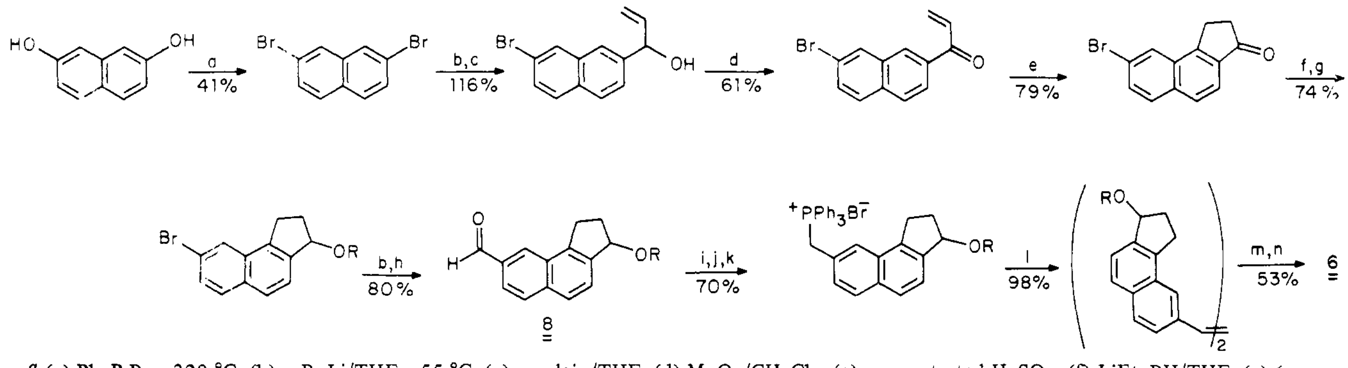
Scheme I[a]



[a] (a) $Ph_3P{\cdot}Br_2$, 320 °C; (b) *n*-BuLi/THF, -55 °C; (c) acrolein/THF; (d) MnO_2/CH_2Cl_2; (e) concentrated H_2SO_4; (f) $LiEt_3BH$/THF; (g) (*t*-Bu)Me_2SiCl, imidazole/DMF; (h) DMF/THF, -70 °C; (i) DIBAL-H/hexane; (j) $(n\text{-}C_8H_{17})_3P$, CBr_4/ether; (k) Ph_3P/C_6H_6, 80 °C; (l) 8, LiOEt/EtOH; (m) $h\nu$, catalytic I_2/C_6H_6; (n) *p*-TsOH·H_2O/C_6H_6, 60 °C. R = (*t*-Bu)Me_2Si.

The methylene hydrogens abut carbons within the helix, splaying the structure considerably. The angle between the outer rings is 69.1°, much greater than in other helicenes.[17] The removal of the methylene hydrogens by base should thereby be facilitated, but in fact the reaction seems difficult to effect. Thus *n*-butyllithium in tetrahydrofuran (THF), which easily deprotonates simpler indenes (including the precursors of **2**[2] and **3**[3]), seems to work only poorly with **6**,[19] but *tert*-butyllithium in THF works well, giving **4** and after quenching with aqueous acetic acid **7**.[20] The implication may be that Coulombic repulsions prevent the splayed structure in **6** from relaxing in **4**, an effect that may account for the course of the reactions discussed below.

When solutions of **4** as its lithium salt in THF are combined at −65 °C with very pure $FeCl_2$,[21] they give as the only product soluble in CS_2 a very dark red crystalline solid[22] in yields of 60%, which mass spectrometry,[23] ^{1}H NMR spectroscopy,[24] and X-ray diffraction analysis[25] identify as **5**. The metal atom presumably bonds to the inside faces of the cyclopentadienyl rings in **4** because the helical structure is splayed, additional evidence for which is the observation that deuterated acids attack almost as often from the inside as from the outside.[26] Drawn by the concentrated negative charge the metal cation moves to a position between the rings, which then clamp at 19.4°, almost parallel,[27] as characteristic of the ferrocenes.[25]

Acknowledgment. We are grateful for the support of the National Science Foundation (CHE 75-20621) and the National Institutes of Health (GM-19173). We thank Dr. John Dewan for the X-ray diffraction analyses.

(17) The corresponding angle in the benzene analogue of **5**, [7]helicene, is 32.4°.[18]

(18) (a) Beurskens, P. T.; Beurskens, G.; van der Hark, Th. E. M. *Cryst. Struct. Commun.* **1976**, *5*, 241, 247. (b) Joly, M. et al. *Helv. Chim. Acta* **1977**, *60*, 537.

(19) Experiments in which **6** was combined with 6 equiv of *n*-BuLi in THF (−78 → 0 °C, 1 h) and then quenched (D_2O) gave impure **7**. The ^{1}H NMR's of some of these impurities fall at 3.0 ppm, obscuring the integration of **7**'s allylic proton resonances. Variations using HMPA and TMEDA as solvents or cosolvents gave **7** or mixtures of **6** and **7**, but impurities blocked our ability to use the integrals of the allylic and olefinic ^{1}H NMR's as measures of the extent of deuteration.

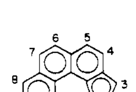
(20) When **6** was combined with 17 equiv of *t*-BuLi in THF (−65 → −20 °C, 45 min; −20 °C, 2.5 h) and quenched with D_2O/CH_3CO_2D, **7**-d_2 was produced. The ratio of the allylic and olefin protons, measured by ^{1}H NMR spectroscopy, was 0.51. The mass spectrum indicated it to be 79.5 ± 2% dideuterated and 11.1 ± 1% monodeuterated (CI, methane).

(21) Commercial $FeCl_2$ gave no metallocene. We used the THF adduct,[1a] which is easy to purify and stable to oxidation.

(22) UV-visible, nm (log ε) in tetrahydrofuran: 261 (4.46), 284 (4.33), 329 (3.85), 391 (3.38), 417 (3.18), 456 (2.69), all shoulders, but with 284 distinct, 261 and 329 less so, and the others less yet.

(23) The mass spectrum (CI, methane) is dominated by the parent peaks (base peak *m/e* 409), and except for a peak attributable to residual **6** (at *m/e* 355, 17%), none are as much as 10% the size of the base peak.

(24) ^{1}H NMR (250 MHz, C_6D_6, see structure i) δ 7.67 (d, *J* = 7.9 Hz, H_7), 7.55 (s, H_8), 7.54 (d, *J* = 8.1 Hz, H_6), integral 5.68; 7.27 (d, *J* = 9.0 Hz, H_5), 7.12 (d of d, *J* = 8.9, 0.8 Hz, H_4), integral 6.16 (augmented by C_6D_5H and minor impurities); 4.39 (d of d, *J* = 2.6, 1.1 Hz, H_3), integral 1.97; 3.88 (t, *J* = 2.5 Hz, H_2), integral 2.45; 3.68 (d of d of d, *J* = 2.6, 1.1, 0.8 Hz, H_1), integral 1.89.[14]



i

(25) Dewan, J., to be published.

(26) In the ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the deuterated product **7** the ratio of the intensities of the exo and endo protons (at δ 3.21 and 3.07) is 0.52. This requires that approximately every third deuteron approach endo to the ring. The possibility was considered that deuterons attach only exo and methylene protons transfer intramolecularly, but the observed couplings exclude this mechanism.

(27) The torsional angles around the inner core of benzenoid C–C bonds are, from terminus to terminus, 15, 20, 27, 17, and 16°.

Catalytic Hydrolysis of Esters of *p*-Nitrophenol Bound by Amylose in the Me_2SO–H_2O Mixed-Solvent System[1]

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Our recent investigations have established that the formation of helical supramolecular complexes of amylose **1** or its derivatives with long-chain substrates in both aqueous and Me_2SO–H_2O mixed-solvent systems is accompanied by conformational changes of the macromolecules.[2] In comparison with the well-studied cyclodextrin and functionalized polymer systems, two merits of our new systems are apparent: (1) binding sites are similar to that of the cyclodextrins and are thus well-defined; (2) the process of substrate binding can be accomplished only by conformational changes which may serve as a mimicry for the "induced fit" of enzymatic processes. Noteworthy rate accelerations with enzymelike kinetics have already been achieved with the hyrolysis of some esters in aqueous phase with sodium carboxymethylamylose (Na-CMA).[2a] The present communication reports similar results from an investigation of the hydrolysis of five esters of *p*-nitrophenol (**2–6**), which have been used in several other investigations,[3] in the Me_2SO–H_2O mixed-solvent system (cf. ref

(1) The Microenvironmental Effects of the Helical Conformations of Amylose and Its Derivatives. 5.

(2) (a) Hui, Yongzheng; Gu, Jianhua *Hua Hsueh Hsueh Pao* **1981**, *39*, 309–318. (b) Hui, Yongzheng; Gu, Jianhua; Jiang, Xikui *Ibid.* **1981**, *39*, 376–381. (c) Hui, Yongzheng; Cheng, Xianen; Gu, Jianhua; Jiang, Xikui *Scienta Sinica*, submitted for publication.

Table I. Rate and Dissociation Constants in 50% Aqueous Me_2SO for Various Ester Substrates, 0.01 M Borate Buffer, 35 °C

substrate	k_{un}, 10^{-2} s^{-1}	k_c, 10^{-2} s^{-1}	K_d, mM	k_c/k_{un}	k_c/K_2, 10^2 s^{-1} M^{-1}	k_2, s^{-1} M^{-1}
2[f]	1.94					0.24
2[b,f]	1.29					0.64
2[c]						1.3
3	1.06	4.6[a]	0.45[a]	4.3[a]	1.0	
4	0.816	4.5	0.22	5.5	2.1	
5	0.837	9.9	0.073	11.8	13.6	
5[b]	0.437	4.6	0.015	10.5	30.7	
5[c]						0.54
6	0.027[d]	4.74	0.036	176	13.2	
6[b]	0.015	1.77	0.0036[e]	118	49.2	
6[c]						0.044

[a] The hydrolysis of **3** may not truly conform to saturation kinetics; thus the k_c and K_d values may involve large uncertainties. For **4**, the uncertainty in k_c is ±20%; all other values are accurate to within ±5%. [b] 0.01 M carbonate buffer was used. [c] The second-order rate constant was obtained in 0.01 M carbonate buffer, with glucose as the catalyst in place of amylose. [d] The experimental uncertainty for this value is ±7%, but all other k_{un} values are accurate to within ±6%. [e] The uncertainty is ±25%; for the other K_d values reading down the column from substrate **4** are accurate to within ±6%. [f] The second-order rate constant was obtained with amylose as the catalyst, and the calculations were based on the number of anhydroglucose units.

4) with amylose **1** itself. The number-average molecular weight of the amylose used is 5.70×10^4, corresponding to a degree of polymerization of 350.

Since the stability of inclusion complexes of **1** increases with the amount of water in the mixed-solvent system,[2c] we chose to use the 1:1 v/v Me_2SO–H_2O system for studying the hydrolysis of five esters of *p*-nitrophenol with various chain lengths,[5] to wit, the acetate **2**, the valerate **3**, the caprylate **4**, the laurate **5**, and the palmitate **6**. Two buffers were used, viz., 0.01 M sodium borate or sodium carbonate; their pH values are 9.5 in pure water. The observed rate constants, k_{obsd}, for the hydrolysis of the substrates were determined by monitoring the absorbance at 410 nm.

At 0.01 M buffer, only substrate **2** shows no kinetic saturation, obviously because it possesses a much shorter chain. With **3** and **4** on the borderline, all others show saturation behavior, and the k_c and K_d values obtained from linear Lineweaver–Burk plots are listed in table I. The distinctively different rate profiles for **5** and **6** under various conditions are shown in Figure 1.

Limitations posed by solubility made it impracticable to make kinetic runs for most of the esters in aqueous buffer systems, but the pH dependence of the buffer on the composition of the Me_2SO–H_2O mixture were known, e.g., for the 0.01 M borate buffer, the pH is 9.5 in pure water, 12.7 in 50% Me_2SO, 13.9 in 60% Me_2SO and >14 in 70% Me_2SO. Since the 12.7 value is higher than the pK_a of the hydroxyl groups in amylose (12.46),[6] the ionized hydroxyl groups of the macromolecules are expected to play vital roles in the catalytic processes.

For the substrate **6**, k_c is over two orders of magnitude larger than k_{un}. More notably, if the bimolecular rate constants of **2**, **5**, and **6** with glucose as the catalyst were taken as the references and compared with the k_2 of **2** and the approximate k_c/K_d^*[7] values

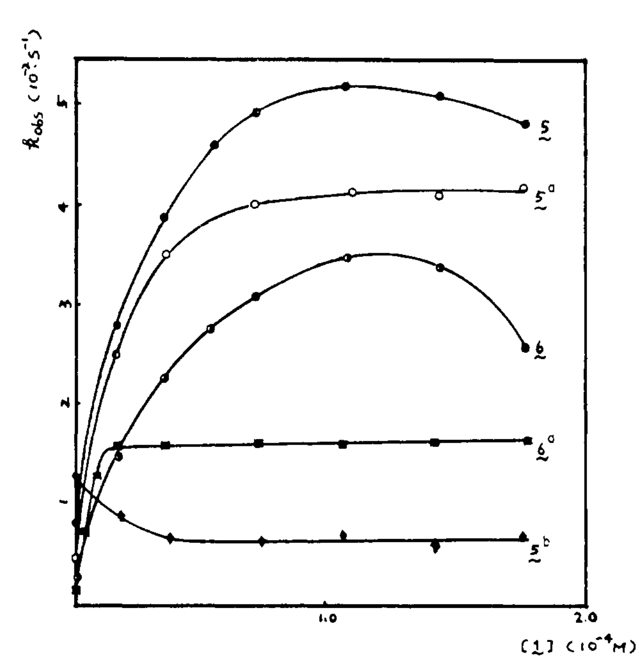


Figure 1. Observed rate constants at 35 °C for the hydrolysis of **5** and **6** as a function of amylose concentration at 0.01 M borate buffer except when (a) 0.01 M carbonate buffer and (b) 0.05 M borate buffer are used.

of **5** and **6** in the carbonate buffer, we found that on **2**, amylose has the same catalytic effect as glucose,[8] but on **5** and **6** it produced remarkable rate accelerations of 2.8×10^2- and 5.6×10^3-fold, in accord with anticipations that more effective inclusion of the longer-chain substrate by the helical conformation of amylose will be accompanied by more effective catalysis of the substrate reaction.[2]

Moreover, the parallel trends in the k_c/k_{un} and k_c/K_d^* values all indicate that the catalytic efficiencies increase with increasing chain lengths of the substrates. The K_d values also show that the stabilities of the inclusion complexes increase with the lengths of the hydrocarbon chains. Thus all facts lead to the same conclusion: the formation of supramolecular complexes is a prerequisite for the catalyzed hydrolysis of the substrates. Indeed, it is rather gratifying to find that actually a linear relationship exists between ln $(1/K_d)$ and the number of carbon atoms of the alkyl groups of these esters. From this linear relationship the free energy change of the process of phase transfer from the bulk phase to the helical cavity for each methylene group can be estimated. The value is –0.15 kcal/mol, much smaller than the corresponding value (–0.88 kcal/mol) for the transfer from aqueous to hydrocarbon phases.[9] Since the polarity differential between our bulk phase (50% aqueous Me_2SO) and the etherlike cavity is small, the observed difference in ΔG values appears natural.

Figure 1 shows two curves (**5** and **6**, 0.01 M borate buffer) which appears puzzling at first sight—the k_{obsd} values drop with increasing host concentration in high-concentration regions. We thought this might be a reflection of the perturbation caused by cross-linking of the macromolecules, since borate anions and amylose are known to form coordination complexes.[10] If we treat this situation by the following scheme, oversimplified as it may be, in a manner somewhat similar to "substrate inhibition"[11] (the present case may be termed "borate-plus-host inhibition"), the inhibition constant, K_d', can be evaluated to be 0.14 and 0.12 mM for **5** and **6** respectively:

(3) (a) Blyth, C. A.; Knowles, J. R. *J. Am. Chem. Soc.* **1971**, *93*, 3021–3027. (b) Ueoka, R.; Shimamoto, K.; Maezato, Y.; Ohkubo, K. *J. Org. Chem.* **1978**, *43*, 1815–1817.

(4) Siegel, B.; Breslow, R. *J. Am. Chem. Soc.* **1975**, *97*, 6869–6870.

(5) The esters were prepared by conventional methods and their structures were established by UV, IR and elemental analysis. Their boiling points or melting points are as follows: **2**, 79–80 °C (mp); **3**, 151–154 °C (3 torr); **4**, 168–169.5 °C (4 torr); **5**, 45.5–46.5 °C (mp); **6**, 63–64.5 °C (mp).

(6) The actual pH of the mixed solvent (0.01 M buffer) are within the range of 12.5–12.7, almost independent of the concentration of amylose.

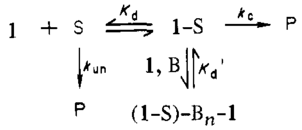
(7) The K_d value determined from the kinetic method is related to the intrinsic dissociation constant, K_d^*, by the expression $K_d = K_d^*/n$, where n is the largest number of binding sites per host molecule. Here n is assumed to be around 20, as based on our previous results.[2c]

(8) The difference of k_2 values can be attributed to the difference in number of hydroxyl groups on free glucose molecules and on anhydroglucose units in amylose.

(9) Tanford, C. "The Hydrophobic Effect", 2nd ed.; Wiley-Interscience: New York, 1980.

(10) (a) Böeseken, J. *Recl. Trav. Chim. Pays-Bas* **1942**, *61*, 82–87. (b) Böeseken, J. *Adv. Carbohydr. Chem.* **1949**, *4*, 189–207. (c) Janado, M.; Azuma, J-i.; Onodera, K. *Agric. Biol. Chem.* **1973**, *37*, 2337–2343.

(11) Piszkiewicz, D. "Kinetics of Chemical and Enzyme Catalyzed Reaction"; Oxford University Press: New York, 1977; pp 91–97.



1, amylose
S, substrate
B, borate ion

Furthermore, curve **5**[b] of the same figure may be called on as a witness to the case in point—a big dose of borate ions simply wrecks the catalysis assembly lines. Finally, as our second witness, curve **5**[a] and **6**[a] show that carbonate ions will do nothing of this sort. Thus we conclude that intrasupramolecular catalysis for the hydrolysis of some long-chain esters can be damaged and even nullified by perturbation of their helical conformations.

Registry No. 1, 9005-82-7; **2**, 830-03-5; **3**, 1956-07-6; **4**, 1956-10-1; **5**, 1956-11-2; **6**, 1492-30-4.

Reduction of Carbon Dioxide and Carbonyl Sulfide by Anionic Group 6B Metal Hydrides and Alkyls. Carbon-Hydrogen and Carbon-Carbon Bond Formation Processes and the Structure of [PNP][Cr(CO)$_5$SC(O)H]

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Considerable interest is being shown in the development of C_1 chemistry, e.g., Fischer-Tropsch (F-T) technology. Recently, we reported on the facile reduction of CO_2 by anionic group 6B metal hydrides to afford metalloformate derivatives (reaction 1).[1]

$$M(CO)_5H^- + CO_2 \rightleftharpoons M(CO)_5O_2CH^- \qquad (1)$$

Because of the great potential for employing not only carbon monoxide but carbon dioxide as a feedstock in the production of reduced carbon containing molecules such as alcohols and hydrocarbons, an investigation on CO_2 insertion processes into metal-carbon bonds has been initiated.[2] Further, in an effort to more fully explore and assimilate the mechanistic aspects of these reactions, as well as to extend their applicability, we have utilized carbonyl sulfide as the substrate in these processes. In this communication we compare and contrast reactions of CO_2 and COS with anionic group 6B metal carbonyl hydrides and alkyls and describe the X-ray structural characterization of the product of carbonyl sulfide insertion into the chromium-hydride bond.

The synthesis of the $Cr(CO)_5SC(O)H^-$ anion was achieved by either exchange of COS for carbon dioxide in the (formato)-pentacarbonylmetalate or by direct reaction of COS with $Cr(CO)_5H^-$. The $[PNP]^+$ or $[Et_4N]^+$ salts of $Cr(CO)_5O_2CH^-$, prepared from $Cr(CO)_5Cl^-$ and TlO_2CH in CH_2Cl_2,[1] reacted cleanly over a 12-h period with COS in CH_3CN at 200 kPa to afford $Cr(CO)_5SC(O)H^-$ (reaction 2). Alternatively, [K(Crypt-222)]-

$$Cr(CO)_5O_2CH^- + COS \xrightarrow{CH_3CN} Cr(CO)_5SC(O)H^- + CO_2 \qquad (2)$$

$[HCr(CO)_5]$, synthesized from $Cr(CO)_6$ and 2 equiv of Crypt 222[3] solubilized KOH in CH_3CN,[1] reacted instantaneously with COS to provide the thioformate species (reaction 3).[4] Both reactions

$$HCr(CO)_5^- + COS \xrightarrow{CH_3CN} Cr(CO)_5SC(O)H^- \qquad (3)$$

gave quantitative spectroscopic yields of the desired product.[5] Since $Cr(CO)_5O_2CH^-$ readily undergoes decarboxylation (i.e., reaction 1 run in the reverse direction), reaction 2 probably proceeds via the $HCr(CO)_5^-$ anionic species as well. On the other hand, because the Mo and W formato analogues are more inert toward CO_2 extrusion, the thioformate derivatives in these instances were prepared according to reaction 3.

Infrared and ^{13}C NMR spectral comparisons of these thioformato complexes with the products arising from CO_2 and CS_2 insertion processes with $HM(CO)_5^-$ species are suggestive of binding of the thioformate ligand to the $M(CO)_5$ moiety through the sulfur atom.[1,6] This mode of binding was confirmed in the [PNP][Cr(CO)$_5$SC(O)H] derivative by X-ray crystallography.[7] The structural results for the anion are depicted in Figure 1.[8] The disposition of the ligands about the chromium atom is that of a

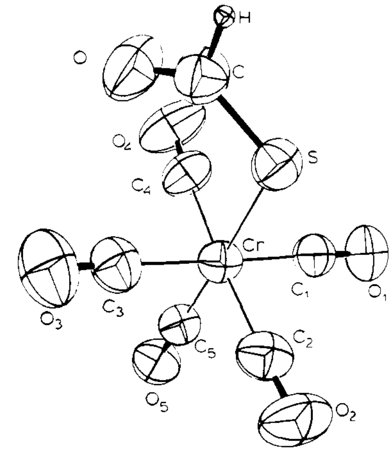

Figure 1. Perspective drawing of the $Cr(CO)_5SC(O)H^-$ anion. Some bond lengths are as follows: Cr-S, 2.447 (1); Cr-C(eq)$_{av}$, 1.894 (4); Cr-C(ax), 1.837 (4); S-C, 1.725 (5); O-C, 1.206 (6); C-H, 1.06 (4) Å.

Table I. Reaction Conditions of CO_2 Insertion into $CH_3W(CO)_5^-$ [a]

no.	additive	time, h	temp, °C	extent of the reaction,[b] %
1	none	24	ambient	~30
2	none	46	ambient	~46
3	none	24	52	100
4	Li salts[c]	20	ambient	100
5	LiCl[d]	6	ambient	100
6	Na^+ [e]	<25	ambient	100[f]

[a] $CH_3W(CO)_5^-PNP^+$, 0.01 M solution in THF, CO_2 pressure 100-300 kPa. [b] By IR spectroscopy of carbonyl region. [c] LiCl, LiBr, LiO_2CCH_3 as byproducts of the $CH_3Li{\cdot}LiBr + ClW(CO)_5^- \rightarrow CH_3W(CO)_5^-$ reaction pressurized in situ with CO_2. [d] 1.1 molar excess with respect to $CH_3W(CO)_5^-$. [e] $NaBPh_4$ 4-fold molar excess with respect to $CH_3W(CO)_5^-$. [f] Determined as $W(CO)_6$.

(1) Darensbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 3223.

(2) For a review of other insertion reactions of CO_2 into transition-metal-carbon bonds, see: Kolomnikov, I. S.; Grigoryan, M. Kh. *Russ. Chem. Rev.* **1978**, *47*, 334.

(3) 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Crypt 222, Kryptofix 222). Supplied by Parish Chemicals, Provo, UT 84601.

(4) For preparative scale syntheses of hydridopentacarbonylmetalates, see: Darensbourg, M. Y.; Deaton, J. C. *Inorg. Chem.* **1981**, *20*, 1644. Darensbourg, M. Y.; Slater, S. *J. Am. Chem. Soc.* **1981**, *103*, 5914.

(5) Anal. Calcd for [PNP][Cr(CO)$_5$SC(O)H]: C, 63.72; H, 3.95; S, 4.05. Found: C, 63.66; H, 4.11; S, 4.13.

(6) For example, the ν(CO) infrared and ^{13}C NMR spectral properties of [K(Crypt-222)][Cr(CO)$_5$SC(O)H] in acetonitrile are 2050 w, 1920 s, and 1861 m cm^{-1} and $\delta(C_{ax})$ 225.7, $\delta(C_{eq})$ 219.1, and δ(SC(O)H) 198.8, respectively.

(7) Single crystals of [PNP][Cr(CO)$_5$SC(O)H] were grown from CD_3CN. They belong to the triclinic space group $P\bar{1}$ with a = 12.671 (5) Å, b = 12.880 (5) Å, c = 15.356 (6) Å, α = 108.01 (3)°, β = 119.61 (3)°, γ = 97.48 (3)°, Z = 2. R = 4.0% for 5811 reflections with $I > 3\sigma(I)$. Crystallographic analysis was carried out by Dr. Cynthia S. Day at Crystalytics Co., Lincoln, NE.

(8) The $[PNP]^+$ counterion was found to be a well behaved group and contained dimensions which are expected for it. The average P-N bond length is 1.582 (3) Å, and the P-N-P angle is 140.1 (2)°.

0002-7863/82/1504-0349$01.25/0