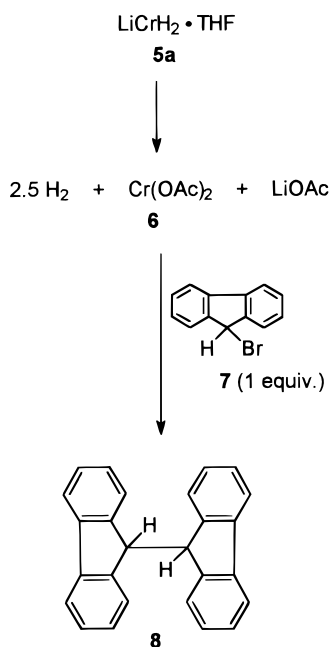




Scheme 4



plex (**5a**),<sup>9</sup> 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  $\text{AgNO}_3$ . Second, its protonolysis with glacial acetic acid yielded  $2.5 \pm 0.05 \text{ mol}$  of  $\text{H}_2$  evolved at STP, whereas 2.5 mol are expected.<sup>10</sup> 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% expected<sup>11</sup> 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)  $\text{cm}^{-1}$ , assignable to the symmetric and asymmetric  $\text{CrH}_2$  stretching vibrations, respectively, and two broad bands of medium intensity at 671 and 805  $\text{cm}^{-1}$ , assignable to  $\text{Cr-H}$  deformations. Bands at 1082, 1462, and 1374  $\text{cm}^{-1}$  were clear evidence for coordinated THF.<sup>12</sup> 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  $\text{D}_2\text{O}$  yielded 96% of 9-fluorenol (**11**) completely deuterated at  $\text{C}_9$ ,<sup>13</sup> 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  $\text{D}_2\text{O}$  gave exclusively undeuterated biphenyl (**14**), consistent with the oxidative addition of **5a** to **12** to form **13** and the reductive elimination of  $\text{LiCrHCl}$  to form the final

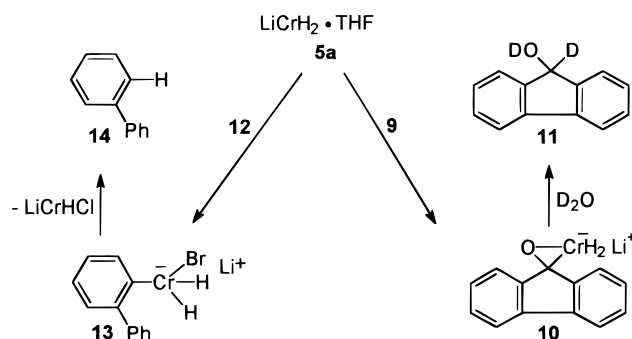
(10) The evolved  $\text{H}_2$  was collected in a gas buret after passage through a cold trap at  $-78^\circ\text{C}$  and was identified by mass spectrometry.

(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  $\text{cm}^{-1}$  to higher frequencies, compared with those of free THF.

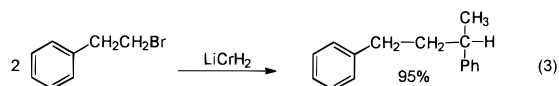
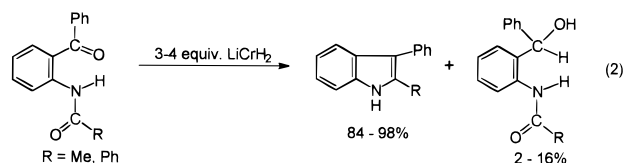
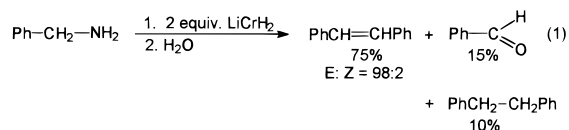
(13) The isolated 9-deuterated derivative of 9-fluorenol was furthermore 65% O-deuterated. That 9-fluorenol was 35% protiated at oxygen can be ascribed to facile H,D-exchange of hydroxyl hydrogen that occurs in moist air upon workup.

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  $^6\text{S}$  state of a  $d^5$  system and a chromium(I) oxidation state.<sup>14</sup> The foregoing chemical analyses and spectroscopic measurements are in excellent agreement with the empirical formulation of  $\text{LiCrH}_2$  for this novel and most versatile reducing and oligomerizing reagent.<sup>15</sup>

The reactivity and hence utility in organic synthesis of  $\text{LiCrH}_2$  (**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  $\text{LiCrH}_2$  (**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.

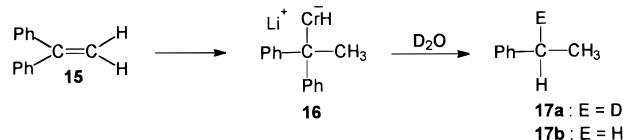
**Table 1. Reductions with Lithium Chromium(I) Dihydride, LiCrH<sub>2</sub> (5)**

entry no.	substrate (S:Cr) <sup>a</sup>	product	yield <sup>b</sup>
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 <sup>c</sup>
18	benzylamine (1:2)	bibenzyl	10
		1,2-diphenylethene <sup>d</sup>	75
		benzaldehyde	15
19	2-acetylaminobenzophenone (1:3)	2-methyl-3-phenylindole <sup>e</sup>	98
20	2-benzoylaminobenzophenone(1:4)	2,3-diphenylindole <sup>e</sup>	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) <sup>f</sup>	2,4,6-triphenyl-1,3,5-triazine	major (1:1)
		2,4,5-triphenylimidazole	major (6:1)
23	diphenylacetylene (10:1)	hexaphenylbenzene <sup>g</sup>	90
24	benzaldehyde	1,2-diphenyl-1,2-ethanediol <sup>h</sup>	75
25	acenaphthylene (2:1)	acenaphthene	85
26	1,1-diphenylethane (2:1)	1,2-diphenylethane	91
27	( <i>E</i> )-1,2-diphenylethane (1:1)	bibenzyl	85
28	styrene <sup>i</sup>	poly(styrene)	100
29	methyl methacrylate <sup>i</sup>	poly(methyl methacrylate)	100
30	9-fluorenone (1:1)	9-fluorenone	98
	9-fluorenone (3:1)	9,9'-bifluorenone	95

<sup>a</sup> The experimental procedure for the generation of LiCrH<sub>2</sub> is straightforward and expeditious: To a stirred suspension of anhydrous chromium(III) chloride in THF at –78 °C (10 mmol of CrCl<sub>3</sub> 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 LiCrH<sub>2</sub>·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. <sup>b</sup> The yields are not yet optimized. <sup>c</sup> Desulfurization was markedly promoted by the addition of 5 mol % of Ni(acac)<sub>2</sub>. <sup>d</sup> A 98:2 *trans,cis*-mixture was obtained. <sup>e</sup> The uncyclized alcohol was a minor product (cf. eq 2). <sup>f</sup> Other unsaturated organonitrogen derivatives, such as imines and azo and nitro compounds, are smoothly reduced by 5 to amines. <sup>g</sup> The minor products were the stilbenes and bibenzyl. <sup>h</sup> A 3:1 mixture of the *racemic*- and *meso*-diols was obtained. <sup>i</sup> 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 LiCrH<sub>2</sub> indicates that hydrochromation can also play a significant role. Thus the 1:1 interaction of LiCrH<sub>2</sub> with 1,1-diphenylethene (15), followed by workup with D<sub>2</sub>O, gave a 95% yield of 1,1-diphenylethane (17), which was 75% deuterated at C<sub>1</sub> (17a), thereby supporting the presence of a large proportion of intermediate 16 at the time of deuteriolysis (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, LiCrH<sub>2</sub> 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 CrCl<sub>6</sub> and CrCl<sub>2</sub>.<sup>16</sup>

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(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.