

Lithium Chromium(I) Dihydride: A Novel Reagent for the Versatile Reductive Metathesis, Reductive Cyclization, Oligomerization, or Polymerization of Diverse Organic Substrates¹

John J. Eisch* and Joseph R. Alila

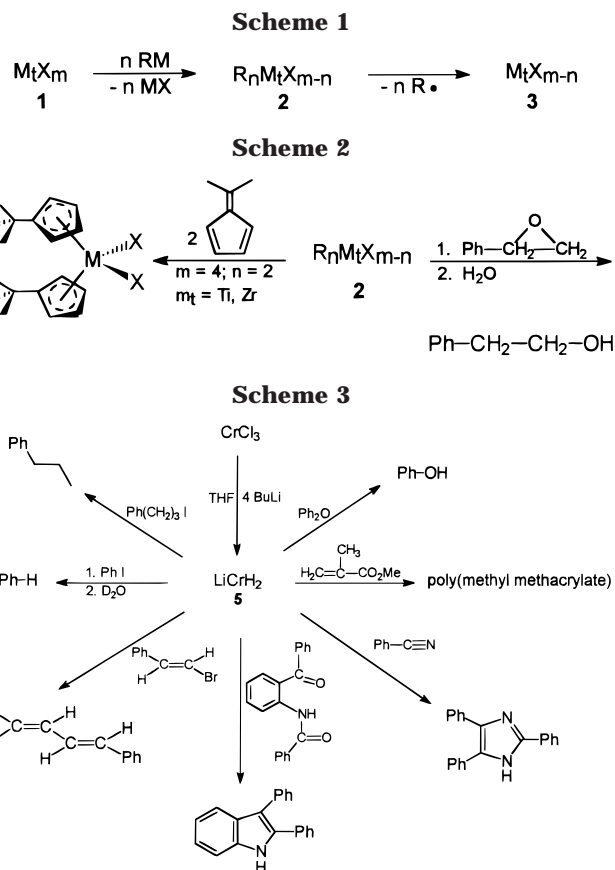
*Department of Chemistry, The State University of New York at Binghamton,
Binghamton, New York 13902-6016*

Received December 23, 1999

Summary: The novel reductant of empirical formula LiCrH_2 has been efficiently generated from CrCl_3 and 4 equiv of *n*-butyllithium in THF and can be isolated and characterized as a dark red-brown LiCl -free complex, $\text{LiCrH}_2 \cdot \text{THF}$, by a combination of elemental, gasometric, chemical, IR, and ESR analyses. Without separation from the LiCl byproduct, this reductant is reactive toward a wide range of σ - and π -heteroatomic bonds, effecting reductive cleavage or coupling, oligomerization, and even polymerization of diverse organic substrates.

Recently we have shown that the interaction of transition metal salts (**1**) with main group metal alkyls (RM) can lead, via transition metal alkyl intermediates (**2**), especially in donor solvents,² to subvalent metal complexes (**3**),^{2,3} which are selective reducing agents for an array of organic substrates (Scheme 1).²⁻⁶ By this process termed alkylative reduction,² reducing agents of the empirical compositions TiCl_2 ,²⁻⁴ ZrCl_2 ,²⁻⁵ HfCl_2 ,^{2,5} CrCl ,⁶ and MoCl_2 ,⁷ can readily be obtained in THF media. By the simple variant of conducting the alkylations of **1** in hydrocarbon media the intermediate transition metal alkyls (**2**) possess sufficient kinetic stability to function instead as hydrometalating agents, via olefin elimination, toward organic substrates as exemplified in Scheme 2 ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{Cr}$) for ketone substrates.⁸

In our continuing search for transition metal reductants of greater scope and versatility, we have sought to overcome the limited solubility and hence lower reactivity of the aforementioned neutral salts, M_tX_{m-n} (**3**) in organic media by converting them into *ate*-complexes of the type MM_tR_{m-n+1} (**4**). Therefore, we are now pleased to report that the alkylative reduction of $CrCl_3$ in THF with 4 equiv of *n*-butyllithium has resulted in the efficient production not of an *ate*-complex



like **4** but of a dark red, THF-soluble complex hydride of empirical formula LiCrH_2 (**5**). This lithium chromium-(I) dihydride is a powerful reductant that far surpasses the reactivity of previously examined neutral salts, M_nX_{m-n} (**3**), in the range of σ - and π -bonds reductively cleaved and in the scope of C–C bonds formed by the cyclization, oligomerization, or polymerization of π -bonded substrates. An overview of the bond cleavage and bond coupling reactions effected by LiCrH_2 is presented in Scheme 3 (products obtained after hydrolytic work-up).

Reagent **5** can be employed without separation from the LiCl byproduct or it can be separated as a pyrophoric, dark red-brown solid monotetrahydrofuran com-

(9) The original THF evaporated from the red solution was found to exhibit bands at 1639 (C=C stretch) and 3040 cm^{-1} (C=C-H stretch).

* Corresponding author. Fax: 607-777-4865. E-mail: jjeisch@binghamton.edu.

(1) Part 19 of the series Organic Chemistry of Subvalent Transition Metal Complexes. Part 18: Eisch, J. J.; Alila, J. R. *Organometallics* **1999**, *18*, 2930.

(2) Eisch, J. J.; Shi, X.; Alila, J. R.; Thiele, S. *Chem. Ber./Recl.* **1997**, *130*, 1175.

(3) Eisch, J. J.; Shi, X.; Lasota, J. Z. *Naturforsch.* **1995**, 50b, 342.

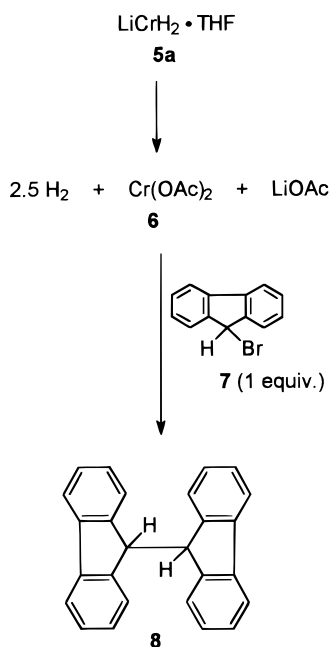
(4) Eischen, J. J.; Polimbrik, S. I.; Sill, A.; Wu, S. C. *Macromol. Symp.* **1995**, *89*, 221.

(5) Eisch, J. J.; Shi, X.; Owuor, F. A. *Organometallics* **1998**, *17*, 5219.
(6) Eisch, J. J.; Alila, J. R. *Organometallics* **1999**, *18*, 2930.

(7) Eisch, J. J.; Patel, Y. Unpublished studies. Analogous alkylative reductions are being examined for the salts of vanadium, tungsten, and manganese.

(8) Eisch, J. J.; Owuor, F. A.; Shi, X. *Organometallics* **1999**, *18*, 1583.

Scheme 4



plex (**5a**),⁹ which was characterized in the following manner (Scheme 4). First, its elemental analysis as $\text{C}_4\text{H}_{10}\text{CrLiO}$ gave these values: calcd, Li, 5.22; Cr, 39.08; found, Li, 4.95; Cr, 38.85; Cl; negative Cl test with AgNO_3 . Second, its protonolysis with glacial acetic acid yielded $2.5 \pm 0.05 \text{ mol}$ of H_2 evolved at STP, whereas 2.5 mol are expected.¹⁰ Third, treatment of the acetolysis solution (**6**) obtained in the foregoing reaction with 2 equiv of 9-bromofluorene (**7**) and subsequent workup gave 46% of 9,9'-bifluorenyl (**8**), close to the 50% expected¹¹ and consistent with the presence of $\text{Cr}(\text{II})$ (**6**) in the acetolysate. Fourth, the infrared spectrum of **5a** displayed bands at 1615(m) and 1631(w) cm^{-1} , assignable to the symmetric and asymmetric CrH_2 stretching vibrations, respectively, and two broad bands of medium intensity at 671 and 805 cm^{-1} , assignable to Cr-H deformations. Bands at 1082, 1462, and 1374 cm^{-1} were clear evidence for coordinated THF.¹² Fifth, the chemical estimation of the reducing action of **5a** in two situations gave the following information: (a) the interaction of equimolar quantities of **5a** and 9-fluorenone (**9**) in THF at 25 °C and subsequent treatment with D_2O yielded 96% of 9-fluorenol (**11**) completely deuterated at C_9 ,¹³ an outcome in accord with the intermediacy of an oxachromacyclopropane, **10**, resulting from the oxidative addition of **5a** to **9** (Scheme 5); and (b) the interaction of equimolar quantities of **5a** and aryl halides such as 2-bromobiphenyl (**12**) and subsequent workup with D_2O gave exclusively undeuterated biphenyl (**14**), consistent with the oxidative addition of **5a** to **12** to form **13** and the reductive elimination of LiCrHCl to form the final

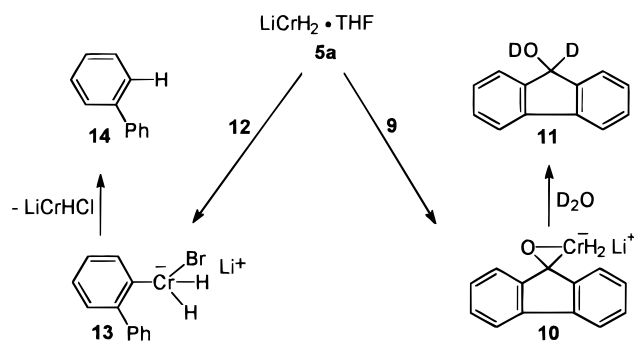
(10) The evolved H_2 was collected in a gas buret after passage through a cold trap at -78°C and was identified by mass spectrometry.

(11) Chromium(II) is known to behave as a one-electron reductant toward allylic or benzylic halides, and thus **6** could transform only 50% of 2 equiv of **7** into **8**.

(12) These IR bands of THF assumed to be coordinated to lithium were shifted by 6 to 15 cm^{-1} to higher frequencies, compared with those of free THF.

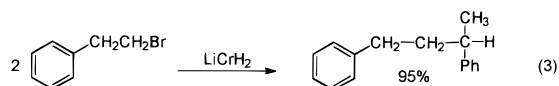
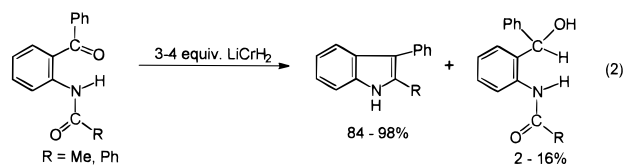
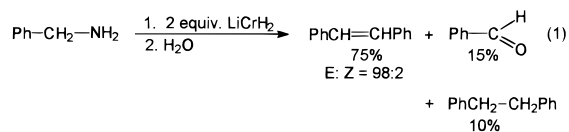
(13) The isolated 9-deuterated derivative of 9-fluorenol was furthermore 65% O-deuterated. That 9-fluorenol was 35% protiated at oxygen can be ascribed to facile H,D-exchange of hydroxyl hydrogen that occurs in moist air upon workup.

Scheme 5



product. Finally, the electron spin resonance spectrum of **5a** in THF solution or as a solid displayed a major singlet, with a g -value of 2.00(2), consistent with the presence of a symmetrical ^6S state of a d^5 system and a chromium(I) oxidation state.¹⁴ The foregoing chemical analyses and spectroscopic measurements are in excellent agreement with the empirical formulation of LiCrH_2 for this novel and most versatile reducing and oligomerizing reagent.¹⁵

The reactivity and hence utility in organic synthesis of LiCrH_2 (**5**) surpass that shown by neutral, subvalent transition metal salts in several respects: (1) the reductive metathesis of carbon–element bonds in aryl or alkyl halides (entries 1–10 in Table 1), in ethers and epoxides (entries 11–16) and their sulfur analogues (entries 17), and even in certain amines (entry 18); (2) the reductive cyclization of keto amides, diketones, and nitriles (entries 19–22); (3) the oligomerization of vinylic halides, alkynes, and aldehydes (entries 5, 23, 24); and (4) the reduction or polymerization of polar olefins such as methyl methacrylate (entries 25–29). Toward aldehydes and ketones reagent **5** shows a remarkable flexibility: low ratios of **5** to carbonyl substrate, fostering pinacol formation and high ratios yielding monomolecular reduction (entry 30, cf. Scheme 5). Finally, unusual C–C bond coupling reactions, involving coupling, cyclization, or rearrangement, can be achieved with **5** with remarkable ease and efficiency (eqs 1–3 and entries 3, 18, 19, 20).



As to the mechanism of reaction of LiCrH_2 (**5**) with organic substrates, the observations portrayed in Scheme

(14) The authors are grateful for the assistance and the interpretations of Professor David C. Doetschman, director of the NSF Regional Center for Pulsed EPR and Photochemical Studies here at SUNY–Binghamton.

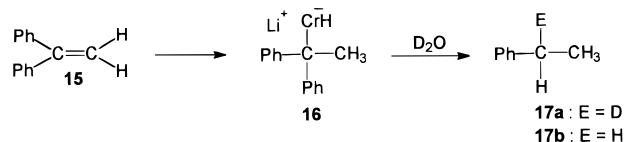
Table 1. Reductions with Lithium Chromium(I) Dihydride, LiCrH₂ (5)

entry no.	substrate (S:Cr) ^a	product	yield ^b
1	benzyl chloride (2:1)	bibenzyl	93
2	1-bromo-1-phenylethane (1:1)	2,3-diphenylbutane (1:1 of <i>racemic:meso</i>)	72
3	2-(bromoethyl)benzene (2:1)	1,3-diphenylbutane	95
4	3-bromo-1-phenylpropane (1:1)	1-phenylpropane	99
5	2-bromostyrene (2:1)	(<i>E,E</i>)-1,4-diphenyl-1,3-butadiene	93
6	4-bromoanisole	anisole	98
7	2-bromobiphenyl (2:1)	biphenyl	98
8	4-iodobiphenyl (2:1)	biphenyl	100
9	4-chloroanisole	anisole	50
10	2,2'-diiodobiphenyl (1:1)	biphenyl	98
11	1,2-epoxydecane (1:1)	1-decanol	10
		2-decanol	90
12	1,2-epoxycyclooctane (1:1)	cyclooctanol	52
		cyclooctene	48
13	1,2-epoxycyclohexane (1:1)	cyclohexanol	99
14	diphenyl ether (2:1)	phenol	92
		benzene	
15	dibenzofuran (2:1)	<i>o</i> -phenylphenol	84
16	tetrahydrofuran (excess:1)	1-butanol	
17	dibenzothiophene (1:3)	biphenyl	50–75 ^c
18	benzylamine (1:2)	bibenzyl	10
		1,2-diphenylethene ^d	75
		benzaldehyde	15
19	2-acetylaminobenzophenone (1:3)	2-methyl-3-phenylindole ^e	98
20	2-benzoylaminobenzophenone(1:4)	2,3-diphenylindole ^e	84
21	<i>meso</i> -1,2,4,5-tetraphenyl-1,5-pentanedione (1:1)	<i>meso</i> -(<i>S,R,S,R</i>)-1,2,4,5-tetraphenyl-1,5-cyclopentanediol	92
22	benzonitrile (1:1–6:1) ^f	2,4,6-triphenyl-1,3,5-triazine	major (1:1)
		2,4,5-triphenylimidazole	major (6:1)
23	diphenylacetylene (10:1)	hexaphenylbenzene ^g	90
24	benzaldehyde	1,2-diphenyl-1,2-ethanediol ^h	75
25	acenaphthylene (2:1)	acenaphthene	85
26	1,1-diphenylethene (2:1)	1,1-diphenylethane	92
27	(<i>E</i>)-1,2-diphenylethene (1:1)	bibenzyl	85
28	styrene ⁱ	poly(styrene)	100
29	methyl methacrylate ⁱ	poly(methyl methacrylate)	100
30	9-fluorenone (1:1)	9-fluorenone	98
	9-fluorenone (3:1)	9,9'-bifluorenone	95

^a The experimental procedure for the generation of LiCrH₂ is straightforward and expeditious: To a stirred suspension of anhydrous chromium(III) chloride in THF at –78 °C (10 mmol of CrCl₃ per 40 mL of THF) were added dropwise 4 molar equiv of butyllithium in hexane. The resulting mixture was further stirred for 0.5 h at –78 °C and then allowed to warm to 25 °C over 2 h to yield the dark red LiCrH₂·THF (5a). Without separating any LiCl a THF solution of the organic substrate was added and the reaction was usually conducted for 12 h at 25 °C, sometimes with subsequent reflux. Hydrolytic workup with 6 N aqueous HCl and isolation of the organic products were carried out in the usual manner. In most reactions the occurrence of THF cleavage was evident by finding 1-butanol among the reaction products. ^b The yields are not yet optimized. ^c Desulfurization was markedly promoted by the addition of 5 mol % of Ni(acac)₂. ^d A 98:2 *trans,cis*-mixture was obtained. ^e The uncyclized alcohol was a minor product (cf. eq 2). ^f Other unsaturated organonitrogen derivatives, such as imines and azo and nitro compounds, are smoothly reduced by 5 to amines. ^g The minor products were the stilbenes and bibenzyl. ^h A 3:1 mixture of the *racemic*- and *meso*-diols was obtained. ⁱ Polymerization proceeded catalytically.

5 make the role of oxidative additions by Cr(I) into C–E and C=E bonds in such reactions most likely. But the behavior of certain substrates toward LiCrH₂ indicates that hydrochromation can also play a significant role. Thus the 1:1 interaction of LiCrH₂ with 1,1-diphenylethene (15), followed by workup with D₂O, gave a 95% yield of 1,1-diphenylethane (17), which was 75% deuterated at C₁ (17a), thereby supporting the presence of a large proportion of intermediate 16 at the time of deuterolysis (Scheme 6).

In conclusion, lithium chromium(I) dihydride (5) has been shown to be a powerful reducing agent for a wide variety of organic substrates either with unsaturated functional groups or groups containing carbon–heteroatom single bonds. Operating by a combination of oxida-

Scheme 6

tive addition and hydrochromation pathways and via organochromium intermediates, LiCrH₂ can variously effect monomolecular reductions, dimerizations, cyclizations, oligomerizations, and polymerizations of great potential utility in organic synthesis. This reagent thereby complements and greatly expands upon the reducing action of other known chromium reducing agents such as CrCl₆ and CrCl₂.¹⁶

Acknowledgment. The foregoing research was initiated under a grant from the National Science Foundation and fostered with support of Solvay S.A., Brussels, Belgium, and the Alexander von Humboldt Senior Scientist Award. Valuable technical and conceptual assistance has been provided by Mr. Fredrick A. Owuor.

OM991028Q

(15) Efforts to obtain suitable crystals of 5a for such a structure determination are being pursued in collaboration with the XRD group of Professor Arnold L. Rheingold of the University of Delaware.

(16) (a) Okude, Y.; Hirano, S.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1977**, *99*, 3180. (b) Jin, H.; Uenishi, J.; Christ, W. J.; Kishi, Y. *J. Am. Chem. Soc.* **1986**, *108*, 5644. (c) Takai, K.; Tagashira, M.; Kuroda, T.; Oshima, K.; Utimoto, K.; Nozaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 6048. (d) Jubert, C.; Nowotny, S.; Kornemann, D.; Antes, I.; Tucker, C. E.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 6384.