O_2H as a solvent; in dilute solution, this acid and I do not react. A possible mechanism of formation involves proton addition to carbon 1 of the free double bond followed by addition of the metal-stabilized carbonium ion another molecule of I. Oxidation by another proton (and its incorporation into the molecule) could occur with concurrent loss of Cr^{2+}, leaving the product with a biacenaphthene ligand and one metal.

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Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and H-atom coordinates and isotropic thermal parameters for IIIb and IVc (10 pages). Ordering information is given on any current masthead page.

Metalation of the Fused Polycyclic Aromatic Ligand in (Arene)chromium Tricarbonyl Complexes: Kinetic and Thermodynamic Site Preferences

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Lithiation of the hydrocarbon ligand in chromium tricarbonyl complexes of naphthalene, 5-methoxynaphthalene, 2,6- and 2,7-dimethoxynaphthalene, and phenanthene is accomplished by reactions of these complexes with lithium diisopropylamide. The lithiated complexes decompose rapidly even at the low temperature of formation (−78 to −95 °C) but can be intercepted in reactions with various species including D_2O, CH_3I, $(CH_3)_3SiCl$, CH_3CHO, or C_6H_5CHO to give substituted derivatives of the starting material. Data are presented which indicate that for $Cr(CO)_3(\eta^6\text{-}C_{10}H_8)$ there is a kinetic preference to lithiation at C(2) and a thermodynamic preference for lithiation at C(1) of the naphthalene ligand. This permits one to optimize the synthesis of either (1-methylnaphthalene)- or (2-methylnaphthalene)chromium tricarbonyl in this reaction sequence.

Introduction

(Arene)chromium tricarbonyl complexes are known to undergo metal–hydrogen exchange (metalation) when treated with certain alkyllithium compounds.[1] It is also possible prepare (lithiobenzene)chromium tricarbonyl in a transmetalation reaction from $Cr(CO)_3(\eta\text{-}C_6H_5HgC_6H_5)$ and *n*-butyllithium.[2] This type of lithiated species has found significant recent application in organometallic and organic syntheses.[3] Complexation of an arene to chromium enhances the reactivity of the aryl protons relative to both the free arene and to other protons in the molecule (in arene substitutent groups, for example). Metalation in these organometallic systems takes place under very mild conditions, and one can exert significant control on the regiospecificity of the reaction.

Until quite recently arene metalation reactions were known only for chromium carbonyl derivatives of benzene or substituted benzenes.[4] Metalation of complexes with fused polycyclic aromatic was conspicuously absent. However, this situation was altered with the appearance of a brief report on the metalation of the naphthalene ligand in $Cr(CO)_3(\eta^6\text{-}C_{10}H_8)$ in 1984.[5] Recently we described lithiation of (2,7-dimethoxynaphthalene)- and (2,6-dimethoxynaphthalene)chromium tricarbonyl, giving a lithiated complex in situ which could then be deuteriated. Regiospecific deuterium incorporation into the ring coordinated to chromium provided labeled complexes that were further used in a study on haptotropic migrations.[6] In the course of that work it seemed reasonable to assume that the metalation of complexes of fused polycyclic aromatic hydrocarbons should be a general phenomenon.[7] Furthermore, when details of these processes were established, the further utility of these lithiated species in organic and organic synthetic projects appears to be a reasonable option.

This paper describes our studies on the metalation reactions of several chromium tricarbonyl complexes with fused polycyclic aromatic hydrocarbon ligands. An unanticipated result emerged in this study when it was observed that the position of lithiation in certain complexes was influenced by reaction conditions. Some effort was then directed to the examination of this phenomenon that is the result of a balance between kinetic vs. thermodynamic control. We will also report studies on several reactions of the lithiated species in this paper.

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(1) (a) Nesmeyanov, A.; Kolobova, N. E. *Izv. Akad. Nauk, SSR, Ser. Khim.* **1968**, 2665. (b) Semmelhack, M. F.; Bisaha, J.; Czarny, M. *J. Am. Chem. Soc.* **1979**, *101*, 768. (c) Card, R. J.; Trahanovsky, W. S. *J. Org. Chem.* **1980**, *45*, 2555. (d) Kausch, M. D.; Moser, G. A.; Lee, W. A. *Synth. React. Inorg. Met.-Org. Chem.* **1979**, *9*, 357.

(2) Rausch, M. D. *Pure Appl. Chem.* **1972**, *30*, 523.

(3) (a) Semmelhack, M. F.; Yamashita, A. *J. Am. Chem. Soc.* **1980**, *102*, 5924. (b) Uemura, M.; Nishikawa, N.; Hayashi, Y. *Tetrahedron Lett.* **1980**, 2069. (c) Nechvatal, G.; Widdowson, D. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1260. (d) Nechvatal, G.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1982**, 467. (e) Uemura, M.; Nishikawa, N.; Take, K.; Ohnishi, M.; Hirotsu, K.; Higuchi, T.; Hayashi, Y. *J. Org. Chem.* **1983**, *43*, 2349. (f) Masters, N. F.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1983**, 955. (g) Uemura, M.; Take, K.; Hayashi, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 858. (h) Semmelhack, M. F.; Zask, A. *J. Am. Chem. Soc.* **1983**, *105*, 2034. (i) Beswick, P. J.; Leach, S. J.; Masters, N. F.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1984**, 46. (j) Uemura, M.; Minami, T.; Hayashi, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 1193.

(4) Metalation of ferrocene and of $Mn(CO)_3(\eta\text{-}C_5H_5)$ preceded the observed metalation of $Cr(CO)_3(\eta\text{-}C_6H_6)$.

(5) Oprunenko, Yu. F.; Malyugina, S. G.; Ustynyuk, Yu A.; Ustynyuk, N. A. *Izv. Akad. Nauk SSR* **1984**, 2199.

(6) Kirss, R. U.; Treichel, P. M. *J. Am. Chem. Soc.* **1985**, *108*, 853.

(7) Kirss, R. U.; Treichel, P. J.; Haller, K. J. *Organometallics*, preceding paper in this issue.

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Experimental Section

All manipulations were carried out under dry nitrogen or under vacuum.

Infrared spectra were recorded on a Beckman Model 4230 spectrometer using solutions of the compound in CH_2Cl_2. ^1H NMR spectra were obtained on either a IBM WP200 or a IBM WP270 spectrometer and are recorded in δ units vs. internal Me_4Si; $CDCl_3$ was chosen as solvent except as noted. ^2D NMR spectra were obtained on a JEOL FX200 spectrometer and are referenced to C_6D_6. High-resolution mass spectra were obtained with either a AEI MS902 or MS80RF spectrometer. Melting points (sealed capillary, Thomas-Hoover apparatus) are uncorrected.

The following starting materials were prepared by the literature procedure given in the cited reference: chromium tricarbonyl complexes of naphthalene,[8] phenanthrene,[9] and 5-methoxynaphthalene.[10] The procedure for the synthesis of several other (new) chromium tricarbonyl complexes of fused polycyclic aromatic hydrocarbon is given below. Other reagents were obtained commercially and used without further purification. Solvents were dried by standard procedures.

Syntheses of (Arene)chromium Tricarbonyl Complexes. **$Cr(CO)_3(\eta^6\text{-}2,6\text{-}(CH_3O)_2C_{10}H_6)$.** A solution of 4.11 g (18.6 mmol) of $Cr(CO)_6$ and 3.58 g (19 mmol) of $2,6\text{-}C_{10}H_6(OCH_3)_2$ in 200 mL of dioxane was heated at reflux for 72 h. After cooling, the red solution was filtered through Celite (a commercial diatomaceous earth) and the filtrate was evaporated to dryness in vacuo. Sublimation of the residue [70–75 °C (0.01 mmHg)] separated the unreacted hydrocarbon. The unsublimed red solid which remained was crystallized from $CHCl_3$/hexane to yield 0.60 g (10% yield) of the product: mp 126–128 °C; IR (CH_2Cl_2) 1962 (s), 1881 (m), 1870 (m) cm^{-1}; ^1H NMR δ 3.78 (s, CH_3O of the coordinated ring), 3.82 (s, CH_3O of the uncoordinated ring), 5.51 (d, $J_{34} = 7.2$ Hz, H_3), 5.76 (s, H_1), 6.16 (d, H_4), 6.63 (s, H_5), 7.06 (d of d, $J_{57} = 1.5$ Hz, $J_{78} = 9.3$ Hz, H_7), 7.43 (d, H_8). Anal. Obsd (Calcd for $C_{15}H_{12}CrO_5$): parent peak 324.0081 (324.0086).

$Cr(CO)_3(\eta^6\text{-}2,7\text{-}(CH_3O)_2C_{10}H_6)$. A similar procedure yielded the product, an orange solid, in 8% yield: mp 134–137 °C; IR 1963 (s), 1877 cm^{-1}; ^1H NMR δ 3.81 (s, CH_3O of the coordinated ring), 3.85 (s, CH_3O of the uncoordinated ring), 5.30 (d of d, $J_{34} = 7.1$ Hz, H_3), 5.75 (d, $J_{13} = 2.0$ Hz, H_1), 6.23 (d, H_4), 6.59 (d, $J_{68} = 2.3$ Hz, H_8), 6.92 (d of d, $J_{56} = 9.2$ Hz, H_6), 7.41 (d, H_5). Anal. Obsd (Calcd for $C_{15}H_{12}CrO_5$): parent peak 324.0090 (324.0086).

$Cr(CO)_3(\eta^6\text{-}1\text{-}C_{10}H_7CH_3)$. A reaction between $Cr(CO)_6$ and 1-methylnaphthalene was carried out as described above. Following filtration and evaporation of solvent a red oil remained. This was dissolved in toluene, and hexane was carefully layered on top of the solution. When the mixture was chilled at −20 °C, red crystals of the product were obtained in 11% yield: mp 126–129 °C dec; IR 1970 (s), 1885 (s) cm^{-1}. Anal. Obsd (Calcd for $C_{14}H_{10}CrO_3$): parent peak 278.0036 (278.0032).

Examination of the ^1H NMR spectrum indicated the presence of two isomers. Fractional crystallization from toluene/hexane yielded a pure sample of the major isomer with the metal bonded to the unsubstituted ring. Major isomer: ^1H NMR (toluene-d_8) δ 2.12 (s, CH_3), 4.47 (d of d, $J_{67} = 6$ Hz, H_6, H_7), 5.36 (pseudo t, $J_{56} = J_{78} = 6$ Hz, H_5, H_8), 6.6–7.2 (m, H_2–H_4). The resonances of the minor isomer can then be identified from the spectrum of the mixture. Minor isomer: ^1H NMR (toluene-d_8) δ 2.06 (s, CH_3), 4.63, 4.77 (m, $J_{23} = 6$ Hz, H_2, H_3), 5.24 (d, $J_{34} = 7$ Hz, H_4), 6.6–7.2 (m, H_5–H_8).

$Cr(CO)_3(\eta\text{-}2\text{-}C_{10}H_7CH_3)$. A similar procedure yielded this product in 28% yield as a mixture of two isomers which were also amenable to partial separation by fractional crystallization; IR 1969 (s), 1894 (s) cm^{-1}. Analysis: Obsd (Calcd for $C_{14}H_{10}CrO_3$): parent peak 278.0047 (278.0032).

Major isomer, metal bonded to substituted ring: ^1H NMR (toluene-d_8) δ 1.78 (s, CH_3), 4.56 (d, $J_{34} = 6.7$ Hz, H_3), 5.21 (s, H_1), 5.38 (d, H_4), 6.73–7.10 (m, H_5–H_8). The resonances of the isomer with chromium bonded to the unsubstituted ring can be partially deduced from the spectrum of the mixture. ^1H NMR (toluene-d_8): δ 1.88 (s, CH_3), 4.63, 4.71 (m, $J_{67} = 7$ Hz, H_6, H_7), 5.40 (d, $J_{56} = J_{78} = 7$ Hz, H_5, H_8). The remaining aromatic resonances cannot be resolved from those of the major isomer.

Lithiation and Reactions of the Lithiated Complexes. The procedure used is illustrated by the example given below.

$Cr(CO)_3(\eta^6\text{-}2,7\text{-}(CH_3O)_2\text{-}3\text{-}DC_{10}H_5)$. Lithium diisopropylamide (LDA) was obtained commercially and weighed out in a nitrogen filled glovebag since this material is highly reactive to oxygen. The sample of LDA (0.108 g, 1.0 mmol) was added to a solution of 0.119 g (0.37 mmol) of $Cr(CO)_3(\eta^6\text{-}2,7\text{-}(CH_3O)_2C_{10}H_6)$ in 12 mL of THF at −78 °C. After the solution was stirred at this temperature for 30 min, an excess of D_2O was added. The solution was stirred, allowed to warm to room temperature over 30 min, and then filtered through Celite. Evaporation in vacuo provided a crude red-orange solid that was recrystallized from $CHCl_3$/hexane to yield 0.073 g (61%) of the product, mp 137–141 °C dec; ^1H NMR: the doublets found at δ 5.75 in the undeuteriated product (assigned to H_1) at δ 6.23 (assigned to H_4) occur as singlets; the doubled of doublet pattern at δ 5.30 (assigned to H_3 in the undeuteriated product) is absent. Anal. Obsd (Calcd for $C_{16}H_{14}CrDO$): parent peak 325.0149 (325.0149).

$Cr(CO)_3(\eta^6\text{-}2,7\text{-}(CH_3O)_2\text{-}3\text{-}CH_3C_{10}H_5)$. The same general procedure was followed. In this instance an infrared spectrum of the solution of the lithiated complex was taken, with new absorptions being seen at 1920 (s) and 1865 (s) cm^{-1} (starting material, 1965 and 1882 cm^{-1}). Methyl iodide replaced D_2O in the second step of this procedure. The product, as orange crystals, was obtained in 10% yield, mp 122–124 °C dec; IR ($CHCl_3$) 1959 (s), 1875 (s), 1861 (m) cm^{-1}; ^1H NMR δ 2.21 (s, CH_3), 3.84 (two singlets separated by 1.4 Hz, CH_3O), 5.78 (s, H_1), 6.17 (s, H_4), 6.59 (d, $J_{68} = 2.1$ Hz, H_8), 6.92 (d of d, $J_{56} = 9.4$ Hz, H_6), 7.41 (d, H_5). Anal. Obsd (Calcd for $C_{16}H_{15}CrO_5$): parent peak 338.0248 (338.0242).

$Cr(CO)_3(\eta^6\text{-}2,7\text{-}(CH_3O)_2\text{-}3\text{-}(HOCH(CH_3)C_{10}H_5)$. The same procedure was followed to lithiate the precursor. Then excess acetaldehyde was added, followed after 25 min by 1.0 mL of H_2O. After the solution was warmed, the solvent was removed in vacuo and the residue that remained was subjected to chromatography on a silica gel column. The product elutes as an orange band by using CH_2Cl_2. It was recrystallized from CH_2Cl_2/hexane (11% yield): mp 145–148 °C dec; IR 1961 (s), 1884 (s), 1866 (m) cm^{-1}; ^1H NMR δ 1.45 (d, $J = 6.3$ Hz, CH_3), 3.85 (s, CH_3O of the coordinated ring), 3.90 (s, CH_3O of the uncoordinated ring), 5.08 (q, $J = 2$ Hz, CH), 5.74 (s, H_1), 6.37 (s, H_4), 6.55 (s, H_4), 6.61 (s, H_8), 6.95 (d, $J_{56} = 9.0$ Hz, H_6), 7.45 (d, H_5). Anal. Obsd (Calcd for $C_{17}H_{16}CrO_6$): parent peak 368.0091 (368.0347).

$Cr(CO)_3(\eta^6\text{-}2,6\text{-}(CH_3O)_2\text{-}3\text{-}DC_{10}H_5)$. Repeating the procedure described for preparation of $Cr(CO)_3(\eta^6\text{-}2,7\text{-}(CH_3O)_2\text{-}3\text{-}DC_{10}H_5)$ led to isolation of this product in 30% yield; mp 126–128 °C. ^1H NMR: the doublet at δ 6.16 in the undeuterated product (assigned to H_4) occurs here as a singlet; the doublet at δ 5.51 assigned to H_3 in the undeuteriated species is absent. Anal. Obsd (Calcd for $C_{15}H_{11}CrDO_5$): parent peak 325.0152 (325.0149).

$Cr(CO)_3(\eta^6\text{-}2,6\text{-}(CH_3O)_2\text{-}3\text{-}CH_3C_{10}H_5)$. The procedure given above for $Cr(CO)_3(\eta\text{-}2,7\text{-}(CH_3O)_2\text{-}3\text{-}CH_3C_{10}H_5)$ was followed except that the oily crude product was purified by chromatograph on silica gel, to separate $N(CH_3)(C_3H_7)_2$ (eluting first with 1:1 CH_2Cl_2). The purified (recrystallized) product was obtained in 15% yield: mp 124–127 °C dec; IR 1957 (s), 1877 (m), 1864 (m) cm^{-1}; ^1H NMR δ 2.28 (s, CH_3), 3.80 (s, CH_3O on the coordinated ring), 3.82 (s, CH_3O of the uncoordinated ring), 5.78 (s, H_1), 6.10 (s, H_4), 6.61 (s, H_5), 7.02 (d, $J_{78} = 9.0$ Hz, H_7), 7.42 (d, H_8). Anal. Obsd (Calcd for $C_{16}H_{14}CrO_5$): parent peak 338.0243 (338.0246).

$Cr(CO)_3(\eta^6\text{-}5\text{-}(CH_3O)\text{-}2\text{-}CH_3C_{10}H_6)$ and $Cr(CO)_3(\eta^6\text{-}5\text{-}(CH_3O)\text{-}3\text{-}CH_3C_{10}H_6)$. The precursor $Cr(CO)_3(\eta^6\text{-}5\text{-}CH_3OC_{10}H_7)$ was allowed to react with LDA at −95 °C for 15 min in THF, as described in the section on kinetic and thermodynamic control, and then CH_3I was added. Workup, as described above, produced a mixture of the two compounds named above; the mixture was not amenable to separation. ^1H NMR: 2-CH_3 isomer, 2.31 (s, CH_3), 3.97 (s, CH_3O), 5.29 (d of d, $J_{34} = 7.0$, $J_{13} = 1.5$ Hz, H_3), 5.93 (s, H_1), 6.5 (m, H_6, H_4), 7.03 (d, H_8), 7.3–7.4 (m, H_7); 3-CH_3 isomer, 2.29 (s, CH_3), 3.99 (s, CH_3O), 5.3–5.6 (m, H_2), 6.05 (d, $J_{12} = 6.7$ Hz, H_1), 6.48 (s, H_4), 6.5 (m, H_6), 7.03 (d, H_8), 7.3–7.4 (m, H_7). Anal. Obsd (Calcd for $C_{15}H_{12}CrO$): parent peak 308.0148 (308.0141).

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[8] Fischer, E. O.; Ofele, K.; Essler, H.; Frohlich, W.; Mortensen, J. P.; Semmlinger, W. *Chem. Ber.* **1958**, *91*, 2763.

[9] Brown, D. A.; Raju, J. R. *J. Chem. Soc. A* **1966**, 1617.

[10] Kundig, E. P.; Simmons, D. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1320.

Table I. Lithiation/Alkylation Reactions of (Naphthalene)chromium Tricarbonyl and (Phenanthrene)chromium Tricarbonyl

reactants	conditns[a]	crude yield, %	1:2 ratio crude product[c]	recryst yield, %	1:2 ratio recryst product
$Cr(CO)_3(\eta^6\text{-}C_{10}H_8)$ + LDA in THF	(1) −95 °C, 15 min	58	22:78	34	4:96
	(2) −95 °C, 4.5 h	54	52:48	24	17:83
	(3) −95 °C, 10 h	*b*	61:39	34	61:39
	(4) −95 °C, 15 min; −62 °C, 15 min	29	22:78	22	10:90
	(5) −95 °C, 15 min; −42 °C, 5 min	*b*	87:13	2	86:14

reactants	conditns[a]	recryst yield, %	1′:2′:3′:4′ ratio[d]
$Cr(CO)_3(\eta^6\text{-}C_{14}H_{10})$ + LDA in THF	(1) −95 °C, 15 min	42	0:14:83:3
	(2) −95 °C, 8 h	36	4:25:43:28
	(3) −95 °C, 15 min; −42 °C, 10 min	37	2:18:64:16
	(4) −95 °C, 15 min	19	5:21:39:35

[a] Initial metalation at −95 °C, followed by stirring and/or warming for the indicated time, and then CH_3I addition. See text for details. For most entries, several independent experiments were performed. [b] Oily residue could not be weighed accurately. [c] 1 and 2 refer to the 1-methyl and 2-methyl isomers. [d] 1′, 2′, 3′, and 4′ refer to isomers with methyl substituents in the 1-, 2-, 3-, and 4-positions, respectively.

The distribution of the individual resonances to these two compounds was based on intensities. The tentative assignments are discussed in the Discussion.

$Cr(CO)_3(\eta^6\text{-}2,4,6\text{-}(CH_3)_3C_{10}H_5)$. Upon attempted lithiation of $Cr(CO)_3(\eta^6\text{-}2,6\text{-}(CH_3)_2C_{10}H_6)$ at −95 °C the solution turned very dark. This color change being a good indication of decomposition, the reaction was terminated by quenching with CH_3I after 2 min. Workup, as described, yielded 0.017 g (~10% yield) of a red solid containing a mixture of unreacted starting material and a product corresponding to (2,4,6-trimethylnaphthalene)$Cr(CO)_3$ by ^1H NMR: ^1H NMR δ 2.44 (s, CH_3), 2.62 (s, CH_3), 5.28 (s, H_3), 5.88 (s, H_1). The resonances of the remaining aromatic protons H_5, H_7, H_8 and the missing CH_3 group are obscured by the resonances of the major product. Reaction times longer than 15 min at −95 °C or longer reaction times at −111 and −130 °C lead to the isolation of uncrystallizable red oils showing resonances characteristic of the same products isolated above, but efforts to purify the oils were unsuccessful. Anal. Obsd (Calcd for $C_{16}H_{14}CrO_3$): parent peak 306.0343 (306.0348).

$Cr(CO)_3(\eta^6\text{-}C_{10}H_7D)$. The procedure described above was followed by using (naphthalene)chromium tricarbonyl as a precursor. The product of monodeuteriation (D_2O addition) was obtained in 16% yield. A parent peak match for this species was obtained (Found 264.9942; calcd 264.9939). The ^1H NMR contained resonances at δ 5.50 (d, J = 6.1 Hz, H_2 and H_3) and at 6.11 (pseudo t, H_1 and H_4). The lower intensity of these resonances relative to the other resonances at δ 7.39 (d, d, H_6 and H_7) and at δ 7.55 (d, d, H_5 and H_8) as well as the multiplicity indicated partial deuteration at positions 1 and 2. A ^2D NMR confirmed deuteriation in these positions in a ratio of approximately 1:4 (δ 5.22 and 4.60).

$Cr(CO)_3(\eta^6\text{-}C_{14}H_9D)$. A similar experiment (−78 °C, quench with D_2O) using (phenanthrene)chromium tricarbonyl yield 74% yield of the monodeuteriated product, again as a mixture of isomers (parent peak found 315.0114; calcd 315.0098).

These results led to the following set of experiments.

Lithiation of $Cr(CO)_3(\eta^6\text{-}C_{10}H_8)$: Kinetic and Thermodynamic Control. Initial studies indicated that it was possible to lithiate (naphthalene)chromium tricarbonyl by the procedures given above. However, deuteriation of the lithiated intermediate produced a mixture of isomers with substituent groups in the 1- and 2-positions. Furthermore the relative amounts of the two isomers appeared to vary depending on conditions. This phenomenon was further studied by the procedure below.

$Cr(CO)_3(\eta^6\text{-}C_{10}H_8)$. A solution of LDA was prepared in situ by addition of a stoichiometric amount of *n*-butyllithium in ether to a solution of diisopropylamine in THF at 0 °C. After 30 min the solution was chilled to −95 °C, and a THF solution of (naphthalene)chromium tricarbonyl at −95 °C was added. A 4:1 ratio of LDA to metal complex was used. The solution was allowed to stir at this temperature for 15 min; this was followed by the addition of an excess of methyl iodide. Alternatively, the solution of the lithiated complex could be warmed to higher temperature or stirred longer at −95 °C and methyl iodide added. After a few minutes the solution was allowed to warm to room temperature and filtered through Celite. Solvent was evaporated from the filtrate and the residue chromatographed in silica gel by using hexane to elute the methyldiisopropylamine followed by diethyl ether to elute a single red-orange fraction. Evaporation of the eluent yields a crude product that can be recrystallized from diethyl ether/hexane. The ratio of $Cr(CO)_3(\eta^6\text{-}1\text{-}CH_3C_{10}H_7)$ to $Cr(CO)_3(\eta^6\text{-}2\text{-}CH_3C_{10}H_7)$ in crude and recrystallized products was evaluated by ^1H NMR spectroscopy; data on these reactions using various conditions are given in Table I.

$Cr(CO)_3(\eta\text{-}C_{14}H_{10})$. A similar series of reactions were carried out by using (phenanthrene)chromium tricarbonyl. A mixture of (methylphenanthrene)chromium tricarbonyl complexes was obtained that could not be separated. Again, ^1H NMR spectroscopy was used to obtain the product ratio which are also given in Table I.

$Cr(CO)_3(\eta^6\text{-}2,6\text{-}(CH_3O)_2C_{10}H_6)$. Lithiation of this compound was carried out at −95 °C by the indicated procedure. The solution was warmed to −42 °C for 5 min before CH_3I was added. The chromatography procedure described earlier resulted in a 37% yield of crude product that was a mixture of $Cr(CO)_3(\eta^6\text{-}2,6\text{-}(CH_3O)_2\text{-}3\text{-}CH_3C_{10}H_5)$ and $Cr(CO)_3(\eta^6\text{-}2,6\text{-}(CH_3O)_2\text{-}1\text{-}CH_3C_{10}H_5)$ in an 86:14 ratio. (In the previously cited experiment the product was recrystallized to give a pure sample of the former isomer. Repeating that experiment, without warming of the solution, and evaluation of the crude product showed that in fact both isomers were present.)

For this second isomer: ^1H NMR δ 2.54 (s, CH_3), 3.83 (s, CH_3O of the coordinated ring), 3.87 (s, CH_3O of the uncoordinated ring), 5.60 (d, J_{34} = 8.2 Hz, H_3), 6.03 (d, H_4), 7.10 (d, J_{78} = 8.8 Hz, H_7), 7.69 (d, H_8). The resonance from H_5 is overlapped by the protons of the other isomer and is probably somewhere under the 7.03 ppm resonance of H_5 of the 3-methyl isomer.

Approximately the same ratio (found 19:81) of these two products was obtained when the reaction was maintained at −95 °C.

The product isolated in this reaction (a mixture of isomers) was subjected to a second lithiation at −95 °C followed after 30 min by methyl iodide addition. Product isolation as described above yielded an ~7% yield of a mixture of $Cr(CO)_3(\eta^6\text{-}2,6\text{-}(CH_3O)_2\text{-}3\text{-}CH_3C_{10}H_5)$ and $Cr(CO)_3(\eta^6\text{-}2,6\text{-}(CH_3O)_2\text{-}1,3\text{-}(CH_3)_2C_{10}H_4)$ in a 2:1 ratio. The latter compound was identified by mass spectrometric peak match (found 352.0407; calcd 352.0403) and by ^1H NMR (δ 2.38 (s, CH_3 in the 3- position), 2.63 (s, CH_3 in the 1-position), 3.74 (s, CH_3O of the coordinated ring), 5.85 (s, H_4), 7.64 (d, H_5)). H_7, H_8, and the CH_3O of the uncoordinated ring are masked by the resonances of the major product.

Discussion

Previously unreported (arene)chromium tricarbonyl complexes were prepared from 1- and 2-methylnaphthalene and from 2,6- and 2,7-dimethoxynaphthalene. The procedure for synthesis involved heating a mixture of the hydrocarbon and $Cr(CO)_6$ in dimethoxyethane for an extended period of time.[11] Relatively low yields of these red or orange crystalline species were obtained, but

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(11) R. U. Kirss, Ph.D. Thesis, University of Wisconsin-Madison, WI, 1986, to be submitted for publication.

otherwise no difficulties were encountered.

In complexes of 2,6- and 2,7-dimethoxynaphthalene there is metal coordination to a ring bearing a methoxy substituent group. This is interesting in the context that chromium tricarbonyl complexes of monosubstituted naphthalenes generally are found with coordination to the unsubstituted ring (except for alkylnaphthalenes). We have not found a literature reference to the chromium tricarbonyl derivative of 1- and 2-methylnaphthalenes. We elected to prepare these species by direct reaction after they were also prepared in the lithiation/alkylation sequence discussed below. Not surprisingly, the syntheses produced two isomers of each product, different by virtue of coordination of the metal to substituted and unsubstituted rings. Previously, two isomeric species had also been characterized in reactions of $Cr(CO)_6$ with 1,4- and 2,3-dimethylnaphthalene.[12] For $Cr(CO)_3(\eta^6\text{-}2\text{-}CH_3C_{10}H_7)$ the isomer obtained in larger amount had the metal coordinated to the substituted ring; for $Cr(CO)_3(\eta^6\text{-}1\text{-}CH_3C_{10}H_7)$ the reverse is true. This observation is in accord with the earlier results on the dimethylnaphthalene complexes.[12]

The position of metal coordination in these two compounds can be ascertained, of course, from the ^{1}H NMR spectra, the three or four protons bonded to the coordinated ring experiencing a significant upfield shift. Assignments of the resonances of the NMR spectra for the four compounds are straightforward and are given in the Experimental Section.

As mentioned in the Introduction, there has been only a small quantity of information on metalation of metal complexes of polycyclic aromatic hydrocarbons,[5-7] and part of this precedence is the communication on this work.[6] However, if the generality of this process can be established and the details of the procedure optimized, lithiated species could become useful in organic syntheses. Thus we chose to investigate the lithiation reactions further in this study.

In most examples on metalation of (arene)chromium tricarbonyl species (with complexes at benzene and substituted benzenes), butyllithium or other alkyllithium reagents have been chosen as bases. However, the use of lithium diisopropylamide, LDA, and lithium 2,2,6,6-tetramethylpiperidide, LTMP, does have some precedence, and when used, these reagents have proven quite satisfactory. Lithium diisopropylamide is somewhat less basic the alkyllithium reagents; it is also less nucleophilic. We were concerned that alkyllithium reagents might add either to the hydrocarbon or to a carbonyl group in preference to deprotonation. As it turned out, LDA was quite satisfactory for intended reactions. We demonstrated first that this reagent successfully deprotonates the chromium tricarbonyl complexes of 2,6- and 2,7-dimethoxynaphthalene.[5] The lithiation reaction requires low temperatures (−78 °C was chosen) and short reaction times, and the lithiated species was quenched with D_2O, giving products with deuterium incorporation at the 3-position of the coordinated ring in relatively low yield. Coordination of chromium activates the coordinated ring (relative to the uncoordinated ring and to the uncomplex hydrocarbon) as expected. The lithiated organometallic complex is not stable however; prolonged times or higher temperature caused a decrease in the amount of product. Further investigation of the non-organometallic products in the lithiation/deuteriation of $Cr(CO)_3(\eta^6\text{-}2,6\text{-}(CH_3O)_2C_{10}H_6)$ showed that $2,6\text{-}(CH_3O)_2\text{-}3\text{-}DC_{10}H_5$ and $2,6\text{-}(CH_3O)_2C_{10}H_6$ are present in an amount which accounted for the low yield. The ratio of d_1 to d_0 species is about 2:1 according to mass spectrometry data. A reasonable hypotheses for the formation of these products can be made as follows. The product of lithiation of the complex is presumed to be unstable even at −78 °C, decomposing to yield $2,6\text{-}(CH_3O)_2\text{-}3\text{-}LiC_{10}H_5$. This anion is this species is a strong enough base to deprotonate the unreacted metal complex, i.e., to compete with LDA in this deprotonation; this produces the undeuteriated hydrocarbon. Assuming comparable rates of deprotonation of the complex by LDA and $2,6\text{-}(CH_3O)_2\text{-}3\text{-}LiC_{10}H_5$, one then expects to obtain at the end of this reaction observed mixture of free ligand (d_0 and d_1) and deuteriated complex.

The lithiated complexes derived from (2,6-dimethoxynaphthalene)-and (2,7-dimethoxynaphthalene)chromium tricarbonyl were also alkylated by using methyl iodide. The latter species was also reacted with CH_3CHO; following protonation a product containing a 1-hydroxyethyl group in the 3-position of the naphthalene ring was obtained.

An instructive example of the influence of a chromium tricarbonyl group to direct metalation to the coordinated ring of a naphthalenic system is seen here in the lithiation of $Cr(CO)_3(\eta^6\text{-}5\text{-}CH_3OC_{10}H_7)$. As noted above, coordination in this complex is to the unsubstituted ring. Lithiation and subsequent methylation using methyl iodide provided two products, $Cr(CO)_3(\eta^6\text{-}2\text{-}CH_3\text{-}5\text{-}CH_3OC_{10}H_6)$ and $Cr(CO)_3(\eta^6\text{-}3\text{-}CH_3\text{-}5\text{-}CH_3OC_{10}H_6)$, in a 26:74 ratio (40% total yield). In contrast the free hydrocarbon is known to undergo lithiation in 4- and 6-positions (the number scheme used for the metal complex is retained in this designation to simplify comparison). Lithiation at positions adjacent to the substituent group is presumably the result of the coordinating ability of oxygen to lithium of the lithiating agent. In the metal complex of this hydrocarbon, the influence of the metal group dominates over the effect of the substituent group.

It is curious that metalation at C(4) is not seen here since this position would seem to be favored by both the methoxy group and the metal. Apparent the metalation is directed by the metal to C(2) and C(3) in preference to C(4).

Structure assignments for the two isomers obtained in the lithiation/methylation of $Cr(CO)_3(\eta^6\text{-}5\text{-}CH_3OC_{10}H_7)$ were based on their ^{1}H NMR spectra. The upfield resonances integrate as three protons, so the methyl and methoxy substituents must be on different rings. Since the metal was initially coordinated to the unsubstituted ring and since the methyl substituent should not cause this coordination to this ring to be disfavored, it is reasonable to assume that the metal is on the ring bearing this substituent. Two pieces of evidence require that the methyl groups are in the 2- and 3-positions of this ring. In complexes with naphthalene ligands the resonances for hydrogens on C(2) and C(3) are always upfield of resonances for hydrogens on C(1) and C(4) by about 1 ppm. In the methyl compounds only one of these upfield resonances is seen. In addition, a methyl group at position 2 or 3 eliminates coupling to hydrogens at either C(1) and C(4), respectively, so these resonances must be seen as singlets. Substitution at either C(1) and C(4) would lead to spectra which do not contain singlet resonances.

Metalation and subsequent preparation of deuterium and methyl derivatives of (naphthalene)chromium tri-

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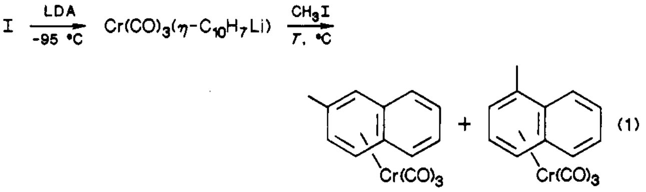
[12] Deubzer, B.; Fritz, H. P.; Kreiter, C. G.; Ofele, K. *J. Organomet. Chem.* **1967**, *7*, 289.

[13] Shirley, D. A.; Chang, C. F. *J. Organomet. Chem.* **1969**, *20*, 251.

[14] (a) Shirley, D. A.; Gray, B. M. *J. Org. Chem.* **1966**, *31*, 1221. (b) Yagupsky, G.; Cais, M. *Inorg. Chim. Acta* **1975**, *12*, L27.

carbonyl was found to be successful and is discussed in detail below. Attempts to metalate various alkylnaphthalene complexes did not yield much success. Even at low temperatures and very short reaction times, decomposition appears to intervene. In these instances the solution rapidly became very dark in color; reactions (e.g., with D_2O) and subsequent work produced neither starting material or product. Illustrative of these difficulties is the lithiation and methylation of $Cr(CO)_3(\eta^6\text{-}2,6\text{-}(CH_3)_2C_{10}H_6)$. When this compound was reacted with LDA at −95 °C, immediate darkening of the solution was seen, and it was necessary to quench the reaction with CH_3I after 2 min. Only a very small amount of solid was obtained upon workup that proved to be a mixture of starting material and a species tentatively identified as $Cr(CO)_3(\eta^6\text{-}2,4,6\text{-}(CH_3)_3C_{10}H_5)$ from NMR data.

The most significant result of this lithiation study was the observation that it is possible to exercise significant control on the position of lithiation in $Cr(CO)_3(\eta^6\text{-}C_{10}H_8)$ in the arene ligand by the choice of conditions. To study this, a series of experiments were carried out. (Naphthalene)chromium tricarbonyl was added to a THF solution containing 4 equiv of LDA at −95 °C; after a specific period of time CH_3I was added (eq 1). Alternatively, the solution of the lithiated complex was warmed to higher temperature before methyl iodide was added. After a few minutes, the solution was allowed to warm to room temperature. Filtration, evaporation of the solvent, and chromatography of the oily residue on silica gel using diethyl ether as an eluent give a single red-orange band from which a crude product was obtained by evaporation. Recrystallization from ether/hexane yielded the final product. Data on yields and isomer distribution for crude and recrystallized products are given in Table I.



When the initial metalation reactions are carried out at temperatures above −78 °C, the solution rapidly darkens, due to decomposition, and diminished yields are obtained. The isomer distribution in the product, however, is similar to that obtained by the procedure described above. Darkening of the solution is sometimes observed when solutions of lithiated complexes were warmed from −95 °C, and this decomposition also conveyed lower isolated yields.

The significant comparison in Table I is between entries 1 and 5. When $Cr(CO)_3(\eta^6\text{-}C_{10}H_7Li)$ is generated at −95 °C and methyl iodide is added at this temperature, $Cr(CO)_3(\eta^6\text{-}2\text{-}CH_3C_{10}H_7)$ is the primary product. If the solution of the lithiated complex is allowed to warm to −42 °C before addition of methyl iodide, the primary product is $Cr(CO)_3(\eta^6\text{-}1\text{-}CH_3C_{10}H_7)$. Further recrystallizations of these products produced pure samples of the indicated isomers. Other entries in Table I indicate that conditions intermediate between these extremes produce the expected mixtures of the two isomers. Rapid isomerization of (2-lithionaphthalene)- to (1-lithionaphthalene)chromium tricarbonyl is seen to require temperatures above −62 °C (entry 4). However, slow isomerization takes place even at −95 °C.

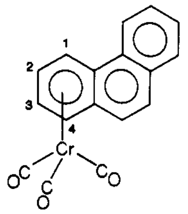
The fact that the chromium tricarbonyl unit is bonded to the methylated ring can readily be verified by the integrated intensities integration of the aromatic protons of the coordinated ring (shifted upfield) and the aromatic protons of the uncoordinated ring.

It is appropriate to recall that direct reaction between 1- and 2-methylnaphthalene and $Cr(CO)_6$ was found to give a mixture of isomers and, indeed, for the complex of 1-methylnaphthalene, the isomer with the metal coordinated to the substituted ring is less abundant (and presumably less stable) than its counterpart with the metal coordinated to the unsubstituted ring.

A reasonable explanation for these results is that preferential lithiation at low temperature at the 2-position of the ring is a kinetic phenomenon; perhaps this is because this position is the least constrained sterically. For reactions of longer duration, or at higher temperature, a thermodynamically favored 1-lithionaphthalene complex results.

Lithiation of free naphthalene is known to occur, but this process requires a stronger base (*n*-butyllithium) and considerably more severe conditions.[15,16] A relatively low yield (20–40%) of a mixture of approximately equimolar amounts of 1- and 2-naphthalenecarboxylic acids was obtained from carbonylation of these species. Both the low reactivity of the naphthalene in this type of reaction and the lack of regioselectivity contrast with the results on the metal complex of this hydrocarbon.

The lithiation/alkylation sequence for (phenanthrene)chromium tricarbonyl produced mixtures of four isomers with methyl groups at each of the possible positions on the coordinated ring. The results are also presented in Table I. It was not possible to separate a single pure isomer from the mixtures, and identification of the isomers was based on ^1H NMR spectra of the mixtures. (Phenanthrene)chromium tricarbonyl



has three multiplets assigned to the aromatic protons of the coordinated ring. The assignments, H_1 at δ 6.6, H_4 at δ 6.0, and H_2, H_3 at δ 5.45, are documented in the literature.[16] The disappearance of one of these resonances as indicative of methylation at that position. Since the products obtained from the methylation reactions contained mixtures of isomers, assignments must also consider the intensities and splitting patterns of the remaining upfield shifted (chromium coordinated) aromatic protons.

The major isomer at short reaction times and low temperature has a methyl resonance at δ 2.35, and there is a decrease in the δ 5.5 resonance. Furthermore, the resonance at δ 6.0 (H_4) is now a singlet while the δ 6.6 resonance (H_1) is a doublet. This is consistent with $Cr(CO)_3(\eta^6\text{-}3\text{-}CH_3C_{14}H_9)$. A second methyl resonance is always observed at δ 2.38 but is of much weaker intensity. The large difference in the chemical shifts of the methyl group in (1-methylnaphthalene) and (2-methylnaphthalene)chromium tricarbonyl suugests that the δ 2.38 resonance is from $Cr(CO)_3(\eta^6\text{-}2\text{-}CH_3C_{14}H_9)$. Furthermore, a singlet is now observed at δ 6.5 (H_1) and a doublet at δ 6.1 (H_4).

A third methyl resonance is observed at δ 2.64. A multiplet is observed at δ 6.5 (H_4) and at δ 5.6 (H_2 and H_3). The downfield shifted methyl resonance relative to the

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[15] Gilman, H.; Bebb, R. E. *J. Am. Chem. Soc.* **1939**, *61*, 109.
[16] Gilman, H.; Gray, S. *J. Am. Chem. Soc.* **1958**, *23*, 1476.

(2-methylphenanthrene)- and (3-methylphenanthrene)chromium tricarbonyl isomers suggests that this isomer could be $Cr(CO)_3(\eta^6\text{-}4\text{-}CH_3C_{14}H_9)$. The splitting pattern is correct for this assignment. Finally, the literature reports the methyl resonance of this compound to be observed at 2.67 ppm in $CDCl_3$.[9] A fourth resonance is observed in the methyl region at δ 2.54 for most of the reaction mixtures. The compound responsible is present in low concentration, never more than 5% of the products, and is tentatively assumed to be $Cr(CO)_3(\eta\text{-}1\text{-}CH_3C_{14}H_9)$. The low concentration of this species precludes assignment or location of the other resonances for this isomer. Steric constraints could be the major reason for the observation of its low concentration.

In other instances the effects of varying temperature and time were less significant. Lithiation of $Cr(CO)_3(\eta^6\text{-}5\text{-}CH_3OC_{10}H_7)$ at −95 °C followed by warming to −42 °C and addition methyl iodide gave the same products, $Cr(CO)_3(\eta^6\text{-}2\text{-}CH_3\text{-}5\text{-}CH_3OC_{10}H_6)$ and $Cr(CO)_3(\eta^6\text{-}3\text{-}CH_3\text{-}5\text{-}CH_3OC_{10}H_6)$, in 25% yield with the amount of the former slightly increased (ratio of 35:65 instead of 26:74). Similarly the ratio of $Cr(CO)_3(\eta^6\text{-}2,6\text{-}(CH_3O)_2\text{-}3\text{-}CH_3C_{10}H_5)$ to $Cr(CO)_3(\eta^6\text{-}2,6\text{-}(CH_3O)_2\text{-}1\text{-}CH_3C_{10}H_5)$ was seen to vary in an insignificant manner. At −95 °C an 81:19 ratio was measured whereas at −42 °C the ratio was 86:14. In neither of these instances was an additional isomer detected.

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Ligand Bridging and Chelation of Tetracobalt Clusters with Difunctional Phosphines

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The interaction of the tetracobalt carbonyl cluster $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ (I) with various bidentate phosphines such as $Ph_2P(CH_2)_nPPh_2$ was examined under both thermal conditions at >80 °C and electron-transfer chain (ETC) catalysis at 25 °C. With diphosphines possessing short carbon backbones (n = 1 and 2), the disubstituted clusters $Co_4(CO)_8(PPh)_2(\widehat{P\ P})$(III) were isolated in high yields under electron-transfer chain catalysis and shown to be the same as those derived in low yields from the thermal reaction. Structure elucidation by X-ray crystallography has established two modes of ligand binding to the tetracobalt cluster, in which the diphosphine either bridged a pair of adjacent cobalt atoms or chelated a single cobalt atom. The dynamic properties of such bridged and chelated clusters in solution were deduced from the temperature-dependent ^{31}P and ^{13}C NMR spectra of the diphosphine and carbonyl (terminal and bridging) ligands, respectively. The higher diphosphine homologues with n = 3 and 4 afforded mono- and disubstituted clusters, the relative amounts of which depended on whether the substitutions were carried out by ETC stimulation or under thermal conditions.

Introduction

Polydentate phosphines can control the stereochemistry and influence the lability of ligands in organometallic complexes.[1-6] The effects of polydentate phosphines in altering the product distributions in catalytic processes are also well-documented.[3,7] Relevant to the latter, polydentate phosphines have been shown to maintain the metal clusters intact under a variety of conditions in which the unsubstituted cluster undergoes fragmentation. For example, the triruthenium cluster capped with a tripod silaphosphine ligand $Ru_3(CO)_9[Si(Me)(PBu_2)_3]$ has been shown to be resistant to fragmentation under the conditions of the Fischer–Tropsch reactions.[8] Furthermore the tetranuclear relatives $M_4(CO)_9[HC(PPh_2)_3]$ where M = Co, Rh, and Ir are stable at high CO pressures.[9] By way of comparison, the parent carbonyl clusters are readily cleaved to species of lower nuclearity upon exposure to carbon monoxide as well as to H_2/CO mixtures.[10]

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[1] Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, Ca, 1980.

[2] McAuliffe, C. A.; Levason, W. "*Phosphine, Arsine and Stilbine Complexes of the Transition Elements*; Elsevier: New York, 1979.

[3] For the use of polydentate phosphines in catalysis, see: (a) *Adv. Chem. Ser.* **1982**, *No. 196* and references within. (b) Pignolet, L. H., Ed. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum: New York, 1983. (c) Valentine, D. S., Jr.; Scott, J. W. *Synthesis* **1976**, 329. (d) Kagan, H. B. *Pure Appl. Chem.* **1975**, *43*, 401. (e) Halpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 8055. (f) Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 838.

[4] (a) King, R. B. *Acc. Chem. Res.* **1972**, *5*, 177. (b) *Acc. Chem. Res.* **1980**, *13*, 243.

[5] Mason, R.; Meek, D. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *18*, 183.

[6] (a) Murata, K.; Matsuda, A. *Bull. Chem. Soc. Jpn.* **1980**, *33*, 214. (b) *Nippon Kagaku Kaishi* **1981**, *8*, 1335. (c) *Kagaku Gijutsu Kenkyusho Hokoku* **1984**, *79*, 155.

[7] (a) Pittman, C. U.; Wilemon, G. M.; Wilson, D. W.; Ryan, R. C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 478. (b) Pittman, C. U.; Richmond, M. G.; Wilemon, G. M.; Absi-Halabi, M. In *Catalysis of Organic Reactions*, Kosak, J. R., Ed.; Marcel Dekker: New York, 1984; Chapter 5.

[8] (a) de Boer, J. J.; van Doorn, J. A.; Masters, C. *J. Chem. Soc., Chem. Commun.* **1978**, 1005. (b) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61.

[9] (a) Arduini, A. A.; Bahsoun, A. A.; Osborn, J. A.; Voelker, C. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1024. (b) Bahsoun, A. A.; Osborn, J. A.; Voelker, C.; Bonnet, J. J.; Lavigne, G. *Organometallics* **1982**, *1*, 1114.

0276-7333/87/2306-0254$01.50/0