addition of Ph_3SnCl.[4,5a,b,8-11,15b,24] Addition of Ph_3SnCl (0.39 g, 1.0 mmol) to a THF solution of **3** (freshly prepared from 0.26 g (1.0 mmol) of **1**) at −78 °C resulted in immediate consumption of the dianion and the appearance of new IR absorptions at 1850 (s) and 1760 (s) cm^{-1} assigned to a monoadduct. The anion was characterized as the $[Et_4N]^+$ salt after room-temperature addition of $[Et_4N]Br$ (0.21 g, 1.0 mmol) to the solution. After 1 h the THF was removed under vacuum and the residue washed (pentane, 2 × 25 mL) to give an orange powder. The orange solution which this formed in THF (20 mL) was filtered and concentrated to about 10 mL before pentane (40 mL) was added to precipitate $[Et_4N][Cr(\eta\text{-}C_6H_6)(CO)_2SnPh_3]$ (**4**)[25] (0.34 g (0.50 mmol) ≡ 50% based on **1**) as orange needles.

Formation of **4** is consistent with the intermediacy of $[Cr(\eta\text{-}C_6H_6)(CO)_2]^{2-}$, and this is further supported by the reaction of **3** (from 0.26 g (1.0 mmol) of **1**) with 2.5 equiv of Ph_3SnCl (0.96 g, 2.5 mmol) at −78 °C. The THF was removed under vacuum (room temperature) and the residue washed with pentane (2 × 50 mL) to give a yellow powder which redissolved in 25 mL of THF. The orange solution was filtered and concentrated to about 10 mL before pentane (30 mL) was added to precipitate spectroscopically pure $[Cr(\eta\text{-}C_6H_6)(CO)_2(SnPh_3)_2]$ (**5**)[26] (0.64 g (0.72 mmol) ≡ 72%).

Double oxidative addition of Ph_3SnCl to trianionic and tetraanionic carbonylmetalates has been reported previously,[8a,9-11] and the intermediacy of $[Cr(\eta\text{-}C_6H_6)(CO)_2SnPh_3]^-$ in the oxidative addition has been confirmed by the isolation of **5** (55% yield) from the reaction of **4** with an additional 1.5 equiv of Ph_3SnCl using a procedure similar to that used for the reaction of excess Ph_3SnCl with **3**.

Facile monoprotonation has previously raised ambiguities in the characterization of extremely basic dianionic carbonylmetalates,[6d-f,27] and monoprotonation was also a problem in early studies of **3**. As indicated above, **3** gradually converts at room temperature in THF to a mixture of **3** and a species with a solution IR spectrum very similar to that of **4**. This was assumed to be $[Cr(\eta\text{-}C_6H_6)(CO)_2H]^-$ (**6**), and IR spectra indicated that **3** was completely replaced by **6** after addition of 1 equiv of NH_4PF_6 (0.06 g, 0.38 mmol) to a THF solution of **3** (freshly prepared from 0.10 g (0.37 mmol) of **1**) at −78 °C.[28]

Attempts to diprotonate **3** by addition of excess NH_4PF_6 gave a species with IR bands at 1878 (s) and 1815 (m) cm^{-1}, which did not, however, give rise to high-field ^1H NMR absorptions. The IR spectrum is close to that of **1**, suggesting that intermediate $[Cr(\eta\text{-}C_6H_6)(CO)_2H_2]$ (**7**) eliminates H_2 and forms $[Cr(\eta\text{-}C_6H_6)(CO)_2(NH_3)]$ (**8**). This interpretation was supported by the observation of an identical IR spectrum when $[Cr(\eta\text{-}C_6H_6)(CO)_3]$ was irradiated in THF with a large excess of NH_3[29] and by the determination (GC) that treatment of **3** with excess NH_4PF_6 gave H_2 (60%).

Bergman has reported that $[Re(\eta\text{-}C_5H_5)(CO)_2H]^-$ reacts with MeI to give $[Re(\eta\text{-}C_5H_5)(CO)_2(Me)_2]$ and $[Re(\eta\text{-}C_5H_5)(CO)_2H_2]$,[27b] but the high overall yield of **5** from **3**, and the absence of IR evidence for the formation of **7** or a derivative of **7**, demonstrate that **5** prepared from fresh **3** at −78 °C was not formed via **6**. Complex **6** does, however, react with 1.5 equiv of Ph_3SnCl in a manner analogous to that reported by Bergman and generates a 1:1 mixture of **5** and **8** (IR).

The preparation of $[Cr(\eta\text{-}C_6H_6)(CO)_2]^{2-}$ by naphthalenide reduction of $[Cr(\eta\text{-}C_6H_6)(CO)_2(py)]$ contrasts with previous reports on the electrochemical and amalgam reduction of $[Cr(\eta\text{-}C_6H_6)(CO)_3]$ and related arene complexes, which have been interpreted in terms of a two-electron reduction to $[(\eta^4\text{-arene})Cr(CO)_3]^{2-}$ species,[30] and it would appear that the labile donor ligand in **1** is an essential feature of the synthesis of **3**.

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Registry No. **1**, 12154-57-3; **2**, 12082-08-5; **3**, 109801-62-9; **4**, 109801-64-1; **5**, 109801-65-2; **6**, 109801-66-3; **8**, 109801-67-4; $NaC_{10}H_7$, 3481-12-7; Ph_3SnCl, 639-58-7.

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(25) IR (THF, ν_{CO}): 1842 (s), 1775 (s) cm^{-1}; ^1H NMR (acetone-d_6) δ 7.05–7.65 (m, 15 H, $SnPh_3$), 4.40 (s, 6 H, C_6H_6); $^{13}C\{^1H\}$ NMR (acetone-d_6) δ 244.0 (s, CO), 157.5, 138.8, 127.5, 126.0 (all s, $SnPh_3$), 82.5 (s, C_6H_6). ^1H and ^{13}C NMR spectra also contained resonances, with the appropriate intensity, characteristic of the tetraethylammonium counterion. Analytical samples were recrystallized from THF/diethyl ether. Anal. Calcd for $C_{34}H_{41}CrNO_2Sn$: C, 61.28; H, 6.20. Found (Galbraith, Knoxville, TN): C, 61.31; H, 6.35.

(26) IR (THF, ν_{CO}): 1900 (m), 1852 (s) cm^{-1}; ^1H NMR (acetone-d_6) δ 7.25–7.70 (m, 30 H, $SnPh_3$), 5.58 (s, 6 H, C_6H_6); $^{13}C\{^1H\}$ (benzene-d_6) δ 233.5 (s, CO), 144.7, 137.4, 128.5, 128.0 (all s, $SnPh_3$) 93.0 (s, C_6H_6). Analytical samples were recrystallized from THF/pentane as yellow needles in 55% overall yield. Anal. Calcd for $C_{44}H_{36}CrO_2Sn_2$: C, 59.58; H, 4.09. Found (Galbraith, Knoxville, TN): C, 59.12; H, 4.02.

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(28) Removal of THF gave a yellow solid with bands (ν_{CO}, Nujol mull) at 1800 (s) and 1700 (s) cm^{-1}. Although attempts to purify this material have been unsuccessful, ^1H NMR spectra in pyridine-d_5 (δ 4.85 (s, 6 H, C_6H_6), −7.66 (s, 1 H, CrH)) confirmed the presence of the hydride ligand. The 1800 cm^{-1} band in the solid sodium salt of **3**[23] can now be assigned to the presence of **6**. Contamination by **6** can be minimized with diethyl ether solvent, since the proton appears to arise from the solvent rather than adventitious water. Solid samples of the sodium salt of **3** dissolve completely and rapidly in CH_3CN to give a species with ν_{CO} at 1830 (s) and 1753 (s) cm^{-1} assigned as **6**.

(29) We have been unable to isolate **8**, which converts to **2** under vacuum.

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Application of High-Performance Liquid Chromatography for the Separation and Study of Organocobaloximes

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Summary: Nine organocobaloximes have been separated by reversed-phase high-performance liquid chromatography. Examples of the application of this newly developed method in the study of axial ligand displacement and decomposition kinetics of organocobaloximes are given.

Although high-performance liquid chromatography (HPLC) is employed mostly for the analysis of organic compounds, it has also been a useful technique for the determination of inorganic and organometallic complexes, such as metallocenes, organolead, organomercury compounds,[1] B_{12} derivatives,[2] etc. To the best of our knowl-

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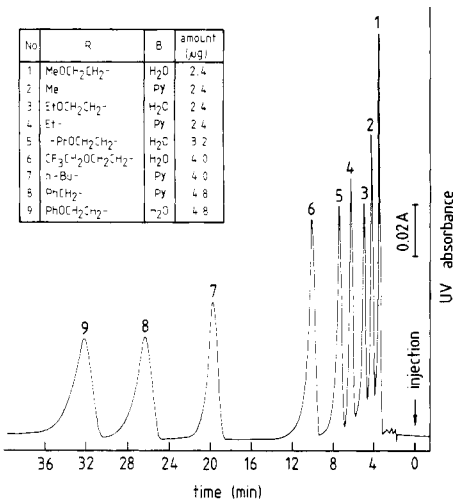

Figure 1. HPLC separation of organocobaloximes (room temperature; column, 250 × 4 mm; packing: 10-μm Chromsil C_{18}; eluent, MeOH:H_2O = 45:55; flow rate, 1.5 cm^3/min; wavelength, 254 nm; injected volume, 20 μL; samples dissolved in 65% MeOH; on column amount indicated in figure).

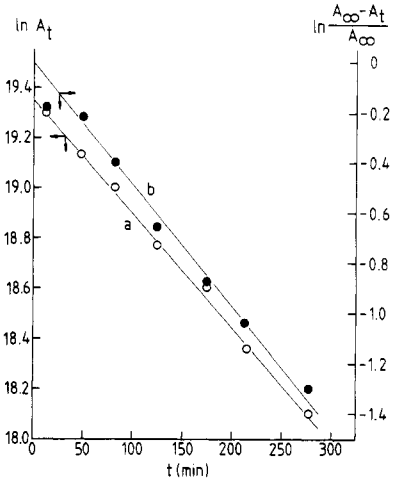

Figure 2. Logarithmic plot of peak areas for (a) $PhOCH_2CH_2Co(Hdmg)_2(H_2O)$ and (b) phenol (Initial concentration of organocobaloxime, 1.16×10^{-3} M).

edge, organocobaloximes[3] also known as vitamin B_{12} model compounds[4] have not been analyzed by this technique. We now report an HPLC method that allows (i) rapid separation of a wide range of organocobaloximes, (ii) simple, simultaneous analysis of their reaction products, and (iii) direct injection of aqueous solutions containing background electrolytes. For this purpose, we have chosen reversed-phase packings (Lichrosorb RP-18, Chromsil C_{18}) and aqueous methanol as a mobile phase.[5] Figure 1 shows that almost complete base-line resolution of nine organocobaloximes[6] can be achieved by this HPLC method. In accordance with the general findings, organocobaloximes with less polar groups elute later, while the more polar organocobaloximes elute earlier. The presence of oxygen in the alkyl group greatly facilitates elution: the retention times decrease in the order $MeOCH_2CH_2$ > Me > $EtOCH_2CH_2$ > Et > *i*-$PrOCH_2CH_2$ > *n*-Pr (t_R of the latter = 10.2 min; peak not shown).

It is a question of considerable interest whether the axial pyridine is displaced by the water molecule before or during analysis. Since the stability constant[9] for the equilibrium $MeCo(Hdmg)_2(H_2O)$ + py ⇄ $MeCo(Hdmg)_2py$ is 2.03×10^3 M^{-1}, ca. 70% dissociation of methyl(pyridine)cobaloxime is expected ($[Co]_T = 3.1 \times 10^{-4}$ M) under the conditions of chromatography; thus free pyridine must be present in the solution. Investgations with Chromsil C_{18} packing have shown that pyridine is retained strongly by this column so that it does not elute under the circumstances of Figure 1. This behavior is probably due to interaction of pyridine with residual silanol groups on the surface of the packing. However, under the same conditions Lichrosorb RP-18 packing has proved to be suitable for the analysis of pyridine (t_R = 6 min). Chromatograms of methyl, ethyl, propyl, butyl, and benzyl derivatives obtained by using Lichrosorb RP-18 have always shown the presence of free pyridine. Thus, it is the aqua complex that is eluted in all cases as no other peaks assignable to (pyridine)cobaloximes can be observed.

HPLC is also suitable for analyzing reaction mixtures of organocobaloximes. This is illustrated by monitoring the known decomposition of (phenoxyethyl)cobaloxime in basic media:

$$PhOCH_2CH_2Co(Hdmg)_2(H_2O) \rightarrow PhOH + CH_2{=}CH_2 + Co(Hdmg)_2OH \quad (1)$$

The kinetics of this reaction has been investigated by measuring the amount of ethylene.[8] Our HPLC method, allowing easy separation of all products and the starting material, is convenient for following the concentration of the species involved, provided the reaction is not too fast compared with the analysis time. Figure 2 shows logarithmic plots of the peak areas for (phenoxyethyl)cobaloxime and phenol.[10] The calculated first-order rate constants are 7.6×10^{-5} s^{-1} (organocobaloxime) and 8.1×10^{-5} s^{-1} (phenol) at 25 °C and pH 10.6 (10% MeOH, K_2HPO_4 + KOH buffer, I = 1 M/KCl), in fair agreement with the value (9.7×10^{-5} s^{-1}) determined earlier volumetrically.

Registry No. $MeOCH_2CH_2Co(hdmg)_2$, 58079-63-3; $MeCo(Hdmg)_2(py)$, 23642-14-0; $EtOCH_2CH_2Co(Hdmg)_2(H_2O)$, 80422-34-0; $EtCo(Hdmg)_2(py)$, 25360-57-0; *i*-$PrOCH_2CH_2Co(Hdmg)_2(H_2O)$, 109637-45-8; $CF_3CH_2OCH_2Co(Hdmg)_2(H_2O)$, 109637-46-9; *n*-$BuCo(Hdmg)_2(py)$, 30974-87-9; $PhCH_2Co(Hdmg)_2(py)$, 27860-79-3; $PhOCH_2CH_2Co(Hdmg)_2(H_2O)$, 64707-51-3; $MeCo(Hdmg)_2(H_2O)$, 25360-55-8; $EtCo(Hdmg)_2(H_2O)$, 26025-30-9; *n*-$BuCo(Hdmg)_2(H_2O)$, 30974-86-8; $PhCH_2Co(Hdmg)_2(H_2O)$, 38721-38-9; PhO, 108-95-2; $CH_2{=}CH_2$, 74-85-1; $Co(Hdmg)_2OH$, 109637-47-0.

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(5) Lichrosorb RP-18 is a trade mark of E. Merck Laboratory, Chromsil C_{18} is manufactured by Labor MIM (Hungary).

(6) Methyl-, ethyl-, propyl-, butyl-, and benzylcobaloximes were prepared by Schrauzer's method.[7] For the preparation of alkoxy derivatives see ref 8.

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(9) Brown, K. L.; Chernoff, D.; Keljo, D. J.; Kallen, R. G. *J. Am. Chem. Soc.* **1972**, *95*, 6697.

(10) To avoid base-line drift and spurious peaks on the chromatogram due to KCl and K_2HPO_4, 55% water containing 0.01 M KCl and 0.01 M KH_2PO_4 + 45% MeOH was used as the mobile phase. Use of KH_2PO_4 also allowed direct injection of the reaction mixture into the HPLC (prior neutralization was unnecessary). The reaction was carried out under nitrogen. Samples were taken via a silicon septum with a 50-μL microsyringe.