The Transformation of Arenes into Acetyl Dienes *via* Nucleophilic Addition to Arene–Cr(CO)$_3$ Complexes and Trapping with MeI

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Anionic cyclohexadienyl–Cr(CO)$_3$ complexes, formed by addition of reactive carbanions to benzene–Cr(CO)$_3$ and naphthalene–Cr(CO)$_3$ complexes, react with MeI by addition and carbonylation to yield disubstituted cyclohexadienes and dihydronaphthalenes, respectively.

Anionic cyclohexadienyl–Cr(CO)$_3$ complexes are important intermediates in the synthesis of substituted arenes by nucleophilic attack on arene–Cr(CO)$_3$ compounds.[1] Their reactions fall into three categories: (a) oxidation of the intermediate

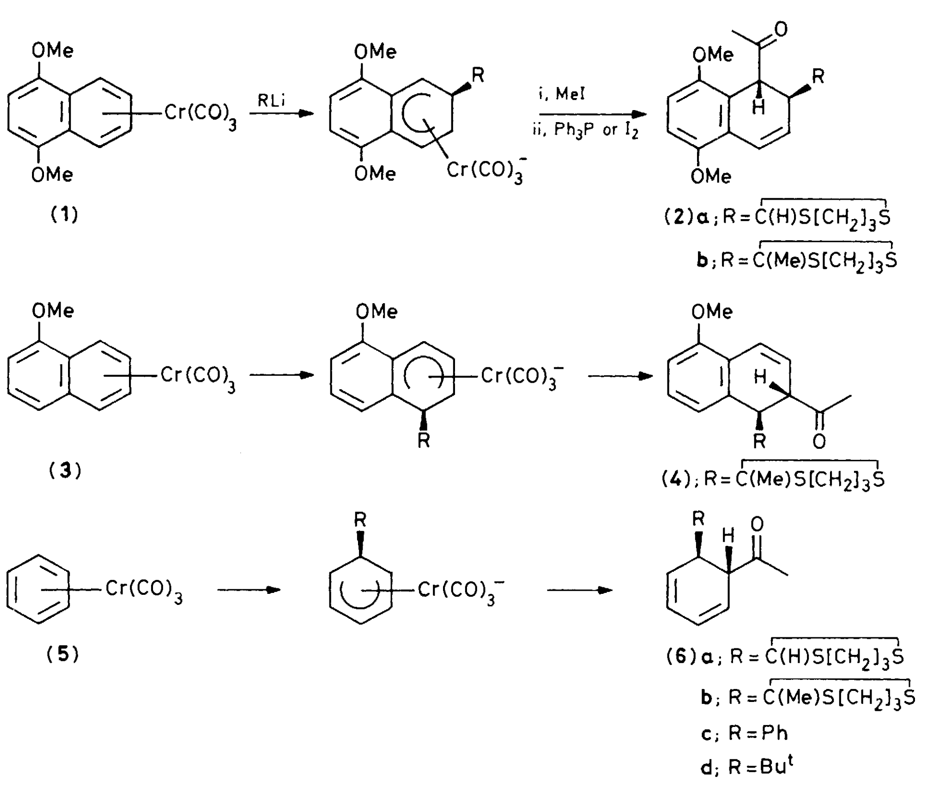

Table 1. Reactions of arene–Cr(CO)$_3$ complexes with reactive nucleophiles and trapping of the cyclohexadienyl intermediates with MeI.

Entry	Complex	RLi	Atmosphere during trapping reaction	Product decomplexation	Product[a]	Yield[b] (%)
1	**(1)**	LiC(H)S[CH$_2$]$_3$S	N$_2$	I$_2$	**(2a)**	42
2	**(1)**	LiC(Me)S[CH$_2$]$_3$S	N$_2$	I$_2$	**(2b)**	76
3	**(3)**	LiC(Me)S[CH$_2$]$_3$S	CO	PPh$_3$	**(4)**	72
4	**(5)**	LiC(H)S[CH$_2$]$_3$S	N$_2$	PPh$_3$	**(6a)**	54
5	**(5)**	LiC(Me)S[CH$_2$]$_3$S	N$_2$	PPh$_3$	**(6b)**	70
6	**(5)**	LiC(Me)S[CH$_2$]$_3$S	CO	PPh$_3$	**(6b)**	89
7	**(5)**	LiPh	CO	PPh$_3$	**(6c)**[c]	47
8	**(5)**	LiBu^t	CO	PPh$_3$	**(6d)**	67

[a] Assignment to the *trans* isomer is tentative; otherwise ^{1}H n.m.r. (360 MHz), i.r., u.v., and mass spectra are in full agreement with the assigned structures. [b] The yields refer to isolated (column chromatography) material. [c] Mixture of **(6c)** and the aromatic analogue. Yield refers to the mixture.

and liberation of the substituted arene; (b) transfer of the nucleophile to an electrophile and regeneration of the starting arene complex; and (c) electrophilic addition to the ligand and formation of a substituted cyclohexadiene. This last category, of considerable potential in organic synthesis, has so far been limited to reactions with strong acids (*e.g.* CF$_3$CO$_2$H). Carbon electrophiles have been reported to react only *via* 'abstraction'[2] [reaction type (b)]. We here report addition reactions of an alkyl halide with CO incorporation to selected cyclohexadienyl–Cr(CO)$_3$ intermediates. This investigation was prompted by our recent observation that sulphur stabilized carbanions add irreversibly to 1,4-dimethoxynaphthalene–Cr(CO)$_3$ **(1)** at the β position, whereas cyano stabilized carbanions and an ester enolate add reversibly and undergo rearrangement from the kinetic β to the thermodynamic α addition product.[3] This suggested the possibility of different behaviour of the intermediates resulting from the addition of the sulphur stabilized carbanions towards electrophiles. This proves to be the case.

Reaction (-78 to 0 °C, 5 h) of the cyclohexadienyl complex, prepared from [C$_{10}$H$_6$(OMe)$_2$]Cr(CO)$_3$ **(1)** and LiC(Me)S[CH$_2$]$_3$S, with MeI in tetrahydrofuran (THF)–hexamethylphosphoric triamide (HMPA) afforded after oxidation with iodine (-78 to 0 °C, 4 h) a single product in 76% yield to which we assign structure **(2b)**† on the basis of ^{1}H

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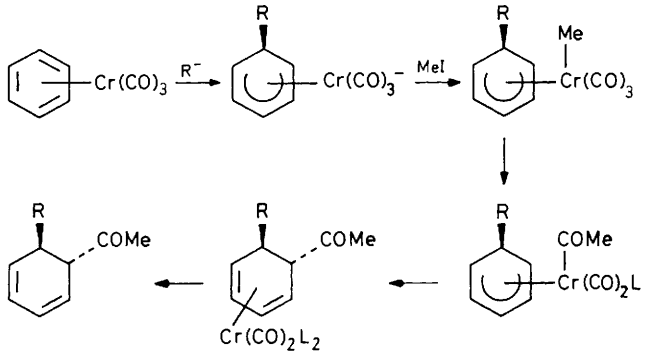
† The *trans* assignment is tentative; it is based on the known stereochemistry of nucleophilic attack on co-ordinated arenes (*exo*) (ref. 2), the requirement of an intermediate interacting with CO in the second step (*endo*), and finally by comparison with the established stereochemistry in an analogous reaction sequence with cyclohexadiene–Fe(CO)$_3$ (ref. 4). The coupling constant ($\leqslant$1 Hz) between the protons of the substituted carbon atoms in **(2a)** is consistent with but does not prove the *trans* structure.

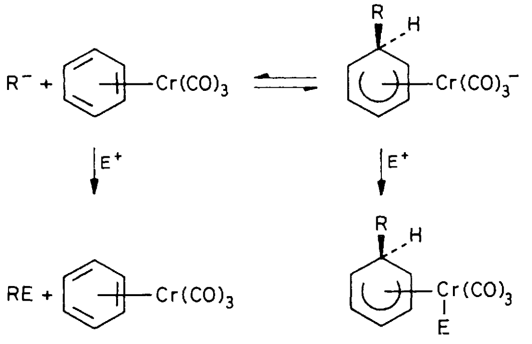


Scheme 1. L = THF or CO.

n.m.r.,‡ i.r., u.v., and mass spectroscopic analysis. Likewise, sequential treatment of the arene complexes (**3**) and (**5**) with reactive nucleophiles and MeI yield, after ligand displacement, the acetyldihydronaphthalene (**4**) and acetyl dienes (**6**),‡ respectively (Table 1).

CO incorporation is observed with or without external CO, although the reactions are cleaner and the yield is higher in the presence of CO during alkylation (see Table 1, entries 5 and 6). Addition of HMPA, known to suppress migratory insertion of CO in anionic complexes,[5] has no observable effect on the outcome of the reaction; *i.e.*, no simple alkyl transfer is observed. Furthermore, it has been noted previously that H$^+$ adds to yield the diene without carbonylation, suggesting a different mechanism for the above reactions to that recently reported for diene–Fe(CO)$_3$ complexes where H$^+$ adds to yield the respective aldehyde.[4] Scheme 1 outlines a mechanism consistent with these observations. Metal alkylation and rapid CO insertion are followed by reductive elimination and displacement of the diene by ligand substitution or oxidation.

In conclusion, the reactivity (towards electrophiles) of anionic cyclohexadienyl–Cr(CO)$_3$ complexes, formed by addition of carbon nucleophiles to arene–Cr(CO)$_3$ compounds, depends to a large extent on the nature of the nucleophile. It can be rationalized in terms of the equilibrium shown in Scheme 2.



Scheme 2

With the very reactive anions used in this study (derived from carbon acids of pK_a >29) addition is essentially irreversible and reaction with MeI follows a pattern typical of anionic carbonyl complexes.[6] Less reactive anions (*e.g.* nitrile stabilized carbanions and ester enolates) add reversibly and react with electrophiles *via* 'transfer' of the nucleophile.§ The borderline of change of reaction pattern and the scope of addition reactions of electrophiles are under investigation.

The reactions described in this communication involve formal addition of R–COMe across an arene π bond and present an interesting addition to the synthetically useful transformations of co-ordinated arenes.

We thank the Swiss National Science Foundation and the Foundation Xavier Givaudan for financial support of this work.

Received, 8th August 1983; Com. 1080

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‡ ^{1}H N.m.r. (in CDCl$_3$ at 360 MHz); compound (**2b**): δ 0.96 (s, 3H, CH$_3$), 1.90 (m, 1H, 5′-H β), 1.96 (s, 3H, COCH$_3$), 2.14 (m, 1H, 5′-H α), 2.68 (m, 2H, 2SCH β), 3.16 (m, 1H, SCH α), 3.28 (m, SCH α), 3.79 (d, 1H, *J* 6 Hz, 6-H), 3.81 (s, 3H, OCH$_3$), 3.85 (s, 3H, OCH$_3$), 4.66 (s, 1H, 5-H), 6.14 (dd, 1H, *J* 6, 10 Hz, 7-H), 6.75 and 6.79 (d, 1H, *J* 9 Hz, 2,3-H), 7.01 (d, 1H, *J* 10 Hz, 8-H); compound (**6b**): δ 1.28 (s, 3H, CH$_3$), 1.87 (m, 1 H, 5′-H β), 2.18 (m, 1H, 5′-H α), 2.27 (s, 3H, COCH$_3$), 2.55 (dt, 1H, *J* 4, 14 Hz, SCH β), 2.67 (dt, 1H, *J* 4, 14 Hz, SCH β), 2.98 (ddd, 1H, *J* 3, 11, 14 Hz, SCH α), 3.09 (ddd, 1H, *J* 3, 11, 14 Hz, SCH α), 3.76—3.83 (m, 2H, 1,2-H), 5.84 (m, 1H, vinyl H), 6.02 (m, 3H, vinyl H's).

§ Rapid equilibrium (Scheme 2) to explain the 'abstraction' of the nucleophile by electrophiles in this reaction was considered earlier but ruled out on the basis of slow anion exchange at room temperature (ref. 2). However, we have recently demonstrated conclusively the reversibility of the addition of stabilized anions to complex (**1**) at low temperatures (ref. 3).