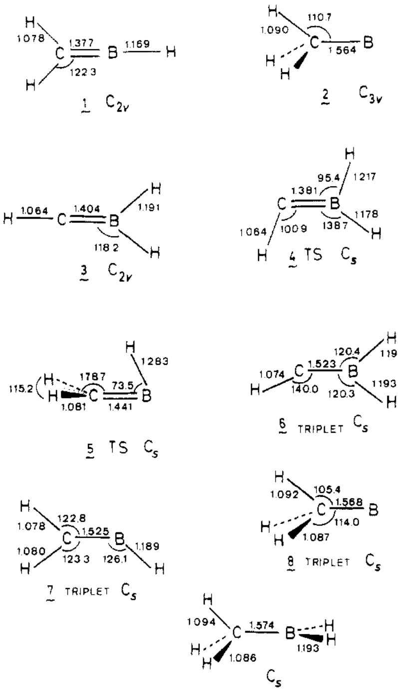

Figure 1. 6-31G* structures of CBH_3 isomers.

arrangement of 2 into 1 has a bridging hydrogen and an intermediate C–B length. The other geometrical data given in Figure 1 (XH bond lengths and angles) reflect the expected effects of hybridization and electronic interactions.

Further Comparisons. Like singlet carbenes, borylenes have both lone pair and empty acceptor orbitals and should exhibit both nucleophilic and electrophilic behavior. Correlated cycloaddition to multiple bonds as well as reactions with both cases and acids is expected. The behavior of protonated methylborylene CH_3–BH^+ (which we have investigated theoretically)[16] contrasts with that of the isoelectronic 2. CH_3–BH^+ is considerably more stable (37.9 kcal/mol at MP4/6-31G*+ZPE) than the isomer $CH_2BH_2^+$, which corresponds to protonated 1. However, $CH_2BH_2^+$ has perpendicular C_{2v} symmetry and lacks the C=B double bond in 1.

Thus, borylenes should be stabilized as complexes with Lewis acids. In addition, π-donor substituents with two sets of electron lone pairs are especially effective, e.g. F in BF ($D_0° = 180$ kcal/mol)[6d] and especially O^- in BO^-, which has the very large electron affinity of 3.12 eV.[6b] We will report the results of a calculational survey of substituted borylenes subsequently.[17]

Postscript. Very recently, Jeong and Klabunde have reported a matrix study[18] that included the reaction of boron atoms with methane. The presence of H_3C–B species was suggested. The spectral lines observed are compared in Table III with those calculated for 2 and its rearrangement product 1. No definite agreement is apparent.

The C=B bond length in a *tetracoordinate* anion, $(mesityl)_2B{=}CH_2^-$, is 1.444 (8) Å by X-ray analysis,[19] but tricoordinate distances are expected to be shorter.

Table III. Frequencies of BCH_3 Species (cm^{-1})

CH_3—B (2)[a]	CH_2=BH (1)[a]	expt[b]
2877 (e)	3010 (b_2)	2500
2813 (a_1)	2952 (a_1)	2134
1390 (e)	2649 (a_1)	2051
1297 (a_1)	1457 (a_1)	2027
865 (a_1)	1248 (a_1)	2007
590 (e)	880 (b_2)	971
	770 (b_1)	909
	652 (b_1)	894
	452 (b_2)	823

[a] 6-31G* harmonic frequencies, scaled by 0.89. [b] Values given in ref 18. Those near 2000 cm^{-1} are ascribed to "δ_{BH}-bridged" vibrations. See text.

Conclusions. The most important conclusion of this work is that methylborylene is a local minimum on the potential surface with a substantial barrier (25.0 kcal/mol) to rearrangement. Being stabilized by π-donation from the methyl group, the singlet state is far below the triplet (by 43.6 kcal/mol).

Acknowledgment. The research was supported at Pittsburgh by the National Science Foundation (Grant CHE-8409405) and at Erlangen by the Fonds der Chemischen Industrie. J.A.P. is indebted to the Alexander von Humboldt Foundation for a Senior Fellowship. We thank P. Budzelaar for helpful suggestions and H. Nöth for information prior to publication.

Registry No. 1, 56125-75-8; 2, 62785-41-5; 3, 78570-06-6; 4, 13766-26-2.

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[16] Pople, J. A.; Apeloig, Y.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1982**, *85*, 489.

[17] Stout, P.; Schleyer, P. v. R., to be submitted for publication. For recent, related studies, see: Armstrong, D. R.; Walker, G. T. *J. Mol. Struct.* **1986**, *139*, 47. Nguyen, M. T. *J. Chem. Soc., Chem. Commun.* **1987**, 342.

[18] Jeong, G. H.; Klabunde, K. J. *J. Am. Chem. Soc.* **1986**, *108*, 7103.

[19] Olmstead, M. M.; Power, P. P.; Weese, K. J.; Doedens, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 2541.

Formation and Characterization of $[Cr(\eta\text{-}C_6H_6)(CO)_2]^{2-}$, a Dianionic η^6-Arene-Substituted Carbonylmetalate

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Summary: Naphthalenide reduction of $[Cr(\eta\text{-}C_6H_6)(CO)_2(py)]$ (**1**) (py = pyridine) gives $[Cr(\eta\text{-}C_6H_6)(CO)_2]^{2-}$ (**3**), which reacts with Ph_3SnCl to give $[Cr(\eta\text{-}C_6H_6)(CO)_2SnPh_3]^-$ (1 equiv) or $[Cr(\eta\text{-}C_6H_6)(CO)_2(SnPh_3)_2]$ (**5**) (excess). Addition of NH_4PF_6 (1 equiv) to **3** gives $[Cr(\eta\text{-}C_6H_6)(CO)_2H]^-$ (**6**), and excess NH_4PF_6 gives $[Cr(\eta\text{-}C_6H_6)(CO)_2(NH_3)]$ (**8**) and H_2. Anion **6** reacts with Ph_3SnCl to give a 1:1 mixture of **5** and **8**.

Mononuclear homoleptic carbonylmetalates can be readily prepared for most transition metals, including group 5,[3] 6,[4] 7,[5] 8,[6] and 9[5a,b,7] metals in low (−1 or −2)

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[3] (a) Werner, R. P. M.; Podall, H. E. *Chem. Ind. (London)* **1961**, 144–145. (b) Ellis, J. E.; Davison, A. *Inorg. Synth.* **1976**, *16*, 68–73. (c) Dewey, C. G.; Ellis, J. E.; Fjare, K. L.; Pfahl, K. M.; Warnock, G. F. P. *Organometallics* **1983**, *2*, 388–391.

[4] Maher, J. M.; Beatty, R. P.; Cooper, N. J. *Organometallics* **1985**, *4*, 1354–1361 and references therein.

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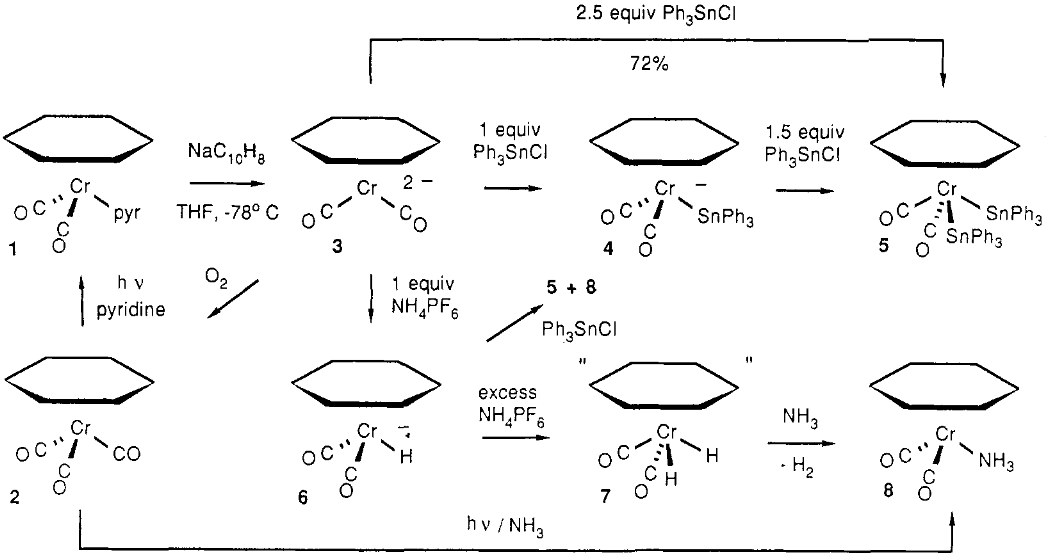
Scheme I



oxidation states and group 5,[8] 6,[9] 7,[10] and 9[11] metals in ultralow (−3 or −4) oxidation states. The extensive chemistry of homoleptic low oxidation state alkene complexes[12] suggests that many substituted carbonylmetalates should also be accessible, and it is well established that cyclopentadienyl-substituted carbonylmetalates ($[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$,[5a,b,13,14] $[Mo(\eta\text{-}C_5H_5)(CO)_3]^-$,[5a,b,13] $[W(\eta\text{-}C_5H_5)(CO)_3]^-$,[5a,13] $[V(\eta\text{-}C_5H_5)(CO)_3]^{2-}$,[15] and $[M(\eta\text{-}C_5R_5)(CO)_4]^-$ with M = Ti or Zr and R = H or Me[16]) are valuable intermediates in organometallic synthesis. With the exception of $[V(\text{mesitylene})(CO)_3]^-$,[17a] however, analogous arene-substituted carbonylmetalates have only recently been reported, and other examples are limited to $[Mn(\eta\text{-}C_6Me_6)(CO)_2]^-$,[17b] $[Mn(\eta\text{-}C_6H_6)(CO)_2]^-$,[17c] $[Cr(\eta^4\text{-naphthalene})(CO)_3]^{2-}$,[18] and dimeric dianions with conjugated ligands like $[\{Cr(CO)_3\}_2(\text{biphenyl})]^{2-}$.[19] We now wish to report the synthesis of $[Cr(\eta\text{-}C_6H_6)(CO)_2]^{2-}$, a dianionic carbonylmetalate containing an η^6-arene ligand, and some of its reactions as summarized in Scheme I.

Our approach to $[Cr(\eta\text{-}C_6H_6)(CO)_2]^{2-}$ is based on naphthalenide reduction of a $[Cr(\eta\text{-}C_6H_6)(CO)_2L]$ complex in which L is a donor ligand which is a poor π-acceptor—this ligand should preferentially dissociate on reduction, and the use of naphthalenide allows reduction under low-temperature conditions such that the second electron transfer can occur before an intermediate radical anion can decompose or dimerize.[4]

A solution of $[Cr(\eta\text{-}C_6H_6)(CO)_2(py)]$ (1)[20] (0.265 g, 1.0 mmol) in 20 mL of tetrahydrofuran (THF) was cooled to −78 °C, and 15.4 mL of a 0.13 M solution of sodium naphthalenide in THF[4] (2 equiv) was syringed in dropwise over 1 min. IR spectra of the dark brown turbid solution indicated complete consumption of 1[21] and initial formation of a new species with carbonyl absorptions at the low frequencies of 1665 (s) and 1550 (m) cm^{-1}, consistent with the formation of $[Cr(\eta\text{-}C_6H_6)(CO)_2]^{2-}$ (3).[22] Two weaker bands grew in at 1840 and 1760 cm^{-1} as the mixture was warmed to room temperature (see below). The dianion is extremely sensitive in solution, oxidizing instantaneously to $[Cr(\eta\text{-}C_6H_6)(CO)_3]$ (2; IR) in air. The sodium salt can be obtained as a pyrophoric dark tan powder,[23] stable for weeks under N_2 (IR), by drying the solution under vacuum at ca. −20 °C and washing the solid with pentane.

The identification of 3 as $[Cr(\eta\text{-}C_6H_6)(CO)_2]^{2-}$ was supported by well-established procedures involving oxidative

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[5] (a) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263–268. (b) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553–558. (c) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 196–201. (d) Hileman, J. C.; Huggins, D. K.; Kaesz, H. D. *Inorg. Chem.* **1962**, *1*, 933–938.

[6] (a) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342–347 and references therein. (b) Cotton, J. D.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2162–2165. (c) Cotton, J. D.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2758–2762. (d) L'Eplattenier, F. *Inorg. Chem.* **1969**, *8*, 965–970. (e) George, R. D.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 972–975. (f) Carter, W. J.; Kelland, J. W.; Okrasinski, S. J.; Warner, K. E.; Norton, J. R. *Inorg. Chem.* **1982**, *21*, 3955–3960.

[7] (a) Edgell, W. F.; Lyford IV, J. *Inorg. Chem.* **1970**, *9*, 1932–1933. (b) Ruff, J. K.; Schlientz, W. J. *Inorg. Synth.* **1974**, *15*, 84–90. (c) Inkrott, K.; Goetze, R.; Shore, S. G. *J. Organomet. Chem.* **1978**, *154*, 337–342.

[8] (a) Ellis, J. E.; Fjare, K. L.; Hayes, T. G. *J. Am. Chem. Soc.* **1981**, *103*, 6100–6106. (b) Warnock, G. F. P.; Sprague, J.; Fjare, K. L.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 672.

[9] Ellis, J. E.; Parnell, C. P.; Hagen, G. P. *J. Am. Chem. Soc.* **1978**, *100*, 3605–3607.

[10] Ellis, J. E.; Faltynek, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 1801–1808.

[11] Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. *J. Chem. Soc., Chem. Commun.* **1977**, 686–687.

[12] Jonas, K. *Adv. Organomet. Chem.* **1981**, *19*, 97–122 and references therein.

[13] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *3*, 104–124.

[14] Fischer, E. O. *Angew. Chem.* **1955**, *67*, 475–482.

[15] (a) Fischer, E. O.; Vigoureux, S. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1958**, *13B*, 2205–2212. (b) Ellis, J. E.; Faltynek, R. A.; Hentges, S. G. *J. Organomet. Chem.* **1976**, *120*, 389–396. (c) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902–7915.

[16] (a) Kelsey, B. A.; Ellis, J. E. *J. Chem. Soc., Chem. Commun.* **1986**, 331–332. (b) Kelsey, B. A.; Ellis, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 1344–1345.

[17] (a) Davison, A.; Reger, D. L. *J. Organomet. Chem.* **1970**, *23*, 491–496. (b) Bernhardt, R. J.; Wilmoth, M. A.; Weers, J. J.; LaBrush, D. M.; Eyman, D. P.; Huffman, J. C. *Organometallics* **1986**, *5*, 883–888. (c) Rush, P. K.; Noh, S. K.; Brookhart, M. *Organometallics* **1986**, *5*, 1745–1747.

[18] (a) Henry, W. P.; Rieke, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 6314–6316. (b) Rieke, R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* **1987**, *26*, 420–427.

[19] (a) Milligan, S. N.; Rieke, R. D. *Organometallics* **1983**, *2*, 171–173. (b) Rieke, R. D.; Milligan, S. N.; Schulte, L. D. *Organometallics* **1987**, *6*, 699–705.

[20] Readily prepared from $[Cr(\eta\text{-}C_6H_6)(CO)_3]$ (2) photochemically in 75% yield: Strohmeier, W.; Hellmann, H. *Chem. Ber.* **1963**, *96*, 2859–2866.

[21] ν_{CO}: 1885 and 1825 cm^{-1}.

[22] Although the reaction must proceed in one electron steps, no intermediates were observed by IR and a single equivalent of naphthalenide led to mixtures of 1 and 3.

[23] ν_{CO} (Nujol mull): 1655 (vs (br)) and 1525 (s (br)) cm^{-1}. Solid material is typically contaminated by 2, and we have been unable to obtain analytically pure samples. There is also a weak band at 1800 cm^{-1} (see below).

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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(24) (a) Chen, Y.-S.; Ellis, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 1141–1143. (b) Ellis, J. E.; Hentges, S. G.; Kalina, D. G.; Hagen, G. P. *J. Organomet. Chem.* **1975**, *97*, 79–93.

(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.

(27) (a) Hoyano, J. K.; Graham, W. A. G. *Organometallics* **1982**, *1*, 783–787. (b) Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *105*, 6500–6501.

(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.

(30) (a) Dessy, R. E.; Stary, F. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 471–476. (b) Rieke, R. D.; Willeford, B. R., Jr.; Arney, J. S.; Rich, W. E.; Poliner, B. S. *J. Am. Chem. Soc.* **1975**, *97*, 5951–5953. (c) Henry, W. P.; Rieke, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 6314–6316.

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-