

Recent advances in arene transformation reactions via chromium complexes

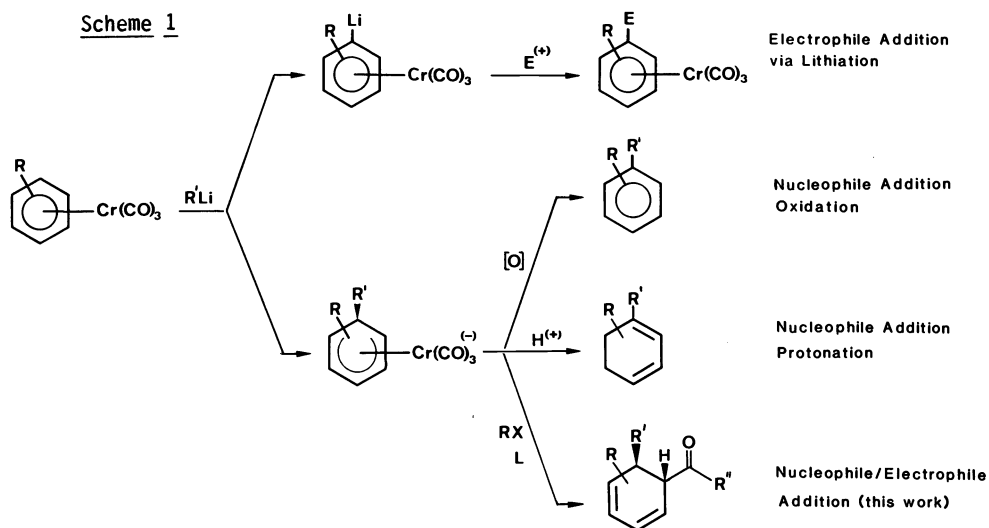
Ernst Peter Kündig

Department of Organic Chemistry, University of Geneva, CH-1211 Geneva 4

ABSTRACT - Sequential addition of reactive carbanions and carbon electrophiles to arene $\text{Cr}(\text{CO})_3$ complexes yield, after decomplexation, trans disubstituted cyclohexadienes. Alkylation of the initially formed anionic cyclohexadienyl complex takes place with high selectivity ($\text{RI} > \text{RBr} \gg \text{RCl}$ (unreactive); $\text{R} = \text{allyl} > \text{prim. alkyl} > \text{sec. alkyl}$; $\text{RI} > \text{RCOR}'$) and is followed by carbonylation and transfer to the six-membered ring. Useful nucleophiles in this reaction appear to be those that react irreversibly with the complexed arene. The question of kinetic vs. thermodynamic control of nucleophilic addition to arene $\text{Cr}(\text{CO})_3$ complexes is discussed, and examples of highly regioselective reactions leading to 3-substituted benzocyclobutenes and 4-substituted indanes are presented.

INTRODUCTION

Arene $\text{Cr}(\text{CO})_3$ complexes are readily prepared by ligand displacement from $(\text{CO})_3\text{CrL}_3$ precursors (e.g. $\text{L} = \text{CO}$ (ref. 1), NH_3 (ref. 2), CNR (ref. 3)) or via arene exchange from labile arene $\text{Cr}(\text{CO})_3$ complexes (e.g. arene = naphthalene (ref. 4)). The $\text{Cr}(\text{CO})_3$ group induces drastic changes in the reactivity of the aromatic ring and of benzylic substituents. The ready access, the ease of manipulation and product decomplexation and, foremost, the interesting and manifold chemistry exhibited by these complexes have led to extensive studies in the field (ref. 5-16). Scheme 1 shows the arene reactivity pattern exhibited by arene $\text{Cr}(\text{CO})_3$ complexes.

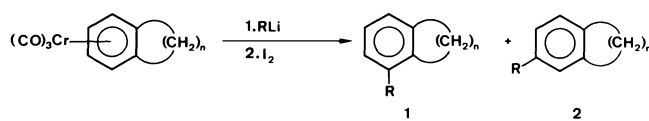


In this article we single out the nucleophilic addition reaction and, in particular, we consider the question of the reversibility of carbanion addition and of the nucleophilicity of the intermediate anionic cyclohexadienyl $\text{Cr}(\text{CO})_3$ complexes.

**REGIOSELECTIVITY AND REVERSIBILITY IN THE ADDITION OF
CARBANIONS TO ARENE Cr(CO)₃ COMPLEXES**

One of the fascinating aspects of the reaction of carbon nucleophiles with substituted arenes coordinated to Cr(CO)₃ is the high regioselectivity of the addition often encountered (ref. 5a, 17-19). Semmelhack and his group noted, and elegantly applied in synthesis, the high meta-selectivity with strong resonance donor groups such as alkoxy, amino and fluoro on the arenes and the para-selectivity with SiMe₃ (ref. 5a, 6). High regioselectivity is also observed with fused ring compounds as indicated in the following recent examples from our laboratory (Table 1). They constitute a ready access to 3-substituted benzocyclobutenes and 4-substituted indanes.

TABLE 1. Regioselectivity in the addition of carbon nucleophiles to benzocyclobutene and indane Cr(CO)₃ complexes



Entry	Carbanion ^a LiR	Product mixture			Yield ^c
		<u>1a</u> (n=2) ^b	<u>1b</u> (n=3)	<u>2b</u> (n=3)	
1	Li CH ₂ CN ^d	65			
2	Li CMe ₂ CN	86	80	: 20	85 ^e
3	Li CMe(CN)OR ^{d, f}	91	90	: 10	95
4	Li CMe ₂ CO ₂ Me ^g	96			
5	Li C[HS(CH ₂) ₃ S] ^d	69	>96 ^h	: <4	88 ^{g, h}
6	Li CMeS(CH ₂) ₃ S ^d	64	>96	: <4	89

^aSolvent for all reactions unless otherwise indicated: THF. ^bNo 4-substituted benzocyclobutenes were observed in these reactions.

^cYields refer to isolated material after chromatographic separation.

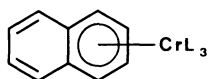
^dMedium: THF/HMPA; 10:1. ^eYield of 4:1 mixture; ratio determined by nmr.

^fR in the product is COCH₃, obtained after hydrolysis of the cyanohydrin acetal; see: G. Stork, L. Maldonado, *J. Am. Soc.* **93**, 5286 (1971).

^gMedium: THF/HMPA; 4:1. ^hThe product was isolated from the crude reaction mixture by crystallization from hexane (m.p. 110-112^o).

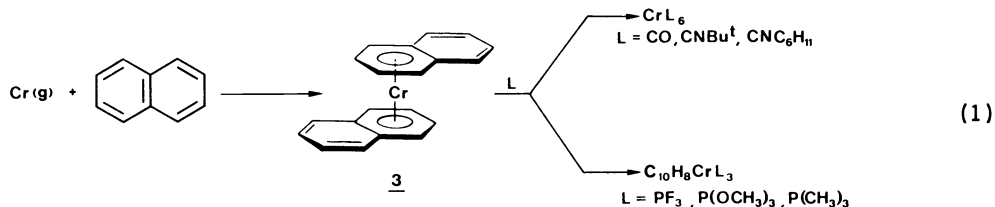
Theoretical rationalization of regioselectivity has been put forward (ref. 19-21). Several factors appear to govern regioselectivity of nucleophilic attack - such as charge polarization induced by the conformation adopted by the Cr(CO)₃ group, coefficient size of the lowest energy arene centered molecular orbital, reactivity of the nucleophile, and steric demands of arene substituent and nucleophile. It has to be pointed out that these analyses assume kinetic control of the addition reaction - an assumption that has not been rigorously established by experiment and, as the reader will see, is by no means generally correct.

Our interest in this question stems from the results of an investigation into the reactivity of a series of naphthalene CrL₃ complexes (ref. 22).



L = CO; PF₃; PF₂OCH₃; P(OCH₃)₃; C₁₀H₈ (=L₃); P(CH₃)₃.

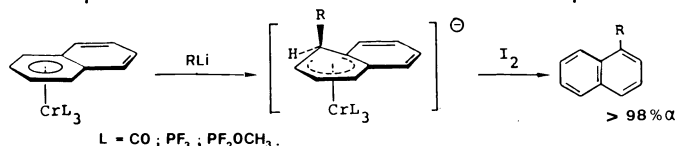
The naphthalene phosphine and phosphite complexes are accessible by displacement under mild conditions of one of the arenes from the sandwich complex **3**. **3** is synthesized by metal evaporation in a simple and versatile rotating solution reactor (eq. 1) (ref. 23-24).



The ease of displacement of naphthalene is a feature common to condensed aromatic ligands. It can be interpreted in terms of a kinetic lability of the naphthalene due to facile slip-page from a η^6 to a η^4 coordination mode (ref. 4).

The nucleophilic addition reaction was used to probe the electrophilic activation of the arene by the electronically very different CrL_3 groups. The reaction is shown to be limited to complexes containing strong acceptor ligands; furthermore, the reaction shows a remarkably high regioselectivity (Table 2) (ref. 22, 25).

TABLE 2. Nucleophilic aromatic substitution for H^- in naphthalene CrL_3 complexes



Entry	Carbanion	Yields of α -substituted naphthalene (%)				
		L = CO	PF_3	PF_2OMe	$\text{P}(\text{OMe})_3$	$\text{C}_8\text{H}_{10}(\text{L}_3)$
1	Li CH_2CN	54	55			
2	Li CMe_2CN	96	90	78	<3	0
3	Li $\overline{\text{CHS}(\text{CH}_2)_3\text{S}}$	83				
4	Li OMe	30				

We next considered the question of the influence of substituents in the α position of the non-complexed ring. It might be expected that superposed on the factors governing regioselectivity in this reaction, steric and electronic effects due to the peri-substituents would become apparent. Steric effects are important as we found 1-substituted naphthalene complexes to react with LiCMe_2CN to yield a mixture of 1.5 and 1.8 disubstituted naphthalenes; the major product being the 1,5 isomer (Table 3) (ref. 26).

Analogously, 1,4-dimethoxynaphthalene $\text{Cr}(\text{CO})_3$ **6**, under the same standard reaction conditions (THF, 0° , 0.5 h), afforded almost entirely the addition product **9** (ref. 27-28). However, inspection of Table 4 shows that the α intermediate is the thermodynamic product. At low temperature (entry 1), the β intermediate is formed predominantly; oxidation yields the mixture of **9** and **10** in the ratio of 38:62 in good yield. Consequently, the different product distribution on increasing reaction time and/or temperature is indicative of a rearrangement of intermediate **8** to **7**. Presumably this transfer occurs via dissociation of the carbanion as depicted in eq. 2. Preliminary results from crossover experiments support this mechanism.

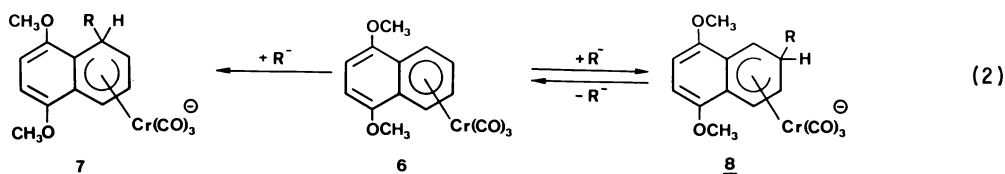
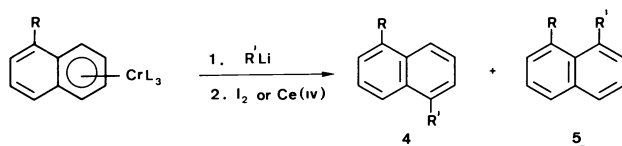
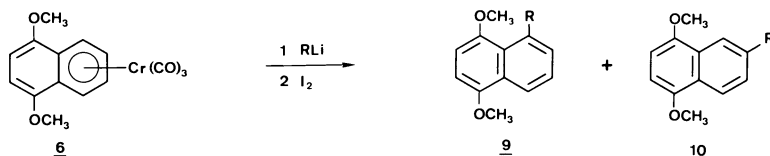


TABLE 3. Regioselectivity in the addition of LiCMe_2CN to 1-substituted naphthalene CrL_3 Complexes ($\text{L} = \text{CO}$ or PF_3)

Entry ^a	Complex	Product distribution		Yield %
		<u>4</u>	<u>5</u>	
1	R=Me, L=PF ₃	98	2	66
2	R=OMe, L=PF ₃	76	24	63
3	R=OMe, L=CO	77	23	70
4	R=F, L=CO	75	25	72

^aThe medium in all reactions was THF; the complex was added as a solid to the solution of the anion at -78° , then brought to 0° for 30 min, recooled to -78° and treated with I_2 or Ce(IV) solution.

TABLE 4. Reactions of carbanions with 1,4-dimethoxynaphthalene Cr(CO)_3 6

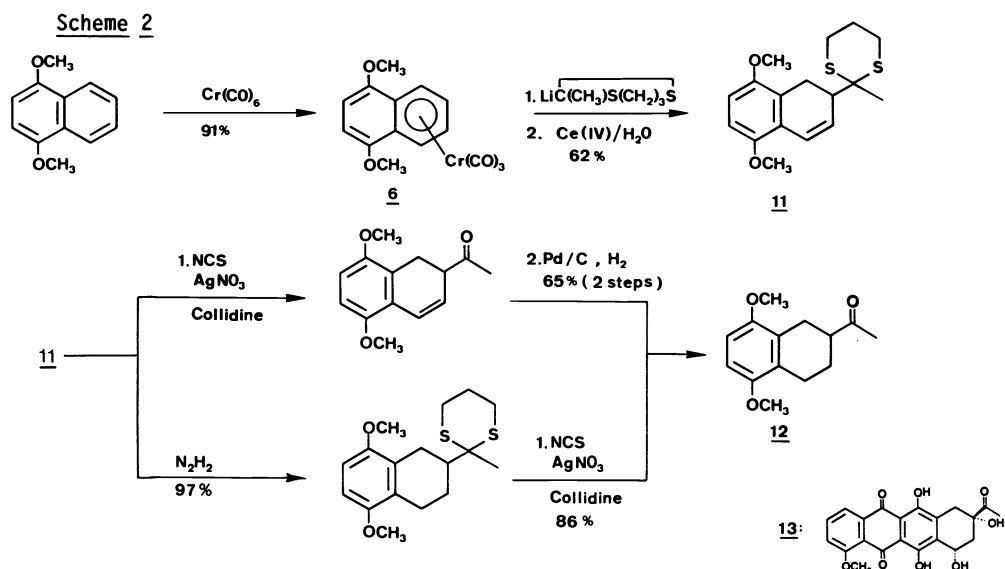
Entry	Carbanion LiR	Medium	Time, h/ temp., °C	Product mixture ^a		Combined yield ^b %
				<u>9</u>	<u>10</u>	
1	LiCMe_2CN	THF ^c	0.1/-72	38	62	81
2	"	"	1/-60	39	61	89
3	"	"	1/-40	79	21	95
4	"	"	1/0	>96 ^d	<4 ^d	78 ^d
5	"	THF/HMPA ^c (2.5/1)	0.5/-60	22	78	69
6	"	"	1/-40	27	73	84
7	"	"	2/0	47	53	76
8	"	"	46/0	>98 ^d	<2 ^d	84 ^d
9	LiCH_2CN	"	1/-50	75 ^d	25 ^d	34 ^d
10	"	"	30/-20	100	0	72
11	$\text{LiCH}_2\text{COO-t-Bu}$	"	1/0	67	33	89
12	"	"	48/0	>98 ^d	<2 ^d	84 ^d
13	$\text{LiC}(\overline{\text{CH}_3})\text{S}(\text{CH}_2)_3\text{S}$	"	1/0	0	100	61
14	"	"	48/0	0	100	71

^aAll compounds were isolated and independently characterized. The product ratios are based on isolated material (unless otherwise noted). ^bThe percentage yield refers to isolated (column chromatography) material after separation into 9 and 10 (unless otherwise indicated). ^cIn all cases the anion and the complex were mixed at -78° . ^dRatio was determined by $^1\text{H-NMR}$ integration; combined yields refer to mixtures of 9 and 10.

The rearrangement follows first-order kinetics with a half-life of the reaction in THF of ca. 40 min at -40° . Addition of hexamethylphosphoric triamide (HMPA) has a pronounced effect on the rate of rearrangement. In THF/HMPA (2.5/1) the half-life for rearrangement is ca. 13 h at 0° . The large (300 fold !) rate decrease on HMPA addition (which causes Li^+ solvation), points to the crucial role of the Lewis acid in the C-C bond breaking step which leads to carbanion dissociation.

Following our first report on the reversibility of nucleophilic addition (ref. 7) a further example of very rapid rearrangement (at -70° of LiCMe_2CN in reaction with N-methyltetrahydroquinoline $\text{Cr}(\text{CO})_3$) appeared in the literature (ref. 9).

Inspection of Table 4 shows the reversibility to be limited to nitrile stabilized carbanions and an ester enolate. Methylthiane anion, on the other hand, adds irreversibly and regio-specifically to the β carbon of **6**. This, as will be discussed in section 3, has important ramifications regarding the chemistry of the cyclohexadienyl $\text{Cr}(\text{CO})_3$ anions. The regio-specific β addition of methylthiane anion can be interpreted in terms of steric and electron pair repulsion between the incoming anion and the methoxy group. Irreversibility may reflect the higher nucleophilicity of the sulfur stabilized carbanion and/or the decreased affinity of sulfur (compared to $-\text{CN}$ and $-\text{OR}$) for the Lewis acid Li^+ . In a synthetic application this reaction provides the key step in a short and novel route to the daunomycinone (**13**) precursor 1,4-dimethyl-6-acetyltetralin (ref. 29) (Scheme 2). Incorporation of the $\text{Cr}(\text{CO})_3$ group in 1,4-dimethoxynaphthalene is regio-specific in the non-substituted ring. Reaction of **6** with 2-lithio-2-methyl-1,3-dithiane in THF/HMPA followed by protonation of the intermediate and decomplexation afforded the dihydronaphthalene **11**. Conversion of **11** to the acetyltetralin **12** can be carried out either by initial dithiane hydrolysis followed by hydrogenation or, with higher yield, by initial reduction of the double bond with diimide followed by dithiane hydrolysis.

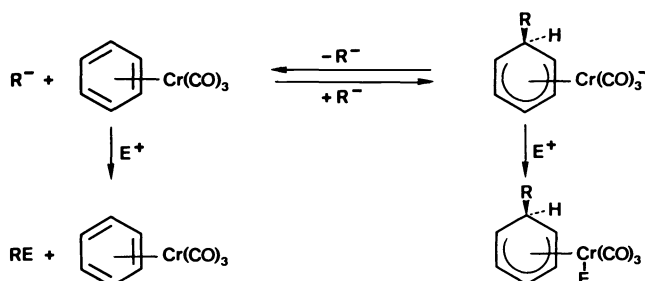


THE ADDITION OF CARBON ELECTROPHILES TO ANIONIC CYCLOHEXADIENYL $\text{Cr}(\text{CO})_3$ COMPLEXES

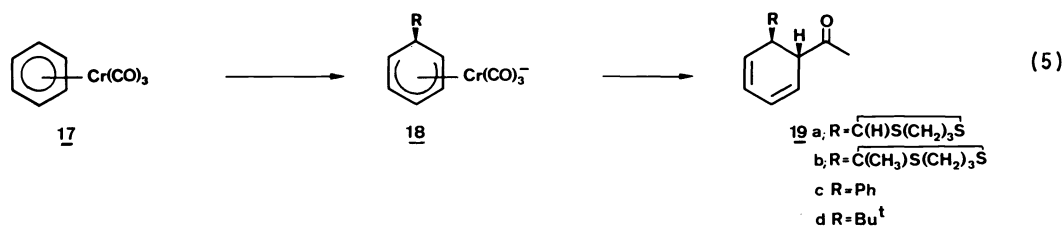
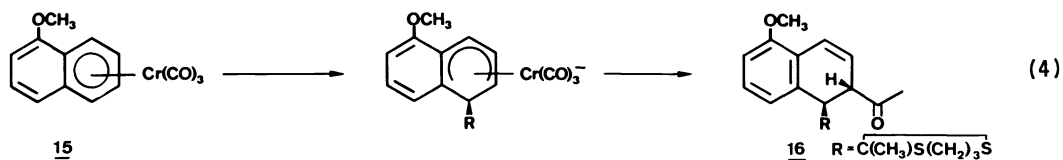
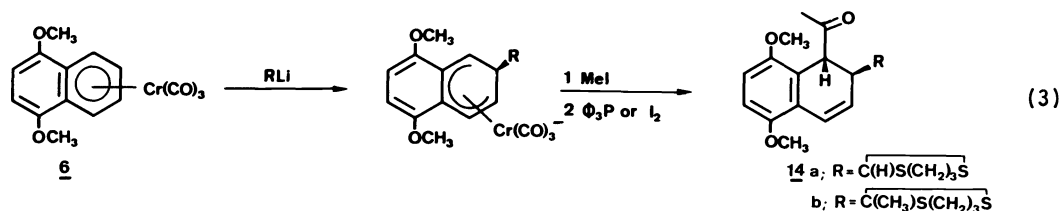
The reversible or, respectively, irreversible addition of carbanions to **6** raised another question. Anionic cyclohexadienyl $\text{Cr}(\text{CO})_3$ complexes have been reported to react with carbon electrophiles via abstraction of the nucleophile with regeneration of the starting arene

complex (ref. 30). This has always been a serious limitation to the synthetic usefulness of these intermediates. Our result suggests that this reflects the reversible nature of the addition reaction (Scheme 3).

Scheme 3



As reactive carbanions such as methylthianellithium appeared to undergo irreversible addition, the possibility of a different reaction path in reactions of the resulting complex anions with carbon electrophiles exists; this proved to be the case. Sequential addition of reactive carbanions and MeI to benzene Cr(CO)_3 and naphthalene Cr(CO)_3 complexes yielded, after ligand displacement or oxidation, trans disubstituted cyclohexadienes and dihydronaphthalenes respectively (ref. 8) (eq. 3-5 and Table 5).



We propose the following mechanism for the transformation (Scheme 4):

Scheme 4

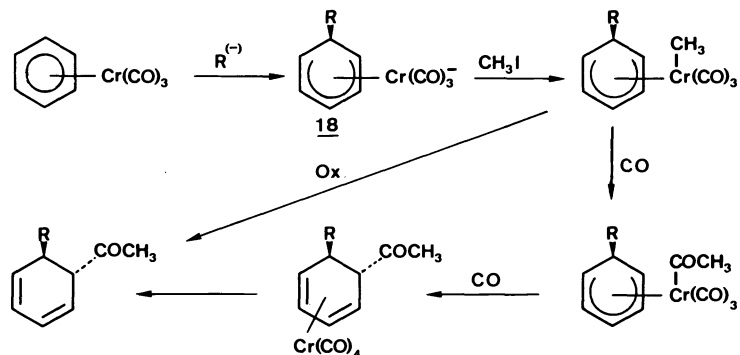
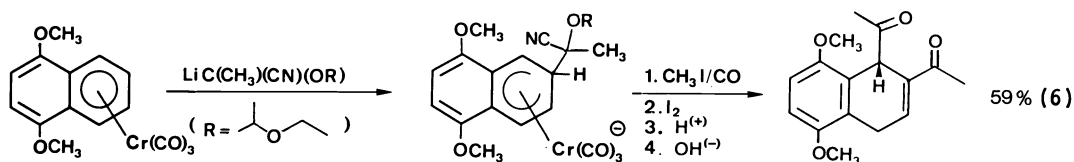


TABLE 5. Reactions of arene-Cr(CO)₃ complexes with reactive nucleophiles and trapping of the cyclohexadienyl intermediates with MeI.

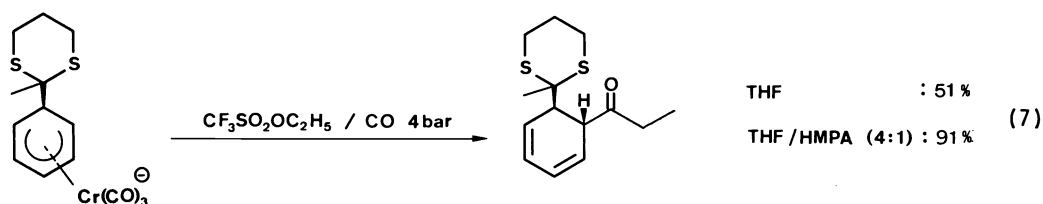
Entry	Complex	RLi	Atmosphere during trapping reaction	Product decomplexation	Product	Yield ^a %
1	<u>6</u>	LiC(H)S[CH ₂] ₃ S	N ₂	I ₂	<u>14a</u>	42
2	<u>6</u>	LiC(Me)S[CH ₂] ₃ S	N ₂	I ₂	<u>14b</u>	76
3	<u>15</u>	LiC(Me)S[CH ₂] ₃ S	CO	PPh ₃	<u>16</u>	72
4	<u>17</u>	LiC(H)S[CH ₂] ₃ S	N ₂	PPh ₃	<u>19a</u>	54
5	<u>17</u>	LiC(Me)S[CH ₂] ₃ S	N ₂	PPh ₃	<u>19b</u>	70
6	<u>17</u>	LiC(Me)S[CH ₂] ₃ S	CO	PPh ₃	<u>19b</u>	89
7	<u>17</u>	LiC(Me)S[CH ₂] ₃ S	CO	CO	<u>19b</u>	88
8	<u>17</u>	LiPh	CO	PPh ₃	<u>19c</u>	47 ^b
9	<u>17</u>	LiBu ^t	CO	PPh ₃	<u>19d</u>	67

^aThe yields refer to isolated (column chromatography) material. ^bMixture of 19c and the aromatic analogue. Yield refers to the mixture.

Reactive anions are required in the addition step. They increase the nucleophilicity of the intermediate 18 and thereby favor alkylation over anion dissociation. HMPA, by cation solvation, assists in the same way. With MeI as electrophile no alkylation takes place in the case of LiCH₂CN or LiCMe₂CN, irrespective of HMPA addition. In its presence however the following sequence could be carried out (eq. 6) (ref. 31):



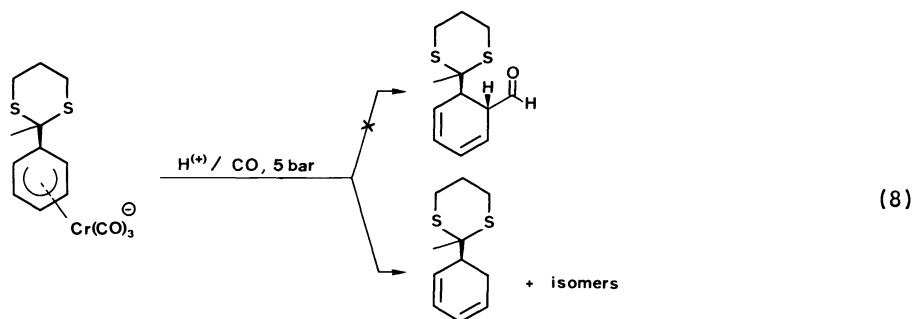
On the other hand, HMPA can be disposed of (albeit with a loss of yield) in the case of a very reactive electrophile (eq. 7).



The two examples underline the sensitivity of the reaction with regard to the nature of the arene, the nucleophile, the electrophile, and the reaction medium.

CO incorporation takes place with or without external CO although the reactions are cleaner and the yield is higher in the presence of CO (or PPh₃) than in the oxidation induced carbonylation (Table 5, entries 5-7). HMPA, known to suppress migratory insertion of CO in anionic complexes (ref. 32), does not suppress this step in this reaction sequence; i.e., no simple alkyl transfer is observed. The only electrophile that adds without CO insertion is H⁺. The formation of isomeric mixtures of cyclohexadienes on treatment of 18b with an excess of strong acid has been reported (ref. 30). We observed no CO insertion on reacting 18b with strong (CF₃COOH) or weak (aq. NH₄Cl) acids under 1 to 5 bar CO (eq. 8).

In this respect the nucleophile/electrophile addition to arene Cr(CO)₃ differs from the closely analogous reaction sequence in diene Fe(CO)₃ chemistry (ref. 33).



The endo migration of the acyl group to the cyclohexadienyl moiety results in a cyclohexadiene chromium complex in which Cr has been formally reduced from Cr(II) to Cr(0) (Scheme 4). On increasing the CO pressure to 4 bar (20°, 1 day) or on addition of an excess of PPh₃ the diene is readily liberated. Precedents have been set (ref. 34) for Cr(CO)₆ recycling although in our cases, in the presence of HMPA, this remains elusive. The trans stereochemistry of nucleophile and electrophile in the product was originally assigned on the basis of the known stereochemistry of nucleophilic addition to coordinated arenes (exo) (ref. 30) and the requirement of an intermediate interacting with a coordinated CO group in the second step (endo). It was recently confirmed by an X-ray structure determination (ref. 31)(Fig. 1):

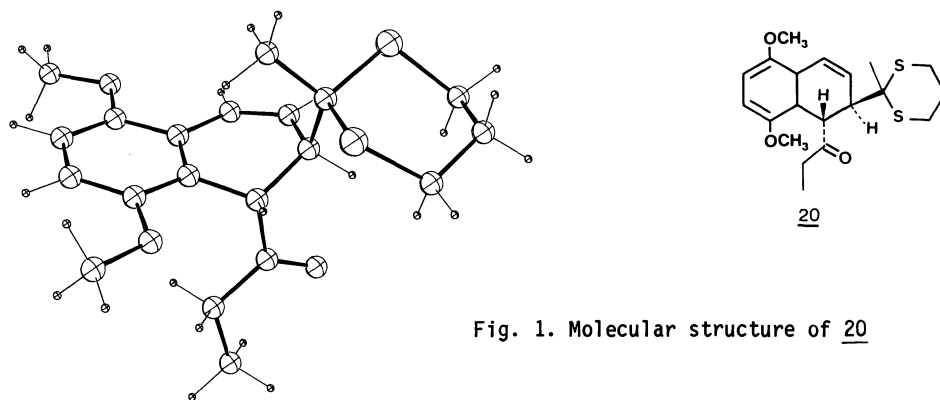


Fig. 1. Molecular structure of 20

Following the brief preliminary survey of nucleophile requirements we focused our attention on selectivity vis-a-vis the electrophile. Fig. 2 summarizes our current results.

Primary iodides and triflates react with the methyldithianylcyclohexadienyl Cr(CO)₃ complex below 0° to give (after CO insertion and decomplexation) the free diene. Ethylbromide only reacted on heating. Secondary iodides and mesylates are less suitable substrates. The main product in these reactions is the mono-substituted dihydro product resulting, presumably, from base induced HX abstraction. This behavior is therefore similar to that of Collman's complex Fe(CO)₄²⁻ (ref. 36). Ready addition to allylic and benzylic bromides is observed - the former occurring in almost quantitative yield. In contrast, allyl chloride does not react readily under these conditions (-78 → 10°), exemplifying the remarkable selectivity of the addition reactions. Further examples include the specific addition to iodide in 1-iodo-4-pentanone and in 1-chloro-5-iodopentane.

The substrate reactivity profile established in these reactions [allylic > primary >> secondary; OTf > OMe ≈ I > Br >> Cl (unreactive)] is consistent with an S_N2 mechanism. There is however a considerable rate difference between iodides and bromides that may indicate a change of mechanism in the two reactions. To test for a competing electron transfer radical mechanism, as was implied in reactions of η⁵-C₅H₅Fe(CO)₂ with alkyl iodides (ref. 35), cyclopropyl methyl iodide was used as electrophile (eq. 9). The absence of homoallyl product mitigates strongly against the intermediacy of an alkyl radical in this reaction.

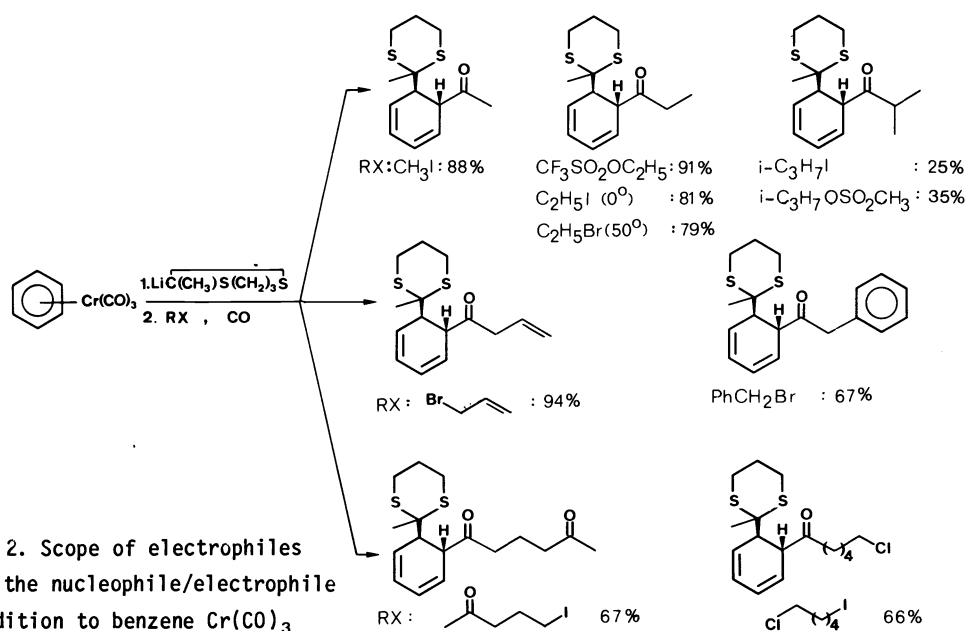
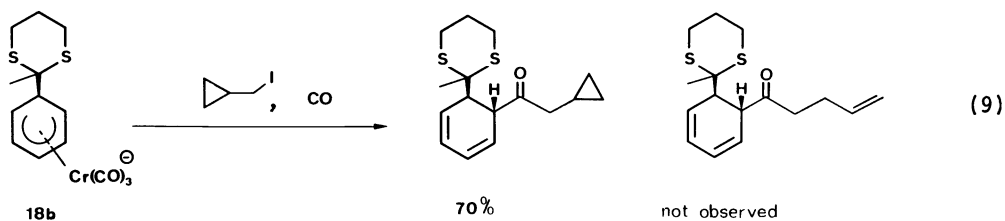


Fig. 2. Scope of electrophiles in the nucleophile/electrophile addition to benzene Cr(CO)₃

The mild decomplexation yields products without double bond isomerization (Fig. 2). They form interesting materials for further elaboration in organic synthesis. This aspect is presently under investigation in our laboratory.



CONCLUSION

Regioselectivity of nucleophilic addition to substituted arene Cr(CO)₃ complexes, in the past interpreted solely in terms of kinetic control, has now been shown to be reversible in several cases. In addition, indirect evidence - such as the effect of the Lewis acid Li⁺ on the rate of nucleophile dissociation in the intermediate - and particularly the course of the reaction of carbon electrophiles with the anionic addition products, indicates reversibility to be far more general than has been previously assumed. Regiocontrol offers new perspectives in arene functionalization, a theme that we shall pursue in the future.

The mechanistic studies presented in section 2 have resulted in the discovery of a synthetically useful transformation of an arene to a trans disubstituted cyclohexadiene (section 3). The simplicity of the one-pot transformation, the high selectivity and the good yields obtained in many cases make this reaction sequence highly attractive for organic synthesis.

ACKNOWLEDGMENTS

It is a pleasure to express my sincere appreciation to my co-workers Vincent Desobry, Patrick Paglia, Dana P. Simmons and Eric Wenger for their enthusiastic work. I am also indebted to Celia Perret, Chantal Grivet and Bruno Rudolph for extremely valuable technical assistance. Financial support of this work by the Swiss National Science Foundation is gratefully acknowledged.

REFERENCES

1. C.A.L. Mahaffy and P.L. Pauson, Inorg. Synth. **XIX**, 154 (1979).
 2. M.D. Rausch, G.A. Moser, E.J. Zaiko, and A.L. Lipman Jr., J. Organomet. Chem. **23**, 185-192 (1970).
 3. I.U. Khand, C.A.L. Mahaffy, and P.L. Pauson, J. Chem. Res., Miniprint 4454 (1978).
 4. E.P. Kündig, C. Perret, S. Spichiger, and G. Bernardinelli, J. Organomet. Chem. **286**, 183 (1985).
 5. a) M.F. Semmelhack, G.R. Clark, J.L. Garcia, J.J. Harrison, Y. Thebtaranonth, W. Wulff, and A. Yamashita, Tetrahedron **37**, 3957 (1981); b) W.E. Watts, "The Organic Chemistry of Metal-Coordinated Cyclopentadienyl and Arene Ligands" in: Comprehensive Organometallic Chemistry, Ed. G. Wilkinson, F.G.A. Stone, E.W. Abel, Pergamon, Vol. 8, pp 1013-1072 (1982); c) J.P. Collman and L.S. Hegeudus, "Principles and Applications of Organotransition Metal Chemistry", University Science Books, Mill Valley, ch. 14 (1980).
- Recent work on:
- a) Nucleophilic addition to arene Cr(CO)₃ complexes
 6. M.F. Semmelhack, and A. Zask, J. Am. Chem. Soc. **105**, 2034-2043 (1983).
 7. E.P. Kündig, V. Desobry, and D.P. Simmons, J. Am. Chem. Soc. **105**, 6962-6963 (1983).
 8. E.P. Kündig, and D.P. Simmons, Chem. Commun. 1320 (1983).
 9. B. Ohlsson and C. Ullenius, J. Organomet. Chem. **267**, C34 (1984).
 - b) Lithiation on the ring
 10. M. Ghavshou and D.A. Widdowson, J. Chem. Soc., Perkin Trans. I 3065 (1983).
 11. P.J. Beswick, S.J. Leach, N.F. Masters, and D.A. Widdowson, Chem. Commun. 46 (1984).
 12. M. Uemura, T. Minami, and Y. Hayashi, Chem. Commun. 1193 (1984).
 - c) Carbanion chemistry in the benzylic position
 13. G. Jaouen, S. Top, A. Laconi, D. Couturier, and J. Brocard, J. Am. Chem. Soc. **106**, 2207-2208 (1984).
 14. J. Blagg, S.G. Davies, and B.E. Mobbs, Chem. Commun. 619 (1985).
 - d) Carbocation chemistry in the benzylic position
 15. M.T. Reetz and M. Sauerwald, Tetrahedron Lett. 2837 (1983).
 16. M. Uemura, K. Isobe, and Y. Hayashi, Chemistry Lett. 91-94 (1985).
 17. J.C. Boutonnet, L. Mordenti, E. Rose, O. Le Martret, and G. Precigoux, J. Organomet. Chem. **221**, 147-156 (1981).
 18. W.R. Jackson, I.D. Rae, M.G. Wong, M.F. Semmelhack, and J.N. Garcia, J. Chem. Soc., Chem. Commun. 1359-1360 (1982).
 19. M.F. Semmelhack, J.L. Garcia, D. Cortes, R. Farina, R. Hong, and B.K. Carpenter, Organometallics **2**, 467-469 (1983).
 20. A. Solladie-Cavallo and G. Wipff, Tetrahedron Lett. 3047-3050 (1980).
 21. T.A. Albright and B.K. Carpenter, Inorg. Chem. **19**, 3092-3097 (1980).
 22. V. Desobry and E.P. Kündig, Helv. Chim. Acta **64**, 1288 (1981).
 23. E.P. Kündig, and P.L. Timms, J. Chem. Soc., Dalton Trans. 991-995 (1980).
 24. For a description of the rotating solution reactor and applications in Grignard reactions see: E.P. Kündig, and C. Perret, Helv. Chim. Acta **64**, 2606-2613 (1981).
 25. For the first example of high α regioselectivity in (C₈H₁₀)Cr(CO)₃ see: M.F. Semmelhack, G.R. Clark, R. Farina, and M. Saeman, J. Am. Chem. Soc. **101**, 217-218 (1979).
 26. V. Desobry, PhD Thesis No 2042, University of Geneva (1982).
 27. E.P. Kündig, V. Desobry, C. Grivet, B. Rudolph, D.P. Simmons, and E. Wenger, to be submitted for publication.
 28. For a preliminary account see ref. 7.
 29. C.M. Wong, D. Popien, R. Schwenk, and J. Te Raa, Can. J. Chem. **49**, 2712-2718 (1971).
 30. M.F. Semmelhack, H.T. Hall Jr., R. Farina, M. Yoshifuji, G. Clark, T. Bargar, K. Hirotsu, and J. Clardy, J. Am. Chem. Soc. 3535-3544 (1979).
 31. E.P. Kündig, P. Paglia, D.P. Simmons, and G. Bernardinelli, submitted for publication.
 32. J.P. Collman, R.G. Finke, J.N. Cawse, and J.I. Brauman, J. Am. Chem. Soc. **100**, 4766-4772 (1978).
 33. a) M.F. Semmelhack, J.W. Herndon, and J.P. Springer, J. Am. Chem. Soc. **105**, 2497-2499 (1983); b) M.F. Semmelhack, J.W. Herndon, and J.K. Liu, Organometallics **2**, 1885-1888 (1983); c) M.F. Semmelhack, and H.T.M. Le, J. Am. Chem. Soc. **106**, 2715-2717 (1984).
 34. J.C. Boutonnet, J. Levisalles, J.-M. Normant, and E. Rose, J. Organomet. Chem. **255**, C21-C23 (1983).
 35. P.J. Krusic, P.J. Fagan, and J. San Filippo Jr., J. Am. Chem. Soc. **99**, 250-252 (1977).
 36. J.P. Collman. Acc. Chem. Res. **8**, 342 (1975).