42. *trans*-Disubstituted Cyclohexadienes *via* Sequential Addition of a Carbon Nucleophile and an Electrophile to (η^6-Benzene)tricarbonylchromium: Scope of Carbon Electrophiles

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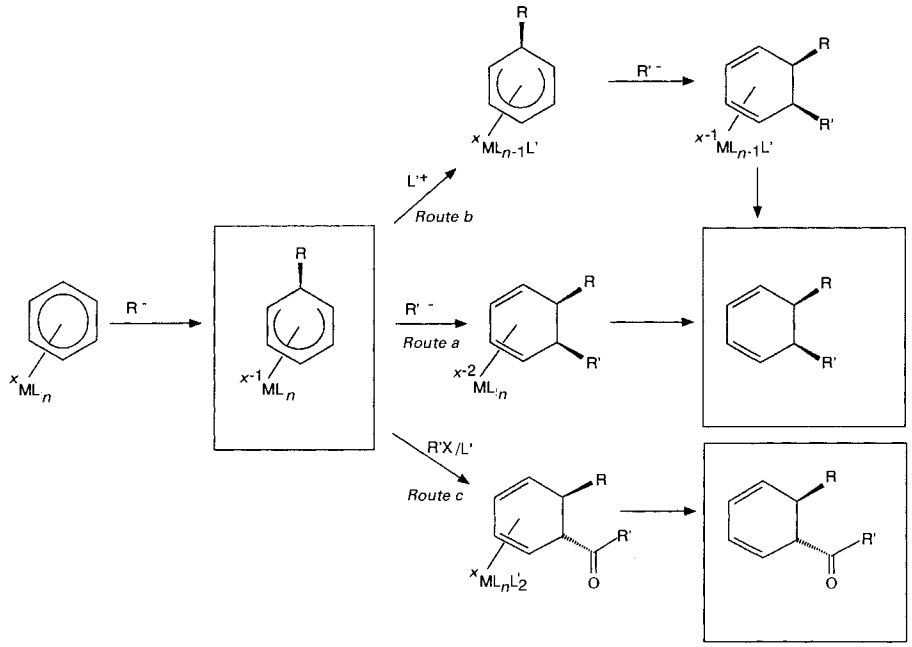
A regio- and stereoselective route from benzene to *trans*-disubstituted cyclohexadienes *via* complexation of the arene to the tricarbonylchromium group is reported. The key step involves an alkylation/carbonylation sequence of the anionic tricarbonyl (η^5-cyclohexadienyl)chromium complex (**3**) which is readily obtained by the addition of 2-lithio-2-methyldithiane (**2**) to (η^6-benzene)tricarbonylchromium (**1**; *cf. Scheme 6*). *In situ* reaction of **3** with alkyl halides (in THF, THF/HMPA, THF/DMPU), followed by oxidation (I_2, Ce(IV)) or ligand exchange (CO, Ph_3P, Et_3N) produced, with complete stereo- and regioselectivity, *trans*-5,6-disubstituted cyclohexadienes (15 examples). The cyclohexadiene substituent originating from the alkyl halide in all cases is an acyl group which shows that CO insertion into the metal–alkyl bond precedes reductive elimination to form the cyclohexadiene product. When, in the reaction of **3** with MeI, NH_3 was used to induce carbonylation und decomplexation, the isomerized, conjugated 1,4-cyclohexadiene **13** was obtained almost exclusively. The electrophile selectivity in the reactions with **3** is consistent with a nucleophilic, S_N2-like mechanism with a high preference for primary iodides. Chloride, ketone, and ester functions in the electrophile are unreactive and are tolerated; a primary alkyl iodide reacted selectively in the presence of a secondary iodide. In one case, the *trans*-configuration in a cyclohexadiene product **7** was demonstrated by the *Diels-Alder* reaction with maleic anhydride. High facial selectivity was observed in this reaction giving a single diastereoisomer resulting from *endo*-addition of the dienophile to the diene face carrying the acyl group. The anionic intermediate **3** was trapped with Ph_3SnCl, and an X-ray analysis of the resulting cyclohexadienyl [$Cr(CO)_3(R)$] complex **15** provides evidence for electrophile addition to the metal. In the solid state, the Ph_3Sn group in **15** is *trans*-configurated to the dithianyl substituent. The ready access to [Cr(arene)$(CO)_3$] complexes, the high selectivity of the reactions reported here and the mild decomplexation provide rapid access to cyclohexadienes that possess functionality and are attractive for further transformation.

Introduction. – Synthetic methods for conversion of arenes into functionalized dihydroarenes *via* regio- and stereoselective addition of substituents across an arene double bond are of interest, because they give direct access to substituted alicyclic rings starting from readily accessible precursors. The complexation of an arene to a transition metal offers several possibilities by which this transformation can be carried out *(cf. Scheme 1)*.

Stable π-arene complexes are known for most transition metals [1–3a] and in complexes in which the arene is bound to an electron-withdrawing group, the arene reactivity is effectively changed. In this class of compounds, the addition of a nucleophile to the arene is extensively studied, providing the most useful reactions for synthesis [4–6]. This addition usually takes place (addition of CO ligand can be competitive; for two examples, see [7]) highly stereoselectively to the *exo*-face of the arene, and numerous examples of isolated and characterized cyclohexadienyl complexes with a wide range of transition-

Scheme 1



metal fragments are known: *e.g.* with $Cr(CO)_3$ [8], $Fecp^+$ [9], $Fe(C_6H_6)^{2+}$ [10] [11], $Mn(CO)_3^+$ [12–15], $Ru(PR_3)X_2$ [16], $M(PR_3)_2X^+$ (Mu = Ru, Os) [17] and Mcp^{*2+} (M = Co, Rh, Ir) [18]. The degree of activation of the arene varies considerably from one fragment to the other [19] and the choice of the transition metal activating group is largely dictated by the accessibility of the complex, the type of nucleophile to be added, and by the further transformation which is to be carried out. For practical reasons, the $Cr(CO)_3$ group is by far the most frequently used in organic applications. The intermediate anionic cyclohexadienyl $Cr(CO)_3$ complexes can be generated, and, without isolation, transformed to the desired substituted arenes by facile oxidative decomplexation. Arene substitution *via* this nucleophile addition/oxidation sequence has been studied thoroughly and has found considerable application in synthesis [20]. Besides the neutral $Cr(CO)_3$ group, the cationic fragments $Mn(CO)_3^+$, $Fe(\eta^5\text{-}C_5H_5)^+$, and $Fe(\eta^6\text{—}C_6H_6)_2^{2+}$ have been receiving increasing attention recently.

Cyclohexadienes are, in principle, accessible *via* the addition of a second nucleophile to the cyclohexadienyl intermediate. Double hydride addition has been accomplished with $(C_6H_6)_2M^{2+}$ (M = Ru [21], Fe [10][1])), and with $[Mn(arene)(CO)_3]^+$ complexes [23] [24]) *(Scheme 1, Route a)*. This reductive synthesis of cyclohexa-1,3-dienes from arenes has been the subject of detailed mechanistic investigation [24].

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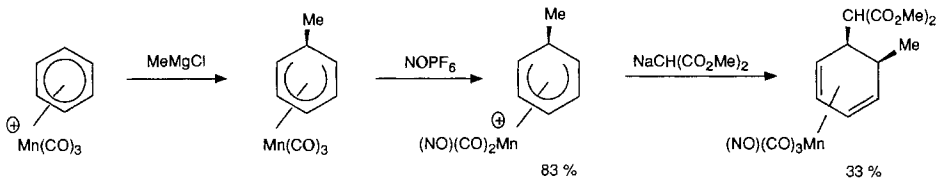
[1]) Nucleophilic addition of hydride and carbanions occur to the *exo*-face of the cyclohexadienyl ligand yielding $[Fe(\eta^6\text{—}C_6H_6)(\eta^4\text{—}C_6H_7R)]$ complexes. This result has been rationalized in terms of orbital control of the reaction [10]. Charge control in this reaction would predict nucleophilic attack to occur on the even (benzene), rather than the odd (cyclohexadienyl) ligand [22].

C–C Bond formation *via* this sequence is more difficult, and the consecutive addition, in a controlled and direct manner, of two different carbanions to a complexed arene has not been achieved to date. The requirement of an activating group that is sufficiently electrophilic to allow the addition of two nucleophiles (*e.g.* the fragments Fe^{2+} (benzene) [10] [11] [25] and $Co(cp)^{2+}$ [26]) imposes severe limitations on the reaction, and instead of addition, electron transfer from carbanions to the arene complexes is observed [10]. To circumvent this difficulty, an alternative stepwise addition of two nucleophiles [27] has been developed *(Scheme 1, Route b)*. This sequence, although necessitating an added intermediate-activation step, yields *cis*-disubstituted cyclohexadienes. Phosphorous, nitrogen, and hydride nucleophiles can be used in this reaction, but carbon nucleophiles usually again react to give electron-transfer products. Nevertheless, some successful examples of the addition of two C nucleophiles have been reported, and one is shown in *Scheme 2* [27b].

Scheme 2

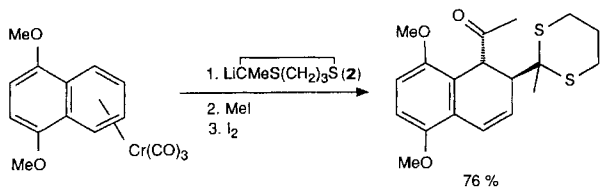


We have adopted a different approach and have discovered a sequential nucleophile/electrophile addition to $[Cr(arene)(CO)_3]$ complexes, yielding *trans*-disubstituted dihydroarenes *(Scheme 1, Route c)*. $[Cr(arene)(CO)_3]$ complexes are accessible in high yield with a wide range of arene substituents [2] [28–30]. Reactive carbanions add readily and often highly regioselectively to give anionic cyclohexadienyl complexes, and these can be reacted with strong acids to yield monosubstituted cyclohexadienes [20b] [31] [32]. First attempts to extend this sequence to carbon electrophiles failed, however, and led to the regeneration of the starting arene complexes [8]. In the light of recent results [33–35], this behavior may be ascribed to the reversibility of the addition. The α-nitrile-stabilized carbanions which were used in the earlier investigation [8] have been shown to dissociate particularly readily from cyclohexadienyl $Cr(CO)_3$ complexes, and high rates have been demonstrated at temperatures well below 0° [33b]. The addition of a C electrophile then merely displaces the equilibrium, until all of the anionic complex has been consumed. The reaction medium plays an important role in this reaction. The dissociation of the carbanion can be slowed down by several orders of magnitude by the appropriate choice of solvent (*e.g.* THF/HMPA instead of THF alone) and with reactive carbanions, irreversible addition occurs [33b].

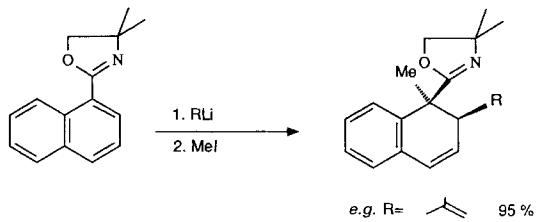
This prompted our reinvestigation of the feasibility of nucleophile/electrophile tandem additions to $[Cr(arene)(CO)_3]$ complexes. A preliminary report on nucleophile requirements for the double addition showed this approach to disubstituted dihydroarenes to be viable *(Scheme 3)* [36].

In parallel, *Meyers et al.* have developed the alternate nucleophile/electrophile double-addition sequence *(Scheme 4)*. The auxiliary in their work is a σ-bound oxazoline or an imine, and the product is either a di- or trisubstituted dihydroarene [37]. A highly

Scheme 3



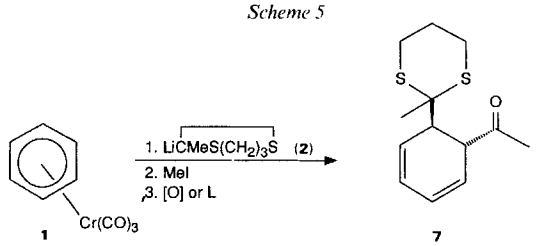
Scheme 4



diastereoselective asymmetric version *via* chiral oxazolines has also been achieved [38]. While very successful for naphthalenes, the method fails, when it is applied to benzene as lithiation rather than addition results [39].

As will be described below, a particularly useful and singular feature of the $Cr(CO)_3$-based method is that it can be applied to [Cr(benzene)$(CO)_3$] (**1**), thus giving direct access to *trans*-disubstituted cyclohexadienes. In the present study, we focus on the stereoselectivity of this tandem 1,2-addition to **1** and on the scope of the alkylation step with C electrophiles[2]). In all reactions described here, 2-lithio-2-methyldithiane (**2**) [41] is used as nucleophile *(Scheme 5)*.

Scheme 5



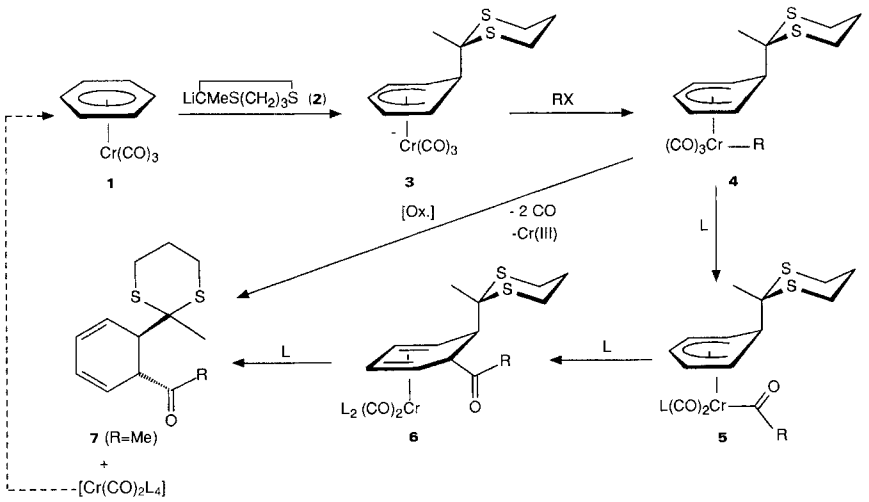
Results and Discussion. – Sequential reaction of complex **1** with nucleophile **2** (−78°/0°, 5 h) and MeI (−78°/0°, 5 h) in THF/HMPA 10:3 afforded, after oxidative decomplexation with I_2, the cyclohexadiene **7** in 63% yield as an single diastereoisomer *(Scheme 5)*.

trans-Configuration in cyclohexadiene **7** was initially assigned on the basis of mechanistic expectation of *exo*-addition of **2** to give the anionic cyclohexadienyl complex **3**, followed by metal alkylation to give **4**. The incorporation of CO in the cyclohexadiene

[2]) For preliminary reports of some results described here, see [40].

product supports this proposition and points to migratory CO insertion and acyl transfer by reductive elimination to the *syn*-face of the cyclohexadienyl moiety. Decomplexation then yields the *trans*-disubstituted cyclohexadiene *(Scheme 6)*.

Scheme 6

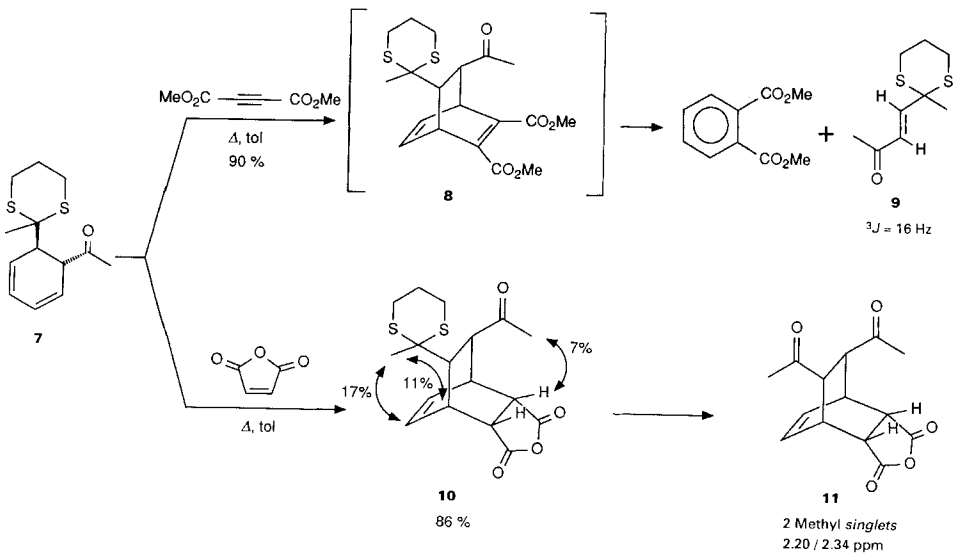


In a separate experiment carried out in THF, **3** was obtained as an oily product from the reaction of nucleophile **2** with [Cr(benzene)$(CO)_3$] (**1**). Slow crystallization from dioxane yielded a yellow crystalline solid. The structure of **3** was assigned on the basis of IR and ^{1}H-NMR spectral data. In the IR, the bands associated with the CO stretching modes are shifted to lower frequencies as expected in a negatively charged complex. The ^{1}H-NMR spectrum agrees with those of other cyclohexadienyl complexes [8–18]. We note here that the dithiane analogue has been described previously by *Semmelhack et al.* [8], and the mode of addition of the nucleophile in this complex has been shown to be *exo* by X-ray diffraction analysis.

A vicinal coupling constant of 3.8 Hz was found for the protons of the substituted C-atoms in **7**. While this is consistent with a *trans*-configuration of the two new C–C bonds in **7**, a more tangible proof was sought and obtained by two cycloaddition reactions *(Scheme 7)*.

Treatment of **7** with dimethyl acetylenedicarboxylate in toluene at 100° for 15 h did not give the expected bicyclic diene **8**. Under the reaction conditions, **8** apparently undergoes a *retro-Diels-Alder* reaction to yield a 1:1 mixture of dimethyl phthalate and (*E*)-vinyl ketone **9**. The (*E*)-configuration of **9** is indicated by the 16 Hz coupling between the vinylic H-atoms. When maleic anhydride was used as dienophile, the *Diels-Alder* reaction gave the bicyclic thioacetal **10** which was isolated in 86% yield as a crystalline solid. Structural assignment of **10** was accomplished on the basis of NOE measurements *(cf. Scheme 7)*. Hydrolysis of the dithiane moiety with *N*-chlorosuccinimide/$AgNO_3$ [42] afforded the unsymmetrical diketone **11**. The two distinct *singlets* of Me groups at 2.20 and 2.34 ppm in the ^{1}H-NMR spectrum of **11** establishes the s-*trans*-configuration of the

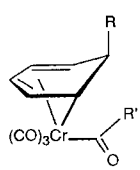
Scheme 7



substituents and lends support to the proposed mechanism for the formation of **7**. Although not critical to the above argument, the formation of a single isomer in the cycloaddition reaction is intriguing. The two faces of diene **7** bear a free and a masked Ac group. Cycloaddition occurs with complete face selectivity *anti* to the dithiane, *syn* to the Ac group. While this would be expected on steric grounds, the single example does not allow generalization on the basis of steric and/or electronic arguments.

Several points in the proposed mechanism *(Scheme 6)* merit comment. On addition of MeI, the initial product formed presumably is the methyl complex **4**. I_2 then prompts migratory CO insertion and reductive elimination before cleaving the diene–metal bond. There are ample precedents for strong acceleration of both CO insertion and reductive elimination reactions on metal oxidation [3b] [43] [44]. Also, reductive elimination of ketones from acyl alkyl transition-metal complexes is known to be a much faster reaction than the reductive coupling of two alkyl ligands to form alkanes[3]). Alkyl/acyl complexes are only rarely amenable to isolation [45], but are, as here, often postulated as intermediates in ketone-forming reactions, typical examples being the reaction of *Collman*'s reagent $Na_2[Fe(CO)_4]$ with alkyl halides to give ketones [46], and the reactions of CO with $[Ti(cp)_2Ph_2]$ [47], with $[NiR_2(2,2'\text{-bipyridine})]$ (R = Me, Et, Pr) [48], and with $[Cocp(PPh_3)Me_2]$ [49]. We attempted unsuccessfully to induce alkyl rather than acyl

[3]) The limiting resonance structure drawn here is helpful when considering the reactivity of the cyclohexadienyl complex.



migration. To avoid oxidation-induced carbonylation, the reaction mixture containing **3** and MeI was warmed to 50° under Ar. Besides much intractable decomposition material, a small amount of **7** was the only cyclohexadiene product isolated. The methylcyclohexadiene product **12** was notably absent. HMPA decreases the extent of ion pairing, and this is known to suppress migratory insertion of CO in anionic complexes [50]. The addition of this co-solvent might, therefore, have been expected to favor the formation of **12** rather than **7**, but in the reaction under investigation this was not the case.

The carbonylation/reductive elimination/decomplexation sequence can also be induced by the addition of an external ligand (L) to the reaction mixture *(cf. Scheme 6)*. N- and P-donor ligands as well as CO can be used, and complexes **5** and **6** are likely intermediates in this sequence. The results are listed in *Table 1*.

Table 1. *The Effect of Oxidation* vs. *Ligand Exchange in the Double Addition Reaction Shown in* Scheme 5

Entry	Ratio of THF/HMPA	Ligand added[a])	Oxidant	Yield [%] of **7**	*Entry*	Ratio of THF/HMPA	Ligand added[a])	Oxidant	Yield [%] of **7**
1	3:1	none	I_2	63	*5*	3:1	CO/Ph_3P[b])	none	89
2	3.1	CO	I_2	59	*6*	3:1	CO/Et_3N[b])	none	90
3	4:1	CO	Ce(VI)	56	*7*	3:1	CO/NH_3[b])	none	77[c])
4	3:1	Ph_3P	none	70	*8*	6:1	CO, 4 bar	none	88

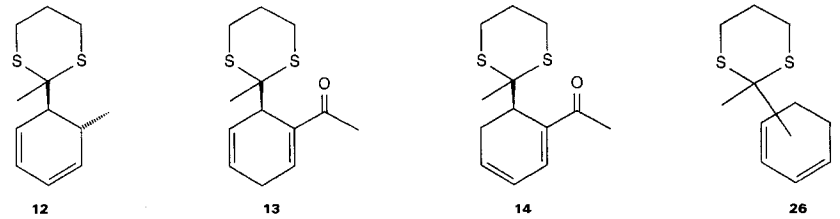
[a]) Large excess.
[b]) Ph_3P, Et_3N, NH_3 were added after a minimum of 5 h reaction time at 0°.
[c]) The product was a 11:1 mixture **13**/**14** (tentative).

In these reactions, the cyclohexadiene product is separated from the metal by ligand exchange, and, particularly with CO, the reaction is cleaner, the yield higher, and product isolation simpler than in the reactions with the oxidizing agents I_2 or Ce(IV). A further advantage over oxidation is the potential for recycling the organometallic fragment. Dienes are readily displaced from Cr(0) and carrying out the reaction under a CO atmosphere should yield $[Cr(CO)_6]$.

Although recycling of $[Cr(CO)_6]$ was not generally the aim in this study, in the reaction of **3** with 1 equiv. of ethyl triflate, attention was paid to this, and $[Cr(CO)_6]$ was isolated in 50% yield together with **7**, when the reaction was carried out under an atmosphere of CO. We note that $[Cr(CO)_6]$ has also been recovered from nucleophilic addition/protonation/ligand exchange reactions by *Rose* and coworkers [32].

Decomplexation under ambient pressure of CO is not very rapid, and we found it more convenient to place the reaction under 4 bar of CO directly after the addition of the electrophile and to isolate the product after a few hours at 20°. The presence of CO does not interfere with the alkylation step, but more nucleophilic ligands, *i.e.* phosphines or Et_3N, can be added only after metal alkylation is complete.

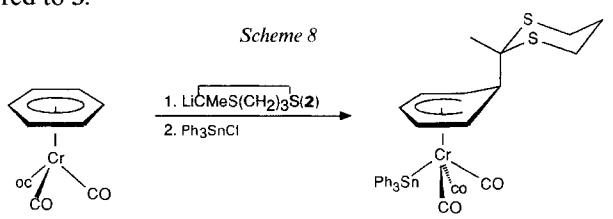
When the decomplexation was carried out with aqueous NH_3, product **13** accompanied by a small amount of isomer **14** (tentative) was isolated in 77% yield. Partial isomerization of **7** to **13** and **14** was also occasionally observed on chromatography, but with **7** and the other cyclohexadiene products described below, this can be completely suppressed by using mild decomplexation under neutral conditions (CO, 4 bar) and expeditious chromatographic purification over silica by flash chromatography [51].



12 13 14 26

The reaction of **3** with Ph_3SnCl yielded complex **15**, a stable and highly crystalline analogue of the proposed alkyl intermediate **4** *(Scheme 8)*. The ^{1}H-NMR signals of the cyclohexadienyl ligand in **15** are shifted downfield, and the C=O stretching frequencies in the IR spectrum are observed at higher wave numbers compared to the corresponding spectra of **3**. Both characteristics are in keeping with the reduced electron density at the metal in **15** compared to **3**.

Scheme 8



1 15

The four sets of ^{1}H-NMR resonances of the cyclohexadienyl attest to the pairwise equivalence of H–C(1) and H–C(5), and H–C(2) and H–C(4). No significant changes were observed on recording the spectrum in the temperature range −60 to 20°, and this points to either a rigid structure containing a plane of symmetry with the Ph_3Sn ligand eclipsed to either C(3) or C(6), or to a rapid rotation around the cyclohexadienyl–metal bond. As the barrier to rotation of the cyclohexadienyl ligand in related $[ML_3]$ complexes is in the range of 9–14 kcal/mol [52–54], the latter interpretation is more likely.

Structure of **15**. The X-ray diffraction analysis of **15** revealed the structure shown in the ORTEP diagrams in the *Figure*.

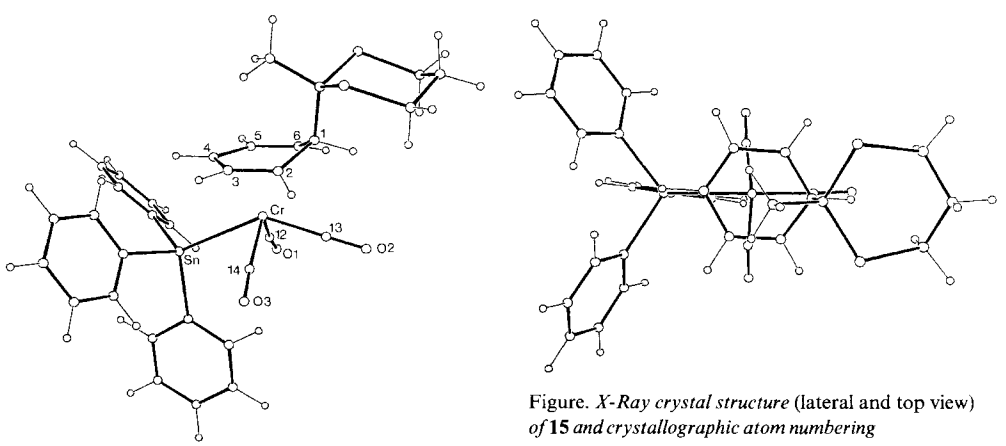


Figure. *X-Ray crystal structure* (lateral and top view) *of* **15** *and crystallographic atom numbering*

The structure shows the $[Cr(CO_3)_3(SnPh_3)]$ fragment in the solid state to be approximately symmetrically oriented with respect to a plane normal to and bisecting the cyclohexadienyl through C(4) and C(1) with the Ph_3Sn ligand *trans*-oriented to the dithianyl substituent. The five unsaturated C-atoms of the cyclohexadienyl ligand lie in a plane (maximum deviation 0.021 Å). The interplanar angle between the pentadienyl plane and the C(1)–C(2)–C(6) plane is 35.1°, in the range of typical values for cyclohexadienyl complexes [14]. Metal–ligand bond length are best discussed with reference to the anionic $\{\eta^5$-[6-(1,3-dithian-2-yl)cyclohexadienyl]$Cr(CO)_3\}$ complex **16** reported by *Semmelhack et al.* [8]. *Table 2* shows a comparison of selected distances of the two complexes. The

Table 2. *Selected Structural Data for Compounds* **15** *and* **16**[a])

	15	**16**[a])	**15**	**16**[a])	
Bond distances [Å]					
Cr···C(2)	2.278 (10)	2.244	Cr···C(5)	2.194 (10)	2.190
Cr···C(3)	2.187 (9)	2.189	Cr···C(6)	2.304 (9)	2.288
Cr···C(4)	2.179 (9)	2.179	Cr···plane(C(2)–C(6))	1.757 (5)	1.747
Cr–Sn	2.719 (2)	–	C(3)–C(4)	1.409 (15)	1.431
Cr–C(12)	1.869 (11)	1.839	C(4)–C(5)	1.411 (13)	1.416
Cr–C(13)	1.836 (10)	1.863	C(5)–C(6)	1.407 (15)	1.419
Cr–C(14)	1.856 (10)	1.737	C(7)–S(1)	1.827 (11)	1.811
C(1)–C(2)	1.507 (12)	1.507	C(7)–S(2)	1.814 (9)	1.817
C(1)–C(6)	1.507 (14)	1.478	C(12)–O(1)	1.152 (13)	1.147
C(1)–C(7)	1.553 (14)	1.530	C(13)–O(2)	1.157 (12)	1.134
C(2)–C(3)	1.400 (14)	1.373	C(4)–O(3)	1.152 (13)	1.220
Bond angles [°]					
C(2)–C(1)–C(6)	104.0 (8)	102.0	C(3)–C(4)–C(5)	117.6 (9)	119.0
C(1)–C(2)–C(3)	120.5 (9)	123.0	C(4)–C(5)–C(6)	119.9 (9)	118.1
C(2)–C(3)–C(4)	121.0 (8)	117.3	C(5)–C(6)–C(1)	121.7 (7)	121.7
Orientation of $Cr(CO)_3$ [°][b])					
C(4)–P–Cr–C(13)	175.6(6)	– 177.7			

[a]) See [8]; the crystal structure of **16** being constituted of 2 molecules by asymmetric unit, the mean geometrical values are reported in this table.

[b]) P is calculated as the centroid of C(2)-, C(3)-, C(4)-, C(5)-, and C(6)-atoms.

distance between the Cr-atom and the pentadienyl-ring plane is 1.757(5) Å in **15** and 1.747 Å in **16**. The mean of the Cr–CO distances in **15** (1.854 Å) is slightly longer than that in **16** (1.813 Å). These changes can be attributed to the reduced electron density available on the Cr for π-back-bonding to the ligands. As in other cyclohexadienyl complexes, two sets of Cr–C(pentadienyl) distances can be identified in **15**. The distances between the Cr-atom and C(3), C(4), and C(5) average 2.19(1) Å and those to C(2) and C(6) average 2.29(2) Å.

Scheme 9 and *Table 3* display the results of a series of reactions with different alkyl halides. All of these reactions were carried out as 'one-pot' procedures without isolation of **3** or of any of the other intermediates. In all cases, the acyl transfer occurred highly regioselectively to yield the products in which formally two substituents are added in a *trans*-stereoselective manner across an arene double bond. The acyl transfer involved in our sequence is most probably irreversible. This contrasts with the protonation of anionic

Scheme 9

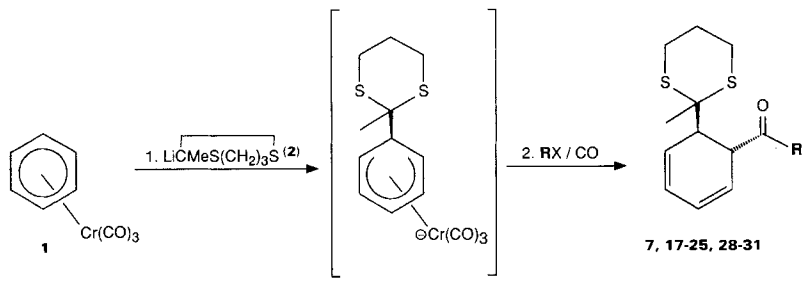
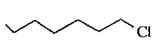
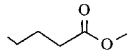
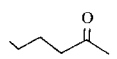
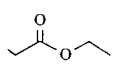
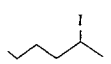


Table 3. *Scope of Electrophiles in the Sequential Addition of 2-Lithio-2-methyldithiane* (**2**) *and Alkyl Halides to [Cr(benzene)(CO)$_3$]* (**1**; *Scheme 9*)

Entry	R	X	Product No.	Yield [%]	*Entry*	R	X	Product No.	Yield [%]
1	Me	I	**7**	89	*12*		I	**25**	51
2	Et	I	**17**	81	*13*		MsO	**25**	35
3	Et	Br	**17**	79[a])					
4	Et	TfO	**17**	82	*14*		I	**27**	66
5		Cl	**18**	25					
6		Br	**18**	94	*15*		I	**28**	70
7		Br	**19**	67	*16*		I	**29**	64
8		Br	**20**	6[b])					
9		Br	**21**	17[c])	*17*		Br	**30**	27
10		I	**21**	90					
11		I	**23**	51	*18*		I	**31**	57

[a]) After heating at 50° for 2 h. Yield at 20° was 28%.
[b]) After heating at 80° for 4 h.
[c]) After heating at 70° for 4 h.

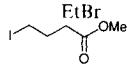
[Cr(CO)$_3$cyclohexadienyl] complexes, usually yielding mixtures of isomeric cyclohexadienes **26**, ascribed to the readily reversible H migration between the metal center and the cyclohexadienyl ligand [8].

Primary iodides and triflates as well as allyl and benzyl bromide react readily in the temperature range of −20 to +20° as indicated by a color change from pale yellow to a deeper yellow-brown (cognac). The addition of EtI proceeded more slowly than did MeI, and a big drop in reactivity was found in going from EtI to EtBr (*Table 3, Entries 2* and *3*). With the latter, and after 40 h at 20°, product **17** was obtained in low yield (28%), but warming to 50° for 2 h raised the yield to 79%. A similar situation was observed with allylic halides. While allyl bromide added efficiently (94% yield of **18**), allyl chloride led to at best a 25% yield at 20° (*Table 3, Entries 5* and *6*). i-PrI and i-PrOMs were less suitable substrates, and yields of **25** were considerably lower than with primary substrates (*Entries 12* and *13*). Isomeric mixtures of (methyldithianyl)-cyclohexadienes **26** were

isolated as major secondary products in several reactions. This could be attributed to the basicity of **3**, a feature common to complexes containing the metal in a low oxidation state. Alternatively, secondary substrates may not react efficiently, and **26** results from protonation of **3** during workup of the reaction mixture. At this stage, we have not attempted to distinguish between the two reaction paths, *e.g.* by analysis for alkene.

We had found previously that the dipolar aprotic solvent HMPA favors the irreversible addition of C nucleophiles to [Cr(arene)(CO)$_3$] complexes [33b]. Its positive and often essential role in the double addition reactions is noted here. While the reactions reported in this paper generally were carried out with HMPA as co-solvent, first results *(Table 4)* indicate that, as in other reactions [55] [56], HMPA can be replaced by the safer 3,4,5,6-tetrahydro-1,3-dimethyl-2(1*H*)-pyrimidinon (DMPU) [57].

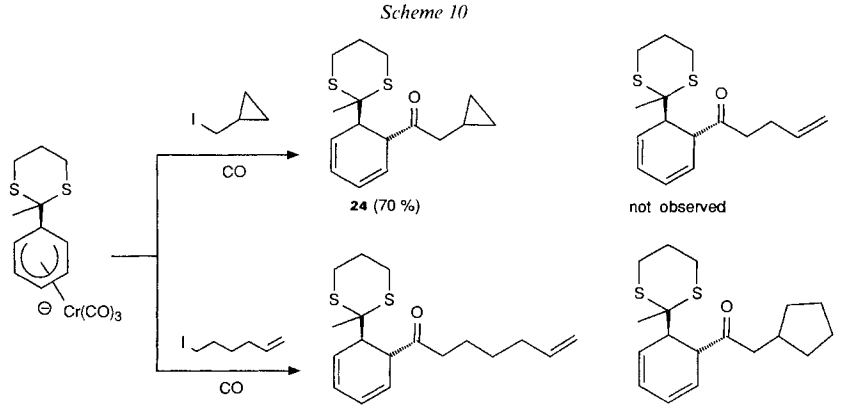
Table 4. *The Effect of HMPA and DMPU on Product Yield*

Entry	Electrophile	THF	Yield [%] in[a])		
			THF/HMPA 5:1	THF/DMPU 5:1	Product
1	MeI	75	88	82	**7**
2	EtBr	traces	28	22	**17**
3		20	62	45	**28**

[a]) Reactions carried out in parallel under identical conditions (20°/40 h/4 bar CO) except for the solvent.

The electrophile selectivity in these reactions follows the order expected for an S_N2-type reaction. The preference of **3** for primary iodides over bromides is much larger than that usually found in S_N2 reactions of organic-reaction partners. There is substantial precedence for this in organometallic chemistry, and it most likely reflects the 'softness' of transition-metal nucleophiles [58]. An S_N2-type mechanism is also consistent with the high efficiency of the allyl-bromide addition. No competing allyl coupling was observed which would have been an expected side product of an electron-transfer mechanism. Finally, strongly supporting evidence stems from the results of the reactions with 6-iodohex-1-ene and (cyclopropyl)methyl iodide *(Scheme 10)*.

Scheme 10



Both substrates would be expected to undergo very fast rearrangement if free radical intermediates were generated during the alkylation [58–61]. The only products isolated in our reactions contained the cyclopropyl, respectively the olefinic group intact (*cf.* **22** and **24**). We note, however, that in the absence of stereochemical verification (inversion at the C-center) and kinetic measurements, to which this sequence is not readily amenable, the evidence for a nucleophilic mechanism must be considered tentative.

A number of electrophiles which were tried in this reaction gave only very low yields of isolated cyclohexadiene or none at all. Thus, the yield with 1-bromo-3-methylbut-2-ene to give **20** was 6%, and reactions with the following electrophiles failed to give disubstituted cyclohexadienes: AcCl, PhCOCl, *N*-methoxy-*N*-methylacetamide [62], methyl cyanoformate [63], PhI, propanal, propene oxide, and cyclopent-2-enone.

The range of electrophiles that add efficiently is, thus, very limited, but the high selectivity can be used to great advantage in reactions with bifunctional reagents. The examples in *Entries 14–18* in *Table 3* demonstrate tolerance of primary chloride, of ester, and ketone groups as well as high selectivity of primary over secondary alkyl iodide.

The results reported here demonstrate the practicality of the *trans*-stereoselective introduction of two C substituents to a benzene double bond. The ready access to [(Cr(arene)$(CO)_3$] complexes, the high selectivity of the reactions and the mild decomplexation provide rapid access to cyclohexadienes that possess functionality and are attractive for further product transformation. We will report in due time on further mechanistic studies, on enantioselective product formation, and on synthetic applications of this sequence.

Generous financial support of this work by the *Swiss National Science Foundation* (grants 2.865-0.85 and 2.639-0.87) is gratefully acknowledged. We also thank Mr. *J.P. Saulnier*, Mr. *A. Pinto*, and Mrs. *D. Clément* for NMR and MS measurements.

Experimental Part

1. General. – All manipulations involving organometallic compounds were carried out under an atmosphere of purified N_2 or Ar and using an inert gas/vacuum double manifold and standard *Schlenk* techniques. [$Cr(CO)_3$-(benzene)] was obtained by thermolysis of [$Cr(CO)_6$] (*Pressure Chemical Company* or *Strem Chemicals*) using the method described by *Mahaffy* and *Pauson* [28]. THF was distilled from 'sodium-benzophenone ketyl' immediately prior to use. Toluene was refluxed for 4 h over Na before distillation. Alkanes were distilled from CaH_2. Hexamethylphosphortriamide (HMPA) *(Fluka)* was stirred with CaH_2 for 15 h at 60° before distillation under a reduced atmosphere (10 mm Hg) of N_2. 3,4,5,6-Tetrahydro-1,3-dimethyl-2(1*H*)-pyrimidinon (DMPU, *Fluka*) was distilled over BaO. (D_6)Benzene was vacuum-transferred after stirring with CaH_2. BuLi *(Fluka)* was titrated before use according to the method of *Gilman* and *Cartledge* [64]. 2-Methyl-1,3-dithiane *(Fluka)* was vacuum-transferred and stored under N_2. MeI, EtI, EtBr, allyl bromide, and i-PrI were obtained from *Fluka* and distilled over P_2O_5 before use. 1-Bromo-3-methylbut-2-ene [65], 4-iodobut-1-ene [66], 6-iodohex-1-ene [66], (cyclopropyl)methyl iodide [67], 1-chloro-6-iodohexane [68], methyl 4-iodobutyrate [69], 5-iodopentan-2-one [70], 1,4-diiodopentane [71], and (cyclohexyl)methyl iodide [67] were prepared according to the methods given in the references. Gas-liquid chromatography (GLC) was carried out on a *Perkin-Elmer-900* spectrometer with flame ionization detector by using a glass column packed with *Chromosorb W/OV 225* (10%). Anal. and prep. TLC were carried out using *Merck* silica gel *60* F_{254}. Column chromatography (CC) was carried out using the flash method described by *Still et al.* [51]. M.p. were determined on a *Büchi 510* apparatus and are not corrected. IR spectra were recorded on a *Perkin-Elmer-681* grating spectrometer or a *Mattson Instruments Polaris Fourier*-transform spectrometer by using NaCl soln. cells. ^1H- and ^{13}C-NMR spectra were recorded on a *Bruker-WM-360* spectrometer (^1H at 360 MHz, ^2H at 55.29 MHz, and ^{13}C at 90.6 MHz) and a *Varian-XL-200* spectrometer (^1H at 200 MHz, ^{13}C at 50.3 MHz). Chemical shifts (δ) are given in ppm relative to Me_4Si. EI-MS (70 eV) were obtained on a *Varian-CH-4* or *SM-1* spectrometer, relative intensities are given in parenthesis. High-resolution (HR) MS were

measured on a *VG* anal. *7070E* instrument (data system 11250, resolution 7000). Elemental analyses were performed by *H. Eder*, Service de Microchimie, Institut de Chimie Pharmaceutique, Université de Genève.

2. General Procedure for the Preparation of Tricarbonyl{η^5-[6-(2-methyl-1,3-dithian-2-yl)cyclohexadienyl]}chromium(0) Lithium Salt (3) *in situ* for Preparative Experiments. – Following the procedure of *Seebach* and *Corey* [41], a soln. of 2-methyl-1,3-dithianelithium was prepared by dropwise addition of BuLi (1.370 ml of a 1.61N soln. in hexane, 2.2 mmol) to a soln. of 2-methyl-1,3-dithiane (0.270 ml, 2.2 mmol) in 20 ml of THF at −78°. After stirring between −30 and −20° for 2 h, the *Schlenk*-reaction vessel was cooled to −78°, and [Cr(benzene)$(CO)_3$] (**1**) (428 mg, 2 mmol) was added in one portion *via* a solid addition tube. When required, HMPA or DMPU was added dropwise at this stage. The mixture was stirred at 0° for 4 h before recooling and reaction with the electrophiles described below.

Isolation of the Complex **3**. The soln. of **3** was prepared as described and then stripped of volatiles at a pressure of $5 \cdot 10^{-2}$ mbar/5 h. Towards the end of the evaporation, the ice-bath was replaced by a water bath of 40°. The dark yellow solid was taken up in 45 ml of dioxane at 40°. On slow cooling to 20°, **3** precipitated as a yellow powdery solid which was separated after 18 h and washed with 3 × 10 ml of pentane. IR: 1900*s*, 1800*s*, 1720*s*. ^{1}H-NMR (360 MHz, (D_6)DMSO): 1.07 (*s*, 3 H); 1.70–1.78 (*m*, 2 H–C(5′)); 2.56–2.70 (*m*, 2 H–C(4′), 2 H–C(6′), H–C(1), H–C(5)); 3.05 (br. *t*, *J* = 2.5, H–C(6)); 4.55 (br. *t*, *J* = 3, H–C(2), H–C(4)); 4.82 (br. *t*, *J* = 3, H–C(3)).

3. Reactions of 3 with MeI. – a) *N_2 Atmosphere: Oxidation with I_2.* Starting with 1.5 mmol of **1**, a soln. of **3** in THF/HMPA (10 ml : 3 ml) was prepared as described above. MeI (0.250 ml) was added to the pale yellow soln. at −78°. After stirring for 5 h at 0°, the now ochre colored soln. was recooled to −78°, treated with 2 g of I_2 in 10 ml of THF, slowly warmed to 0°, and left at that temp. for *ca.* 4 h. The mixture was concentrated *in vacuo*, the crude product taken up in Et_2O (40 ml) and washed sequentially with aq. $NaHSO_3$ soln. (10%, 10 ml), 1N HCl (3 × 10 ml), aq. $NaHCO_3$ soln. (sat., 10 ml), H_2O (2 × 10 ml), and aq. NaCl soln. (sat., 10 ml). The org. phase was dried ($MgSO_4$), and Et_2O was removed in a rotavapor. Chromatography on silica gel (hexane/toluene 1:1) of the crude product yielded 242 mg (63%) of **7** as an oil.

1-[6-(2-Methyl-1,3-dithian-2-yl)cyclohexa-2,4-dien-1-yl]ethanone (**7**). UV (cyclohexane): 268 (41600), 208 (50000). IR (film): 3039*m*, 2965*m*, 2920*m*, 2905*m*, 2825*m*, 1707*s*, 1585*w*, 1435*m*, 1420*s*, 1368*m*, 1350*s*, 1310*m*, 1275*m*, 1230*m*, 1175*s*, 1122*m*, 1110*m*, 1065*m*, 983*m*, 900*m*, 710*s*. ^{1}H-NMR ($CDCl_3$): 1.28 (*s*, CH_3); 1.80–1.93 (*m*, H–C(5″)); 2.03–2.13 (*m*, H–C(5″)); 2.27 (*s*, $COCH_3$); 2.55 (*dt*, *J* = 4, 14, 1 H, SCH_2); 2.67 (*dt*, *J* = 4, 14, 1 H, SCH_2); 2.98 (*ddd*, *J* = 3, 11, 15, 1 H, SCH_2); 3.09 (*ddd*, *J* = 3, 11, 15, 1 H, SCH_2); 3.74–3.80 (*m*, 1 allylic H); 3.82–3.85 (*m*, 1 allylic H); 5.82–5.88 (*m*, 1 vinylic H); 5.96–6.08 (*m*, 3 vinylic H). MS: 133 (100), 59 (11). Anal. calc. for $C_{13}H_{18}S_2O$ (254.40): C 61.38, H 7.13; found: C 61.69, H 7.39.

b) *N_2 Atmosphere: Reaction with Ph_3P.* The reaction was carried out as described in *Sect. 3a*, but instead of I_2, a soln. of Ph_3P (2 g, 7.6 mmol) in 10 ml of THF was added and the mixture stirred at 0° overnight. Workup as described, but foregoing washing with aq. $NaHSO_3$ soln., yielded, after chromatography, 266 mg (70%) of **7**.

c) *CO Atmosphere: Reaction with Ph_3P.* As described before, a soln. of 1.5 mmol of **3** in THF/HMPA was prepared and treated with MeI at −78°. The N_2 atmosphere was then removed by a freeze/pump cycle, and the reaction mixture was placed under an atmosphere of CO. After stirring for 5 h at 0° and recooling to −78°, a soln. of Ph_3P (2 g, 7.6 mmol) in THF (10 ml) was added, and the mixture was left overnight at 0°. Workup followed by CC yielded 340 mg (89%) of **7**.

d) *CO Atmosphere: Reaction with Et_3N.* Proceeding exactly as described in *Sect. 3c*, but adding, instead of Ph_3P, NEt_3 (2 ml) yielded 341 mg (89%) of **7**.

e) *CO Atmosphere: Reaction with NH_3.* The reaction was carried out as described in 3a. After stirring overnight at 0°, the mixture was poured on conc. NH_3 and stirred for 3 h before extraction with Et_2O. Chromatography of the crude product yielded 292 mg (77%) of a mixture **13**/**14** (tentative) in the ratio (^{1}H-NMR) of 11:1. Crystallization from Et_2O/hexane yielded pure **13**.

1-[6-(2-Methyl-1,3-dithian-2-yl)cyclohexa-1,4-dien-1-yl]ethanone (**13**). M.p. 112–115°. IR (CH_2Cl_2): 3040*m*, 2980*w*, 2930*m*, 2910*m*, 1672*s*, 1660*s*, 1625*w*, 1415*m*, 1370*m*, 1350*m*, 1290*w*, 1240*s*, 1070*m*, 975*m*, 940*m*, 905*m*, 850*w*. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.23 (*s*, CH_3); 1.76–1.90 (*m*, H–C(5″)); 2.04–2.14 (*m*, H–C(5″)); 2.39 (*s*, $COCH_3$); 2.40–2.50 (*m*, 1 H, SCH_2); 2.60–2.67 (*m*, 1 H, SCH_2); 2.78–2.86 (*m*, 2 H–C(3)); 2.98–3.16 (*m*, SCH_2); 4.41 (*dd*, *J* = 4,7, H–C(6′)); 5.92–5.98 (*m*, 1 vinylic H); 6.05–6.14 (*m*, 1 vinylic H); 6.70–6.75 (*m*, 1 vinylic H). MS: 43 (22), 59 (26), 133 (100).

f) *4 Bars CO*. The reaction was carried out in a heavy wall 40 ml *Schlenk* tube fitted with a 8-mm O-ring tap (*Youngs*) and an adapter with a small pressure gage. As described before, a soln. of **3** (1 mmol) in THF/HMPA (10 ml : 1.7 ml) was prepared. The mixture was frozen (N_2 liq. bath), and an excess of MeI (0.6 ml) was added *via* syringe. After a freeze/pump cycle, 4.5 bar CO was pressed onto the mixture, and the magnetically stirred mixture

left to warm up to ambient temp. overnight. Excess CO was vented, Et_2O (50 ml) was added and the soln. washed sequentially with 1N HCl (3 × 10 ml), aq. $NaHCO_3$ soln. (sat., 10 ml), H_2O (2 × 10 ml), and aq. NaCl soln. (sat., 10 ml). Chromatography on silica gel (hexane/toluene, 1:1) of the crude product obtained after drying and solvent removal yielded 224 mg (88%) of **7**. This general procedure was used with the range of C electrophiles described in *Sect. 6*.

Analogous reactions were carried out with the following modifications of the above procedure: *i*) medium THF (no HMPA), decomplexation for 40 h (4.4 bar CO): 75% yield of **7**. *ii*) Medium THF/DMPU (5:1), decomplexation for 44 h (4 bar CO): 82% yield of **7**.

4. *Diels-Alder* Reactions of 7 with Dimethyl Acetylenedicarboxylate and Maleic Anhydride. – a) *Dimethyl acetylenedicarboxylate*. A soln. of **7** (40 mg, 0.157 mmol) and dimethyl acetylenedicarboxylate (0.06 ml, 0.48 mmol) in toluene (0.5 ml) was degassed *via* a freeze/thaw cycle and then heated in a closed tube at 110° for 14 h. Chromatography in a pipette over silica gel (hexane/Et_2O 10:1) yielded 58 mg (90%) of a product which was a 1:1 mixture of dimethyl phthalate and **9** (^{1}H-NMR).

4-(2-Methyl-1,3-dithian-2-yl)but-3-en-2-one (**9**). ^{1}H-NMR ($CDCl_3$, 360 MHz): 1.61 (*s*, CH_3); 1.78–1.92 (*m*, H–C(5′)); 2.02–2.12 (*m*, H–C(5′)); 2.32 (*s*, $COCH_3$); 2.64–2.74 (*m*, 2 H, 2 SCH_2); 2.84–2.94 (*m*, 2 H, 2 SCH_2); 6.37 (*d*, *J* = 16, 1 H, CH=CH); 6.85 (*d*, *J* = 16, 1 H, CH=CH).

b) *Maleic Anhydride*. A soln. of **7** (100 mg, 0.42 mmol) and maleic anhydride (70 mg, 0.66 mmol) in toluene (1.5 ml) was degassed and then heated in a closed tube at 110° for 21 h. The mixture was concentrated, dissolved in CH_2Cl_2, filtered, concentrated (1 ml) with heating, and then diluted with Et_2O (2 ml). Upon cooling, crystallization occurred, and the solid was filtered, washed Et_2O, and dried to give anal. pure **10** (130 mg, 86%).

endo-*8-Acetyl-7-(2-methyl-1,3-dithian-2-yl)bicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Anhydride* (**10**). M.p. 223–224° (CH_2Cl_2/Et_2O). IR ($CHCl_3$): 3020*w*, 1870*w*, 1785*s*, 1710*m*, 1085*m*, 925*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.20 (*s*, CH_3); 1.70–1.88 (*m*, H–C(5′)); 1.93–2.10 (*m*, H–C(5′)); 2.38 (*s*, $COCH_3$); 2.44–2.72 (*m*, 3 H (dithian), H–C(1)); 2.86–3.10 (*m*, 1 H (dithian), H–C(2)); 3.15 (*dd*, *J* = 3, 9, H–C(5)); 3.24–3.34 (*m*, H–C(6), H–C(4)); 3.70–3.77 (*m*, H–C(3)); 6.26–6.39 (*m*, C*H*=C*H*). MS: 52 (32), 133 (100), 211 (33), 235 (21), 278 (7), 309 (5). HR-MS: calc. for $C_{17}H_{20}O_4S_2$: 352.0802; found: 352.0786. Anal. calc. for $C_{17}H_{20}O_4S_2$: C 57.93, H 5.72; found: C 57.86, H 5.72.

Hydrolysis of **10** *to Yield* **11**. To a soln. of 50 mg (0.14 mmol) of **10** (50 mg, 0.14 mmol), *N*-chlorosuccinimide (82 mg, 0.61 mmol), and collidine (172 mg, 0.19 ml, 1.42 mmol) in MeCN/H_2O 4:1 (4 ml) at 20° was added $AgNO_3$ (108 mg, 0.63 mmol). A white solid precipitated immediately, and the mixture was stirred for 0.5 h. At this time, the mixture was diluted with 10% aq. $Na_2S_2O_3$ and extracted with CH_2Cl_2 (3 × 10 ml). The combined org. extracts were dried ($MgSO_4$) and concentrated to give a gummy solid. This material was filtered through silica gel (CH_2Cl_2), and the residue was triturated with Et_2O (3 × 1 ml) to give **11** (20 mg, 54%) as an anal. pure white solid.

endo-*7,8-s*-trans-*Diacetylbicyclo[2.2.2]oct-2-ene-5,6-dicarboxylic Anhydride* (**11**). M.p. 149–150° (CH_2Cl_2/Et_2O). IR ($CHCl_3$): 3020*m*, 2930*w*, 1870*w*, 1785v*w*, 1715*s*, 1360*m*, 1225*m*, 1085*m*, 925*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 2.20 (*s*, 3 H); 2.34 (*s*, 3 H); 3.12 (*dd*, *J* = 3.5, 9, 1 H); 3.22 (*dd*, *J* = 2, 5.5, 1 H); 3.27 (*dd*, *J* = 2.5, 5.5, 1 H); 3.34 (*dd*, *J* = 3,9, 1 H); 3.52–3.58 (*m*, 1 H); 3.69–3.74 (*m*, 1 H); 6.25 (br. *t*, *J* = 8, 1 H); 6.46 (br. *t*, *J* = 7, 1 H). MS: 78 (100), 121 (93), 219 (46), 262 (3). HR-MS: calc. for $C_{14}H_{14}O_5$: 262.0841; found: 262.0832. Anal. calc. for $C_{14}H_{14}O_5$: C 64.12, H 5.38; found: C 63.84, H 5.37.

5. Reaction of 7 with Ph_3SnCl. Isolation and X-Ray Structure of the Ph_3Sn Adduct 15. – Ph_3SnCl (578 mg, 1.5 mmol) was added *via* a solid transfer tube to a soln. of **3** (1 mmol) in THF (10 ml) at −78°, prepared as described in *Sect. 2*. The mixture was stirred, and over a period of 1 h, the temp. was raised to 20°. Volatiles were then removed *in vacuo*, the yellow residue washed with pentane, taken up in THF, and filtered over *Celite*. The soln. was concentrated to *ca.* 3 ml and hexane was added. On cooling first to 4°, then to −30°, **15** (495 mg, 71%) precipitated as fine yellow needles.

Tricarbonyl{η^5-[6(2-methyl-1,3-dithian-2-yl)cyclohexadienyl}(triphenylstannyl)chromium (**15**). M.p. 190–192° (dec.). IR (THF): 1987*s*, 1982*s*, 1930*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.53 (*s*, CH_3); 1.68–2.14 (*m*, 2 H); 2.54–2.89 (*m*, 2 H, 2 SCH_2); 3.52–3.61 (*t*, H–C(6)); 3.79–3.89 (*t*, H–C(1), H–C(5)); 4.27–4.37 (*t*, H–C(2), H–C(4)); 5.96–6.05 (*t*, H–C(3)); 7.31 (*m*, 10 arom. H); 7.55–7.64 (*m*, arom. H). Anal. calc. for $C_{32}H_{30}O_3CrSn$: C 55.11, H 4.34; found: C 55.19, H 4.49.

Crystallographic Data of **15**. Cell parameters and reflection intensities were measured at r.t. on a *Nonius CAD4* diffractometer with graphite monochromated Mo*Kα* radiation. A summary of crystal data, intensity measurements, and structure refinement is given in *Table 5*, and selected geometrical parameters are reported in *Table 2*. The structure was solved by direct methods (MULTAN-87) [72] and refined by least-square analysis with X-TAL program [73]. Crystallographic data have been deposited with the *Cambridge Crystallographic Data Center*, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.

Table 5. *Summary of Crystal Data, Intensity Measurement, and Structure Refinement for Complex* **15**

Formula	$C_{32}H_{30}CrO_3S_2Sn$	μ [mm^{-1}]	1.36
Molecular weight	697.4	$(\sin\theta/\lambda)_{max}$(Å^{-1})	0.51
Crystal system	Monoclinic	No. of measured reflections	3582
Space group	$P2_1/c$	No. of observed reflections	2532
Crystal size (mm)	0.20 × 0.20 × 0.45	Criterion for observed	$\|F_o\| > 4\sigma(F_o)$
a [Å]	19.604(2)	No. of parameters	352
b [Å]	10.4201(7)	Refinement (on F)	full-matrix
c [Å]	15.107(5)	Weighting scheme	$\omega = 1/\sigma^2(F)$
β [°]	104.56(1)	H-atoms	calculated
V [Å^3]	2986.9(11)	Max. and average Δ/σ	0.316, 0.046
Z	4	Max. and min. $\Delta\rho$ [eÅ^{-3}]	0.74, −0.33
D_c [g · cm^{-3}]	1.55	S	1.51
F_{000}	1408	R, ωR (%)	5.1, 4.0

6. Reactions of 3 with Other C Electrophiles. – a) *EtI/CO/Ph$_3$P.* The procedure and quantities used were identical to those described in *Sect. 3c* except for the electrophile which was EtI (0.300 ml). Chromatography on silica gel (toluene/hexane 1:1) gave 325 mg (81%) of **15** as an oil.

1-[6-(2-Methyl-1,3-dithian-2-yl)cyclohexa-2,4-dien-1-yl]propan-1-one (**17**). UV (cyclohexane): 267 (44000), 206 (58000). IR (CH_2Cl_2): 3020*m*, 2980*m*, 2940*m*, 2925*m*, 2905*m*, 1710*s*, 1460*m*, 1445*m*, 1425*s*, 1370*m*, 1345*s*, 1315*m*, 1110*m*, 1070*m*, 940*m*, 910*m*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 1.08 (*t*, J = 7, CH_3); 1.30 (*s*, CH_3); 1.80–1.92 (*m*, H–C(5″)); 2.04–2.13 (*m*, H–C(5″)); 2.50–2.74 (*m*, 4 H, 2 SCH_2, CH_2CO); 2.98–3.15 (*m*, 2 H, 2 SCH_2); 3.74–3.80 (*m*, 1 allylic H); 3.85–3.90 (*m*, 1 allylic H); 5.81–5.88 (*m*, 1 vinylic H); 5.96–6.08 (*m*, 3 vinylic H). MS: 133 (100), 105 (23), 77 (23), 59 (100). Anal. calc. for $C_{14}H_{20}OS_2$ (268.43): C 62.67, H 7.51; found: C 62.49, H 7.77.

b) *Ethyl Triflate/CO.* The procedure and quantities applied were identical to those described in *Sect. 3f* except for the solvent which was THF/HMPA 4:1 and the electrophile which was ethyl trifluoromethanesulfonate (0.646 ml, 5 mmol). Decomplexation (4.5 bar CO), workup, and chromatography yielded 217 mg (82%) of **17** as an oil.

The above procedure was repeated without HMPA and with the addition of only 1 equiv. of ethyl triflate (0.130 ml, 1 mmol). The mixture was stirred under 4.5 bar CO for 2 days, vented, diluted with pentane (25 ml), and cooled to −78°. From the precipitate, $[Cr(CO)_6]$ (115 mg, 52%) was isolated by sublimation. Workup of the mother liquor provided 131 mg (49%) of **17**.

c) *EtBr/CO.* Under the conditions described in the *General Procedure* in *Sect. 3f*, except for the solvent which was THF/HMPA (10 ml: 1.7 ml) and the electrophile which was EtBr (1 ml), 76 mg (28%) of **17** were obtained (after 44 h at 20° under 4.8 bar CO) together with dithianecyclohexadiene (mixture of isomers). Repeating this experiment but warming the reaction mixture to 50° for 2 h yielded 212 mg (79%) of **17**.

d) *Allyl Bromide/CO.* Applying the *General Procedure* on a 1.5-mmol scale, allyl bromide (0.8 ml) was added as the electrophile. The solvent was THF/HMPA, 4:1, and the reaction was left under 4.5 bar CO for 24 h before workup. Chromatography on silica gel using hexane/Et_2O 4:1 yielded **18** (394 mg, 94%) as an oil.

When *allyl chloride* was used under otherwise identical conditions, **18** was isolated in 25% yield.

1-[6-(2-Methyl-1,3-dithian-2-yl)cyclohexa-2,4-dien-1-yl]but-3-en-1-one (**18**). IR (CH_2Cl_2): 3040*m*, 2920*m*, 1710*s*, 1580*m*, 1440*m*, 1340*m*, 1310*m*, 1120*w*, 1070*w*, 990*m*, 920*m*. ^{1}H-NMR ($CDCl_3$, 360 MHz); 1.27 (*s*, CH_3); 1.71–1.88 (*m*, H–C(5″)); 2.00–2.12 (*m*, H–C(5″)); 2.51 (*dt*, J = 4, 15, 1 H, SCH_2), 2.64 (*dt*, J = 4, 15, 1 H, SCH_2); 2.94 (*ddd*, J = 3, 12, 15, 1 H, SCH_2); 3.06 (*ddd*, J = 3, 12, 15, 1 H, SCH_2); 3.37 (*dt*, J = 2.5, 14, $COCH_2$); 3.78–3.82 (*m*, H–C(1′), H–C(6′)); 5.10–5.22 (*m*, 2 H–C(4)); 5.80–5.94 (*m*, 5 vinylic H). MS: 133 (100), 69 (8), 57 (57). HR-MS: calc. for $C_{15}H_{20}OS_2$ (M^+): 280.0956; found: 280.0972.

e) *PhCH$_2$Br/CO.* The scale and conditions were identical to those described in *Sect. 6d.* $PhCH_2Br$ (0.5 ml, 4.20 mmol) was used as electrophile to yield, after chromatography on silica gel (toluene/hexane 1:1, toluene), **19** (333 mg, 67%) as an oil.

Benzyl 6-(2-Methyl-1,3-dithian-2-yl)cyclohexa-2,4-dien-1-yl Ketone (**19**). UV (cyclohexane): 270 (54000), 208 (170000). IR (film): 3020*m*, 2960*m*, 2920*m*, 2860*w*, 1712*s*, 1605*w*, 1585*w*, 1495*m* 1450*m*, 1420*m*, 1370*m*, 1310*m*, 1275*m*, 1240*m*, 1185*w*, 1070*m*, 950*m*, 755*m*, 705*s*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 1.28 (*s*, CH_3); 1.78–1.90 (*m*, H–C(5′)); 2.00–2.10 (*m*, H–C(5′)); 2.45 (*d*, J = 14, 1 H, SCH_2); 2.64 (*d*, J = 14, 1 H, SCH_2); 2.89 (*ddd*, J = 3, 13, 14, 1 H, SCH_2); 3.05 (*ddd*, J = 2, 13, 14, 1 H, SCH_2); 3.85–3.92 (*m*, 1 allylic H); 3.92–3.96 (*m*, 1 allylic H); 3.94 (*s*, CH_2CO); 5.80–5.88 (*m*, 1 vinylic H); 6.00–6.10 (*m*, 3 vinylic H); 7.18–7.37 (*m*, 5 arom. H). MS: 49 (88), 59 (100), 65

(45), 77 (52), 84 (58), 91 (100), 105 (83), 133 (100), 223 (8). Anal. calc. for $C_{19}H_{22}OS_2$ (330.50): C 69.05, H 6.71; found: C 69.06, H 6.73.

f) *1-Bromo-3-methylbut-2-ene/CO.* To a soln. of **3** (1 mmol), prepared as described above, in THF/HMPA 2:1, 1-bromo-3-methylbut-2-ene (0.400 ml, 3.8 mmol) was added at −78°. The mixture was heated under CO pressure (3 bar) to 80° for 4 h. Workup as described and filtration over silica gel yielded the crude product which was purified by prep. TLC (hexane/Et_2O 4:1) to yield 17.2 mg (5.6%) of **20.**

4-Methyl-1-[6-(2-Methyl-1,3-dithian-2-yl)cyclohexa-2,4-dien-1-yl]pent-3-en-1-one (**20**). IR (CH_2Cl_2): 3040*w*, 2980*m*, 2920*m*, 2860*w*, 1710*s*, 1450*w*, 1375*m*, 1310*w*, 1110*m*, 1080*m*, 910*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.25 (*s*, CH_3); 1.60 (*s*, allylic CH_3); 1.75 (*s*, allylic CH_3); 1.77–1.96 (*m*, H–C(5″)); 1.98–2.13 (*m*, H–C(5″)); 2.51 (*ddd*, J = 4, 4, 14.5, 1 H, SCH_2); 2.63 (*ddd*, J = 4, 4, 14.5, 1 H, SCH_2); 2.97 (*ddd*, J = 3, 12, 15, 1 H, SCH_2); 3.07 (*ddd*, J = 3, 12, 15, 1 H, SCH_2); 3.30 (*d*, J = 7, CH_2CO); 3.76–3.85 (*m*, 2 allylic H); 5.31 (br. *t*, J = 7, H–C(3)); 5.76–5.85 (*m*, 1 vinylic H); 5.94–6.05 (*m*, 3 vinylic H). MS: 59 (23), 105 (27), 133 (100), 175 (56), 201 (74), 227 (36). Anal. calc. for $C_{17}H_{24}OS_2$ (308.51): C 66.19, H 7.84; found: C 66.28, H 7.85.

g) *4-Iodobut-1-ene/CO.* Following the *General Procedure* on a 1-mmol scale, 4-iodobut-1-ene (0.370 ml, 3.76 mmol) was added as the electrophile. The solvent was THF/HMPA 5:1, and the reaction mixture was left under 4.8 bar CO for 40 h before workup. Chromatography on silica gel using hexane/Et_2O 8:1 yielded **21** (265 mg, 90%) as an oil.

1-[6-(2-Methyl-1,3-dithian-2-yl)cyclohexa-2,4-dien-1-yl]pent-4-en-1-one (**21**). IR (CH_2Cl_2): 3040*m*, 2920*s*, 2860*m*, 1720*s*, 1640*m*, 1590*w*, 1440*m*, 1420*m*, 1370*m*, 1360*w*, 1115*m*, 1075*m*, 1000*m*, 940*m*, 915*m*. ^{1}H-NMR ($CDCl_3$): 1.30 (*s*, CH_3); 1.80–1.92 (*m*, H–C(5″)); 2.05–2.12 (*m*, H–C(5″)); 2.32–2.38 (*m*, CH_2CO); 2.56 (*dt*, J = 4, 15, 1 H, SCH_2); 2.62–2.75 (*m*, 3 H, SCH_2, 2 H–C(3)); 2.98 (*ddd*, J = 4, 12, 15, SCH_2); 3.09 (*ddd*, J = 4, 12, 15, 1 H, SCH_2); 3.75–3.80 (*m*, 1 allylic H); 3.83–3.88 (*m*, 1 allylic H); 4.96–5.08 (*m*, 2 H–C(5)); 5.78–5.90 (*m*, 2 vinylic H); 5.97–6.10 (*m*, 3 vinylic H). MS: 59 (22), 133 (100), 161 (20), 211 (10), 227 (9), 239 (3). Anal. calc. for $C_{16}H_{22}OS_2$ (294.479): C 65.29, H 7.53; found: C 65.67, H 7.81.

h) *6-Iodohex-1-ene/CO.* The reaction was carried out exactly as described before (1-mmol scale) except that 6-iodohex-1-ene (0.6 ml) was added as electrophile. The mixture was stirred under 4.5 bar CO for 23 h before workup. Chromatography over silica gel (hexane/Et_2O 20:1) yielded 286 mg (89%) of **22.**

1-[6-(2-Methyl-1,3-dithian-2-yl)cyclohexa-2,4-dien-1-yl]hept-6-en-1-one (**22**). IR (CH_2Cl_2): 3080*w*, 3040*m*, 2975*w*, 2930*vs*, 2860*m*, 1710*vs*, 1675*w*, 1640*m*, 1430*m*, 1380*m*, 1280*m*, 1070*m*, 1000*m*, 950*m*, 920*s*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 1.25 (*s*, CH_3); 1.30–1.42 (*m*, CH_2); 1.52–1.64 (*m*, CH_2); 1.78–1.82 (*m*, H–C(5″)); 2.00–2.13 (*m*, H–C(5″), 2 H–C(5)); 2.48–2.70 (*m*+*dt*, J = 2.5, 7.5, SCH_2, CH_2CO); 2.98 (*ddd*, J = 3, 12, 14.5, 1 H, SCH_2); 3.08 (*ddd*, J = 3, 12, 14.5, 1 H, SCH_2); 3.74–3.78 (*m*, 1 allylic H); 3.84–3.87 (*m*, 1 allylic H); 4.92–5.08 (*m*, 2 vinylic H): 5.74–5.86 (*m*, 2 vinylic H), 5.88–6.10 (*m*, 3 vinylic H). MS: 59 (12), 105 (8), 133 (100). Anal. calc. for $C_{18}H_{26}OS_2$ (322.52): C 67.03, H 8.13; found: C 67.28, H 8.37.

i) *(Cyclohexyl)methyl Iodide.* Following the *General Procedure* (1-mmol scale), (cyclohexyl)methyl iodide (1.2 ml, 6.5 mmol) was added to a soln. of **3** in THF/HMPA 5:1. Carbonylation and decomplexation was induced by CO (4 bar). FC on silica gel using hexane/Et_2O 20:1 yielded **23** (171 mg, 51%).

2-Cyclohexyl-1-[6-(2-methyl-1,3-dithian-2-yl)cyclohexa-2,4-dien-1-yl]ethanone (**23**). IR (CH_2Cl_2): 3050*m*, 2930*vs*, 2850*s*, 1710*s*, 1450*m*, 1430*w*, 1380*m*, 1350*w*, 1280*w*, 1080*m*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.80–2.15 (*m*, 13 H); 1.25 (*s*, CH_3); 2.46 (*dd*, J = 2, 7, CH_2CO); 2.52–2.75 (*m*, SCH_2); 2.97 (*ddd*, J = 3, 11, 14, 1 H, SCH_2); 3.08 (*ddd*, J = 3, 11, 14, 1H, SCH_2); 3.69–3.76 (*m*, 1 allylic H); 3.82–3.87 (*m*, 1 allylic H); 5.75–5.83 (*m*, 1 vinylic H); 5.92–6.03 (*m*, 3 vinylic H). MS: 59 (52), 133 (100), 211 (6), 229 (3).

j) *(Cyclopropyl)methyl Iodide.* Proceeding as before, (cyclopropyl)methyl iodide (0.500 ml, 5 mmol) was added to a cold (−78°) soln. of **3** (1 mmol) in THF/HMPA (12.5 ml, 4:1). Decomplexation under CO (4 bar, 48 h), workup as described followed by distillation of the volatiles and chromatography (silica gel, toluene/hexane 1:1, toluene) yielded 206 mg of **24** (70%).

2-Cyclopropyl-1-[6-(2-methyl-1,3-dithian-2-yl)cyclohexa-2,4-dien-1-yl]ethanone (**24**). IR (CH_2Cl_2): 3080*w*, 3050*m*, 3010*m*, 2960*s*, 2930*s*, 2860*s*, 1715*vs*, 1430*w*, 1375*m*, 1315*m*, 1075*m*, 1020*m*, 940*w*, 830*w*.^{1}H-NMR ($CDCl_3$, 360 MHz): 0.05–0.16 (*m*, CH_2 (cyclopropyl)); 0.52–0.60 (*m*, CH_2 (cyclopropyl)); 1.00–1.10 (*m*, CH (cyclopropyl)); 1.30 (*s*, CH_3); 1.80–1.92 (*m*, H–C(5″)); 2.04–2.13 (*m*, H–C(5″)); 2.51 (*dd*, J = 7, 3, $COCH_2$); 2.54 (*dt*, J = 4, 15, 1 H, SCH_2); 2.67 (*dt*, J = 4, 15, 1 H, SCH_2); 3.00 (*ddd*, J = 3, 12, 15, 1 H, SCH_2); 3.10 (*ddd*, J = 3, 12, 15, 1 H, SCH_2); 3.78–3.87 (*m*, 1 allylic H); 3.85–3.90 (*m*, 1 allylic H); 5.75–5.80 (*m*, 1 vinylic H); 5.95–6.06 (*m*, 3 vinylic H). MS: 59 (33), 77 (6), 133 (100), 159 (6), 207 (11), 239 (8). Anal. calc. for $C_{16}H_{22}OS_2$ (294.47): C 65.29, H 7.53; found: C 65.34, H 7.71.

k) *i-PrI/CO.* Complex **3** was prepared as before (1-mmol scale, solvent THF/HMPA 5:1) and reacted with the electrophile which was i-PrI (1 ml, 5.9 mmol). The mixture was placed under 3 bar CO and brought to 70° for 7 h to yield, after workup and chromatography (silica gel, hexane/Et_2O 1:1), 144 mg (51%) of **25.**

An analogous reaction with i-PrOMs (1.38 g, 10 mmol) with warming to 50° under 5 bar CO yielded **25** in 35% yield.

3-Methyl-1-[6-(2-methyl-1,3-dithian-2-yl)cyclohexa-2,4-dien-1-yl]butan-1-one (**25**). IR (film): 3040*m*, 2970*s*, 2930*s*, 2870*m*, 1710*s*, 1465*m*, 1435*m*, 1420*m*, 1380*m*, 1370*m*, 1275*w*, 1115*m*, 1070*m*, 1050*w*, 945*m*, 900*w*, 715*w*, 700*m*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 1.08 (*d*, *J* = 7, CH_3); 1.17 (*d*, *J* = 7, CH_3); 1.30 (*s*, CH_3); 1.80–1.92 (*m*, H–C(5″)); 2.02–2.10 (*m*, H–C(5″)); 2.55 (*dt*, *J* = 14, 3, 1 H, SCH_2); 2.68 (*dt*, *J* = 14.3, 1 H, SCH_2); 2.90–3.15 (*m*, 2 SCH_2, H–C(3)); 3.80–3.85 (*m*, 1 allylic H); 3.94–3.98 (*m*, 1 allylic H); 5.80–5.86 (*m*, 1 vinylic H); 5.96–6.16 (*m*, 3 vinylic H): MS: 43 (23), 59 (17), 133 (100). Anal. calc. for $C_{16}H_{22}OS_2$ (282.46): C 63.78, H 7.85; found: C 63.80, H 7.99.

1) *1-Chloro-6-iodohexane/CO*. Using the same procedure, 1-chloro-6-iodohexane (1.2 ml) was added to a soln. of **3** (1 mmol) in THF/HMPA 4:1). The mixture was placed under CO (4 bar) for 48 h to yield, after workup and chromatography on silica gel (hexane/Et_2O 4:1), 354 mg (66%) of **27**.

7-Chloro-1-[6-(2-methyl-1,3-dithian-2-yl)cyclohexa-2,4-dien-1-yl]heptan-1-one (**27**). IR (CH_2Cl_2): 3040*m*, 2940*s*, 2840*m*, 1710*s*, 1480*m*, 1370*m*, 940*w*, 900*w*, 640*w*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 1.3 (*s*, CH_3); 1.32–1.38 (*m*, CH_2); 1.42–1.50 (*m*, CH_2); 1.53–1.66 (*m*, CH_2); 1.73–1.93 (*m*, CH_2, H–C(5″)); 2.03–2.13 (*m*, H–C(5″)); 2.52–2.71 (*m*, SCH_2, CH_2CO); 3.00 (*ddd*, *J* = 3, 12, 15, 1 H, SCH_2); 3.10 (*ddd*, *J* = 3, 12, 15, 1 H, SCH_2); 3.50 (*t*, *J* = 7, 2 H, CH_2Cl); 3.73–3.80 (*m*, 1 allylic H); 3.85–3.90 (*m*, 1 allylic H); 5.78–5.86 (*m*, 1 vinylic H); 5.96–6.08 (*m*, 3 vinylic H). MS: 105 (12), 120 (8), 133 100), 179 (1), 189 (1), 255 (20). Anal. calc. for $C_{18}H_{27}ClOS_2$ (358.98): C 60.22, H 7.58; found: C 60.42, H 7.76.

m) *Methyl 4-Iodobutyrate/CO*. Using the *General Procedure* on a 1-mmol scale, methyl 4-iodobutyrate (0.150 ml, 1.3 mmol) was added as the electrophile. The solvent was THF/HMPA 5:1, and the reaction mixture was left under 3.6 bar CO for 44 h at 22° before workup. Chromatography on silica gel using hexane/Et_2O 1:1 yielded **28** (224 mg, 70%).

Methyl 4-{[6-(2-Methyl-1,3-dithian-2-yl)cyclohexa-2,4-dien-1-yl]carbonyl}butyrate (**28**): IR (CH_2Cl_2): 3140*m*, 2960*s*, 2930*s*, 2800*m*, 1740*vs*, 1710*vs*, 1440*s*, 1370*m*, 1320*w*, 1240*w*, 1205*w*, 1170*w*, 1100*w*, 945*w*, 900*w*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 1.28 (*s*, CH_3); 1.82–1.96 (*m*, H–C(5″), 2 H–C(3)); 2.03–2.13 (*m*, H–C(5″)); 2.35 (*t*, *J* = 7, 2 H–C(2)); 2.56 (*dt*, *J* = 4, 15, 1 H, SCH_2); 2.63–2.75 (*m*, 3 H, SCH_2, 2 H–C(4)); 2.98 (*ddd*, *J* = 3, 12, 15, 1 H, SCH_2); 3.08 (*ddd*, *J* = 3, 12, 15, 1 H, SCH_2); 3.67 (*s*, CH_3O); 3.72–3.78 (*m*, 1 allylic H); 3.83–3.88 (*m*, 1 allylic H); 5.78–5.83 (*m*, 1 vinylic H); 5.96–6.07 (*m*, 3 vinylic H). MS: 59 (18), 133 (100), 159 (10), 175 (12), 203 (8), 281 (7), 309 (21). HR-MS calc. for $C_{16}H_{21}O_2S_2$: 309.0983; found 309.0925 ($[M - OCH_3]^+$); calc. for $C_{15}H_{21}OS_2$: 281.1034; found: 281.0996 ($[M - CO_2CH_3]^+$).

n) *5-Iodopentan-2-one*. 5-Iodopentan-2-one (0.5 ml) was added to a cold (−78°) soln. of **3** (1.5 mmol) in THF/HMPA 4:1 (12.5 ml) under an atmosphere of CO. The mixture was stirred at 0° overnight and then slowly heated to 70° (2 h). After cooling to 0°, Ph_3P(2 g) were added. After 5 h, the mixture was poured onto HCl (1N) and extracted with Et_2O. Workup as described in the *General Procedure* and chromatography on silica gel (hexane/toluene 1:1, toluene) yielded 310 mg (64%) of **29**.

1-[6-(2-Methyl-1,3-dithian-2-yl)cyclohexa-2,4-dien-1-yl]hexane-1,5-dione (**29**). M.p. 55–57° (pentane). IR (CH_2Cl_2): 3045*m*, 2930*m*, 1712*s*, 1435*m*, 1425*m*, 1410*m*, 1370*m*, 1310*w*, 1170*w*, 1100*w*, 945*w*. ^{1}H-NMR ($CDCl_3$, 360 MHz): 1.28 (*s*, CH_3); 1.82–1.90 (*m*, CH_2, H–C(5″)); 2.03–2.10 (*m*, H–C(5″)); 2.12 (*s*, CH_3–C(5)); 2.46 (*t*, *J* = 7, 2 H–C(4)); 2.50–2.60 (*m*, 1 H, SCH_2); 2.60–2.72 (*m*, 3 H, SCH_2, 2 H–C(2)); 2.97 (*ddd*, *J* = 2, 13, 14, 1 H, SCH_2); 3.08 (*ddd*, *J* = 2, 13, 14, 1 H, SCH_2); 3.70–3.76 (*m*, 1 allylic H); 3.80–3.84 (*m*, 1 allylic H); 5.75–5.82 (*m*, 1 vinylic H); 5.95–6.07 (*m*, 3 vinylic H). MS: 43 (12), 59 (12), 133 (100). Anal. calc. for $C_{17}H_{24}O_2S_2$ (324.50): C 62.92, H 7.45; found: C 63.05, H 7.63.

o) *Ethyl Bromoacetate*. Following the *General Procedure* (1-mmol scale), ethyl bromoacetate (0.600 ml, 5.4 mmol) was added to a soln. of **3** in THF/HMPA 5:1. The mixture was placed under 1.5 bar of CO and gradually brought from −78 to 55°. After stirring at this temp. for 2 h, the mixture was recooled to 0° and worked up as described in the *General Procedure*. Chromatography over silica gel (hexane/Et_2O 12:1, 4:1) yielded 88 mg (27%) of **30**.

Ethyl 2-{[6-(2-Methyl-1,3-dithian-2-yl)cyclohexa-2,4-dien-1-yl]carbonyl}acetate (**30**). IR (CH_2Cl_2): 3040*w*, 2980*w*, 2930*w*, 2900*w*, 1740*w*, 1710*s*, 1370*m*, 1320*m*, 1030*s*, 910*s*. ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.25 (*t*, *J* = 7, CH_3); 1.25 (*s*, CH_3); 1.78–1.95 (*m*, H–C(5″)); 2.0–2.15 (*m*, H–C(5″)); 2.47–2.70 (*m*, SCH_2); 2.91–3.14 (*m*, SCH_2); 3.56 ([*AB*] *d*, *J* = 15, 1 H–C(2)); 3.67 ([*AB*] *d*, *J* = 15, 1 H–C(2)); 3.76–3.82 (*m*, 1 allylic H); 3.88–3.95 (*m*, 1 allylic H); 4.18 (*q*, *J* = 7, CH_2); 5.73–5.84 (*m*, 1 vinylic H); 6.00–6.09 (*m*, 3 vinylic H). MS: 59 (32), 115 (4), 133 (100), 163 (4), 181 (4), 192 (6), 210 (2), 281 ([*M* − Et]$^+$, < 1). Anal. calc. for $C_{16}H_{22}O_3S_2$ (326.47): C 58.86, H 6.79; found: C 58.76, H 6.80.

p) *1,4-Diiodopentane/CO*. Complex **3** was prepared exactly as before (1-mmol scale, solvent THF/HMPA 5:1) and reacted with 1,4-diiodopentane (0.500 ml, 4 mmol). The mixture was stirred for 21 h under 5 bar CO at 22°. Chromatography on silica gel (hexane/Et_2O 25:1) yielded 247 mg (57%) of **31**.

5-Iodo-1-[6-(2-methyl-1,3-dithian-2-yl)cyclohexa-2,4-dien-1-yl]hexan-1-one (**31**). IR (CH_2Cl_2): 3040*m*, 2960*s*, 2930*s*, 2860*m*, 1715*s*, 1450*m*, 1375*m*, 1315*w*, 1240*w*, 1225*w*, 1160*m*, 1075*m*, 945*m*, 905*m*, 865*w*, 815*w*, 675*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 1.34 (*s*, CH_3); 1.60–2.00 (*m*, 2 H–C(4), 2 H–C(3), H–C(5″)); 1.97 (*d*, $J = 7$, CH_3–C(5)); 2.08–2.18 (*m*, H–C(5″)); 2.56–2.77 (*m*, 2 H–C(2), SCH_2); 3.04 (*ddd*, $J = 3$, 12, 15, 1 H, SCH_2); 3.14 (*ddd*, $J = 3$, 12, 15, 1 H, SCH_2); 3.78–3.84 (*m*, 1 allylic H); 3.86–3.94 (*m*, 1 allylic H); 4.18–4.28 (*m*, H–C(5)); 5.80–5.88 (*m*, 1 vinylic H); 6.00–6.12 (*m*, 3 vinylic H). MS: 59 (18), 105 (12), 133 (100), 155 (15), 175 (46), 197 (24), 225 (19), 331 (8). Anal. calc. for $C_{17}H_{25}IOS_2$ (436.41): C 46.79, H 5.77; found: C 46.79, H 5.72.

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