synthesis but also the bonus of immediately increasing the availability of didemnin B, since didemnin A was the major component in the *T. solidum* extract (A/B, ca. 3:1).

Note Added in Proof. Very recently, the structure of didemnin B was also assigned as **2** by X-ray crystallography (Hossain, M. B.; van der Helm, D.; Antel, J.; Sheldrick, G. M.; Sanduja, S. K.; Weinheimer, A. J. 14th Meeting International Union of Crystallography, Perth, Australia, August 12–20, 1987).

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Substitution Reactions of Sodium Tetracarbonylcobaltate(1–)

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Salts of $[Co(CO)_4]^-$ have been extensively used in the synthesis of various cobalt(I) carbonyl derivatives via oxidative addition reactions[1,2] and in catalytic carbonylation of aliphatic and aromatic halides, where an oxidative addition step is critical to the catalytic cycle.[3] Recently, the possibility of ligand substitution in $[Co(CO)_4]^-$ upon irradiation was proposed based on the observation that alcoholic solutions of $[Co(CO)_4]^-$ catalyze the hydroformylation of olefins under photochemical conditions.[4] However, salts of $[Co(CO)_4]^-$ have been regarded as inert to substitution of the carbonyl groups under thermal conditions.[5]

Herein we report the first[6] direct evidence of the facile substitution of CO in $Na[Co(CO)_4]$ by ^{13}CO, phosphites, phosphines, and activated olefins which may provide new impetus for catalytic applications.

Solutions of $Na[Co(CO)_4]$ in THF under 1 atm of ^{13}CO undergo rapid equilibration according to eq 1.[7] The presence of

$$Na[Co(CO)_4] + x\,^{13}CO \rightleftarrows Na[Co(^{13}CO)_x(CO)_{4-x}] + xCO \tag{1}$$

15-crown-5 ether dramatically slows down the exchange, and use of PPN^+[8] as the counterion affords no observable reaction at room temperature in 48 h. The lability of the Li^+ and K^+ salts of $[Co(CO)_4]^-$ is qualitatively similar to that of $Na[Co(CO)_4]$. These results indicate that ion-pairing phenomena[9] play an important role in ligand replacement reactions of $[Co(CO)_4]^-$. ^{13}CO exchange is inhibited by the presence of PPh_3[10] to suggest that a 16-electron $[Co(CO)_3]^-$ may be involved in the reaction.

If a stream of Ar is used to remove CO, $Na[Co(CO)_4]$ readily reacts with phosphites and phosphines according to eq 2, with the

$$Na[Co(CO)_4] + PR_3 \rightleftarrows Na[Co(CO)_3PR_3] + CO \tag{2}$$

$$R = OPh,\ O\text{-}n\text{-}Bu,\ Ph,\ n\text{-}Bu$$

most facile substitution occurring for $P(OPh)_3$.[11] UV irradiation of the reaction mixtures accelerates these substitution processes. The reverse reaction proceeds readily; e.g., a 0.005 M solution of $Na[Co(CO)_3PPh_3]$ in THF absorbs 1 mol of CO in less than 2 min at –10 °C.[12-14] The uptake of CO is slower in the presence of PPh_3. The kinetics of this reaction, measured by following the initial rates of absorption of CO, show first-order dependence on the concentration of each of $Na[Co(CO)_3PPh_3]$ and CO and an inverse first-order dependence on the concentration of PPh_3.[15,16]

The PR_3 in $Na[Co(CO)_3PR_3]$ can be replaced not only by CO but also by a less basic ligand PR'_3. IR and ^{31}P NMR spectra of a reaction mixture derived from a 1:1 molar ratio of $Na[Co(CO)_3PPh_3]$ and $P(OPh)_3$ at 25 °C under Ar showed that ligand exchange (eq 3) is essentially complete in 30 min. Similar ex-

$$Na[Co(CO)_3PPh_3] + P(OPh)_3 \rightleftarrows Na[Co(CO)_3P(OPh)_3] + PPh_3 \tag{3}$$

periments with different combinations of free and ligated $P(n\text{-}Bu)_3$, PPh_3, $P(O\text{-}n\text{-}Bu)_3$, and $P(OPh)_3$ revealed that the more basic ligand can be replaced by a less basic one[17] to establish equilibrium.

Activated olefins (L) react with $Na[Co(CO)_4]$ in THF solution to form mono- and disubstituted derivatives in equilibrium re-

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† On leave from the University of Veszprēm, Hungary.

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(5) (a) For example, in a recent review the following is stated: "Ionic $[Co(CO)_4]^-$ salts do not undergo substitution reactions"; see ref 1, p 14. (b) Howell, J. A.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557–599.

(6) After this paper was submitted for publication, we have learned that thermal and photochemical substitution reactions of $[Co(CO)_4]^-$ were studied by Ellis and Winzenburg who isolated salts of several $[Co(CO)_3PR_3]^-$: Winzenburg, M. L. Ph.D. Thesis, University of Minnesota, 1979. We thank Professor J. E. Ellis for making this information available to us.

(7) Complete scrambling was observed in 10 min at 25 °C for a 0.04 M solution: $Na[Co(^{13}CO)_4]$ IR (THF) 1845 (vs br), 1814 (s) cm^{-1}.

(8) PPN^+ = bis(triphenylphosphine)nitrogen(1+) ion.

(9) (a) Schussler, D. P.; Robinson, W. R.; Edgell, W. F. *Inorg. Chem.* **1974**, *13*, 153–158. (b) Recent review: Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221–274.

(10) No incorporation of ^{13}CO could be detected after 10 min in the IR spectrum of a 0.03 M solution of $Na[Co(CO)_4]$ in THF at 28 °C in the presence of a 38-fold molar excess of PPh_3 under 1 atm of ^{13}CO. After 60 min of reaction time, ν (^{13}CO) bands appeared at 1862, 1851, and 1820 cm^{-1}, and the intensity of the original ν (^{12}CO) band at 1888 cm^{-1} decreased by about 20%. Essentially complete scrambling was observed after 20 h.

(11) Refluxing a 1:1 molar mixture of $Na[Co(CO)_4]$ and $P(OPh)_3$ (0.06 M) in THF with a slow passage of Ar for 30 min gave virtually complete monosubstitution: IR (THF) 1959 (s), 1883 (vs), 1842 (s), 1594 (m) cm^{-1}; ^{31}P NMR (THF, 100 MHz, 200 K) δ 175. These spectra are identical with those of the Na/Hg reduction product of $Co_2(CO)_6[P(OPh)_3]_2$: Hieber, W.; Lindner, E. *Chem. Ber.* **1961**, *94*, 1417–1425.

(12) It has been shown that PMe_3 in $K[Co(PMe_3)_4]$[13] and $P(OPh)_3$ in $Na[Co(P(OPh)_3)_4]$[14] can be successively replaced by CO.

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(16) Solubility (0.0073 M) of CO in THF at 0 °C and P_{CO} 1 atm was extrapolated from measured values at 25 and 30 °C: Payne, M. W.; Leussing, D. L.; Shore, S. G. *J. Am. Chem. Soc.* **1987**, *109*, 617–618.

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actions (eq 4 and 5). The stoichiometry and the reversibility of

$$Na[Co(CO)_4] + L \rightleftarrows Na[Co(CO)_3L] + CO \qquad (4)$$

$$Na[Co(CO)_4] + 2L \rightleftarrows Na[Co(CO)_2L_2] + 2CO \qquad (5)$$

L = maleic anhydride, dimethyl maleate (DM),
dimethyl fumarate (DF)

these reactions were established by gas evolution and IR spectral measurements. Selective conversions of $Na[Co(CO)_4]$ and L into $Na[Co(CO)_3L]$[18] at 1:1 molar ratio or into $Na[Co(CO)_2L_2]$[19] at 1:2 molar ratio were realized by using UV irradiation or thermolysis at reflux, respectively. The Li^+ and K^+ salts of $[Co(CO)_4]^-$ react similarly to $Na[Co(CO)_4]$. By contrast, $PPN[Co(CO)_4]$ does not react with the aforementioned olefins under comparable thermal conditions.

The IR spectra of these $Na[Co(CO)_3L]$ and $Na[Co(CO)_2L_2]$ olefin complexes show metal carbonyl absorptions shifted to higher frequencies compared with those of $Na[Co(CO)_4]$. This indicates substantial cobalt-to-olefin π back-donation. Consistently, the C=O stretching frequencies of the olefins move to lower values upon ligation.

The ^1H and ^{13}C NMR spectra in CD_2Cl_2 or $CDCl_3$ solution reveal expected changes in the chemical shifts of the olefins upon coordination.[20] Interestingly and significantly, however, there is a doubling (with equal intensity) of signals for each of the otherwise equivalent H and C nuclei. This effect may be attributed to the coordination of the counterion to only one carbonyl group of each olefin in forming a tight ion pair in these solvents. Preliminary X-ray crystallographic results show that the Na^+ ion in $Na[Co(CO)_2(DF)_2]\cdot THF$ is surrounded by the THF oxygen and by one oxygen atom from each of four COOMe groups of different dimethyl fumarate ligands belonging to two anions. By contrast, the NMR spectra of $Na[Co(CO)_2L_2]$ in D_2O show only one signal for each kind of H and C nucleus which also has a normal chemical shift for coordinated olefins. Here, solvent separated ion pairs are probably present.

Studies are in progress to delineate the scope of substitution reactions of $[Co(CO)_4]^-$ and other metal carbonyl anions and to explore the chemistry of the substituted anionic products.

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Registry No. DM, 624-48-6; DF, 624-49-7; $Na[Co(CO)_4]$, 14878-28-5; $P(OPh)_3$, 101-02-0; $P(O\text{-}n\text{-}Bu)_3$, 102-85-2; PPh_3, 603-35-0; $P(n\text{-}Bu)_3$, 998-40-3; maleic anhydride, 108-31-6.

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[18] E.g., a THF solution (50 mL) of equimolar amounts (8.6 mmol) of $Na[Co(CO)_4]$ and dimethyl maleate in a quartz Schlenk tube was irradiated under Ar with 254-nm lamps in a Rayonet reactor for 5 days at 25 °C. Concentration to 12 mL and crystallization at −78 °C afforded 3.51 g (77%) of orange crystals of $Na[Co(CO)_3(DM)]\cdot 3THF$: mp ~ 25 °C; IR (THF) 1997 (s), 1918 (vs), 1904 (vs) 1706 (s) cm^{-1}; ^1H NMR (CD_2Cl_2, 250 MHz) δ 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 NMR (CD_2Cl_2, 63 MHz) δ 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 $C_{21}H_{32}CoNaO_{10}$: Co, 11.20. Found: Co, 11.51.

[19] E.g., a THF solution (30 mL) of $Na[Co(CO)_4]$ (8.5 mmol) and dimethyl fumarate (17.7 mmol) was refluxed under Ar for 24 h. Concentration to 15 mL and filtration of the slurry at 25 °C gave 3.98 g (94%) of orange crystals of $Na[Co(CO)_2(DF)_2]\cdot THF$: IR (THF) 1998 (s), 1946 (s), 1731 (vw), 1701 (sh), 1692 (s), 1657 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 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); ^1H NMR (D_2O, 250 MHz) δ 4.02 (s br, 4 H, CH_2), 3.90 (s, 12 H, Me), 3.68 (s, 4 H, CH), 2.16 (s br, 4 H, CH_2); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 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); ^{13}C NMR (D_2O, 63 MHz) δ 178.5 (COO), 67.8 (CH_2), 51.5 (Me), 45.1 (CH), 25.2 (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.

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Uranyl Ion As a Probe of the Conduction Plane of β'' Alumina

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The fast ion conductor, sodium β'' alumina, is well known for its transport properties and rich ion exchange chemistry.[1] The latter aspect has led to the synthesis of a number of compounds which possess interesting transport and optical properties.[2–4] In this communication we present the first report of the ion exchange of a luminescent molecule, the uranyl ion, and show that it is a sensitive probe of the sites and the interaction of ions in the conduction plane of β'' alumina.

The structure of the β'' aluminas is anistropic with a strong two-dimensional character. The conduction planes are loosely packed regions that contain the mobile cation (i.e., Na^+ in sodium β'' alumina) and O^{2-} (see Figure 1). Alternating with the conduction planes are dense regions, called spinel blocks, composed of Al^{3+} and O^{2-} in close-packed arrangements. The large vacancy concentration in the conduction plane leads to high ionic mobilities in two dimensions. The sodium ions in the plane occupy sites of distorted tetrahedral (C_{3v}) symmetry known as Beevers–Ross (BR) sites. A second site in the conduction plane which possesses octahedral symmetry is known as the mid-oxygen (mO) site. Although the β'' alumina exchange chemistry permits a wide range of monatomic ions to be introduced, the incorporation of complex ions or molecules in the conduction plane is rare. Water is readily incorporated, and various hydration effects have been studied by vibrational spectroscopy.[5]

The luminescence spectrum of the uranyl ion in β'' alumina is shown in Figure 2. Single crystals of sodium β'' alumina (2 × 2 × 0.2 mm) were prepared by the flux evaporation technique.[6] The exchange process, uranyl–sodium, was accomplished by immersing the precursor single crystals in sodium nitrate melts containing either 0.2% or 2% uranyl nitrate. The crystals were held in the melt between 2 and 18 h at 350 °C. A maximum of 4% of the sodium ions was replaced by uranyl ions. X-ray diffraction results indicate that the β'' alumina structure was retained without any significant change in lattice parameters from the parent crystal.[7] The spectra were obtained at 10K by excition at 351 nm with an Ar^+ laser. The spectrum shows the signature Franck–Condon progression in the symmetric O–U–O stretch with a frequency of 860 cm^{-1} and the origin at 19 840 cm^{-1}. A second progression (the primed labels) is also observed with the same frequency but with an origin at about 19 560 cm^{-1}. When the concentration of the uranyl ion is varied, the positions of the primed and unprimed peaks remain fixed, but the relative intensities change.

The origin of the vibronic progression in the luminescence spectra of uranyl compounds changes as a function of the environment.[8,9] Two extremes are shown in Figure 2 for comparison

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