an equimolar mixture of $Li[Co(CO)_4]$ and DM in THF at ca. 25 °C gave a practically complete conversion to $Li[Co(CO)_3(DM)]$ as indicated by the appearance of the $\nu$(CO) bands at 2002 (s), 1920 (vs br), and 1693 (s br) $cm^{-1}$. However, unlike its $Na[Co(CO)_3(DM)]$ counterpart, which is stable, this complex underwent disproportionation (eq 24) during an attempt at crystallization.

$$2Li[Co(CO)_3(DM)] \rightarrow Li[Co(CO)_4] + Li[Co(CO)_2(DM)_2] \quad (24)$$

A reaction between $Na[Co(CO)_2(DF)_2]$ and $HCo(CO)_4$ was conducted in THF at −20 °C to ascertain whether transfer of the hydrogen ligand occurs between the two different Co centers. However, the wine-red reaction mixture showed the formation of $Na[Co_3(CO)_{10}]$ (by IR spectroscopy[19]) as well as DF and dimethyl succinate (DS) (by gas chromatography) to indicate that the hydrogen instead added to the alkene (eq 25).

$$Na[Co(CO)_2(DF)_2] + 2HCo(CO)_4 \rightarrow Na[Co_3(CO)_{10}] + DF + DS \quad (25)$$

**Reactions with Fumaronitrile.** Reactions of $Na[Co(CO)_4]$ with FN are very similar to those with MA. Accordingly, UV irradiation of an equimolar mixture of $Na[Co(CO)_4]$ and FN in THF at 10 °C affords the monosubstituted product (eq 26), whereas a room-temperature reaction of a 2:1 molar mixture of FN and $Na[Co(CO)_4]$ within 5–10 min shows the formation of $Na[Co(CO)_3(FN)]$ and then of $Na[Co(CO)_2(FN)_2]$ (eq 27). The

$$Na[Co(CO)_4] + FN \xrightarrow{h\nu} Na[Co(CO)_3(FN)] + CO \quad (26)$$

$$Na[Co(CO)_4] \xrightarrow[-CO]{+FN} Na[Co(CO)_3(FN)] \xrightarrow[-CO]{+FN} Na[Co(CO)_2(FN)_2] \quad (27)$$

disubstituted product is best prepared by conducting the thermal reaction in THF at reflux under a slow stream of Ar and is isolated in high yield (84%) as the dark yellow $Na[Co(CO)_2(FN)_2]\cdot THF$. Under 1 atm of CO in 1 h at ca. 25 °C, this complex is in part converted to $Na[Co(CO)_3(FN)]$ and FN.

The behavior of $Na[Co(CO)_3(FN)]$ toward other activated alkenes (eqs 28–30) parallels that of $Na[Co(CO)_3(MA)]$.

$$Na[Co(CO)_3(FN)] + MA \xrightarrow{25\ °C} Na[Co(CO)_2(MA)(FN)] + CO \quad (28)$$

$$Na[Co(CO)_3(FN)] + TCNE \xrightarrow{-40\ °C} Na[Co(CO)_3(TCNE)] + FN \quad (29)$$

$$Na[Co(CO)_3(FN)] + TCNE \xrightarrow{-40\ °C} Na[Co(CO)_2(FN)(TCNE)] + CO \quad (30)$$

**Reactions with Tetracyanoethylene.** Reactions of $Na[Co(CO)_4]$ with TCNE were carried out under different experimental conditions and always resulted in the formation of $Na[Co(CO)_3(TCNE)]$ and an unidentified noncarbonyl decomposition product.

When equimolar amounts of $Na[Co(CO)_4]$ and TCNE reacted in THF at ca. 25 °C, within 5 min 1.4 equiv of CO was evolved. The IR spectrum of the turbid yellow solution showed that ca. 50% of the original cobalt complex remained unreacted and that $Na[Co(CO)_3(TCNE)]$ was present. Addition of a further equivalent of TCNE again resulted in a rapid evolution of CO (1.5 equiv) and the formation of a dark brown precipitate. The IR spectrum revealed a complete disappearance of $Na[Co(CO)_4]$ and a decrease in the concentration of $Na[Co(CO)_3(TCNE)]$. In addition, a product was observed with $\nu(CN)$ bands at 2227 (w br), 2177 (m br), and 2149 (w) $cm^{-1}$. Treatment of this mixture with yet another equivalent of TCNE resulted in a rapid loss of 0.9 equiv of CO, disappearance of all $\nu(CO)$ absorptions, and a growth of the aforementioned $\nu(CN)$ absorptions. No $\nu(CO)$ bands of any other carbonylcobaltate(1–) complex were noted in the course of this experiment.

The monosubstituted complex can be isolated in good yield as the brown microcrystalline $Na[Co(CO)_3(TCNE)]\cdot 3THF$ from the reaction of equimolar amounts of $Na[Co(CO)_4]$ and TCNE in THF at –60 °C, with slow warming to 0 °C (eq 31). This procedure gives only a small quantity of the dark brown precipitate, which is sparingly soluble in THF but highly soluble in $H_2O$. Its IR spectrum shows absorptions associated with $\nu(CN)$, $\nu(C{=}C)$ (of TCNE), $\nu(CH)$, and $\delta(CH)$ (of THF) vibrations. The product was not further characterized.

$$Na[Co(CO)_4] + TCNE \rightarrow Na[Co(CO)_3(TCNE)] + CO \quad (31)$$

**Concluding Remarks on Reactions.** Reactions of $Na[Co(CO)_4]$ with activated alkenes to give $Na[Co(CO)_{4-x}(alkene)_x]$, where $x = 1$ or 2, and the behavior of the resultant products toward CO and other activated alkenes, represent equilibrium-controlled processes. Salts of various alkenecarbonylcobaltate(1–) complexes have been prepared and isolated by carefully controlling experimental conditions for their synthesis. The chemistry described in some detail in the foregoing sections is generalized below.

The average energy of the two IR-active CO stretching modes, av $\nu(CO)$, of $Na[Co(CO)_{4-x}(alkene)_x]$, where $x = 1$ and 2, depends on the degree of substitution and on the nature of the alkene. For the same alkene, av $\nu(CO)$ is higher for $Na[Co(CO)_2(alkene)_2]$ than for $Na[Co(CO)_3(alkene)]$. This suggests that the alkenes utilized in our study are superior $\pi$-acceptor ligands and compete favorably with CO for $\pi$ electrons of cobalt. Among the alkenes investigated, av $\nu(CO)$ ($cm^{-1}$) increases in the order alkene = DF (1947.5) < DM (1954) < FN (1963.5) < MA (1969) < TCNE (2007) for $Na[Co(CO)_3(alkene)]$, alkene = DF (1972) < MA (1995) ~ FN (1995.5) for $Na[Co(CO)_2(alkene)_2]$, and $alkene_1$, $alkene_2$ = MA, FN (1995) < MA, TCNE (2031) < FN, TCNE (2037) for $Na[Co(CO)_2(alkene_1)(alkene_2)]$. These data indicate that DM and DF are the weakest $\pi$ acceptors, MA and FN are very similar and stronger than DM and DF, and TCNE is by far the best $\pi$ acid of the five alkenes examined. In fact, the values of av $\nu(CO)$ for $Na[Co(CO)_2(MA)(TCNE)]$ and $Na[Co(CO)_2(FN)(TCNE)]$ are unrealistically high for cobalt(1–) compounds. We believe that a better formulation of these complexes is as bis(cobaltacyclopropane) species with the metal being formally cobalt(III).

Interestingly, the chemistry of the various $Na[Co(CO)_{4-x}(alkene)_x]$ complexes reflects quite well the $\pi$-bonding strength of the constituent alkenes. The unusual properties associated with the TCNE ligand in these complexes were presented and discussed earlier in the paper; thus, only the complexes of MA, DM, DF, and FN will be considered further.

The complexes $Na[Co(CO)_3(alkene)]$ and $Na[Co(CO)_2(alkene)_2]$ undergo substitution by CO and other activated alkenes. The behaviors of the complexes $Na[Co(CO)_2(alkene)_2]$, where alkene = MA or FN, are very similar ; both react with CO at 1 atm to give only $Na[Co(CO)_3(alkene)]$, and both yield the mixed alkene-ligand complexes $Na[Co(CO)_2(alkene_1)(alkene_2)]$ when treated with $alkene_2$ = MA (or FN) or TCNE. By contrast, $Na[Co(CO)_3(DM)]$ and $Na[Co(CO)_2(DF)_2]$ react with CO at 1 atm with complete displacement of the alkene to give $Na[Co(CO)_4]$, and $Na[Co(CO)_2(DF)_2]$ reacts analogously with $alkene_2$ = MA or FN to afford $Na[Co(CO)_2(alkene_2)_2]$. Therefore, in these systems, the equilibrium favors the presence in the complex of the stronger $\pi$ acceptors MA and FN rather than of the weaker $\pi$ acceptors DM and DF. Stated differently, the more oxidized complexes appear to have higher stability to alkene replacement than the less oxidized ones.

**Crystal Structure of $Na[Co(CO)_2(DF)_2]\cdot THF$.** ORTEP drawings of the asymmetric unit and of anion A of $Na[Co(CO)_2(DF)_2]\cdot THF$ are given in Figures 1 and 2, respectively. Selected bond distances and angles are listed in Table V. Figure 1 shows that the two Co complexes (A and B) form a dimer through their bonding interactions with the $Na^+$ ions. Each $Na^+$ ion is coordinated to the oxygen atoms of two fumarate C=O groups from each Co complex and to the oxygen atom of a THF molecule, for a total coordination number of five. The arrangement of these oxygen atoms around the $Na^+$ ion is trigonal bipyramidal. For Na1A, the atoms O9A and O5B are apical and the atoms O5A, O9B, and O11A are equatorial, whereas for Na1B the atoms O4A and O8B are apical, with the atoms O8A, O4B, and O11B being equatorial. The average Na–O separation is 2.30 (2) Å, which is in the range of Na–O distances observed in other five-coordinate, $O_5$-ligated $Na^+$ complexes, $[Na(THF)_2]_2[Hg(Fe(CO)_4)_2]$[30] and $[Na(THF)_2][Fe_2(CO)_5(COMe)(\mu\text{-}PPh_2)_2]$.[31] The geometry about the Co atom is approximately tetrahedral if one considers the midpoints of the C5–C6 bond (labeled as CM1) and the C11–C12 bond (labeled as CM2) and atoms C1 and C2 as comprising the coordination sphere for the metal.

The geometry associated with the constitution of the dimer of $Na[Co(CO)_2(DF)_2]\cdot THF$ is such that a sub-

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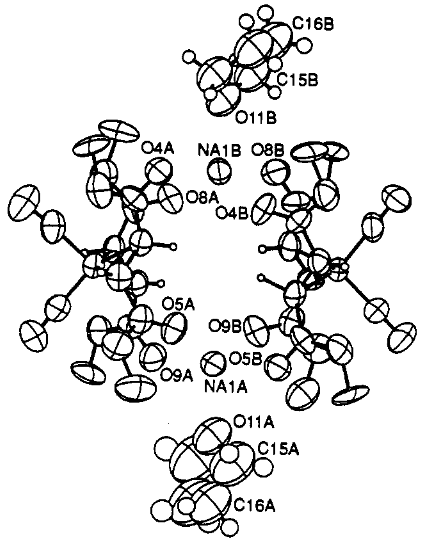


**Figure 1.** ORTEP drawing of the asymmetric unit of Na[Co(C-O)$_2$(DF)$_2$]·THF. Only selected atoms are numbered. (For a complete numbering scheme, see Figure 2.) Atoms are drawn at the 50% probability level.

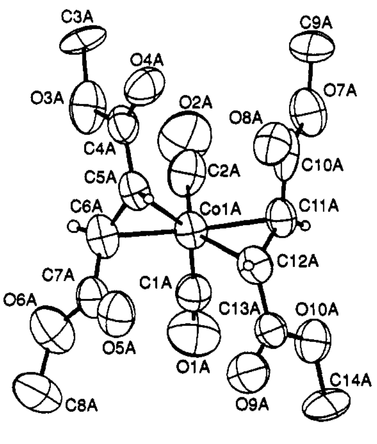


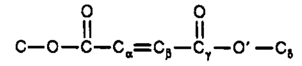
**Figure 2.** ORTEP drawing of anion A of Na[Co(CO)$_2$(DF)$_2$]·THF showing atom numbering scheme. Atoms are drawn at the 50% probability level.

structure exists within the asymmetric unit. The Co atoms, Na$^+$ ions, the O11 atoms of the THF molecules, and the C≡O groups (carbonyl ligands) are related in pairs by a pseudoinversion center of the dimer. However, the DF ligands themselves are not related in this manner.

The asymmetric centers of the DF ligands, viz., atoms C5, C6, C11, and C12, are all of the same absolute configuration for ions A and B of one dimer unit as depicted in Figure 1. Therefore, the dimer unit itself is optically active, but since the space group is centrosymmetric, the dimer of opposite chirality is also present in the unit cell. As a result, the crystals of Na[Co(CO)$_2$(DF)$_2$]·THF cannot be optically active.

The torsion angles about the C=C bond of the DF ligands indicate the degree of distortion that these ligands undergo upon complexation to the Co atom. These angles are C4–C5–C6–C7 -150° and C10–C11–C12–C13 -153° for anion A and C4–C5–C6–C7 -150° and C10–C11–C12–C13 -155° for anion B. A similar distortion (torsion angles 151 and 152°) has been reported for bis(acetonitrile)bis(diethyl fumarate)cobalt(0),[32] and an even larger one (145 (2)°) for racemic tetracarbonyl(fumaric acid)iron(0).[33]

**Table V. Selected Bond Distances (Å) and Angles (deg) for Na[Co(CO)$_2$(DF)$_2$]•THF**

| | anion A | anion B |
|---|---|---|
| Bond Distances Involving Co and CO | | |
| Co–C1 | 1.773 (20) | 1.731 (20) |
| Co–C2 | 1.750 (21) | 1.752 (19) |
| Co–C5 | 2.074 (18) | 2.048 (18) |
| Co–C6 | 2.036 (19) | 2.066 (16) |
| Co–CM1[a] | 1.934 (19) | 1.935 (18) |
| Co–C11 | 2.029 (16) | 2.072 (18) |
| Co–C12 | 2.048 (19) | 2.038 (17) |
| Co–CM2[a] | 1.918 (19) | 1.940 (18) |
| C1–O1 | 1.155 (18) | 1.162 (18) |
| C2–O2 | 1.164 (18) | 1.153 (17) |
| Average Bond Distances for the DF Ligand[b] | | |
|  $C{-}O{-}C(=O){-}C_\alpha{=}C_\beta{-}C_\gamma(=O){-}O'{-}C_\delta$ | | |
| $C_\gamma$–O | 1.217 (19) | |
| $C_\delta$–O′ | 1.486 (21) | |
| $C_\gamma$–O′ | 1.342 (20) | |
| $C_\beta$–$C_\gamma$ | 1.480 (25) | |
| $C_\alpha$–$C_\beta$ | 1.381 (22) | |
| Bond Angles Involving Co | | |
| C1–Co–C2 | 96.3 (8) | 98.8 (8) |
| C1–Co–CM1 | 122.0 (8) | 117.4 (8) |
| C1–Co–CM2 | 101.9 (8) | 103.6 (8) |
| C2–Co–CM1 | 103.4 (8) | 104.9 (8) |
| C2–Co–CM2 | 119.2 (8) | 117.0 (8) |
| CM1–Co–CM2 | 113.8 (8) | 114.6 (8) |
| Co–C1–O1 | 178.6 (18) | 175.2 (19) |
| Co–C2–O2 | 175.7 (19) | 177.4 (20) |
| Average Bond Angles for the DF Ligand[b] | | |
| $C_\gamma$–O′–$C_\delta$ | 116.3 (16) | |
| $C_\beta$–$C_\gamma$–O | 124.2 (21) | |
| $C_\beta$–$C_\gamma$–O′ | 113.8 (31) | |
| O–$C_\gamma$–O′ | 121.9 (22) | |
| $C_\alpha$–$C_\beta$–$C_\gamma$ | 122.0 (19) | |
| Co–$C_\beta$–$C_\gamma$ | 111.7 (26) | |

[a] CM1 and CM2 are the midpoints of the C5–C6 and C11–C12 bonds, respectively. [b] Average values are weighted and result from summing over the four DF ligands in the asymmetric unit; the error is the larger of the unweighted estimated standard deviation of a single observation and that estimated from the least-squares inverse matrix.

The average of the C=C bond distances in Na[Co(C-O)$_2$(DF)$_2$]·THF (1.38 (2) Å) is essentially identical with that reported for acetonitrilobis(diethyl fumarate)nickel(0) (1.39 (1) Å).[34] However, as expected, it is longer than the C=C bond distance in the free ligands fumaric acid (1.348 Å)[35] and dimethyl 2,3-bis(diphenylphosphino)fumarate (1.349 (7) Å).[36] Interestingly, in the complexes Co(MeCN)$_2$-(diethyl fumarate)$_2$[32] and MeIr(CO)(PPh$_3$)$_2$(DM),[37] this bond length increases to 1.42 (1) and 1.45 (1) Å, respectively. The shorter C=C bond distances in Na[Co(C-O)$_2$(DF)$_2$]·THF than in Co(MeCN)$_2$(diethyl fumarate)$_2$ probably result from the nature of the other ligands present in these complexes. Thus, in the former complex, the DF ligands compete with CO for $\pi$ electrons of the metal, whereas in the latter complex metal-to-ligand $\pi$ bonding occurs only for the diethyl fumarates. This results in the stronger cobalt-to-alkene $\pi$ bonding in Co-(MeCN)$_2$(diethyl fumarate)$_2$ and hence the observed longer C=C bond distances.

The average Co–C(alkene) distance of 2.05 (2) Å in Na[Co(CO)$_2$(DF)$_2$]·THF is comparable to that in [Li(TH-

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$F)_2][Co(COD)_2]$ (2.026–2.090 Å)[38] and $Co(MeCN)_2$(diethyl fumarate)$_2$ (2.060 (9) Å).[32]

**Acknowledgment.** We gratefully acknowledge the financial support of the National Science Foundation (through Grant CHE-8420806 to A.W.) and the Hungarian Academy of Science (through Grant OTKA 138 to F.U. at Veszprêm). High-field NMR spectra were obtained at The Ohio State University Chemical Instrument Center (funded in part by National Science Foundation Grant 79-10019).

**Supplementary Material Available:** A stereodrawing of the unit cell and tables of anisotropic thermal parameters, hydrogen atom coordinates, and additional bond distances and angles for the complex $Na[Co(CO)_2(DF)_2]\cdot THF$ (9 pages); a table of observed and calculated structure factors for the complex $Na[Co(CO)_2(DF)_2]\cdot THF$ (15 pages). Ordering information is given on any current masthead page.

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# Understanding Reactivity Trends by Structural and Theoretical Studies of Distortions in Ground-State Reagents

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*Received April 18, 1991*

Distortions of the carbonyl ligands in $RM(CO)_n$ ($M = Mn$, $n = 5$; $M = Co$, $n = 4$) are examined by studying published structural data. The more electropositive the R group, the more the equatorial CO groups are found to bend toward the R group. The results can be understood in terms of a simple model: for example, in $RMn(CO)_5$ the more electropositive the R group, the more the $Mn(CO)_5$ group departs from the octahedral structure expected for a $d^6$ system and approaches the distorted trigonal bipyramidal (TBP) or square pyramidal (SP) geometry expected for a $d^8$ configuration. In a similar way the TBP $RCo(CO)_4$ undergoes distortions leading toward $d^{10}$ tetrahedral geometry when R is electropositive. The effect is found to be more pronounced for late transition metals and for TBP over $O_h$ coordination modes. EHT calculations validate and amplify this simple model and are used to identify the main orbital interactions. On Bürgi–Dunitz ideas, the above distortions are correlated with the carbonyl insertion into a M–R bond for which larger reaction rates are found for more electropositive R groups. These results suggest that the electronic factors that favor distortion also favor the insertion reaction. Distortion analysis allows us to understand why nucleophiles sometimes substitute and sometimes abstract R in $RCo(CO)_3$.

## Introduction

An important goal in chemistry is understanding the factors that affect reaction rates and product ratios as the structure of the reaction partners is changed. In order to do this, we need to identify and understand key electronic and steric effects in the transition state. Such an analysis is particularly difficult because few experimental studies are available that give a detailed insight into the structural or electronic properties of the transition structure. Direct spectroscopic study is not possible and thus only indirect evidence can be used. High-level quantum chemical calculations have been done to determine the geometries and energies of transition structures. However, in the case of organometallic systems such studies are still difficult and certain well-marked reactivity trends remain unexplained.

In this paper, we describe a method for gaining a better understanding of electronic effects that influence chemical reactions by a combination of structural and theoretical studies. Bürgi and Dunitz showed how a quantitative comparison of a series of structural data can help define reaction pathways.[1] For example, a study of the $N\cdots C{=}O$ spatial arrangements in several molecules containing a carbonyl function and an amino group was used to define the reaction path of the addition of nucleophiles to a carbonyl function. Several other organic reactions ($S_N2$, isomerization, proton transfer) were analyzed in a similar manner.[1,2] In contrast, similar investigations in the area of organometallic reactions are still scarce. To our knowledge two studies have been conducted: hydrolysis of hexacoordinated Ni complexes[1] and oxidative addition of a C–H bond to a metal.[3] Another study examined the relationship between structure and activation energy, providing an estimate of transition-state structures in the ring inversion of (*s-cis*-$\eta^4$-butadiene) complexes.[4] In each of these examples, structures frozen in the crystalline state were considered to be successive snapshots of a reaction pathway. Theoretical studies have supported this view.[5] However, few attempts have been made to analyze the factors that make a structure freeze in the crystal on a

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