case of 8-NMe_2 or 8-*p*-$SnMe_3$, the methylene signal of the methyl ethers **16** and **22** could be used as the internal standard. Rate constants were calculated by the method of least squares. Correlation coefficients were greater than 0.999. Rate constants given represent the average of at least two runs.

Rearrangement of 11-*p*-CH_2SiMe_3 and 11-*p*-cyclopropyl. Kinetics Procedures. Rearrangements rates of these substrates in isooctane were monitored in sealed cuvettes by ultraviolet spectroscopy as previously described.[25] The absorbance change for 11-*p*-CH_2SiMe_3 was monitored at 245 nm and 11-*p*-cyclopropyl was monitored at 246 nm. After 10 half-lives, an infinity reading was taken. Rate constants were calculated by standard methods and represent an average of at least 2 runs.

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Alkylations of Tetracarbonyl(phosphine)chromium and Pentacarbonylchromium Carbene Complexes and Their Reactions with Selected Acetylenes

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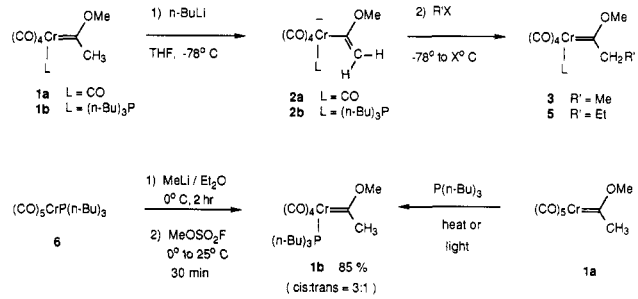
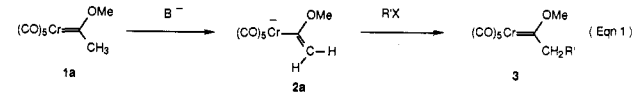
The thermodynamic acidity of (methylmethoxymethylene)tetracarbonyl(tri-*n*-butylphosphine)chromium (**1b**) was found to be 6 orders of magnitude less than that of (methylmethoxymethylene)pentacarbonylchromium (**1a**). The anion **2b** is generated from **1b** by deprotonation with *n*-butyllithium. The difference in acidity of **1a** and **1b** is reflected in an increase in the reactivity of **2b** with alkyl halides and sulfonate esters that is sufficient to allow for the efficient preparation of elaborated carbene complexes from simple precursors. Since the anion **2a**, generated from pentacarbonyl complex **1a**, can only be effectively alkylated with trifluoromethanesulfonate esters, methods are developed for the conversion of tetracarbonyl phosphine carbene complexes to pentacarbonyl carbene complexes such that the former can serve as synthons for the latter. Several reactions of tetracarbonyl phosphine carbene complexes were investigated, including the benzannulation reaction with acetylenes, the reaction of acetylenes with alkyl-substituted complexes to produce stable vinylketenes, and two-alkyne annulations with 1,6-heptadiyne that provide for the first time selective synthesis of bicyclo[4.3.0]nonadien-2-ones.

Shortly after it was discovered[1] that the protons on carbons α to the carbene carbon in several transition-metal Fischer carbene complexes are acidic, the chemistry of stoichiometrically generated anions of alkyl carbene complexes (such as **2a**) was investigated.[2] From an examination of the equilibrium of the bis(triphenylphosphine)nitrogen(1+) salt of **2a** with various phenols, it was established that the pK_a of **1a** was approximately 8.[3] Given the acidity of **1a**, it is to be expected that its conjugate base **2a** would be relatively unreactive with most electrophiles, and the extensive studies by Casey reveal that this is indeed the case.[2] Methyl iodide and primary halides either give very poor yields or fail to give detectable amounts of alkylated products in their reactions with anion **2a**.[2f,j,k] Methyl fluorosulfate gives moderate yields with **2a** but ethyl tosylate fails to alkylate **2a**.[2j] Alkylations with allylic and benzylic halides give improved yields but this is offset by severe problems with dialkylation.[2f] Condensation products can be obtained from the reaction of **2a** with nonenolizable aldehydes but under the same conditions ketones do not react.[2b,e,g,i-k] Certain electrophiles such as epoxides[2h] α-bromo esters,[2h] and α-chloro ethers[2g] give moderate yields of interesting and/or synthetically useful carbene complexes.

Scheme I





Due to the increasing value of transition-metal carbene complexes in organic synthesis,[4,5] there is consequently a

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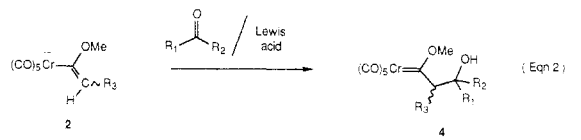
0022-3263/87/1952-3263$01.50/0

Table I. Alkylations of the Pentacarbonyl and *cis*-Tetracarbonyl Tri-*n*-butylphosphine Complexes 1a and 1b

complex	L	R^1X (equiv)	conditions[a] (temp/time/[1])	product	% yield	% recvry of 1
1a	CO	MeI (1.0)	0 °C, 30 min, 0.75 M	3a	22[b]	9
1a	CO	$MeSO_3F$ (1.0)[f]	0 °C, 30 min, 0.15 M	3a	50[c]	10
1a	CO	$MeSO_3CF_3$ (1.5)	0 C, 15 min, 0.07 M	3a	83[g]	0
1a	CO	$EtSO_3PhCH$ (1.3)	0 °C, 30 min, 0.18 M	5a	0[c]	50
1b	P(*n*-Bu)$_3$[d]	MeI (10.0)[e]	0 °C, 60 min, 0.05 M	3b	93	0
1b	P(*n*-Bu)$_3$[d]	MeI (1.0)	0 °C, 50 min, 0.09 M	3b	74	18
1b	P(*n*-Bu)$_3$[d]	$MeSO_3F$ (2.4)	−78 °C, 2 min, 0.05 M	3b	93	0
1b	P(*n*-Bu)$_3$[d]	$MeSO_3CF_3$ (2.0)	0 °C, 8 min, 0.13 M	3b	99[h]	0
1b	P(*n*-Bu)$_3$[d]	$EtSO_3PhCH_3$ (2.5)	22 °C, 10 h, 0.05 M	5b	17	43

[a] Unless otherwise specified all alkylations were performed by adding the electrophile all at once to a solution of the anion 2 in THF at −78 °C followed by warming to the indicated temperature. [b] Reference 2j, p 83. [c] Reference 2j, p 84. [d] Reactions of the purified cis isomer of 1b. [e] Addition of anion 2 to the electrophile. [f] Diethyl ether solvent. [g] 94:6 mixture of mono- to dialkylated product, ref 10c. [h] 2:1 mixture of cis/trans isomers.

growing need to synthesize more elaborate complexes. The alkylation of anions of transition-metal carbene complexes would provide a versatile method for the transformation of a single readily available complex such as **1a** into a variety of elaborated complexes, and thus it would be desirable to find solutions to the general unreactivity of these anions toward most electrophiles. Two conceptually straightforward solutions to this problem would be to increase either the reactivity of the electrophile or of the carbene complex anion. We have employed the former tactic in the aldol condensation reaction of these "carbenylate" anions where the reactions of anion **2a** was extended to include ketones and enolizable aldehydes by activating the carbonyl compound by pretreatment with a Lewis acid.[5f] However, for alkylations with alkyl halides or activated derivatives of alkyl alcohols, the more successful tactic is most likely to follow from efforts directed toward increasing the reactivity of the anions of these carbene complexes.



It should be possible to enhance the reactivity of anions of the type **2** without any structural changes in the carbene ligand by replacing one of the five carbon monoxide ligands on the chromium with the more electron-releasing tri-*n*-butylphosphine (Scheme I). Tetracarbonyl(phosphine)-chromium carbene complexes have been previously prepared[6] but the acidity of alkyl-substituted complexes has not been examined. It is to be expected that they would be less acidic due to the destabilizing effect that the phosphine ligand would have on their conjugate bases. As a consequence it can further be expected that anions bearing phosphine ligands (such as **2b**) will be more reactive toward electrophiles than their pentacarbonyl analogues (i.e., **2a**). Herein is described the first examination of the acidity of tetracarbonyl(phosphine)chromium carbene complexes, the reactivity of their corresponding "enolates", and a preliminary comparison of the synthetic potential of these phosphine complexes with that established for their pentacarbonyl analogues.

Tetracarbonyl(phosphine)chromium carbene complexes have been prepared by either the thermal or photoinduced reactions of pentacarbonyl carbene complexes with phosphines or by employing the standard Fischer synthesis starting with pentacarbonyl(phosphine)chromium.[6a-d] We have found that the best method for the synthesis of the tri-*n*-butylphosphine complex **1b**[6c] is via the addition of methyllithium to pentacarbonyl(tri-*n*-butylphosphine)-chromium which in turn can be prepared in quantitative yield from chromium hexacarbonyl and tri-*n*-butylphosphine.[6e] Significantly improved yields can be achieved when the methyllithium employed is halide free. By this method the phosphine complex **1b** can be obtained in 85% yield as a 3:1 mixture of cis and trans isomers.

The cis and trans isomers of tetracarbonyl phosphine carbene complexes have previously been characterized. The isomers can be distinquished by ^{13}C NMR and have been characterized by X-ray crystallographic analysis[6f] and routinely can be identified by ^1H NMR since the methoxyl absorption for the cis isomers are upfield from those for the trans isomers. Fischer observed that the purified isomers rapidly undergo isomerization to give an equilibrium mixture that is dependent on the structure of the complex and on the solvent.[7] Formation of the cis isomer has been found to be preferred kinetically; however, as the size of the carbene ligand increases, a greater proportion of the trans isomer is observed.[8] The rate of the isomerization of the cis isomer of (methoxymethylmethylene)(triethylphosphine)tetracarbonylchromium(0) was found

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Table II. Alkylations of the *cis*-Tetracarbonyl Tri-*n*-butylphosphine Complexes 1b, 3b, 5b, and 8b

entry	complex	R	R^1X (equiv)	conditions[a]	product	yield, % (cis/trans)	% recvry of 1
1	**1b**	H	MeI (10)[b]	0 °C, 1 h	**3b**	93 (2:1)	
2			MeI (10[b,c]	0 °C, 1 h	**3b**	94 (2:1)	
3			MeI (1.0)	0 °C, 50 min	**3b**	74 (2:1)	18
4			$MeOSO_2F$ (2.4)	−78 °C, 2 min	**3b**	93 (2:1)	
5			$MeOSO_2CF_3$ (2.0)	0 °C, 8 min	**3b**	99 (2:1)	
6			CH_3CH_2Br (3.0)[b]	22 °C, 10 h	**5b**	47 (1.6:1)[d]	25
7			CH_3CH_2I (4.0)[b]	0 °C, 6 h	**5b**	44 (1.6:1)[e]	16
8			CH_3CH_2OTs (2.5)	22 °C, 10 h	**5b**	17 (1.6:1)	43
9			$CH_3CH_2OSO_2F$ (2.5)	0 °C, 3 min	**5b**	97 (1.6:1)	
10			$(CH_3)_2CHI$ (1.1)	0 °C, 5 h	**7b**	26 (2.9:1)	47
11			$(CH_3)_2CHOSO_2CF_3$ (2.0)	0 °C, 10 min	**7b**	94 (2.9:1)	
12			$PhCH_2Cl$ (2.0)	0 °C, 3 h[f]	**8b**	90 (4:1)	
13			$HC{\equiv}C(CH_2)_3OSO_2CF_3$ (1.6)	0 °C, 20 min	**9b**	90 (15:1)	
14			$CH_2{=}CH(CH_2)_2OSO_2CF_3$ (1.1)	0 °C, 25 min	**10b**	95 (5:1)	
15			$CH_3C{\equiv}C(CH_2)_2OSO_2CF_3$ (2.0)	0 °C, 30 min	**11b**	91 (2.5:1)	
16			$Me_3SiC{\equiv}C(CH_2)_3OSO_2CF_3$ (1.5)	0 °C, 10 min	**12b**	98 (3:1)	
17	**3b**[g]	CH_3	$HC{\equiv}C(CH_2)_3OSO_2CF_3$ (1.5)	0 °C, 10 min	**13b**	97 (1:1)	
18	**8b**[h]	CH_2Ph	$HC{\equiv}C(CH_2)_3OSO_2CF_3$ (2.0)	0 C, 15 min	**14b**	74 (1:10)	
19	**5b**[i]	CH_2CH_3	CH_3CH_2I (3.0)	0 °C, 5 h	**15b**	87 (1:11)	

[a] Unless otherwise specified all alkylations were performed by adding the electrophile all at once to a 0.05–0.10 M THF solution of the anion **2** generated from the purified cis isomer at −78 °C followed by warming to the indicated temperature. [b] Inverse addition. [c] Alkylation of a 11:1 mixture of trans and cis **1b**. [d] An 18% yield of the dialkylated product **15b** was also obtained. [e] A 23% of the dialkylated product **15b** was also obtained. [f] Diethyl ether solvent. [g] 2:1 mixture of cis/trans isomer. [h] 4:1 mixture of cis/trans isomer. [i] 1.6:1 mixture of cis/trans isomers.

to be $k_1 = 5.7 \times 10^{-4}$ s^{-1} at 46 °C in methylcyclohexane.[7a] The cis and trans isomers of the tri-*n*-butylphosphine complex **1b** were separated by flash chromatograhy on silica gel and all of the reactions summarized in Table I and II were carried out on the purified cis isomer unless otherwise specified.

A comparison of the reactivity of the pentacarbonyl anion **1a** and the tetracarbonyl tri-*n*-butylphosphine anion **2b** is provided by the data in Table I. The reaction of anion **2a** with methyl iodide has been reported to give a 22% yield of the corresponding ethyl carbene complex **3a** and a 9% recovery of the methyl complex **1a**.[2j] The phosphine-substituted anion **2b** was generated by deprotonation of **1b** with *n*-butyllithium in THF at −78 °C and was found to be highly reactive by comparison, and one of the manifestations of this is the greatly increased yields in reactions with electrophiles. Alkylation with methyl iodide gave a 93% yield of the corresponding ethyl complex **3b**. The rate enhancement is dramatically exemplified in the reaction of methyl fluorosulfate with **2b**, which is complete in 2 min at −78 °C to give **3b** in 93% yield. We have confirmed that the same reaction with **2a** requires 30 min at 0 °C to go to completion.[2j] We have repeated the reported alkylation of **1a** with methyl fluorosulfate on a number of occasions and obtained yields in the range of 40–50% and have further found that under the reported conditions[2d,j] approximately 3% of the dialkylated product is obtained.[10b] The reaction of the pentacarbonyl anion **2a** with ethyl tosylate was reported to fail[2j] and although the same reaction with **2b** does give the *n*-propyl carbene complex **5b**, the yield is not synthetically useful.

The data in Table I reveal that the alkylations of the tetracarbonyl tri-*n*-butylphosphine anion **2b** with alkyl halides, fluorosulfates, and tosylsulfates are clearly superior to those of the pentacarbonyl anion **1a**; however, both anions give high yields with methyl trifluoromethanesulfonate. Complex **1b** gives a 99% yield of **3b** as a 2:1 mixture of cis/trans isomers, whereas **1a** gives an 83% yield[10c] of **3a** as a 94:6 mixture of mono- to dialkylated product. If inverse addition is employed (addition of **2a** to $MeSO_3CF_3$), then the yield of **3a** is 75% and the amount of dialkylated product is reduced to 1.2% of the isolated material.[10c] It was not surprising to find that this alkylation proceeded in 83% yield since trifluoromethanesulfonates are generally observed to be more reactive alkylating reagents than fluorosulfates.[11] Another explanation for this difference in yields may be attributed to the observation that methyl fluorosulfate will dissociate to dimethyl sulfate and sulfuryl fluoride at ambient temperatures.[12] As can be seen from the reactions in Scheme IV the pentacarbonyl complex **1a** can be successfully alkylated in high yields with other trifluoromethanesulfonates (triflates) as well. This represents the first good synthetic method for the preparation of pentacarbonyl Fischer carbene complexes of the group 6 metals via the direct alkylation of other pentacarbonyl complexes.

The data from a larger survey of the reactions of the tri-*n*-butylphosphine-substituted anion **2b** are presented in Table II. Moderate yields are obtained with primary halides although the total yields of alkylated products are high since in the case of ethyl iodide and ethyl bromide substantial amounts of dialkylated products are also produced. Ethyl tosylate alkylates the anion poorly but the fluorosulfate ester of ethanol gives a nearly quantitative yield of the *n*-propyl carbene complex **5b**. In addition to the dialkylated product **15b**, substantial amounts of the starting methyl complex **1b** can be recovered from the reactions with ethyl bromide and ethyl iodide. It was demonstrated that the recovered **1b** is not produced in this reaction by a dehydrohalogenation reaction initiated by deprotonation of ethyl iodide by the anion **2b**. The reaction of **2b** with ethyl-d_5 iodide produced the deuteriated mono- and dialkylated products **5b′** and **15b′**, but the recovered starting material **1b** was found not to contain any deuterium (eq 3). The isolation of **1b** from this reaction is thus either the consequence of deprotonation of the product **5b** (a necessary step in dialkylation) or to the fact that the anion **2b** has not completely reacted. That

(10) (a) McEwen, W. K. *J. Am. Chem. Soc.* **1936**, *58*, 1124. (b) Presumably if the reaction were carried out by addition of the anion **2b** to the electrophile this small amount of dialkylation could be prevented. (c) Xu, Y. C.; Anderson, B. A.; Wulff, W. D., manuscript in preparation.

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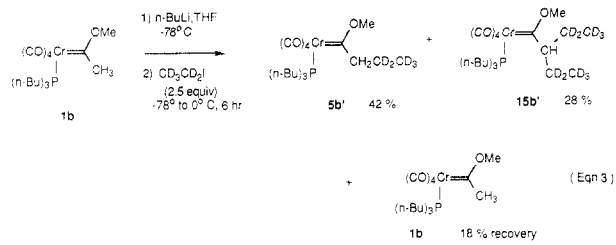


the former is the case is suggested by the high yield of the reaction of the anion derived from the *n*-propyl complex **5b** with ethyl iodide from which none of the starting complex **5b** can be reisolated (entry 19) or from which no dialkylated product can be detected. This indicates either that proton transfer to form a tertiary anion α to the carbene carbon is unfavorable or that the tertiary anion derived from **15b** is much less reactive than the secondary anion derived from **5b**. As indicated by entry 10, the synthetic utility of the alkylation of these anions with secondary halides is limited. However, the alkylation of the anion **2b** with isopropyl triflate (entry 11) gives a 94% yield of isobutyl carbene complex **7b**.

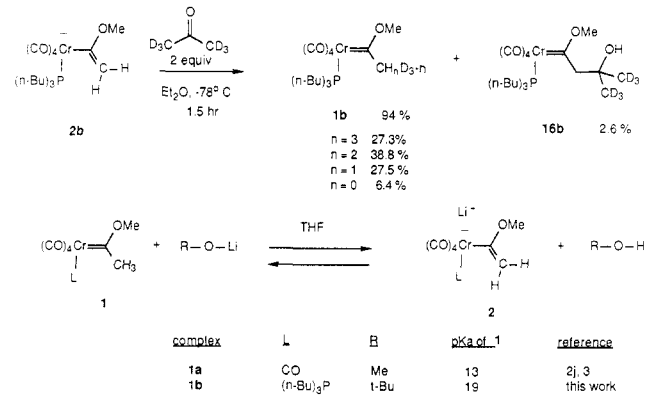
Clearly, the most synthetically useful alkylations are with triflates since they are readily preparable from most alcohols and as indicated in the table, seven out of the eight triflates that we have tried gave greater than 90% yields of the alkylated carbene complexes with no evidence for the formation of any dialkylated products in any of these reactions. It is interesting to note that the reaction of anion **2b** with primary triflates proceeds in high yields even if the triflate contains a relatively acidic acetylenic proton (entries 13 and 19).

For the purposes of producing consistent data, all of the reactions with the electrophiles indicated in Tables I and II were carried out on the purified cis isomer of **1b** and the alkylated products were obtained as mixtures of cis and trans isomers in the ratios indicated in the table. It was found that both the cis and trans isomers of **1b** are alkylated with equal facility. An enriched sample of *trans*-**1b** (trans/cis = 11:1) was deprotonated and treated with methyl iodide to give the ethyl complex **3b** in 94% yield as a 2:1 mixture of isomers (entry 2), which is essentially identical with the results obtained with the cis isomer of **1b** (entry 1). For preparative purposes, it was thus not necessary to separate the cis and trans isomers of **1b** that are produced in the synthesis from pentacarbonyl(phosphine)chromium (Scheme I).

The aldol condensation of the anion **2b** was attempted with acetone; however, under several conditions the only result from this reaction was the near quantitative recovery of the carbene complex **1b** after the reaction mixture was quenched. The basicity of the tri-*n*-butylphosphine-substituted complex **1b** is expected to be much higher than the pentacarbonyl complex **1a** and it could be sufficiently high to permit deprotonation of acetone. In order to test for this possibility, the anion **2b** was treated with 2 equiv of deuteriated acetone in ether at −78 °C and the reaction mixture was quenched after 1.5 h. The starting material was recovered in 94% yield and was found to be extensively deuteriated with the distribution of mono-, di-, and trideuteriated compounds indicated in Scheme II. A small amount of the aldol product **16b** was isolated from the reaction mixture.

This result suggests that the pK_a of the tri-*n*-butylphosphine complex **1b** is near acetone and that it is significantly higher than that for the pentacarbonyl complex **1a**. In order to quantify the destabilizing effect that the tri-*n*-butylphosphine ligand has on the anion **2** relative to a carbon monoxide ligand, the acidity of the tri-*n*-butyl-

Scheme II



phosphine complex **1b** was determined. The thermodynamic acidity of the pentacarbonyl complex **1a** had previously been determined in tetrahydrofuran with lithium methoxide as base and from the data reported the pK_a can be calculated to be 13 (pK_a(MeOH) = 16 in benzene[10a]).[2j] The same experiment was carried out with the phosphine complex **1b** in tetrahydrofuran with lithium *tert*-butoxide as base and the same equilibrium concentrations of **1b** and **2b** were found (**1b**:**2b** = 0.79) by ^{1}H NMR from the reaction of **1b** and lithium *tert*-butoxide and from the reaction of **2b** and *tert*-butyl alcohol. When these reactions where quenched, a high recovery of **1b** was obtained (84%), indicating that there are no side reactions significantly obscuring the measurement. Replacing a carbon monoxide ligand by tributylphosphine thus decreases the acidity of **1** by a factor of 10^6 given that the pK_a of *t*-BuOH in benzene is 19[10a] and that the 3 pK_a unit differential between MeOH and *t*-BuOH observed in benzene holds also for THF.

If tetracarbonyl phosphine carbene complexes could be converted to pentacarbonyl complexes after the alkylation step, advantage could be taken of both the established and still growing importance of a variety of reactions of pentacarbonylchromium carbene complexes in organic synthesis[2] and of the range of alkylation reactions that are made possible by substituting one of the five carbon monoxide ligands for a phosphine. As indicated above in Scheme I, a number of reports have described the conversion of pentacarbonyl carbene complexes to tetracarbonyl(phosphine)chromium complexes;[6] however, there are no examples of the reverse transformation in the literature. Our first attempt was to exchange the tri-*n*-butylphosphine in complex **1b** by exposure to a carbon monoxide atmosphere. After **1b** had been exposed to 250 psi of carbon monoxide for 12 h at room temperature, only a trace of the pentacarbonyl complex **1a** could be detected. The complete conversion of the starting material was observed when the pressure was raised to 800 psi; however, the only compound that could be isolated from the reaction was tri-*n*-butylphosphine, apparently the result of displacement of both the phosphine and carbene ligand from **1b**.

Given the general observation that triphenylphosphine participates in dissociative processes more readily than tri-*n*-butylphosphine in a number of organometallic complexes,[9] we turned our attention to the triphenylphosphine-substituted methylmethoxychromium carbene complex **1c**. The preparation of this compound has been reported by both of the procedures outlined in Scheme I for **1b**.[6] However, we have found that the best procedure in this case involves ligand exchange of the pentacarbonyl complex **1a** with triphenylphosphine (Scheme III). Complex **1c** can be obtained in 88% yield as a 5:1 mixture of

Scheme III

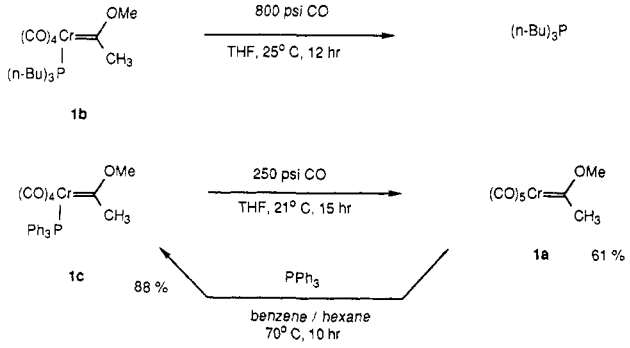


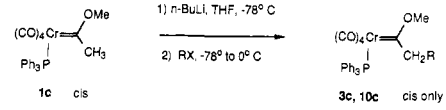
Table III. Alkylations of the Tetracarbonyl Triphenylphosphine Complex 1c

RX (equiv)	conditions[a]	product[b]	yield, %
MeI (5.0)	0 °C, 30 min	**3c**	96
$MeOSO_2CF_3$ (2.0)	0 °C, 10 min	**3c**	84
$H_2C{=}CHCH_2CH_2OSO_2CF_3$ (1.5)	0 °C, 15 min	**10c**	86

[a] All alkylations were performed by adding the electrophile all at once to a 0.06 M solution of the anion **2c** generated from the purified cis isomer of **1c** at −78 °C and warming to 0 °C for the indicating time. [b] All products were obtained exclusively as the cis isomer.

cis and trans isomers, from which the cis isomer can be selectively crystallized from pentane. Exposure of the cis isomer of **1c** to an atmosphere of carbon monoxide at 250 psi and room temperature for 15 h resulted in complete conversion of the starting material and the isolation of the pentacarbonyl complex **1a** in 61% yield. It is expected that the trans isomer of **1c** would also be converted to **1a**, if for no other reason than these isomers can equilibrate at room temperature. These results prompted us to consider the development of tetracarbonyl triphenylphosphine complexes as synthons for pentacarbonyl complexes in alkylation reactions.

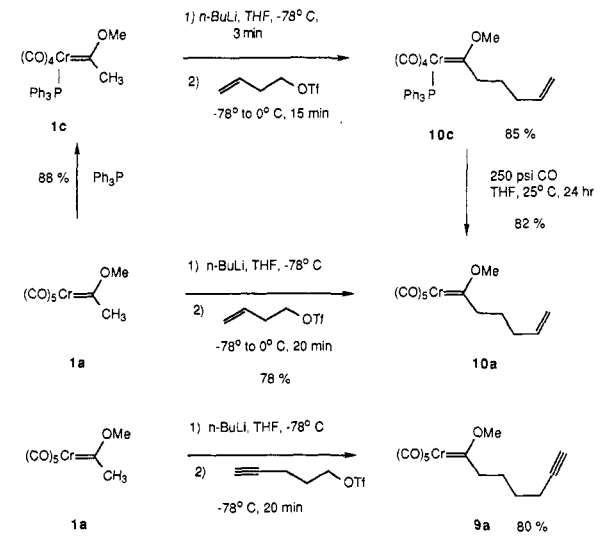
It must, of course, first be demonstrated that the tetracarbonyl triphenylphosphine complexes will undergo facile alkylations before they can be utilized as synthons for pentacarbonyl complexes. Like tri-*n*-butylphospine, the triphenylphosphine ligand should have a considerable destabilizing effect on the anion **2** when compared to carbon monoxide, and this is borne out in the reactions of anion **2c** with the electrophiles indicated in Table III. Only the cis isomers of the alkylated products **3c** and **10c**



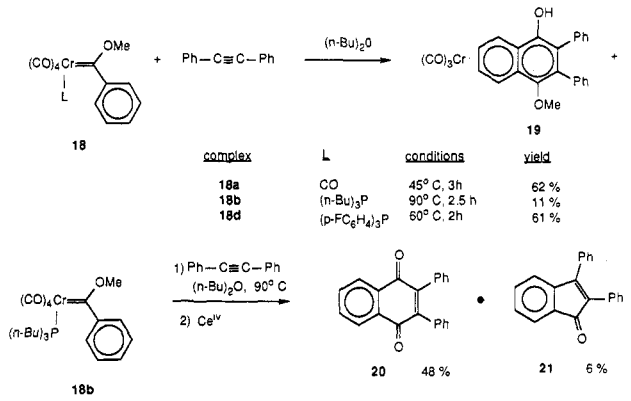
were isolated from these reactions. By comparison with the data in Tables I and II, it can be seen that the anion **2c** is dramatically more reactive than the pentacarbonyl anion **2a** and comparable with the reactivity of the tetracarbonyl tri-*n*-butylphosphine anion **2b**.

The reactions presented in Scheme IV demonstrate the synthetic utility of the alkylations of the anions of the pentacarbonyl complex **1a** and the tetracarbonyl triphenylphosphine complex **1c** with functionalized triflates and the interconversions of these two classes of carbene complexes. The anion generated by deprotonation of **1c** with *n*-butyllithium will react cleanly with 3-butenyl triflate to give the complex **10c** in 85% yield as exclusively the cis isomer. Ligand exchange proceeds efficiently with carbon monoxide to provide an 82% yield of the pentacarbonyl complex **10a**. Alternatively, the anion generated

Scheme IV



Scheme V

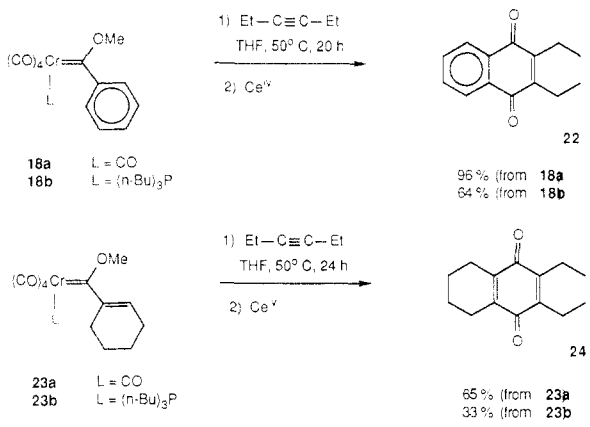


from complex **1a** can be alkylated with 3-butenyl triflate to give complex **10a** in 78% yield. The preparation of the alkynyl complex **9a** can be accomplished in a similar reaction in 80% yield.

The inherent value of the reactions of pentacarbonyl Fischer chromium carbene complexes in organic synthesis has been well-established.[2] The reactions of tetracarbonyl(phosphine)chromium carbene complexes, on the other hand, have scarcely been examined and can be found in three reports in the literature.[13-15] One report described the phosphine-induced acid cleavage of the carbene ligand in phosphine-substituted complexes.[13] A second report describes an asymmetric induction in a cyclopropanation reaction of a complex bearing an optically active phosphine.[14] The third report involves the benzannulation reaction which for pentacarbonyl chromium carbene complexes has become quite important synthetically and has been employed in the synthesis of a number of natural products.[5] The benzannulation reactions of diphenylacetylene with the phosphine complexes **18b** and **18d** have been described and compared to the same reaction of the corresponding pentacarbonyl complex **18a**.[15] The reaction of the tris(*p*-fluorophenyl)phosphine complex **18d** was reported to give essentially the same yield of the naphthol chromium tricarbonyl complex **19** as the pentacarbonyl complex **18a** (Scheme V). The reaction of complex **18b** bearing the less electron-accepting tri-*n*-butylphosphine

(13) Schubert, U.; Fischer, E. O. *Chem. Ber.* **1973**, *106*, 3882.
(14) Cooke, M. D.; Fischer, E. O. *J. Organomet. Chem.* **1973**, *56*, 279.
(15) Dotz, K. H.; Dietz, R. *Chem. Ber.* 1977, *110*, 1555.

Scheme VI



ligand, however, was reported to be seriously negatively affected by the presence of this ligand as the yield of the naphthol **19** dropped to 11%. However, in our hands we found that the reaction of complex **18b** with diphenylacetylene when carried out under the same conditions and oxidatively worked up with cerium(IV) ammonium nitrate gave the naphthoquinone **20** in only a slightly lower yield of 48% and in addition gave the indenone **21** in 6% yield. Therefore, the total organic yield from the reaction of the tetracarbonyl tri-*n*-butylphosphine complex **18b** is thus not significantly different than that for the reaction of the pentacarbonyl complex **18a**.

Further investigations of the benzannulation reaction of tetracarbonyl tri-*n*-butylphosphine complexes does reveal that they are less useful than the reactions of the corresponding pentacarbonyl complexes. The yields of the annulated product for both of the examples indicated in Scheme VI drop off when a carbon monoxide ligand is substituted for a tri-*n*-butylphosphine. It is not known at this point why tri-*n*-butylphosphine has this effect; however, we are continuing the study of tetracarbonyl phosphine complexes of molybdenum and tungsten, particularly with triarylphosphine complexes since we are especially encouraged by some of the advantageous characteristics of these compounds to be discussed below.

From what is known about the mechanism[5a,16] of the reaction of pentacarbonylchromium carbene complexes with acetylenes, it is expected that the first step in the reaction of the methylmethoxy chromium carbene complex **1a** with acetylenes is the dissociation of a carbon monoxide ligand. From the kinetic measurements that have been made for **1a** on carbon monoxide exchange,[17] any reaction of **1a** with acetylenes should require 70 °C for a reasonable rate. The reaction of **1a** with either trimethylsilylacetylene or bis(trimethysilyl)acetylene at 70 °C is complete after 24 h; however, no silica gel mobile compounds could be isolated from the reaction mixture.[18] The reactions of the corresponding triphenylphosphine complex **1c** with both acetylenes were complete in 1.5 h at room temperature which gave the vinylketenes **25** and **26** in 65% and 70% yields, respectively (Scheme VII). We have found that these vinylketenes are not very thermally stable above room temperature and thus it is the high reactivity of the triphenylphosphine complex **1c** that makes the isolation of these ketenes possible. The high reactivity of **1c** is undoubtedly due to the ease of the dissociation of the triphenylphosphine ligand that creates an open coordination site on the metal at low temperatures.[9] Silylvinylketenes of this type are known,[19,20] including examples from the reactions of chromium carbene complexes.[19] The silylketenes **25** and **26** could be interesting synthetic intermediates. It has been demonstrated that the influence of the Me_3Si group in the parent (trimethylsilyl)vinylketene[20] is responsible for its novel [4 + 2] cycloaddition reactions with olefins rather than the expected [2 + 2] cycloadditions. Other silylvinylketenes have been observed to react with ynamines to give bicyclo[3.1.0]hexanes.[21]

Scheme VII

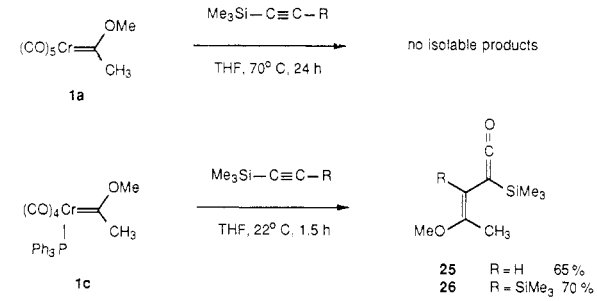
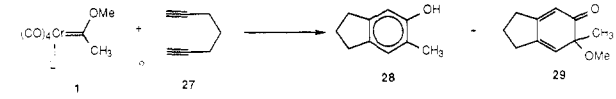


Table IV. Two Alkyne Annulations of Complexes 1a-c with 1,6-Heptadiyne

complex	equiv 27	solvent	temp, °C	time, h	yield, % 28	29
1a	1.2	THF	70	6	57[a]	0
1a	1.2	CH_3CN	70	6	39[a]	26
1b	2.8	THF	70	12	48	0
1b	3.2	CH_3CN	70	7	49	0
1c	2.0	THF	21	5	60	0
1c	0.8	CH_3CN	22	2	8	54

[a] Reference 5.

A final example illustrating the synthetic potential of tetracarbonyl phosphine carbene complexes is their influence on the two-alkyne annulation reaction with 1,6-heptadiyne. We have previously reported that the reaction of the pentacarbonyl chromium complex **1a** will react with 1,6-heptadiyne to give 3-methyl-2-indanol **28** in 57% yield.[5i] It was suspected that phenol **28** was generated by an in situ reduction of the dienone **29** by a chromium(0) species. If this were the case, it was reasoned that a more



coordinating solvent such as acetonitrile may help to prevent this reduction. It was found that the dienone **29** could indeed be isolated from the reaction in acetonitrile, but even under the best of conditions it was still the minor product. All attempts to further optimize this reaction failed which included examining the reactions of the corresponding molybdenum and tungsten analogues of **1a**. It seemed possible that if acetonitrile could stablize the unspecified chromium(0) species responsible for the reduction of the dienone **29**, then a good coordinating phosphine present in the starting carbene complex might also prevent this reduction. As can be seen from the data in Table IV, the tri-*n*-butylphosphine complex **1b** gave only the phenol **28** in both THF and acetonitrile. Although the reasons

(16) (a) Fischer, H.; Mulhemeier, J.; Markl, R.; Dotz, K. H. *Chem. Ber.* **1982**, *115*, 1355. (b) Casey, C. P. *React. Intermed. (Wiley)* **1981**, 2.
(17) Casey, C. P.; Cesa, M. C. *Organometallics* **1982**, *1*, 87.
(18) Wulff, W. D.; Chan, K. S., unpublished results.
(19) Dotz, K. H.; Fugen-Koster, B. *Chem. Ber.* **1980**, *113*, 1449.
(20) Danheiser, R. L.; Sard, H. *J. Org. Chem.* **1980**, *45*, 4810.
(21) Dotz, K. H.; Muhlemeier, J.; Trenkle, B. *J. Organomet. Chem.* **1985**, *289*, 257.

are not yet understood, the reaction of the triphenylphosphine complex **1c** gave the first synthetically useful selectivity (54:8) in favor of the dienone **29**, which has potential for a number of attractive synthetic applications.[5u] An additional advantage of the triphenylphosphine complex **1c** is that since this reaction can be carried out at room temperature in a few hours and since these complexes are stable to air in solution under these conditions, there is no special handling required so that these reactions can be simply carried out in an open flask on the benchtop.

Summary

This initial survey of the reactions of tetracarbonyl(phosphine)chromium carbene complexes reveals that there are significant differences with the reactions of their corresponding pentacarbonyl analogues. The acidity of alkyl complexes is greatly reduced for the tetracarbonyl phosphine complexes, a factor of 10^6 for the tri-*n*-butylphosphine complex **1b**. As expected the anions generated from these complexes are superior in their reactions with a number of alkylating agents as compared to the anions of pentacarbonyl complexes. These alkylation reactions make possible the preparation of elaborated carbene complexes (**9b**, **11b**, **14b**) for the examination of some novel intramolecular reactions of alkyl carbene complexes and acetylenes. The tetracarbonyl triphenylphosphine complexes can serve as synthons for pentacarbonyl complexes in alkylation reactions since the triphenylphosphine ligand can be easily displaced by carbon monoxide. It was found that the tetracarbonyl tri-*n*-butylphosphine complexes are not as useful as the pentacarbonyl complexes in the benzannulation reaction; however, the tetracarbonyl triphenylphosphine complex **1c** was found to be superior in it's reaction with diynes leading to the formation of bicyclo[4.3.0]nonadien-2-ones and also in the preparation of vinylketenes from silylacetylenes where it was observed that the corresponding pentacarbonyl complex failed. These observations should encourage the continued investigations of the chemistry of tetracarbonyl phosphine carbene complexes, particularly of those reactions that have already been demonstrated to be of synthetic value for the pentacarbonyl complexes such as Diels–Alder reactions,[5o,22] aldol condensations,[5f] and cyclobutanone formation.[5h] There is also the potential for asymmetric synthesis in the reactions of these complexes bearing chiral phosphine ligands.

Experimental Section

Unless otherwise noted all reagents were obtained from commercial supplier and used without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately prior to use. Unless otherwise specified, all reactions were carried out under either argon or nitrogen. Flash column chromatography was carried out as described by Still[23] in the presence of air even for the various carbene complexes. The solvent for chromatographic separations and to which all R_f values refer is a ternary mixture of ether, methylene chloride, and hexane. All melting points are uncorrected. Routine proton NMR spectra were recorded either on a Bruker 270-MHz or a DS 1000 500-MHz spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. The ^{13}C NMR spectra were recorded on a Varian XL-400 spectrometer. Infrared spectra were recorded either on a Perkin-Elmer Model 283 spectrophotometer or a Nicolet 20 SXB FTIR spectrometer. Low resolution mass spectra were recorded on a Finnigan 1015 instrument and high resolution mass spectra were recorded on a VG 70-250 mass spectrometer. Elemental analysis were carried out either by Galbraith, Inc. or Micro-Tech Lab., Inc.

Preparation of (Methylmethoxymethylene)(triphenylphosphine)tetracarbonylchromium(0) (1c). The following procedure was first described by Fischer.[6d] A solution of the carbene complex **1a** (1.765 g, 7.06 mmol) and triphenylphosphine (2.223 g, 8.47 mmol) in 60 mL of benzene/hexane (1:1) was heated at reflux for 10 h under a nitrogen atmosphere with a nitrogen sweep across the top of the reflux condensor. The solvents were removed under reduced pressure and the residue was eluted with a 5:1 pentane/benzene solvent mixture through silica gel to give 2.501 g (5.16 mmol, 73%) of the cis isomer of **1c** and 0.517 g (1.07 mmol, 15%) of the trans isomer of **1c**. The cis isomer may need to be further purified by crystallization from pentane. *cis*-**1c**: mp 105–107 °C (lit.[6d] mp 107 °C); ^1H NMR ($CDCl_3$) δ 2.56 (s, 3 H), 4.18 (s, 3 H), 7.30–7.40 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 34.87, 63.63, 128.24 (d, $J_{c\text{-}p}$ = 6.9 Hz), 129.55, 132.91 (d, $J_{c\text{-}p}$ = 10.0 Hz), 136.34 (d, $J_{c\text{-}p}$ = 30.3 Hz), 221.07 (d, $J_{c\text{-}p}$ = 12.9 Hz), 226.41 (d, $J_{c\text{-}p}$ = 9.0 Hz), 230.06 (d, $J_{c\text{-}p}$ = 13.5 Hz), 359.78 (d, $J_{c\text{-}p}$ = 11.6 Hz); IR (neat) 3075–3045 br m, 2992 w, 2944 w, 2005 s, 1914–1849 br s, 1480 s, 1445 m, 1434 s, 1236 m, 1157 m, 1089 s, 749 s, 670 s cm^{-1}. *trans*-**1b**: mp 98–100 °C (lit.[6d] mp 100 °C); ^1H NMR ($CDCl_3$) δ 2.96 (s, 3 H), 4.62 (s, 3 H), 7.30–7.40 (m, 15 H).

Preparation of (Methylmethoxymethylene)(tri-*n*-butylphosphine)tetracarbonylchromium(0) (1b). The preparation of **1b** was accomplished by utilizing a slight modification of a procedure reported by Fischer.[6c,d] To a solution of (tri-*n*-butylphosphine)pentacarbonylchromium[6e] (5.8 g, 14.7 mmol) in 100 mL of anhydrous diethyl ether was added 9.2 mL of a solution of methyllithium (1.6 M, 14.7 mmol; halide free) in diethyl ether at 0 °C under an argon atmosphere. The solution was warmed to room temperature, stirred for 3 h, and methylated by the dropwise addition of 1.4 mL of methyl fluorosulfate (2.0 g, 17.5 mmol). The reaction was stopped after 30 min and the excess methyl fluorosulfate was quenched by shaking with 50 mL of saturated aqueous sodium carbonate. The organic phase was washed with water and saturated brine and dried over magnesium sulfate. After removal of the organic solvents, the oily residue was eluted through a silica gel column with hexane to give *cis*-**1b** (4.00 g, 9.4 mmol, 64%; R_f 0.12) as a red solid (mp 51 °C; lit.[6b] mp 54 °C) and *trans*-**1b** (1.35 g, 3.2 mmol, 22%; R_f 0.3) as a red oil. The ^1H NMR and ^{13}C NMR data for the cis isomer **1b** were extracted from the spectra of a mixture of the cis and trans isomers which was predominantly cis (a small amount of isomerization of *cis*-**1b** occurs during the NMR experiment). *cis*-**1b**: ^1H NMR ($CDCl_3$) δ 0.85–1.0 (m, 9 H), 1.30–1.50 (m, 12 H), 1.55–1.75 (m, 6 H), 2.88 (s, 3 H), 4.41 (s, 3 H); ^{13}C NMR ($CDCl_3$)[24] δ 13.74, 24.38 (d, $J_{c\text{-}p}$ = 12.5 Hz), 25.29, 28.05 (d, $J_{c\text{-}p}$ = 15.5 Hz), 46.28, 63.5, 221.95 (d, $J_{c\text{-}p}$ = 14.4 Hz), 225.81 (d, $J_{c\text{-}p}$ = 7.5 Hz), 230.80 (d, $J_{c\text{-}p}$ = 14.7 Hz), 358.58 (d, $J_{c\text{-}p}$ = 12.9 Hz). The ^1H NMR data for *trans*-**1b** is indistinguishable from that of *cis*-**1b** with the exception of the methoxy absorption at δ 4.60. The IR data and mass spectrum were recorded on a 3:1 mixture of *cis*- and *trans*-**1b**: IR (neat) 2959–2935 br s, 2873 s, 2005 s, 1910–1851 br s, 1457 s, 1420 m, 1221 s, 1160 s, 1094 s, 985 s, 899 s, 668 s cm^{-1}; mass spectrum, *m/e* (rel intensity) 456 (48), 424 M^+ (45), 396 (30) 394 (34), 375 (38), 312 (24), 283 (11), 254 (55), 228 (13), 202 (20), 189 (27), 173 (35), 162 (20), 146 (20), 134 (19), 120 (32), 104 (36), 92 (65), 76 (100). The absorption at *m/e* 456 is due to bis(tri-*n*-butylphosphine)tetracarbonylchromium. This type of decomposition in the mass spectrometer has been observed previously for phosphine-substituted carbene complexes.[14]

In large-scale reactions, *trans*-**1b** is obtained usually contaminated by starting material; however, the cis isomer of **1b** can be conveniently recovered from the flash chromatography fractions containing both isomers by crystallization from pentane since *cis*-**1c** is substantially higher melting than *trans*-**1c**. Halide-free methyllithium generally gives a 10–20% higher yield of **1b** compared to methyllithium-containing lithium bromide.

Reaction of the Anion 2b with Acetone-d_6. A solution of *n*-butyllithium (0.19 mL, 1.50 m, 0.28 mmol) in hexane was added to a solution of *cis*-**1b** (118.8 mg, 0.28 mmol) in 5 mL of anhydrous diethyl ether at −78 °C under argon. After the mixture was stirred

(22) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726.
(23) Still, Ww. C.; Kahn, M.; Metra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(24) Pregosin, P. S.; Kunz, R. W. *NMR: Basic Princ. Prog.* **1979**, *16*, 63.

for 10 min, acetone-d_6 (40 μL, 0.54 mmol) was added at −78 °C by syringe. The reaction was stopped after 1.5 h by addition of 2 mL of aqueous 5% $NaHCO_3$ solution. The organic layer was washed with water and brine and dried over magnesium sulfate. After the volatiles were removed under reduced pressure, the residue was flash chromatographed on silica gel with a 1:1:50 mixture of ether, methylene chloride, and hexane as eluent to afford the deuterium exchanged product **1b′** (112.0 mg, 0.264 mmol, 94%) as a mixture of cis and trans isomers (cis/trans = 3:1). The following spectral data were obtained on a 3:1 mixture of *cis*- and *trans*-**1b′**: ^{1}H NMR ($CDCl_3$, *c*-**1b′**) δ 0.85–1.0 (m, 9 H), 1.30–1.50 (m, 12 H), 1.55–1.75 (m, 6 H), 2.88, 2.84, 2.81 (3 singlets, 1.9 H, due to the resonances of $-CH_nD_{3-n}$, n = 1, 2, 3), 4.41 (s, 3 H); ^{1}H NMR ($CDCl_3$, *trans*-**1b′**) δ 0.85–1.0 (m, 9 H), 1.30–1.50 (m, 12 H), 1.55–1.75 (m, 6 H), 2.88, 2.84, 2.81 (3 singlets, 1.9 H), 4.60 (s, 3 H); mass spectrum, m/e (rel. intensity) 456 (0.56),[14] 427 $M^+_{n=0}$ (0.25), 426 $M^+_{n=1}$ (0.50), 425 $M^+_{n=2}$ (0.55), 424 M^+_n = 3 (0.34), 394 (17.0), 315 (1.85), 314 (4.5), 313 (5.3), 312 (3.1), 283 (5.3), 254 (38.1), 228 (7.7), 212 (8.3), 202 (18.4), 198 (6.6), 160 (5.9), 146 (14.5), 131 (17.0), 118 (26.0), 104 (32.3), 76 (100.0). From the peak intensities of m/e 312–315, the relative percentages of the different deuterium exchange products **1b′** were determined: n = 3, 27.3%; n = 2, 38.8%; n = 1, 27%; n = 0, 6.4%.

In addition to the deuterium exchanged products **1b′**, there was another minor product which (R_f 0.03 (1:1:50), R_f 0.23 (1:1:5)) was tentatively assigned as the aldol adduct **16b** (3.5 mg, 0.07 mmol, 2.6%) on the basis of the following ^{1}H NMR data. **16b**: ^{1}H NMR ($CDCl_3$) δ 0.87–0.98 (m, 9 H), 1.30–1.50 (m, 12 H), 1.55–1.75 (m, 6 H), 3.48 (s, 2 H), 3.57 (s, 1 H), 4.73 (s, 3 H).

Determination of the pK_a of 1b. Lithium *tert*-butoxide was prepared by adding a solution of *n*-butyllithium (0.509 mmol) in 2 mL of THF-d_8 to a solution of *tert*-butyl alcohol (37.5 mg, 0.509 mmol) in 3 mL of THF-d_8 at room temperature under argon. The carbene complex *cis*-**1b** (216.0 mg, 0.509 mmol) was then added to the lithium *tert*-butoxide solution and the resulting mixture was stirred at room temperature for 20 min. Integration of either the methoxy peak or the methyl peak in the ^{1}H NMR spectrum of this mixture revealed that the ratio of anion **2b** to complex **1b** was 1.2:1.0. The ^{1}H NMR data for the following compounds were obtained separately: lithium salt **2b**, ^{1}H NMR (THF-d_8) δ 0.85–0.95 (m, 9 H), 1.25–1.40 (m, 11 H), 1.48–1.68 (m, 6 H), 3.29 (s, 3 H) 3.79 (s, 1 H) 4.45 (s, 1 H); *cis*-**1b**, ^{1}H NMR (THF-d_8) δ 0.90–1.0 (m, 9 H), 1.37–1.50 (m, 12 H), 1.65–1.78 (m, 6 H), 2.93 (s, 3 H), 4.36 (s, 3 H); *trans*-**1b**, ^{1}H NMR (THF-d_8) δ 0.90–1.0 (m, 9 H), 1.37–1.50 (m, 12 H), 1.65–1.78 (m, 6 H), 2.93 (s, 3 H), 4.60 (s, 3 H).

The reaction of anion **2b** with *tert*-butyl alcohol provided a similar result. Lithium salt **2b** was made by adding a solution of 0.388 mmol of *n*-butyllithium in 2 mL of THF-d_8 to **1b** in 2 mL of THF-d_8 at room temperature under argon. Complete deprotonation of **1b** was checked by ^{1}H NMR, which revealed the exclusive presence of anion **2b**. *tert*-Butyl alcohol (36.6 μL, 28.8 mg, 0.358 mmol) was added to the solution of anion **2b** and the resulting mixture was stirred at room temperature for 20 min. Integration of the ^{1}H NMR spectrum of the reaction mixture in the same manner showed the ratio of anion **2b** to complex **1b** was 1.32:1.0. After 2 mL of an aqueous $NaHCO_3$ solution (5%) was added to the mixture the organic layer was washed with water and brine and dried over magnesium sulfate. The residue was flash chromatographed on silica gel with hexane as solvent to give compound **1b** as a 3:1 mixture of cis and trans isomers (138.2 mg, 0.326 mmol, 84%) in good recovery, which ensures that there is no appreciable side reaction obscuring the measurement. On the basis of these results and on the acidity of *tert*-butyl alcohol (pK_a 19[10a]), the pK_a of complex **1b** can be calculated to be 18.8. Thus complex **1b** has approximately the same acidity as *tert*-butyl alcohol.

Alkylation of *cis*-1b with Methyl Iodide, Methyl Fluorosulfate, and Methyl Triflate. (a) Normal Addition of Methyl Iodide. To a solution of the carbene complex *cis*-**1b** (148.3 mg 0.35 mmol) in 4 mL of THF was added 0.22 mL of *n*-butyllithium (1.6 M, 0.35 mmol) at −78 °C under argon. Methyl iodide (20 μL, 45.6 mg, 0.35 mmol) was then introduced at −78 °C by syringe and the solution was stirred at 0 °C for 50 min. After 3 mL of an aqueous $NaHCO_3$ solution (5%) was added, the organic layer was washed with water and brine and dried over magnesium sulfate. The residue was eluted with 1:1:100 mixture of ether, methylene chloride, and hexanes through a silica gel column to give both the starting material **1b** (26.2 mg, 0.062, 17.6%) and the alkylated product **3b** (114.0 mg, 0.26 mmol, 74.3%; cis, R_f 0.29; trans, R_f 0.47; cis/trans = 2:1) as a red oil. The following data were obtained on a 2:1 mixture of *cis*- and *trans*-**3b**: ^{1}H NMR ($CDCl_3$, *cis*-**3b**) δ 0.88–1.05 (m, 12 H), 1.35–1.45 (m, 12 H), 1.53–1.76 (m, 6 H), 3.19 (q, 2 H, J = 7.47 Hz), 4.61 (s, 3 H); ^{1}H NMR ($CDCl_3$, *trans*-**3b**) δ 0.88–1.05 (m, 12 H), 1.35–1.45 (m, 12 H), 1.53–1.76 (m, 6 H), 3.25 (q, 2 H, J = 7.46 Hz), 4.63 (s, 3 H); IR (neat) 2950 s, 2875 m, 2000 s, 1920–1860 br s, 1455 m, 1200 m cm^{-1}; mass spectrum, m/e (rel intensity) 568 (6),[14] 456 (3), 438 M^+ (38), 410 (30), 394 (10), 382 (4), 354 (8), 362 (32), 259 (12), 245 (53), 220 (40), 203 (100), 202 (85), 173 (22), 146 (25) 89 (44). Anal. Calcd for $C_{20}H_{35}O_5PCr$: C, 54.76; H, 8.05; P, 7.07; Cr, 11.86. Found: C, 54.53; H, 8.12; P, 7.40; Cr, 11.37.

(b) Inverse Addition of Methyl Iodide. A solution of the anion **2b** (0.258 mmol) in 5 mL of diethyl ether was generated according to the procedure described in part a and was transferred via a cannula to a solution of methyl iodide (160.6 μL, 366.1 mg, 2.58 mmol) in 4 mL of THF at 0 °C under argon. After the mixture was stirred at 0 °C for 1 h, 3 mL of an aqueous $NaHCO_3$ solution (5%) was added. The organic layer was washed with water and brine and dried over magnesium sulfate. The alkylated product was purified by flash chromatography as described above to give the ethyl complex **3b** (104.9 mg, 0.24 mmol, 93%; cis/trans = 2:1).

(c) Alkylation with Methyl Fluorosulfate. Methyl fluorosulfate (50.1 μL, 71.3 mg, 0.625 mmol) was added to a −78 °C solution of the anion **2b** (0.259 mmol) in 4 mL of THF that was made by the procedure described in part a. The reaction mixture was then stirred at −78 °C for 2 min. Employing the workup and purification procedures described in part a afforded **3b** (105.0 mg, 0.240 mmol, cis/trans = 2:1) in 93% yield.

(d) Alkylation with Methyl Triflate. Methyl trifluoromethanesulfonate (60 μL, 87.0 mg, 0.53 mmol) was added to a −78 °C solution of the anion **2b** (0.263 mmol) in 4 mL of THF that was made by the procedure described in part a. The solution was stirred at 0 °C for 10 min. Following the purification procedures in part a, the ethyl complex **3b** (114.0 mg, 0.260 mmol; cis/trans = 2:1) was obtained in 99% yield.

Alkylation of *trans*-1b with Methyl Iodide. To a solution of *trans*-**1b** (112.5 mg, 0.265 mmol) in 5 mL of anhydrous diethyl ether at −78 °C under argon was added 0.166 mL of *n*-butyllithium (1.6 M, 0.265 mmol). The resulting solution was stirred for 10 min and then transferred via cannula to a solution of methyl iodide (164.9 μL, 376.0 mg, 2.65 mmol) in 4 mL of THF at 0 °C under argon. After the mixture was warmed to 0 °C for 1 h, 3 mL of an aqueous $NaHCO_3$ solution was added. The organic layer was washed with water and brine and dried over magnesium sulfate. The residue was flash chromatographed by elution through silica gel with a 1:1:100 mixture of ether, methylene chloride, and hexane to give the carbene complex **3b** as a mixture of cis and trans isomers (109.4 mg, 0.250 mmol; cis/trans = 2:1) in 94% yield.

Alkylation of *cis*-1b with Ethyl Fluorosulfate, Ethyl Iodide, Ethyl Bromide, and Ethyl Tosylate. (a) Alkylation with Ethyl Fluorosulfate. The anion **2b** was generated by adding a solution of *n*-butyllithium (0.184 mL, 1.52 M, 0.279 mmol) in hexane to a solution of the carbene complex **1b** (118.3 mg, 0.279 mmol) in 4 mL of THF at −78 °C under argon. After 10 min, ethyl fluorosulfate (62.4 mg, 0.487 mmol) was added and the resulting solution was warmed to 0 °C and stirred for 3 min. After the solution was quenched with 3 mL of a buffer solution (pH 7.0), the organic layer was washed with water and brine and dried over magnesium sulfate. The volatiles were removed under reduced pressure and the residue was purified by flash chromatography on silica gel with a 1:1:100 mixture of ether, methylene chloride, and hexane as eluent to give the *n*-propyl carbene complex **5b** as a mixture of cis and trans isomers (122.1 mg, 0.27 mmol, 97%; cis, R_f 0.34; trans, R_f 0.49; cis/trans = 1.6:1). The following spectral data were obtained for a 1.6:1 mixture of *cis*- and *trans*-**5b**: ^{1}H NMR ($CDCl_3$, *cis*-**5b**) δ 0.90–1.00 (m, 12 H), 1.32–1.48 (m, 12 H), 1.51–1.68 (m, 6 H), 1.70–1.78 (m, 2 H), 3.12 (t, 2 H, J = 7.5 Hz), 4.61 (s, 3 H); ^{1}H NMR ($CDCl_3$, *trans*-**5b**) δ 0.90–1.00 (m, 12 H), 1.32–1.48 (m, 12 H), 1.51–1.68 (m, 6 H), 1.70–1.78 (m, 2 H), 3.22 (t, 2 H, J = 7.5 Hz), 4.65 (s, 3 H); IR (neat)

2950 s, 2873 m, 2002 m, 1908–1865 br s, 1455 m, 1212 s cm^{-1}; mass spectrum, *m/e* (rel intensity) 456 (35),[14] 452 M^+ (3.0), 443 (18), 417 (7), 368 (5), 340 (20), 317 (11), 295 (8), 282 (5), 267 (11), 254 (60), 228 (30), 202 (55), 173 (95), 162 (38), 141 (48), 131 (50), 118 (77), 104 (95), 76 (100); calcd for $C_{21}H_{37}O_5PCr$ *m/e* 452.1738, found *m/e* 452.1768. Anal. Calcd for $C_{21}H_{37}O_5PCr$: C, 55.72; H, 8.25. Found: C, 55.67; H, 8.59.

(b) Alkylation with Ethyl Iodide. To a solution of the anion **2b** (0.26 mmol) in 4 mL of THF at −78 °C under argon (prepared as described in part a) was added ethyl iodide (70 μL, 136.5 mg, 0.875 mmol). The solution was brought to 0 °C and stirred for 6 h and then quenched with 3 mL of a buffer solution (pH 7.0). Employing the workup and purification procedure described in part a, monoalkylated product **5b** (51.7 mg, 0.114 mmol, 44%; cis/trans = 1.6:1), dialkylated product **15b** (29.1 mg, 0.06 mmol, 23.3%; cis, R_f 0.54; trans, R_f 0.59; cis/trans = 1:11), and recovered starting material **1b** (17.8 mg, 0.042 mmol, 16.1%, cis/trans = 3:1) were isolated from the reaction mixture. The following spectral data were obtained from a 1:11 mixture of *cis*- and *trans*-**15b**: ^1H NMR ($CDCl_3$, *cis*-**15b**) δ 0.88–0.98 (m, 15 H), 1.25–1.32 (m, 4 H), 1.40–1.60 (m, 12 H), 1.70–1.78 (m, 6 H), 3.86 (m, 1 H), 4.62 (s, 3 H); ^1H NMR ($CDCl_3$, *trans*-**15b**) δ 0.88–0.89 (m, 15 H), 1.25–1.32 (m, 4 H), 1.40–1.60 (m, 12 H), 1.70–1.78 (m, 6 H), 3.86 (m, 1 H), 4.65 (s, 3 H); IR (neat) 2966–2944 br s, 2874 s, 2056 m, 2001 s, 1928–1850 br s, 1458 s, 1206 s cm^{-1}; mass spectrum, *m/e* (rel intensity) 480 M^+ (26), 560 (17),[14] 394 (6), 368 (30), 282 (16), 254 (100), 228 (6), 202 (28), 173 (47), 146 (23), 104 (35), 76 (90); calcd for $C_{23}H_{41}O_5PCr$ *m/e* 480.2096, found *m/e* 480.2080. Anal. Calcd for $C_{23}H_{41}O_5PCr$: C, 57.46; H, 8.60. Found: C, 57.33; H, 8.60.

(c) Alkylation with Ethyl Bromide. The procedure described in part a was employed. Ethyl bromide (60 μL, 87.6 mg, 0.80 mmol) was added to a solution of the anion **2b** (0.27 mmol) in 4 mL of THF at −78 °C. The solution was warmed to room temperature and stirred for 10 h and then quenched with 3 mL of a buffer solution (pH 7.0). After workup the monoalkylated complex **5b** (57.9 mg, 0.128 mmol, 47.4%; cis/trans = 1.6:1), the dialkylated complex **15b** (22.8 mg, 0.048 mmol, 17.6%; cis/trans = 1:11), and recovered starting material (28.7 mg, 0.68 mmol, 25%; cis/trans = 3:1) could be separated from the reaction mixture.

(d) Alkylation with Ethyl Tosylate. This reaction was carried out with the procedure described in part a. Ethyl *p*-toluenesulfonate (176.1 mg, 0.88 mmol) was added to a solution of the anion **2b** (0.32 mmol) in 6 mL of THF at −78 °C. The resulting solution was stirred at room temperature for 10 h and then quenched with 5 mL of buffer solution (pH 7.0). After workup, flash column chromatography gave **5b** (12.3 mg, 0.05 mmol, 17%; cis/trans = 1.6:1) and recovered starting material **1b** (55.2 mg, 0.13 mmol, 43.8%; cis/trans = 3:1).

Alkylation of *cis*-1b with Ethyl-d_5 Iodide. The procedure follows that described for unlabeled ethyl iodide. To a solution of the anion **2b** (0.257 mmol) in 4 mL of THF at −78 °C under argon was added ethyl-d_5 iodide (136.5 mg, 0.848 mmol). The resulting solution was stirred at 0 °C for 6 h and then quenched with 3 mL of a buffer solution (pH 7.0). The organic layer was washed with water and brine and dried over magnesium sulfate. After removal of the solvents, the residue was flash chromatographed to afford the monoalkylated product **5b′** (49.4 mg, 0.108 mmol, 42.1%; cis/trans = 1.6:1), the dialkylated product **15b′** (35.6 mg, 0.073 mmol, 28.3%; cis/trans = 1:10), and recovered starting material **1b** (19.4 mg, 0.046 mmol, 18.0%; cis/trans = 3:1). The following spectral data were obtained from a mixture of *cis*- and *trans*-**5b′**: ^1H NMR ($CDCl_3$, *cis*-**5b′**) δ 0.90–1.0 (m, 9 H), 1.32–1.48 (m, 12 H), 1.50–1.68 (m, 6 H), 3.11 (s, 2 H), 4.60 (s, 3 H); ^1H NMR ($CDCl_3$, *trans*-*5b′*) δ 0.90–1.0 (m, 9 H), 1.32–1.48 (m, 12 H), 1.50–1.68 (m, 6 H), 3.21 (s, 2 H), 4.63 (s, 3 H). **15b′**: ^1H NMR n$CDCl_3$, *cis*-**15b′**) δ 0.89–0.98 (m, 9 H), 1.40–1.60 (m, 12 H), 1.60–1.74 (m, 6 H), 3.78 (s, 1 H), 4.62 (s, 3 H); ^1H NMR ($CDCl_3$, *trans*-**15b′**) δ 0.89–0.98 (m, 9 H), 1.40–1.60 (m, 12 H), 1.60–1.74 (m, 6 H), 3.84 (s, 1 H), 4.65 (s, 3 H). The ^1H NMR and mass spectra of the recovered **1b** revealed that no detectable amount of deuterium had been incorporated in the starting material.

Alkylation of *cis*-1b with Isopropyl Triflate and Isopropyl Iodide. (a) Alkylation with Isopropyl Triflate. A solution of the anion **2b** (0.269 mmol) was prepared by the addition of 0.18 mL of a hexane solution of *n*-butyllithium (1.52 M, 0.269 mmol) to a solution of 114.4 mg of *cis*-**1b** (0.269 mmol) in 4 mL of THF at −78 °C under argon. Isopropyl trifluoromethanesulfonate[25] (103.7 mg, 0.54 mmol) was added at −78 °C. After the reaction mixture was warmed to 0 °C for 10 min, 5 mL of a buffer solution (pH 7) was poured into the flask. The organic layer was washed with water and brine and dried over magnesium sulfate. Purification of the crude product was accomplished by flash chromatography on silica gel with a 1:1:100 ternary mixture of ether, methylene chloride, and hexane as eluent and resulted in the isolation of complex **7b** (118.1 mg, 0.253 mmol, cis, R_f 0.33; trans, R_f 0.47; cis/trans = 2.9:1) in 94% total yield. The following spectral data were obtained for a 2.9:1 mixture of *cis*- and *trans*-**7b**: ^1H NMR ($CDCl_3$, *cis*-**7b**) δ 0.88–0.98 (m, 15 H), 1.30–1.48 (m, 12 H), 1.60–1.78 (m, 6 H), 2.13–2.25 (m, 1 H), 3.04 (d, 2 H, *J* = 6.69 Hz), 4.64 (s, 3 H); ^1H NMR ($CDCl_3$, *trans*-**7b**) δ 0.88–0.98 (m, 15 H), 1.30–1.48 (m, 12 H), 1.60–1.78 (m, 6 H), 2.13–2.25 (m, 1 H), 3.18 (d, 2 H, *J* = 6.69 Hz), 4.66 (s, 3 H); IR (neat) 2935 s, 2860 m, 1995 m, 1915–1840 br s, 1450 m, 1200 m cm^{-1}. Anal. Calcd for $C_{22}H_{39}O_5PCr$: C, 56.62; H, 8.43. Found: C, 56.47; H, 8.62.

(b) Alkylation with Isopropyl Iodide. Isopropyl iodide (30 μL, 51.1 mg, 0.30 mmol) was added at −78 °C to a solution of the anion **2b** (0.270 mmol) prepared by addition of *n*-butyllithium (0.18 mL, 1.52 M, 0.27 mmol) to a solution of **1b** (113.7 mg, 0.270 mmol) in 3 mL of THF under argon. The reaction mixture was warmed to 0 °C and stirred for 5 h. Following the workup and purification procedure described in part a afforded **7b** (32.5 mg, 0.070 mmol, 26%; cis/trans = 2.9:1) and recovered starting material **1b** (52.8 mg, 0.124 mmol, 46.5%; cis/trans = 3:1).

Alkylation of *cis*-1b with Benzyl Chloride. The anion **2b** was made by adding a solution of *n*-butyllithium (0.71 mL, 1.52 M, 1.08 mmol) in hexane to a solution of *cis*-**1b** (459.5 mg, 1.08 mmol) in 16 mL of anhydrous diethyl ether at −78 °C under argon. Benzyl chloride (0.25 mL, 275.0 mg, 2.17 mmol) was then introduced by syringe and the reaction mixture was allowed to warm at 0 °C for 3 h. The reaction was stopped by the addition of 5 mL of an aqueous $NaHCO_3$ solution (5%). The organic layer was washed with water and brine and dried over magnesium sulfate. Flash elution of the residue on a silica gel column with a 1:1:100 solvent mixture of ether, methylene chloride, and hexane afforded the β-phenethyl complex **8b** (500.7 mg, 0.97 mmol, 90.2%; cis, R_f 0.23; trans, R_f 0.39; cis/trans = 4:1). The following spectral data were collected on a 4:1 mixture of *cis*- and *trans*-**8b**: ^1H NMR ($CDCl_3$, *cis*-**8b**) δ 0.88–0.98 (m, 9 H), 1.25–1.48 (m, 12 H), 1.52–1.76 (m, 6 H), 2.79 (t, 2 H, *J* = 8.0 Hz), 3.42 (t, 2 H, *J* = 8.0 Hz), 4.64 (s, 3 H), 7.15–7.30 (m, 5 H); ^1H NMR ($CDCl_3$, *trans*-**8b**) δ 0.88–0.98 (m, 9 H), 1.25–1.48 (m, 12 H), 1.52–1.76 (m, 6 H), 2.79 (t, 2 H, *J* = 8.0 Hz), 3.52 (t, 2 H, *J* = 8.0 Hz), 4.67 (s, 3 H), 7.15–7.30 (m, 5 H); ^{13}C NMR ($CDCl_3$, *cis*-**8b**)[14] δ 13.76, 24.41 (d, $J_{c\text{-}p}$ = 12.2 Hz), 25.28, 28.35 (d, $J_{c\text{-}p}$ = 14.7 Hz), 33.81, 64.08, 65.72, 126.05, 128.42, 128.54, 141.18, 222.11 (d, $J_{c\text{-}p}$ = 14.1 Hz), 225.41 (d, $J_{c\text{-}p}$ = 7.6 Hz), 230.29 (d, $J_{c\text{-}p}$ = 12.2 Hz), 361.84 (d, $J_{c\text{-}p}$ = 12.2 Hz); ^{13}C NMR ($CDCl_3$, *trans*-**8b**) δ 14.14, 24.52 (d, $J_{c\text{-}p}$ = 12.0 Hz), 25.43, 28.22 (d, $J_{c\text{-}p}$ = 19.0 Hz), 33.20, 64.00, 64.72, 125.81, 128.37, 128.46, 141.69, 223.37 (d, $J_{c\text{-}p}$ = 12.2 Hz), 352.31 (d, $J_{c\text{-}p}$ = 9.0 Hz); IR (neat) 3030 w, 2950 s, 2870 m, 2010 m, 1925–1865 br s, 1460 m, 1215 m cm^{-1}. Anal. Calcd for $C_{26}H_{39}O_5CrP$: C, 60.66; H, 7.64. Found: C, 60.08, H, 7.78.

Alkylation of *cis*-1b with 4-Pentynyl Triflate, 3-Pentynyl Triflate, and 5-(Trimethylsilyl)-4-pentynyl Triflate. (a) Alkylation with 4-Pentynyl Triflate. 4-Pentynyl trifluoromethanesulfonate[26] (58.8 mg, 0.272 mmol) was added to a −78 °C solution of the anion **2b** prepared by the addition of *n*-butyllithium (0.11 mL, 1.6 M, 0.170 mmol) to a solution of *cis*-**1b** (72.1 mg, 0.170 mmol) in 3 mL of THF at −78 °C under argon. After the solution was warmed to 0 °C for 15 min, it was quenched with 3 mL of an aqueous $NaHCO_3$ solution (5%). The organic layer was washed with water and brine and dried over magnesium sulfate. The residue was flash eluted with a 1:1:100 mixture of ether, methylene chloride, and hexane on silica gel to afford the alkylated product **9b** (75.2 mg, 0.153 mmol, 90%; cis, R_f 0.26; trans, R_f 0.43; cis/trans = 15:1). The following spectral data were obtained on a 15:1 mixture of *cis* and *trans*-**9b**: ^1H NMR ($CDCl_3$, *cis*-**9b**) δ 0.90-0.98

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(m, 9 H), 1.32–1.48 (m, 14 H), 1.52–1.76 (m, 8 H), 1.94 (t, 1 H, J = 2.45 Hz), 2.20 (dt, 2 H, J = 6.8 Hz, 2.43 Hz), 3.17 (t, 2 H, J = 7.00 Hz), 4.62 (s, 3 H); ^{1}H NMR ($CDCl_3$, *trans*-**9b**) δ 0.90–0.98 (m, 9 H), 1.32–1.48 (m, 14 H), 1.52–1.76 (m, 8 H), 1.94 (t, 1 H, J = 2.45 Hz), 2.20 (dt, 2 H, J = 6.8 Hz, 2.43 Hz), 3.28 (t, 2 H, J = 7.00 Hz), 4.65 (s, 3 H); IR (neat) 3310 s, 2960–2930 br s, 2860 s, 2000 s, 1920–1860 br s, 1450 s, 1225 s cm^{-1}. Anal. Calcd for $C_{24}H_{39}O_5PCr$: C, 58.73; H, 8.02. Found: C, 58.35; H, 8.30.

(b) Alkylation with 3-Pentynyl Triflate. The reaction of 3-pentynyl triflate and *cis*-**1b** was carried out by utilizing the procedure described in part a. 3-Pentynyl trifluoromethanesulfonate[27] (315.4 mg, 1.46 mmol) was added neat to a −78 °C solution of the anion **2b** prepared by the addition of *n*-butyllithium (0.48 mL, 1.52 M, 0.73 mmol) to a solution of *cis*-**1b** (311.0 mg, 0.73 mmol) in 8 mL of THF at −78 °C under argon. The reaction mixture was warmed to 0 °C for 30 min and quenched with 10 mL of an aqueous $NaHCO_3$ solution (5%). After workup and purification the complex **11b** (325.7 mg, 0.665 mmol; cis, R_f 0.19; trans, R_f 0.29; cis/trans = 2.5:1) was obtained in 91% yield. The following spectral data were obtained on a 2.5:1 mixture of *cis*- and *trans*-**11b**: ^{1}H NMR ($CDCl_3$, *cis*-**11b**) δ 0.90–0.98 (m, 9 H), 1.35–1.48 (m, 12 H), 1.52–1.74 (m, 8 H), 1.76 (t, 3 H, J = 2.2 Hz), 2.10–2.17 (m, 2 H), 3.28 (t, 2 H, J = 8.5 Hz), 4.61 (s, 3 H); ^{1}H NMR ($CDCl_3$, *trans*-**11b**) δ 0.90–0.98 (m, 9 H), 1.35–1.48 (m, 12 H), 1.52–1.74 (m, 8 H), 1.76 (t, 3 H, J = 2.2 Hz), 2.10–2.27 (m, 2 H), 3.32 (t, 2 H, J = 8.5 Hz), 4.63 (s, 3 H); IR (neat) 2958–2938 br s, 2873 m, 2100 w, 2002 s, 1910–1860 br s, 1456 m, 1221 m cm^{-1}.

(c) Alkylation with 5-(Trimethylsilyl)-4-pentynyl Triflate. The preparation of 5-(trimethylsilyl)-4-pentynyl triflate follows from a general procedure that has been utilized for other triflates.[11] A solution of 5-(trimethylsilyl)-4-pentyn-1-ol (2.78 g, 17.8 mmol) in 20 mL of methylene chloride was treated with trifluoromethanesulfonic anhydride (3.6 mL, 6.04 g, 21.4 mmol) in the presence of triethylamine (2.49 mL, 1.81 g, 17.8 mmol) at 0 °C for 2 h. After the solvent was removed, the crude triflate was eluted by flash column chromatography with a 1:1:20 mixture of ether, methylene chloride, and hexane as eluent to afford the purified product (1.06 g, 3.68 mmol, 21%): ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9 H), 1.92 (p, 2 H, J = 7.2 Hz), 2.30 (t, 2 H, J = 7.3 Hz), 4.45 (t, 2 H, J = 7.2 Hz); IR (neat) 2960 m, 2910 m, 2850 s, 2170 s, 1416 m, 1294 s, 1210 s, 1144 m cm^{-1}.

The alkylation of the anion **2b** (1.04 mmol) with 5-(trimethylsilyl)-4-pentynyl triflate (449.3 mg, 1.56 mmol) was carried out according to the procedure described in part a. After the reaction mixture was stirred at 0 °C for 30 min, 10 mL of an aqueous $NaHCO_3$ solution (5%) was added to quench the reaction. After workup and purification, the alkylated product **12b** (574.5 mg, 1.02 mmol, cis/trans = 3:1) was obtained in 98% yield. The following spectral data were collected on a 3:1 mixture of *cis*- and *trans*-**12b**: ^{1}H NMR ($CDCl_3$, *cis*-**12b**) δ 0.14 (s, 9 H), 0.88–0.98 (m, 9 H), 1.26–1.48 (m, 14 H), 1.50–1.78 (m, 8 H), 2.21 (t, 2 H, J = 7.0 Hz), 3.15 (t, 2 H, J = 7.2 Hz), 4.60 (s, 3 H); ^{1}H NMR ($CDCl_3$, *trans*-**12b**) δ 0.14 (s, 9 H), 0.88–0.98 (m, 9 H), 1.26–1.48 (m, 14 H), 1.50–1.78 (m, 8 H), 2.21 (t, 2 H, J = 7.0 Hz), 3.26 (t, 2 H, J = 7.2 Hz), 4.63 (s, 3 H); IR (neat) 2965–2935 br s, 2865 m, 2150 m, 2008 s, 1924–1860 br s, 1450 s, 1228 m cm^{-1}.

Alkylation of *cis*-1b with 3-Butenyl Triflate. The preparation of 3-butenyl trifluoromethanesulfonate was accomplished with a general procedure for the preparation of triflates.[11] A solution of 3-buten-1-ol (2.15 mL, 1.80 g, 25.0 mmol) in 45 mL of methylene chloride was reacted with trifluoromethanesulfonic anhydride (4.2 mL, 7.04 g, 25.0 mmol) in the presence of 1 equiv of triethylamine for 2 h. After removal of the solvents, bulb-to-bulb distillation of the crude residue gave pure 3-butenyl triflate (3.36 g, 16.5 mmol) in 66% yield: ^{1}H NMR ($CDCl_3$) δ 2.55–2.64 (m, 2 H), 4.56 (t, 2 H, J = 6.60 Hz), 5.68–5.76 (m, 2 H), 5.70–5.85 (m, 1 H); IR (neat) 3084 s, 2977 m, 2913 s, 1640 m, 1412 s, 1248 s, 1208 s, 1146 s, 940 s cm^{-1}.

To a solution of anion **2b** (0.31 mmol) prepared by the reaction of *n*-butyllithium (0.194 mL, 1.6 M, 0.31 mmol) in hexane with a solution of *cis*-**1b** (132.7 mg, 0.31 mmol) in 5 mL of THF at −78 °C under argon was added 3-butenyl trifluoromethanesulfonate (69.6 mg, 0.34 mmol). After the reaction mixture was warmed to 0 °C for 25 min, 5 mL of an aqueous $NaHCO_3$ solution (5%) was poured into the flask. The organic layer was washed with water and brine and dried over magnesium sulfate. The residue was purified by flash column chromatography on silica gel with a 1:1:100 mixture of ether, methylene chloride, and hexane to give **10b** (141.0 mg, 0.29 mmol, 95%; cis, R_f 0.33; trans, R_f 0.52; cis/trans = 5:1) as a red oil. The following spectral data were obtained on a 5:1 mixture of *cis*- and *trans*-**10b**: ^{1}H NMR ($CDCl_3$, *cis*-**10b**) δ 0.92–0.99 (m, 9 H), 1.32–1.50 (m, 12 H), 1.58–1.75 (m, 8 H), 2.02–2.10 (m, 2 H), 3.14 (t, 2 H, J = 7.85 Hz), 4.59 (s, 3 H), 4.94–5.06 (m, 2 H), 5.72–5.84 (m, 1 H); ^{1}H NMR ($CDCl_3$, *trans*-**10b**) δ 0.92–0.99 (m, 9 H), 1.32–1.50 (m, 12 H), 1.58–1.75 (m, 8 H), 2.02–2.10 (m, 2 H), 3.24 (t, 2 H, J = 7.85 Hz), 4.62 (s, 3 H), 4.94–5.06 (m, 2 H), 5.72–5.84 (m, 1 H); ^{13}C NMR ($CDCl_3$, *cis*-**10b**) δ 13.73, 24.40 (d, $J_{c\text{-}p}$ = 12.5 Hz), 25.29, 26.62, 28.32 (d, $J_{c\text{-}p}$ = 20.1 Hz), 33.51, 61.36, 65.58, 115.18, 138.05, 222.09 (d, $J_{c\text{-}p}$ = 14.4 Hz), 225.48 (d, $J_{c\text{-}p}$ = 6.8 Hz), 230.38 (d, $J_{c\text{-}p}$ = 12.8 Hz), 364.00 (d, $J_{c\text{-}p}$ = 12.5 Hz); ^{13}C NMR ($CDCl_3$, *trans*-**10b**) δ 13.73, 24.40 (d, $J_{c\text{-}p}$ = 12.5 Hz), 25.43, 26.33, 28.16 (d, $J_{c\text{-}p}$ = 16.8 Hz), 28.42, 61.80, 64.63, 114.70, 138.55, 223.47 (d, $J_{c\text{-}p}$ = 12.2 Hz), 354.55 (d, $J_{c\text{-}p}$ = 9.7 Hz); IR (neat) 3080 w, 2959–2953 br s, 2870 m, 2002 s, 1915–1860 br s, 1635 w, 1456 s, 1220 s cm^{-1}. Anal. Calcd for $C_{22}H_{39}O_5PCr$: C, 57.70; H, 8.22. Found: C, 57.20; H, 8.03.

Alkylation of 3b with 4-Pentynyl Triflate. To a solution of the carbene complex **3b** (230.0 mg, 0.52 mmol) in 5 mL of THF at −78 °C under an argon atmosphere was added a solution of *n*-butyllithium (0.34 mL, 1.52 M, 0.53 mmol) in hexane. After the solution was stirred for 10 min, 4-pentynyl trifluoromethanesulfonate[26] (177.1 mg, 0.82 mmol) was then introduced by syringe and the reaction mixture was warmed to 0 °C for 5 min. The organic layer was washed with water and brine and dried over magnesium sulfate. Upon elution of the residue from a flash silica gel column with a 1:1:50 mixture of ether, methylene chloride, and hexane the alkylated complex **13b** (255.1 mg, 0.51 mmol, cis/trans = 1:1; trans, R_f 0.42; cis, R_f 0.31) was isolated in 97% yield as a red oil. The following spectral data were obtained on a 1:1 mixture of *cis*- and *trans*-**13b**: ^{1}H NMR ($CDCl_3$, *cis*-**13b**) δ 0.90–1.00 (m, 12 H), 1.23–1.31 (m, 2 H), 1.34–1.50 (m, 12 H), 1.61–1.78 (m, 8 H), 1.92 (t, 1 H, J = 2.3 Hz), 2.18 (dt, 2 H, J = 7.5 Hz, 2.3 Hz), 3.87–3.95 (m, 1 H), 4.62 (s, 3 H); ^{1}H NMR (*trans*-**13b**) δ 0.90–1.00 (m, 12 H), 1.23–1.31 (m, 2 H), 1.34–1.50 (m, 12 H), 1.61–1.78 (m, 8 H), 1.92 (t, 1 H, J = 2.3 Hz), 2.18 (dt, 2 H, J = 7.5 Hz, 2.3 Hz), 4.01–4.08 (m, 1 H), 4.64 (s, 3 H); IR (neat) 3300 m, 2960–2940 br s, 2870 m, 2000 m, 1920–1825 br s, 1440 s, 1200 cm^{-1}.

Alkylation of 8b with 4-Pentynyl Triflate. To a solution of the carbene complex **8b** (480.6 mg, 0.935 mmol) in 15 mL of THF at −78 °C under an argon atmosphere was added a hexane solution of *n*-butyllithium (0.615 mL, 1.52 M, 0.935 mmol) in hexane. After the solution was stirred for 10 min, 4-pentynyl trifluoromethanesulfonate[26] (432.0 mg, 2.0 mmol) was then introduced by syringe and the reaction mixture was warmed to 0 °C for 15 min. The reaction was stopped by quenching with 10 mL of water. The organic layer was washed with water and brine and dried over magnesium sulfate. The alkylated product was purified by flash chromatography on silica gel with a 1:1:50 mixture of ether, methylene chloride, and hexane to give complex **14b** (400.8 mg, 0.691 mmol; cis/trans 1:10) in 74% yield as a red oil. The following spectral data were obtained on a 1:10 mixture of *cis*- and *trans*-**14b**: ^{1}H NMR ($CDCl_3$, *cis*-**14b**) δ 0.87–0.98 (m, 9 H), 1.25–1.32 (m, 2 H), 1.35–1.50 (m, 14 H), 1.55–1.78 (m, 6 H), 1.91 (t, 1 H, J = 2.3 Hz), 2.10 (dt, 2 H, J = 7.6 Hz, 2.3 Hz), 3.33 (dd, 1 H, J = 16.2 Hz, 9.7 Hz), 2.99 (dd, 1 H, J = 16.2 Hz, 5.4 Hz), 4.18–4.28 (m, 1 H), 4.67 (s, 3 H), 7.18–7.26 (m, 5 H); ^{1}H NMR ($CDCl_3$, *trans*-**14b**) δ 0.87–0.98 (m, 9 H), 1.25–1.32 (m, 2 H), 1.35–1.50 (m, 14 H), 1.55–1.78 (m, 6 H), 1.91 (t, 1 H, J = 2.3 Hz), 2.10 (dt, 2 H, J = 7.6 Hz, 2.3 Hz), 3.33 (dd, 1 H, J = 16.2 Hz, 9.7 Hz), 2.99 (dd, 1 H, J = 16.2 Hz, 5.4 Hz), 4.18–4.28 (m, 1 H), 4.71 (s, 3 H), 7.18–7.26 (m, 5 H); IR (neat), 3300 s, 3040 m, 2930–2830 br s, 1995 s, 1920–1830 br s, 1440 s, 1200 s cm^{-1}. Anal. Calcd for $C_{31}H_{45}O_5CrP$: C, 64.09; H, 7.83. Found: C, 63.67; H, 8.13.

Alkylation of 5b with Ethyl Iodide. To a solution of compound **5b** (93.0 mg, 0.206 mmol) in 3.5 mL of THF at −78 °C under argon was added a solution of *n*-butyllithium (0.130 mL, 1.6 M, 0.206 mmol) in hexane. After 10 min at −78 °C, ethyl iodide (49.4 μL, 0.618 mmol) was introduced by syringe and the resulting

(27) Stutz, H.; Hannack, M. *Tetrahedron Lett.* **1974**, *28*, 2457.

solution was warmed to 0 °C for 5 h. The reaction mixture was quenched with 5 mL of water and the organic layer was washed with water and brine and dried over magnesium sulfate. Purification of the crude product by flash column chromatography gave the complex **15b** (86.1 mg, 0.179 mmol, 87%; cis/trans = 1:11), which had spectral properties identical with a complex that had been characterized as **15b** from the reaction of anion **2b** with ethyl iodide.

Reaction of *cis*-1c with Methyl Iodide and Methyl Fluorosulfate. A solution of *n*-butyllithium (0.34 mL, 1.52 M, 0.517 mmol) in hexane was added to a solution of *cis*-**1c** (250.4 mg, 0.517 mmol) in 8 mL of THF at −78 °C under argon. The solution was stirred for 10 min and then methyl iodide (0.16 mL, 364.8 mg, 2.57 mmol) was introduced by syringe. The reaction flask was transferred to an ice bath and the solution was stirred for 30 min. After 3 mL of a buffer solution (pH 7) was added, the organic layer was then washed with water and brine and dried over magnesium sulfate. The product was purified by flash chromatography on silica gel with a 1:1:50 mixture of ether, methylene chloride, and hexane to give the ethyl complex **3c** (247.0 mg, 0.496 mmol; R_f 0.19) in 96% yield as a red oil, which was exclusively the cis isomer: ^{1}H NMR ($CDCl_3$) δ 0.83 (t, 3 H, J = 7.8 Hz), 2.92 (q, 2 H, J = 7.8 Hz), 4.48 (s, 3 H), 7.25–7.41 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ = 11.74, 55.04, 66.33, 128.53 (d, $J_{c\text{-}p}$ = 11.1 Hz), 129.93, 133.14 (d, $J_{c\text{-}p}$ = 9.4 Hz), 136.41 (d, $J_{c\text{-}p}$ = 32.5 Hz), 221.06 (d, $J_{c\text{-}p}$ = 12.5 Hz), 226.12 (d, $J_{c\text{-}p}$ = 8.0 Hz), 229.43 (d, $J_{c\text{-}p}$ = 9.7 Hz), 364.20 (d, $J_{c\text{-}p}$ = 9.2 Hz); IR (neat), 3070 m, 2940–2910 br m, 2054 m, 2006 s, 1917–1881 br s, 1434 s, 1208 s cm^{-1}. Anal. Calcd for $C_{26}H_{23}O_5PCr$: C, 62.83; H, 4.65. Found: C, 63.04; H, 4.67.

A similar procedure was employed for the reaction of *cis*-**1c** with methyl trifluoromethanesulfonate. Addition of *n*-butyllithium (0.21 mL, 1.52 M, 0.31 mmol) in hexane to a solution of *cis*-**1c** (152.3 mg, 0.31 mmol) in 5 mL of THF at −78 °C, followed in 10 min by the addition of 70 μL of methyl trifluoromethanesulfonate (101.5 mg, 0.62 mmol), and after the workup and purification procedure described above produced the carbene complex **3c** (130.0 mg, 0.26 mmol) in 84% yield.

Reaction of *cis*-1c with 3-Butenyl Triflate. *n*-Butyllithium (0.254 mL, 1.6 M, 0.407 mmol) in hexane was added to a solution of *cis*-**1c** (197.3 mg, 0.407 mmol) in 7 mL of THF at −78 °C under an argon atmosphere. After 5 min, 124.5 mg (0.61 mmol) of 3-butenyl trifluoromethanesulfonate (see above) was introduced by a syringe. The solution was warmed to 0 °C for 15 min and then quenched with 5 mL of a buffer solution (pH 7). The organic layer was washed with water and brine and dried over magnesium sulfate. After removal of the volatiles, the residue was eluted on a flash silica gel column with a 1:1:50 mixture of ether, methylene chloride, and hexane to provide an 85% yield of a red solid (mp 108–110 °C) that was identified as the cis isomer of **10c** (185.1 mg, 0.344 mmol; R_f 0.20): ^{1}H NMR ($CDCl_3$) δ 1.32–1.40 (m, 2 H), 1.76–1.84 (m, 2 H), 2.84 (t, 2 H, J = 7.5 Hz), 4.50 (s, 3 H), 4.70–4.89 (m, 2 H), 5.52–5.63 (m, 1 H), 7.25–7.40 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 26.45, 33.91, 61.69, 66.33, 115.31, 128.55 (d, $J_{c\text{-}p}$ = 11.4 Hz), 129.95, 133.19 (d, $J_{c\text{-}p}$ = 9.1 Hz), 136.33 (d, $J_{c\text{-}p}$ = 32.6 Hz), 138.11, 221.00 (d, $J_{c\text{-}p}$ = 12.8 Hz), 226.14 (d, $J_{c\text{-}p}$ = 10.0 Hz), 229.39 (d, $J_{c\text{-}p}$ = 13.1 Hz), 363.79 (d, $J_{c\text{-}p}$ = 12.3 Hz); IR (neat) 3070 m, 2938–2912 br m, 2056 m, 2006 s, 1892–1884 br s, 1434 m, 1210 m cm^{-1}. Further characterization of this compound was achieved by ligand exchange to give complex **10a**, which was completely characterized. Crude TLC indicated the possible presence of a trace of *trans* **10c**; however, this component was lost on the silica gel column.

Ligand Exchange of 1b and 1c with Carbon Monoxide. Carbene complex **1c** (302.3 mg, 0.62 mmol) was placed in a Paar bomb as a solution in 8 mL of THF. The bomb was pressurized to 250 psi with carbon monoxide and the solution was then stirred at room temperature for 15 h. The bomb was opened and after removal of the solvent from the reaction mixture, the residue was eluted with a 1:1:100 mixture of ether, methylene chloride, and hexane from a silica gel column to afford the carbene complex **1a** (94.6 mg, 0.38 mmol, 61.3%).

A ligand displacement reaction of the carbene complex **1b** with carbon monoxide was carried out in a similar manner. A solution of **1b** in THF under a pressure of 250 psi of carbon monoxide was stirred at room temperature for 12 h. TLC of the reaction mixture revealed the presence of only the starting material. The bomb was charged with a higher pressure of carbon monoxide (800 psi) and the solution was stirred for another 12 h. Tri-*n*-butylphosphine was the only observable and isolable product from this reaction.

Ligand Exchange of 10c with Carbon Monoxide. Carbene complex **10c** (144.0 mg, 0.26 mmol) was dissolved in 3 mL of THF and placed in a bomb which was then filled with carbon monoxide to a pressure of 250 psi. The solution was stirred at room temperature for 24 h. The bomb was opened and after removal of the THF solvent, elution of the residue with a 1:1:50 mixture of ether, methylene chloride, and hexane on a silica gel column afforded the pentacarbonyl complex **10a** (65.1 mg, 0.214 mmol) in 82% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.55–1.62 (m, 2 H), 2.02–2.09 (m, 2 H), 3.31 (t, 2 H, J = 7.7 Hz), 4.76 (s, 3 H), 4.96–5.05 (m, 2 H), 5.69–5.78 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.47, 33.21, 62.51, 67.71, 115.60, 137.59, 216,42, 223.17, 363.39; IR ($CDCl_3$) 3080 w, 2960–2920 br m, 2860 m, 2060 s, 1980–1890 br s, 1645 m, 1450 s, 1265 s cm^{-1}; mass spectrum, m/e (rel intensity) 304 M$^+$ (18), 248 (13), 220 (28), 215 (8) 214 (37), 192 (72), 165 (18), 164 (100), 162 (78), 132 (53), 130 (63), 112 (25), 111 (22), 97 (23); calcd for $C_{12}H_{12}O_6Cr$ m/e 304.0039, found m/e 304.9990. Anal. Calcd for $C_{12}H_{12}O_6Cr$: C, 47.35; H, 3.98. Found: C, 47.30; H, 3.99.

Alkylation of 1a with 4-Pentynyl Triflate. To a solution of **1a** (108.4 mg, 0.43 mmol) in 6 mL of Et_2O at −78 °C under argon was added a solution of *n*-butyllithium (0.27 mL, 1.6 M, 0.43 mmol) in hexane. After 10 min, 4-pentynyl trifluoromethanesulfonate[26] (149.0 mg, 0.69 mmol) was added by syringe. The resulting solution was warmed to 0 °C for 20 min and then quenched with 5 mL of an aqueous $NaHCO_3$ solution (5%). The organic layer was washed with water and brine and dried over magnesium sulfate. The residue was purified by flash column chromatography on silica gel with a 1:1:50 mixture of ether, methylene chloride, and hexane to give the alkylated complex **9a** (108.1 mg, 0.342 mmol; R_f 0.27) in 80% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.49–1.67 (m, 4 H), 1.96 (t, 1 H, J = 2.62 Hz), 2.20 (td, 2 H, J = 6.60 Hz, J = 2.61 Hz), 3.34 (t, 2 H, J = 7.30 Hz), 4.97 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 18.99, 25.98, 28.58, 62.96, 68.23, 69.28, 84.21, 216.25, 222.93, 362.14; IR (neat) 3312 s, 2962–2944 br s, 2863 m, 2110 w, 2063 s, 1970–1890 br s, 1457 s, 1250 s cm^{-1}; mass spectrum, m/e (rel intensity) 316 M$^+$ (18), 232 (7), 204 (37), 176 (100), 161 (67), 148 (23), 146 (39), 144 (54), 131 (15), 118 (28), 105 (20), 93 (28), 91 (48), 82 (32), 80 (37), 69 (33); calcd for $C_{13}H_{12}O_6Cr$ m/e 316.0039, found m/e 316.0035.

Alkylation of 1a with 3-Butenyl Triflate. To a solution of **1a** (103.4 mg, 0.41 mmol) in 6 mL of Et_2O at −78 °C under an argon atmosphere was added a solution of *n*-butyllithium (0.26 mL, 1.6 M, 0.41 mmol) in hexane. After stirring for 10 min, 140.0 mg (0.69 mmol) of 3-butenyl trifluoromethanesulfonate (see above) was introduced. The resulting solution was warmed to 0 °C for 20 min and then quenched with 5 mL of an aqueous $NaHCO_3$ solution (5%). The organic layer was washed with water and brine and dried over magnesium sulfate. Flash elution of the residue from a silica gel column with a 1:1:50 mixture of ether, methylene chloride, and hexane afforded the carbene complex **10a** (96.4 mg, 0.32 mmol) in 78% yield, which had spectral properties identical with the compound that was characterized as **10a** from the ligand exchange reaction of complex **10c**.

Reaction of (Phenylmethoxymethylene)(tri-*n*-butylphosphine)tetracarbonylchromium(0) (18b) with Diphenylacetylene. A solution of the carbene complex **18b** (300.0 mg, 0.62 mmol) and diphenylacetylene (104.0 mg, 0.58 mmol) in 15 mL of *n*-butyl ether was deoxygenated by the freeze–thaw method (−196 °C/25 °C, 3 cycles). The reaction mixture was heated under an argon atmosphere at 90 °C for 3 h. A solution of 0.5 M ceric ammonium nitrate (10 mL) was added to the cooled reaction mixture, which was then stirred in air for 30 min. The organic phase was diluted with ether, washed with water and brine, and dried over magnesium sulfate. After removal of the solvents, the products were separated by flash column chromatography on silica gel with a 1:1:10 mixture of ether, methylene chloride, and hexane. The first compound to elute from the column (R_f 0.33) was obtained in 6.5% yield as a red solid (10.5 mg, 0.04 mmol) and identified as the indenone **21**: mp 148–150 °C (lit.[29] mp

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149–151 °C); ^{1}H NMR ($CDCl_3$) δ 7.12 (d, 1 H, J = 7.25 Hz), 7.21–7.28 (m, 6 H), 7.33–7.40 (m, 6 H), 7.56 (d, 1 H, J = 6.95 Hz); IR (neat) 3070–3029 br m, 1701 s, 1686 s, 1604 s, 1479 m, 1456 s, 1438 s, 1339 s, 1182 m, 1077 m, 701 s cm^{-1}; mass spectrum, m/e (rel intensity) 282 M$^+$ (100), 265 (12), 252 (48), 240 (12), 178 (15), 165 (10), 126 (17), 105 (87), 91 (14), 77 (48), 69 (22); calcd for $C_{21}H_{14}O$ m/e 282.1045, found m/e 282.1033. The second compound off the column (R_f 0.25) was obtained in 48% yield as a yellow solid (85.6 mg, 0.28 mmol) and identified as the quinone **20**: mp 137–139 °C (lit.[28] mp 138–140 °C); ^{1}H NMR ($CDCl_3$) δ 7.02–7.10 (m, 4 H), 7.18–7.26 (m, 6 H), 7.75–7.82 (m, 2 H), 8.15–8.22 (m, 2 H); IR (neat) 3058 s, 1757 w, 1661 s, 1560 s, 1570 w, 1492 m, 1443 m, 1345 m, 1322 m, 1290 s, 1211 m, 1062 m, 756 s, 701 s cm^{-1}.

Reaction of 18b with Diethylacetylene. A solution of complex **18b** (271.6 mg, 0.558 mmol) and diethylacetylene (100.0 mg, 1.22 mmol) in 11 mL of THF was deoxygenated by the freeze–thaw method (–196 °C/25 °C, 3 cycles). The reaction mixture was heated at 50 °C under an argon atmosphere for 20 h. After addition of 10 mL of a 0.5 M aqueous solution of ceric ammonium nitrate, the mixture was stirred in air for 30 min. The organic layer was diluted with ether, washed with water and brine, and then dried over magnesium sulfate. The residue was eluted with a 1:1:20 mixture of ether, methylene chloride, and hexane through silica gel to afford quinone **22**[5t] (76.0 mg, 0.355 mmol, 63.6%): mp 67–69 °C (lit.[30] mp 72–73 °C); ^{1}H NMR ($CDCl_3$) δ 1.16 (t, 6 H, J = 7.5 Hz), 2.66 (q, 4 H, J = 7.5 Hz), 7.67–7.72 (m, 2 H), 8.06–8.09 (m, 2 H); IR (neat) 3063 w, 2977 s, 2938 s, 2874 m, 1662 s, 1614 m, 1596 s, 1463 s, 1345 m, 1329 m, 1298 s, 1257 m cm^{-1}.

Reaction of 23b with Diethyleneacetylene. The phosphine complex **23b** was prepared from the pentacarbonyl complex **23a**[5t] by the Fischer thermolysis procedure.[6d] A solution of the carbene complex **23a** (323.1 mg, 1.02 mmol) and tri-*n*-butylphosphine (206.0 mg, 1.02 mmol) in 15 mL of hexane was stirred at 50 °C for 3 h under a nitrogen flow across the top of the reflux condensor. The solvent was removed by reduced pressure and the residue was eluted with 1:1:100 mixture of ether, methylene chloride, and hexane through silica gel to give complex **23b** as a mixture of cis and trans isomers (377.6 mg, 0.77 mmol, 75.5%, cis/trans = 5:3; cis, R_f 0.18; trans, R_f 0.26; red oil). The following spectral data were obtained on a 5:3 mixture of *cis*- and *trans*-**23b**: ^{1}H NMR ($CDCl_3$, *cis*-**23b**) δ 0.87–0.95 (m, 9 H), 1.25–1.45 (m, 12 H), 1.57–1.68 (m, 6 H), 1.68–1.76 (m, 4 H), 2.07–2.30 (m, 4 H), 4.17 (s, 3 H), 5.45 (s, 1 H); ^{1}H NMR ($CDCl_3$, *trans*-**23b**) δ 0.87–0.95 (m, 9 H), 1.25–1.45 (m, 12 H), 1.57–1.68 (m, 6 H), 1.68–1.76 (m, 4 H), 2.07–2.30 (m, 4 H), 4.44 (s, 3 H), 5.58 (s, 1 H); IR (neat) 2959 s, 2934 s, 2872 s, 2008 s, 1940–1857 br s, 1613 w, 1459 s, 1190 s, 1090 s, 976 s cm^{-1}. Anal. Calcd for $C_{24}H_{39}O_5PCr$: C, 58.76; H, 8.01; P, 6.31; Cr, 10.60. Found: C, 58.27; H, 7.93; P, 6.52; Cr, 10.32.

The reaction of **23b** with diethylacetylene was carried out according to the procedure described for the reaction of **18b** with diethyacetylene. A deoxygenated solution of **23b** (368.5 mg, 0.75 mmol) and diethylacetylene (307.5 mg, 3.75 mmol) in 7 mL of THF was heated at 60 °C under argon for 12 h. Oxidative workup involved the addition of 8 mL of an aqueous 0.5 M ceric ammonium nitrate solution and stirring for 30 min. The same purification procedure provided the quinone **24**[5t] in 33% yield (53.5 mg, 0.245 mmol): mp 78–79 °C; ^{1}H NMR ($CDCl_3$) δ 1.09 (t, 6 H, J = 7.6 Hz), 1.64–1.72 (m, 4 H) 2.35–2.44 (m, 4 H), 2.46 (q, 4 H, J = 7.6 Hz); IR ($CHCl_3$) 2940 m, 2880 w, 1645 s, 1612 m, 1430 m, 1295 w, 1255 w, 960 w, 822 m cm^{-1}; mass spectrum, m/e (rel intensity) 218 M$^+$ (12), 203 (20), 190 (22) 189 (19), 175 (100), 161 (40), 105 (28), 91 (35), 79 (80). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.06; H, 8.26. Found: C, 77.16; H, 8.38.

Reaction of the Triphenylphosphine Carbene Complex 1c with (Trimethylsilyl)acetylene. A solution of the complex **1c** (902.1 mg, 1.86 mmol) and (trimethylsilyl)acetylene (262.3 mg, 2.67 mmol) in 18 mL of THF was deoxygenated by the freeze–thaw method (–196 °C/25 °C, 3 cycles). The reaction mixture was stirred under argon at room temperature for 1.5 h. The THF was removed under reduced pressure with care since the product is volatile. The residue was eluted from a silica gel column with a 1:1:100 mixture of ether, methylene chloride, and pentane to give a 65% yield of the vinylketene **25** (219.0 mg, 1.20 mmol) as a relatively stable oil: ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 1.84 (s, 3 H), 3.54 (s, 3 H), 4.16 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 1.14, 13.75, 17.39, 54.60, 82.23, 156.50, 181.55; IR (neat) 2950 br m, 2080 s, 1250 s, 840 s cm^{-1}; mass spectrum, m/e (rel intensity) 184 M$^+$ (4), 169 (30), 157 (23), 151 (10), 141 (20), 131 (77), 119 (100), 109 (14), 98 (9), 89 (32), 83 (24), 73 (89); calcd for $C_8H_{13}O_2Si$ m/e 169.0685, found m/e 169.0707. The stereochemistry of the double bond was assigned on the basis of the following NOE experiment. A 12.3% enhancement of the olefinic absorption (δ = 4.16 ppm) was observed when the methoxyl absorption (δ = 3.54 ppm) was irradiated. No enhancement of the olefinic absorption was observed when the methyl absorption (δ = 1.84 ppm) was irradiated.

Reaction of Complex 1c with Bis(trimethylsilyl)acetylene. A procedure similar to that used for the reaction of **1c** and (trimethylsilyl)acetylene was employed. A deoxygenated solution of **1c** (304.0 mg, 0.63 mmol) and bis(trimethylsilyl)acetylene (159.8 mg, 0.94 mmol) in 5 mL of THF was stirred under argon at room temperature for 1.5 h. After removal of the solvent, the crude product was purified in the same manner to give the vinylketene **26** (112.5 mg, 0.44 mmol, R_f 0.54) in 70% yield as a oil: ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9 H), 0.15 (s, 9 H), 1.96 (s, 3 H), 3.52 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ –0.24, –0.05 15.30, 15.41, 55.65, 103.06, 164.37, 179.67; IR (neat) 2960 br m, 2080 br m, 2080 s, 1600 m, 1240 s, 830s cm^{-1}; mass spectrum, m/e (relative intensity) 256 M$^+$ (37), 241 (12) 213 (25), 185 (42), 157 (18), 155 (15), 152 (26), 147 (26), 124 (17), 89 (53), 73 (100); calcd for $C_{12}H_{12}O_2Si_2$ m/e 256.1315, found m/e 256.1316. Anal. Calcd for $C_{12}H_{24}O_2Si_2$: C, 56.17; H, 9.44. Found: C, 56.13; H, 9.18.

Reaction of the Tri-*n*-butylphosphine Complex 1b with 1,6-Heptadiyne in THF and Acetonitrile. A solution of complex **1b** (122.9 mg, 0.29 mmol) and 1,6-heptadiyne (73.6 mg, 0.80 mmol) in 65 mL of THF was deoxygenated by the freeze–thaw method (–196 °C/25 °C, 3 cycles). The reaction mixture was heated at 70 °C under an argon atmosphere for 12 h. The solvent was removed under reduced pressure, and the residue was eluted from a flash silica gel column with a 1:1:10 mixture of ether, methylene chloride, and hexane to give the indanol **28** (20.3 mg, 0.14 mmol) in 48% yield: mp 84–86 °C; ^{1}H NMR ($CDCl_3$) δ 2.04 (quint, 2 H, J = 7.4 Hz), 2.21 (s, 3 H), 2.76–2.87 (m, 4 H), 4.50 (s, 1 H), 6.67 (s, 1 H), 6.97 (s, 1 H); IR ($CHCl_3$) 3400–3200 br s, 3000 m, 2940 m, 1500 s, 1325 m cm^{-1}; mass spectrum, m/e (rel intensity) 148$^+$ (85), 133 (100), 105 (12), 91 (20); calcd for $C_{10}H_{12}O$ m/e 148.0888, found m/e 148.0892. Anal. Calcd for $C_{10}H_{12}O$: C, 81.08; H, 8.11. Found: C, 80.74; H, 8.07.

The reaction of **1b** with 1,6-heptadiyne in acetonitrile as also examined and carried out with the same procedure as for the reaction in THF. A deoxygenated solution of **1b** (133.6 mg, 0.315 mmol) and 1,6-heptadiyne (94.5 mg, 1.03 mmol) was heated under argon at 70 °C for 7 h. After workup and purification the indanol **28** was isolated in 49% yield (22.7 mg, 0.153 mmol).

Reaction of the Triphenylphosphine Complex 1c with 1,6-Heptadiyne in THF. A solution of **1c** (141.4 mg, 0.29 mmol) and 1,6-heptadiyne (65.3 mg, 0.71 mmol) in 65 mL of THF was deoxygenated by the freeze–thaw method (–196 °C/25 °C, 3 cycles). The reaction mixture was then stirred under argon at room temperature for 5 h. After removal of the solvent, the residue was eluted with a 1:1:10 mixture of ether, methylene chloride, and hexane on silica gel to give a compound that had spectral data identical with that described above for indanol **28** (26.1 mg, 0.18 mmol, 61%).

It was found that this reaction need not be protected from air. The indanol **28** could be isolated in 45% yield (not optimized) by simply dissolving complex **1c** and 1,6-heptadiyne (1.4 equiv) in THF (0.03 M in **1c**) and allowing the solution to stand in an open flask on the bench-top for 2 h.

Reaction of the Triphenylphosphine Complex 1c with 1,6-Heptadiyne in Acetonitrile. A solution of **1c** (232.0 mg, 0.48 mmol) and 1,6-heptadiyne (34.0 mg, 0.37 mmol) in 70 mL of acetonitrile was deoxygenated by the freeze–thaw method (–196 °C/25 °C, 3 cycles). The solution was then stirred at room temperature under argon for 2 h. After removal of the solvent, the residue was purified by flash column chromatography (1:1:5,

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Et_2O/CH_2Cl_2/hexane) to give two compounds.

The minor component was found to have spectral data identical with that described above for **28** (4.5 mg, 0.03 mmol, 8.2%). The major product was identified as the cyclohexadienone **29**[5u] (35.9 mg, 0.202 mmol, 55%): mp 33 °C; ^1H NMR ($CDCl_3$) δ 1.30 (s, 3 H), 1.86–1.98 (m, 2 H), 2.54–2.61 (m, 2 H), 2.66 (t, 2 H, J = 7.2 Hz), 3.09 (s, 3 H), 6.02 (s, 1 H), 6.09 (s, 1 H); IR ($CHCl_3$) 3000 s, 1675 m, 1652 s, 1600 m, 1360 m, 1245 m, 1095 s, 1030 w, 850 m cm^{-1}; mass spectrum, m/e (rel intensity) 178 M^+ (100), 163 (15), 147 (20), 135 (40) 121 (58), 119 (60), 91 (50) 43, (40); calcd for $C_{11}H_{14}O_2$ m/e 178.0994, found m/e 178.0988. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.16; H, 7.87. Found: C, 74.14; H, 8.04.

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Evidence Supporting Two-Electron Nucleophilic Displacement in Reactions of Unhindered Alkyl Bromides and Iodides with Boron and Aluminum Hydride Reducing Agents

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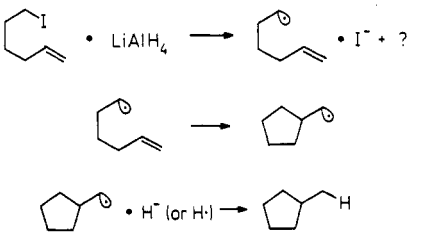
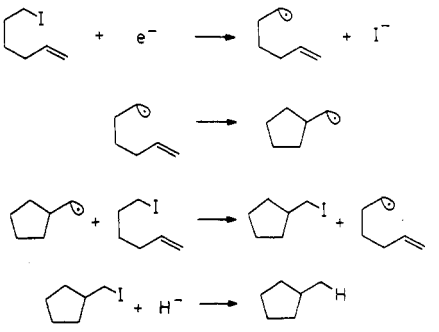
7-Bromo- and 7-iodo-2-methoxy-2-heptenenitrile were used as mechanistic probes in reactions with a variety of boron and aluminum hydride reducing agents. No radical-derived cyclized products were observed in the reductions. The reactions with these probes are best explained as conventional two-electron nucleophilic displacements of halide ion by hydride. Previous work had indicated that electron transfer (SET) from boron and aluminum hydride reducing agents to unhindered alkyl halides is not a predominant reaction, and this work supports that conclusion and sets a lower limit on the amount of SET.

The reactions of boron and aluminum hydride reducing agents with primary and secondary alkyl halides can produce hydrocarbon products. These reactions have generally been thought to occur by a conventional two-electron nucleophilic displacement of halide by hydride.[2] However, recent results with alkyl halide mechanistic probes have suggested that radicals can be formed in reactions of $LiEt_3BH$, $LiAlH_4$, and AlH_3 with simple alkyl iodides and bromides and have led to conclusions that the initial reactions involve electron transfer from the metal hydride to the alkyl halide.[3-5] In the probe studies an alkyl halide is used which, if converted to a radical, will lead to a rearranged product. The presence of rearranged reduction products thus implicates radical intermediates and by inference this has been taken as evidence of an electron transfer process. A typical reaction sequence that incorporates such an electron-transfer step is exemplified in Scheme I for reaction of the common mechanistic probe 6-iodo-1-hexene with LAH. In most probe studies quantitation of electron-transfer processes has not been attempted.

Scheme I



Scheme II



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