188. Addition of Carbon Nucleophiles to Tricarbonylchromium Complexes of 1,2-Dihydrocyclobutabenzene, Indane, 1,2,3,4-Tetrahydronaphthalene and *ortho*-Xylene

by **E. Peter Kündig***, **Chantal Grivet**, **Eric Wenger**[1]), and **Gérald Bernardinelli**

Department of Organic Chemistry and Laboratory of X-ray Crystallography, University of Geneva, 30, quai Ernest Ansermet, CH-1211 Geneva 4

and **Alan F. Williams***

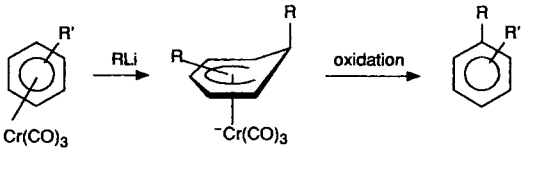
Department of Analytical, Inorganic and Applied Chemistry, University of Geneva, 30, quai Ernest Ansermet, CH-1211 Geneva 4

(11.X.91)

3-Substituted 1,2-dihydrocyclobutabenzenes (bicyclo[4.2.0]octa-1,3,5-triene) are readily accessible from $[Cr(CO)_3$(1,2-dihydrocyclobutabenzene)] (**1**) *via* a two-step sequence which involves addition of a nucleophile and oxidation of the intermediate anionic cyclohexadienyl complex. Nucleophiles used include $LiCMe_2CN$ (**A**), $LiCH_2CN$ (**B**), LiC(Me)(OR)CN (**C**), $Li\overline{CHS(CH_2)_3S}$ (**D**), $Li\overline{CMeS(CH_2)_3S}$ (**E**), $LiCMe_2CO_2Me$ (**F**), and $LiCH_2CO_2(t\text{-Bu})$ (**G**). $[Cr(CO)_3$(Indane)] (**2**) also reacts highly regioselectively to give α-substitution, whereas $[Cr(CO)_3$(tetrahydronaphthalene)] (**3**) and $[Cr(CO)_3$(*o*-xylene)] (**4**) give mixtures of products. In several cases, the mixtures of the intermediate anionic cyclohexadienyl complexes can be equilibrated to give, after oxidation, β-substituted derivatives of 1,2,3,4-tetrahydronaphthalene and *ortho*-xylene selectively. EHMO calculations were carried out, and they rationalize the observed α-regioselectivity of nucleophilic addition under kinetic control. The X-ray structures of **1** and **4** are reported and in both compounds the $Cr(CO)_3$ group adopts in the solid state a staggered *syn*-conformation with respect to the substituted aromatic C-atoms.

Introduction. – Aromatic substitution under mild conditions can be achieved *via* complexation of the arene to the electron-withdrawing $Cr(CO)_3$ fragment, followed by the addition of a C-nucleophile and oxidative decomplexation (*Scheme 1*). Reactions with substituted arenes are often highly regioselective and give products with a substitution pattern which is complementary to that found in electrophilic aromatic substitution [1] [2]. Equilibration between different regioisomers of anionic $[Cr(CO)_3$(cyclohexadienyl)] intermediates can be rapid even at low temperature [3] [4]. Characteristically, this behavior is found in reactions of α-cyano C-nucleophiles and ester enolates, and we have shown that the product mixtures isolated from reactions with these nucleophiles at 0° in

Scheme 1



[1]) Part of the Ph. D. thesis of *E. W.*, Université de Genève, 1990.

THF reflect the distribution of isomers at equilibrium. On the other hand, some S-stabilized carbanions[2]), and alkyl- and aryllithium compounds add irreversibly. In reactions of other C-nucleophiles, dissociation can be suppressed by the addition of polar aprotic solvents (HMPA, DMPU) [3b]. In these cases, product distribution reflects kinetic control, and observed regioselectivity can be rationalized by assuming either charge or orbital control of the addition [6–8].

Earlier reports on regioselectivity of addition/oxidation reactions include reactions of $[Cr(CO)_3(indane)]$ (**2**) [9], 1-substituted derivatives of **2** [9–11], $[Cr(CO)_3(1,2,3,4\text{-tetrahydronaphthalene})]$ (**3**) [12] and 1,5-disubstituted derivatives of **3** [13]. In this paper, we describe the results of a systematic study of regioselectivity of nucleophilic addition to $[Cr(CO)_3(1,2\text{-dihydrocyclobutabenzene})]$ (**1**[2]), **2**, **3**, and $[Cr(CO)_3(o\text{-xylene})]$ (**4**). The regioselectivity in this closely related series is particularly instructive, and should lead to a more detailed knowledge of the factors which govern regioselectivity. The next target then is the control of the addition reaction to form single regioisomers. We here show that this can indeed be achieved. A few of the results described here have been published in preliminary form [14].

Results and Discussion. – *Nucleophilic Addition Reactions.* The addition of **1** as a solid to a solution of $LiCMe_2CN$ (**A**) kept at −78° in THF followed by warm up to −20° and oxidative decomplexation (I_2) gave the 3-substituted cyclobutabenzene **5** as a single product. To probe the effect of temperature, a separate experiment was carried out. A THF solution of **1** was cooled to −90° and rapidly transferred into a solution of the C-nucleophile at the same temperature. After 5 min, the reaction mixture was partitioned. Half of the mixture was immediately treated with I_2, while the other half was stirred for 2 h at 0° prior to quenching with I_2 at −78°. Both reactions yielded **5** exclusively (*Table 1, Entries 3* and *4*).

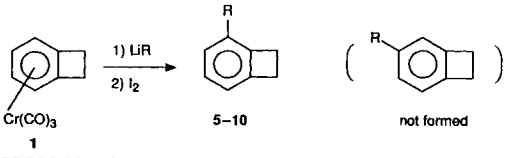


Table 1. *Synthesis of 3-Substituted 1,2-Dihydrocyclobutabenzenes* via *the Addition of C-Nucleophiles to Complex* **1**

Entry	Nucleophile LiR	Conditions [°C/h]	Medium	Product	Yield[c]) [%]
1	$LiCMe_2CN$ (**A**)	−20/0.5	THF	**5**	86
2	$LiCMe_2CN$ (**A**)	−90/0.1[a])	THF	**5**	76
3	$LiCMe_2CN$ (**A**)	0/2[b])	THF	**5**	67
4	$LiCH_2CN$ (**B**)	−20/0.5	THF/HMPA 10:1	**6**	65
5	LiC(Me)(CN)OR (**C**[d]))	−20/0.5	THF/HMPA 10:1	**7**[e])	91
6	$LiCHS(CH_2)_3S$ (**D**)	0/0.5	THF	**8**	69
7	$LiC(CH_3)S(CH_2)_3S$ (**E**)	0/4	THF/HMPA 4:1	**9**	64
8	$LiCMe_2CO_2Me$ (**F**)	−30/0.3	THF	**10**	71

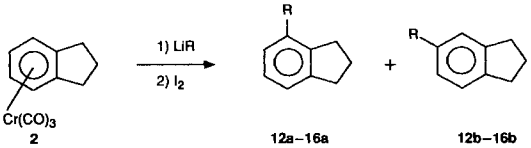
[a]) Complex added as THF solution at −90°. [b]) From the same reaction mixture as in *Entry 2*. [c]) Isolated yield after chromatography. [d]) R = $CH(CH_3)OCH_2CH_3$. [e]) The product is the acetyl derivative, obtained by the hydrolysis of the cyanohydrin.

[2]) 1,3-Dithiane- and 2-methyl-1,3-dithiane-Li add irreversibly, 2-(trimethylsilyl)-1,3-dithiane- and tris(methylthio)methane-Li add reversibly to $[Cr(CO)_3(1\text{-methoxynaphthalene})]$ [5].

[3]) *IUPAC* name of **1**: Tricarbonyl{(1-6-η)-bicyclo[4.2.0]octa-1,3,5-triene)}chromium(0).

Complex **1** also reacted with the nucleophiles $LiCH_2CN$ (**B**), LiC(Me)(CN)(CH(Me)OEt) (**C**), $LiCHS(CH_2)_3S$ (**D**), $LiC(CH_3)S(CH_2)_3S$ (**E**), and $LiCMe_2CO_2Me$ (**F**) highly regioselectively to give, after oxidation, single products **6–10** (*Table 1, Entries 4–8*). The substitution pattern can be readily deduced by inspection of the ^{1}H-NMR spectra and comparison to analogous compounds synthesized by different routes [16]. Hydrolysis of the dithiane derivative **8** gave 1,2-dihydrocyclobutabenzene-3-carbaldehyde (**11**).

In the reactions of $[Cr(CO)_3$(indane)] (**2**), addition to the site α to the ring junction largely prevails over that to the β-site. With nucleophiles **B**, **D**, and **E**, single products were formed while **A** and **C** reacted at low temperature to afford 10:1 mixtures of regioisomers (*Table 2, Entries 1* and *5*). We have shown previously that in reactions with nucleophile **A**, the product isomer distribution depends on reaction time and temperature. These were varied from 0.1 h at −90° to 15 h at 0° and were shown to lead very rapidly from an initial 10:1 to a final 3:1 mixture of the intermediates and, after oxidation, the substituted arenes (*Table 2, Entries 1* and *2*). Hydrolysis of the dithiane derivative **15a** gave indane-4-carbaldehyde (**17**).



2 **12a–16a** **12b–16b**

Table 2. *Substituted Indanes* via *the Addition of C-Nucleophiles to Complex* **2**

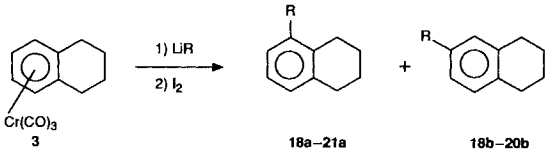
Entry	Nucleophile LiR	Conditions [°C/h]	Medium	Product distribution		Yield[a] [%]
1[b]	$LiCMe_2CN$ (**A**)	−90/0.1[c]	THF	91 (**12a**)	9 (**12b**)[d][e]	90[f]
2[b]	$LiCMe_2CN$ (**A**)	0/2	THF	75 (**12a**)	25 (**12b**)[d][e]	90
3	$LiCH_2CN$ (**B**)	−40/1	THF/HMPA 3:1	100 (**13a**)	0 (**13b**)[e]	95
4	$LiCH_2CN$ (**B**)	−20/0.5	THF	100 (**13a**)	0 (**13b**)[e]	89
5	LiC(Me)(CN)OR (C)[g]	−20/0.5	THF/HMPA 10:1	90 (**14a**)	10 (**14b**)[d][h]	95
6	$LiCHS(CH_2)_3S$ (**D**)	−10/1	THF/HMPA 10:1	> 96 (**15a**)	< 4 (**15b**)[f]	89
7	$LiC(Me)S(CH_2)_3S$ (**E**)	0/16	THF/HMPA 10:1	> 96 (**16a**)	< 4 (**16b**)[d][i]	90

[a]) Yields refer to isolated mixtures of isomers **a** and **b** (unless otherwise noted). [b]) Data from [9]. [c]) Complex added as THF solution at −90°. [d]) Mixture ratio determined by ^{1}H-NMR. [e]) Mixture ratio determined by GLC. f) GLC yield, *trans*-decaline as internal standard. [g]) R = $CH(CH_3)OCH_2CH_3$. [h]) The product is the acetyl derivative, obtained by the hydrolysis of the cyanohydrin. [i]) Estimated limit of detection (by ^{1}H-NMR).

Results of reactions carried out with $[Cr(CO)_3$(1,2,3,4-tetrahydronaphthalene)] (**3**) and $[Cr(CO)_3$(*o*-xylene)] (**4**) are shown in *Tables 3* and *4*.

The low-temperature (−90°) reactions with nucleophile **A** afforded mixtures of regioisomers. As with complexes **1** and **2**, addition of **A** to the C-atom α to the ring junction of the 1,2,3,4-tetrahydronaphthalene complex **3** was predominant. In contrast, this was the minor isomer in the reaction of **A** with **4**. In the presence of the polar, non-nucleophilic cosolvent HMPA, **23a** and **23b** were formed in equal proportions. On warming the reaction mixtures, complete rearrangement to the intermediate leading to the β-regioisomer took place with both **3** and **4**. Different isomer distributions upon change of reaction temperature also resulted with the smaller nucleophiles **B** and **G**, but these were much less pronounced than with **A**.

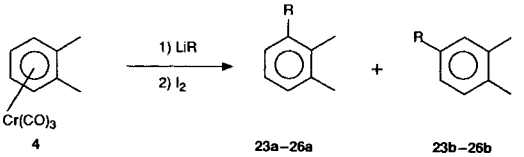
Table 3. *Substituted 1,2,3,4-Tetrahydronaphthalenes* via *the Addition of C-Nucleophiles to Complex* **3**



Entry	Nucleophile LiR	Conditions [°C/h]	Medium	Product distribution		Yield[a] [%]
1	$LiCMe_2CN$ (**A**)	–90/0.1[b]	THF	73 (**18a**)	27 (**18b**)[c]	80[e]
2	$LiCMe_2CN$ (**A**)	–30/1	THF	< 2 (**18a**)	< 98 (**18b**)[d]	88[e]
3	$LiCH_2CN$ (**B**)	–78/1	THF/HMPA 4:1	100 (**19a**)	0 (**19b**)	69[f]
4	LiC(Me)(CN)OR (**C**)[g]	–20/0.5	THF/HMPA 10:1	67 (**20a**)[a]	33 (**20b**)[c])[h]	58
5	$LiC(Me)S(CH_2)_3S$ (**E**)	30/15	THF	100 (**20a**)	0 (**20b**)	24[i]
6	$LiC(Me)S(CH_2)_3S$ (**E**)	0/4	THF/HMPA 4:3	100 (**20a**)[k]	0 (**20b**)	81[f])[k]

[a]) Yields refer to isolated mixtures of isomers **a** and **b** (unless otherwise noted). [b]) Complex added as THF solution at –90°. [c]) Mixture ratio determined by ^{1}H-NMR. [d]) Mixture ratio determined by GLC. [e]) Yield calculated by GLC with *trans*-decaline as internal standard. [f]) Data from [12]. [g]) R = $CH(CH_3)OCH_2CH_3$. [h]) The product is the acetyl derivative, obtained by the hydrolysis of the cyanohydrin. [i]) Acetyl derivative. [k]) Mixture (2.7:1) of acetyl (**20a**) and methyldithiane (**21a**) product.

Table 4. *Substituted 1,2-Dimethylbenzenes* via *the Addition of C-Nucleophiles to Complex* **4**

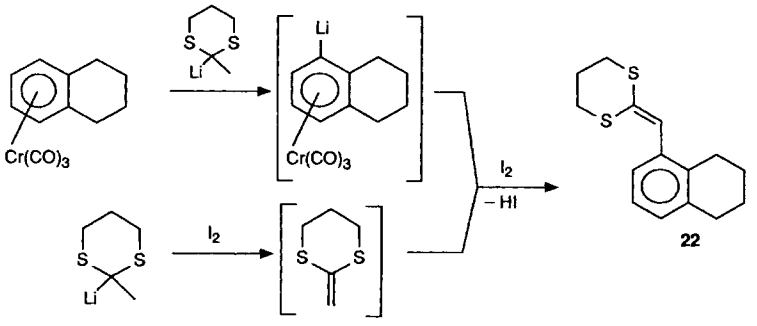


Entry	Nucleophile LiR	Conditions [°C/h]	Medium	Product distribution		Yield[a] [%]
1	$LiCMe_2CN$ (**A**)	–90/0.03[b]	THF	20 (**23a**)	80 (**23b**)[c])[d]	85
2	$LiCMe_2CN$ (**A**)	0/1.5	THF	> 2 (**23a**)	< 98 (**23b**)[c]	87
3	$LiCMe_2CN$ (**A**)	–55/0.3	THF/HMPA 2.5:1	47 (**23a**)	53 (**23b**)[c]	96
4	$LiCMe_2CN$ (**A**)	0/24	THF/HMPA 2.5:1	13 (**23a**)	87 (**23b**)[c]	91
5	$LiCH_2CN$ (**B**)	–40/1	THF/HMPA 3:1	100 (**24a**)	0 (**24b**)[d]	69
6	$LiCH_2CN$ (**B**)	–50/0.1	THF/HMPA (1 equiv.)	89 (**24a**)	11 (**24b**)[d]	45
7	$LiCH_2CN$ (**B**)	–20/2	THF/HPMA (1 equiv.)	60 (**24a**)	40 (**24b**)[d]	83
8	LiC(Me)(CN)OR (**C**[e])	–20/0.5	THF/HMPA 10:1	32 (**25a**)	69 (**25b**)[c])[f]	65
9	$LiCH_2CO_2(t\text{-Bu})$ (**G**)	–55/1.5	THF/HMPA 3:1	78 (**26a**)	22 (**26b**)[c]	57
10	$LiCH_2CO_2(t\text{-Bu})$ (**G**)	0/1.5	THF/HMPA 3:1	70 (**26a**)	30 (**26b**)[c]	44

[a]) Yield refers to isolated mixtures of isomers **a** and **b**. [b]) Complex (in THF) added at –90°. [c]) Mixture ratio determined by ^{1}H-NMR. [d]) Mixture ratio determined by GLC. [e]) R = $CH(CH_3)OCH_2CH_3$. [f]) The product is the acetyl derivative, obtained by the hydrolysis of the cyanohydrin.

Two earlier results by *Cambie et al.* with $LiCH_2CN$ and $LiCMeS(CH_2)_3S$ and complex **3** are included in *Table 3* for comparison (*Entries 3* and *6*) [12]. In the absence of HMPA, only low yields of addition of the C-nucleophile **E** were obtained, and, during workup, complete hydrolysis of the dithiane group took place. A side product, frequently present in low yield but occasionally formed in up to 30%, was isolated, and it was assigned structure **22**. A tentative rationalisation of this product is shown in *Scheme 2*. Surprisingly, nucleophile **E** did not add to the *o*-xylene complex **4** under a number of different

Scheme 2



conditions. Intractable products were formed in most cases, some resulting from competitive deprotonation rather than addition.

Regioselectivity of the Nucleophilic Addition. Carbanion addition to complexes **1**–**4** always takes place at the unsubstituted C-atoms of the aromatic rings. The nucleophile addition/oxidation sequence, when applied to complex **1**, provides ready access to the 3-substituted derivatives, a substitution pattern complementary to that of electrophilic aromatic substitution[4]). We note in passing that 3-substituted 1,2-dihydrocyclobutabenzenes are also accessible *via* lithiation/electrophile addition to **1** [16] and *via* zirconocene metallacycles [17]. Before considering the origins of the regioselectivity of nucleophilic addition to complex **1**, we examine the reactions of complexes **2**–**4**. The data show that under conditions favoring kinetic control of regioselectivity, C-nucleophiles add predominantly (**A**, **C**) or exclusively (**B**, **D**, **E**) to the C-atoms α to the ring junction in **2** and **3**. The high regioselectivity is exemplified by the efficient addition of dithiane to complex **2**. Oxidative workup, extraction, and crystallization from hexane gave **15a** as single product in good yield (*Table 2, Entry 6*).

With complex **3**, and much more clearly with complex **4**, we notice that addition of tertiary C-nucleophiles to the C(α)-atom becomes more difficult (*Table 4, Entries 1, 3,* and *8*), but the primary carbanions **B** and **G** still add with fair to excellent regioselectivity to this center (*Entries 5* and *9*). It was suggested that nucleophilic addition to [$Cr(CO)_3$(1,2-disubstituted arene)] complexes should occur to that C-atom which carries the H-atom, which undergoes the smallest upfield shift on complexation [18]. While the complexation shifts of the α-H-atoms are smaller than those of the β-H-atoms in complexes **1** and **2**, this is no longer the case for **3** and **4**, and thus no forecast of regioselectivity can be made on this basis.

In the addition of α-cyano C-nucleophiles and ester enolates to complexes **2**–**4**, but not to **1**, rearrangement to the thermodynamically favored regioisomeric β-addition intermediate takes place on warming up. As can be expected on the grounds of steric interactions, the extent of this migration increases from **2** to **4** and also strongly depends on the nucleophile. With the tertiary carbanion **A** and complex **2**, the change is relatively modest resulting in a 3:1 equilibrium. In its reactions with complex **3**, the same carbanion undergoes almost complete reversal of regioselectivity (*Table 3, Entries 1* and *2*).

[4]) Electrophilic aromatic substitution of 1,2-dihydrocyclobutabenzene yields the 4-substituted derivatives highly regioselectively [15].

Complete rearrangement to the β-isomer also takes place very rapidly with complex **4**. The S-stabilized carbanions **D** and **E** always add selectively to the C-atom α to the ring junction, and product distribution is invariant with time and temperature. The primary carbanion **B** also always adds to the α-position. While it is probable that this addition becomes reversible at higher temperatures, this is not accompanied by a rearrangement except in the case of complex **4**, where a 3:2 equilibrium of α- and β-addition is attained at $-20°$ (*Entry 7*).

We may compare the reactions of **3** to those reported by *Grundy et al.* for the addition of alkyl lithium and hydride reagents to the [Fe(cp)](1,2,3,4-tetrahydronaphthalene)[BF_4] complex [19]. Although regioselectivity in the Fe complex was shown to vary from one nucleophile to the other, the range was relatively small (1:1 to 2:1 mixtures of α- and β-addition products). Also, hydride addition to [Fe(cp)(*o*-xylene)][BF_4] was reported to give a 1:1 mixture of the cyclohexadienyl complexes [20]. This ties in with observations that the (cyclopentadienyl)iron-mediated reactions give low regioselectivity in nucleophilic additions of C-nucleophiles to coordinated arenes [21], but the question of reversibility of the addition of C-nucleophiles has as yet not been investigated in this series [22]. In the $Cr(CO)_3$-mediated reactions, the kinetically preferred site of attack on **1**–**4** is α to the ring junction, but, as the above results show, bulk of the arene substituent and the carbanion can bring about changes in regioselectivity.

Complex **1** stands out in that its reactions with carbanions of different size and reactivity are regiospecific at C(3). Moreover, this selectivity holds both under conditions favoring kinetic control and under those where equilibration of the intermediate cyclohexadienyl complexes is typically observed. It is, thus, likely that for **1** both kinetically and thermodynamically controlled addition favor the same intermediate. This has precedent in the reactions of nucleophile **A** with [Cr(anisole)$(CO)_3$] [3b]. Under conditions of a reversible carbanion addition, product distribution is determined by the relative thermodynamic stabilities of the isomeric intermediate, while for kinetic control (*e.g.* the experiments in *Entries 2, 6,* and *7* in *Table 1*), we assume a frontier-orbital-controlled reaction. We note that charge control of nucleophilic addition is generally limited to complexes which adopt a strongly preferred eclipsed conformation. For reasons of symmetry, this is not the case in the series of complexes under investigation here. The known structures for symmetrically *ortho*-disubstituted [Cr(arene)$(CO)_3$] complexes show them to adopt either the staggered *syn*-conformation or the *anti*-conformation[5]). In the *anti*-conformation, the symmetry-unique carbonyl ligand is pointed away from the substituents, in the *syn* conformation it is bisecting the disubstituted or fused C–C bond (*Fig. 1*).

anti *syn*

Fig. 1. anti- *and* syn-*staggered conformations of* ortho-*disubstituted [Cr(arene)$(CO)_3$] complexes*

[5]) In symmetrically *ortho*-disubstituted complexes, the Cr-atom is displaced from the center of gravity of the arene ring, away from the sites of ring fusion. Provided that the $Cr(CO)_3$ tripod remains undistorted, this, in a staggered conformation, could bring the CO vectors closer to one set of ring C-atoms than to the other. The displacement is very small, and we think it unlikely, but cannot rule out, that this has an effect on regioselectivity.

X-Ray Crystal Structures of Complexes **1** *and* **4**. The crystal structures of **1** and **4** were determined in order to detect any structural difference which might account for the difference in regioselectivity. Selected bond distances and angles are given in *Tables 5* and *6*, respectively. *Figs. 2* and *3* show the structures and the atomic numbering schemes used for the two complexes.

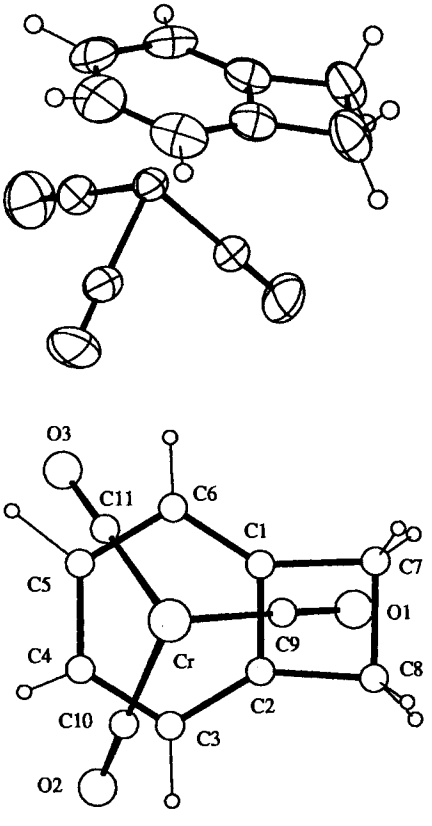


Fig. 2. *X-Ray crystal structure and numbering scheme for complex* **1**

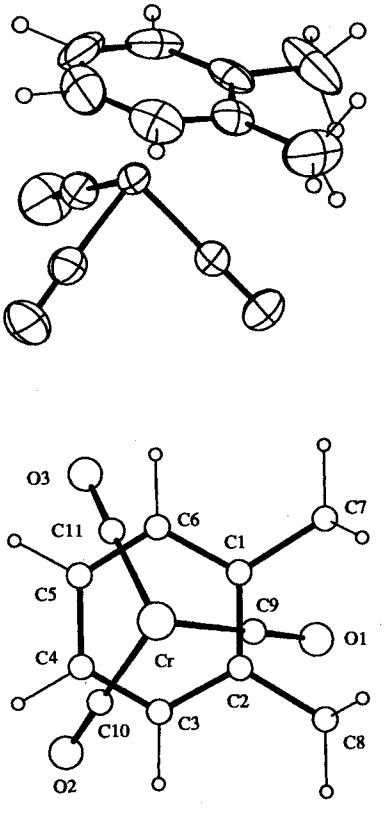


Fig. 3. *X-Ray crystal structure and numbering scheme for complex* **4**

Table 5. *Selected Interatomic Distances* [Å] *and Angles* [°] *for Complex* **1**

Cr–C(1)	2.230(7)	C(1)–C(2)	1.405(9)	C(1)–C(2)–C(3)	121.1(7)	C(9)–Cr–C(10)	88.5(3)
Cr–C(2)	2.228(8)	C(2)–C(3)	1.393(11)	C(2)–C(3)–C(4)	116.5(8)	C(9)–Cr–C(11)	90.0(3)
Cr–C(3)	2.225(9)	C(3)–C(4)	1.401(14)	C(3)–C(4)–C(5)	122.5(8)	C(10)–Cr–C(11)	90.0(3)
Cr–C(4)	2.196(8)	C(4)–C(5)	1.392(14)	C(4)–C(5)–C(6)	120.8(8)	C(2)–C(1)–C(7)	91.5(6)
Cr–C(5)	2.190(9)	C(5)–C(6)	1.434(13)	C(5)–C(6)–C(1)	115.7(7)	C(1)–C(7)–C(8)	87.7(6)
Cr–C(6)	2.241(8)	C(6)–C(1)	1.379(10)	C(6)–C(1)–C(2)	123.3(7)	C(7)–C(8)–C(2)	87.2(6)
Cr–C(9)	1.826(8)	C(1)–C(7)	1.525(11)	C(6)–C(1)–C(7)	145.2(7)	C(7)–C(8)–C(1)	93.6(6)
Cr–C(10)	1.839(8)	C(7)–C(8)	1.541(13)	C(3)–C(2)–C(8)	145.3(7)		
Cr–C(11)	1.833(7)	C(8)–C(2)	1.506(12)				
C(9)–O(1)	1.155(10)	C(10)–O(2)	1.143(10)				
C(11)–O(3)	1.159(9)						

Table 6. *Selected Interatomic Distances* [Å] *and Angles* [°] *for Complex* **4**

Cr–C(1)	2.229(7)	C(1)–C(2)	1.42(1)	C(6)–C(1)–C(2)	119.3(7)	C(9)–Cr–C(10)	88.0(3)
Cr–C(2)	2.232(7)	C(2)–C(3)	1.38(1)	C(1)–C(2)–C(3)	118.2(7)	C(9)–Cr–C(11)	90.7(3)
Cr–C(3)	2.223(9)	C(3)–C(4)	1.34(2)	C(2)–C(3)–C(4)	121.2(9)	C(10)–Cr–C(11)	89.2(3)
Cr–C(4)	2.20(1)	C(4)–C(5)	1.36(2)	C(3)–C(4)–C(5)	121.2(9)	C(2)–C(1)–C(7)	121.6(7)
Cr–C(5)	2.19(1)	C(5)–C(6)	1.37(2)	C(4)–C(5)–C(6)	120.8(9)	C(1)–C(2)–C(8)	121.9(7)
Cr–C(6)	2.198(7)	C(6)–C(1)	1.40(1)	C(5)–C(6)–C(1)	119.3(8)	C(6)–C(1)–C(7)	119.1(8)
Cr–C(9)	1.811(7)	C(1)–C(7)	1.52(1)			C(3)–C(2)–C(8)	119.9(7)
Cr–C(10)	1.830(8)	C(2)–C(8)	1.49(1)				
Cr–C(11)	1.828(7)	C(9)–O(1)	1.164(8)				
C(10)–O(2)	1.154(9)	C(11)–O(3)	1.152(9)				

Both complexes show the expected structure for a [Cr(arene)$(CO)_3$] [23] with a tripodal $Cr(CO)_3$ fragment coordinated in a η^6 mode to the arene. The distance from the Cr-atom to the plane of the arene is 1.720(8) Å for **1** and 1.728(2) for **4**. In both cases, the $Cr(CO)_3$ is displaced from the centre of the ring away from the substituents. This presumably arises from slight steric repulsion which is also shown by the fact that the substituents lie out of the least-squares plane defined by the arene and on the opposite side to the Cr-atom. The average displacement is 0.04 Å for **1** and 0.02 Å for **4**. Both compounds show the *syn*-staggered conformation in which one of the CO groups lies in between and below the two substituted C-atoms of the arene.

The geometry of the coordinated 1,2-dihydrocyclobutabenzene is similar to that of the free ligand [24]. The bond angles are identical within experimental error to those of the free ligand, and show a 'squeezing' of the benzene ring resulting in the C–C–C angles at the α-positions being reduced to 116.1° compared with the expected value of 120°. The C–C bond distances are slightly longer than those in the free ligand, and show alternance, the average value for the bond *trans* to a Cr–CO bond (1.388 Å) being shorter than those eclipsed by a Cr–CO bond (1.401 Å). This alternance has been observed for [Cr(benzene)$(CO)_3$] [25], and has been rationalized by extended *Hückel* (EHMO) calculations [26].

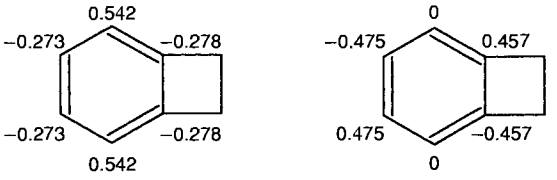
We conclude that there is no obvious structural difference in the coordination of the two arenes that can explain the different regioselectivity. However, the constraints of the four-membered ring in **1** result in the substituent being bent away from the α-position when compared with **4**. The average value of the difference in angle is 25.7(8)° which is likely to exert a considerable effect on interactions between the substituent and a nucleophile attacking the α-position.

Calculations. To identify any electronic origin for the observed *syn*-conformation of the $Cr(CO)_3$ unit and the change in regioselectivity between **1** and **4**, calculations on these systems were performed using the EHMO method [27]. This method has previously been used succesfully to discuss the conformational preferences [26] [28] of the $Cr(CO)_3$ unit and the regioselectivity of nucleophilic attack on [Cr(arene)$(CO)_3$] complexes [6–8].

For both the 1,2-dihydrocyclobutabenzene and the *o*-xylene complexes the calculations show the *anti*-conformer to be more stable than the *syn* or eclipsed conformations, but the barriers to rotation are very small, of the order of 0.5 kcal/mol. The small barriers to rotation were predicted by *Albright et al.* [26] for 1,2-disubstituted arenes. We suspect that the apparent contradiction with the results of *Rogers et al.* [28], who observed and calculated a *syn*-conformation for [Cr(biphenylene)$(CO)_3$], may arise from the greater interaction of the aromatic 1,2-substituent with the coordinated arene orbitals in this latter case than that between the arene and the aliphatic substituents in the complexes studied here.

Three different approaches were used to investigate the regioselectivity of nucleophilic attack:

a) The localization of the arene LUMO has been shown to be a useful indication of the site of nucleophilic attack [6] [8]. For both **1** and **4**, the LUMO is strongly localized at the α-position, the next arene unoccupied MO (SLUMO) lying *ca.* 1 kcal/mol higher in energy as a result of interaction with the aliphatic substituents:



b) The attack of a nucleophile on an [Cr(arene)$(CO)_3$] complex will lead to an η^5-cyclohexadienyl complex [29]. Calculations were carried out on the relative stabilities of the η^5-cyclohexadienyl complexes formed by attack of a hydride ion on complexes **1** and **4** using a geometry based on the crystal structure of the 1,3-dithiane adduct of [Cr(benzene)$(CO)_3$] [29]. The results showed no difference between **1** and **4**, with attack at the β-position being slightly more favorable in both cases by *ca.* 1/10 kcal. As observed [29] and predicted by EHMO calculations [30], there is a strong preference for the $Cr(CO)_3$ moiety to adopt a conformation in which a CO ligand eclipses the C-atom bearing the nucleophile.

c) Finally a method developed by *Weber et al.* in which the interaction energy between an incoming nucleophile (H^-) and the complex is mapped over the molecular surface [31] was applied. For all complexes attack at the α-position was predicted.

Conclusion. – Nucleophilic addition of stabilized carbanions to the arene complexed to the $Cr(CO)_3$ group is an expedient route to 3-substituted 1,2-dihydrocyclobutabenzenes and 4-substituted indanes. By varying reaction conditions and nucleophile, good regiocontrol can also be achieved with *o*-xylene. This is demonstrated by the addition of the primary C-nucleophile **B** to complex **4** to give **24a** selectively (*Table 4, Entry 5*), while the opposite regioselectivity is obtained with the tertiary C-nucleophile **A** (product **23b**, *Table 4, Entry 2*).

Calculations correctly predict α-selectivity under kinetic control, but they are unable to predict the observed differences in regioselectivity for nucleophilic attack, suggesting that these do not arise from electronic effects associated with the change of substituents from the four-membered ring in **1** to the two Me groups in **4**. It seems reasonable to suppose that some steric effect is operative, since it is for complex **1** where the substituents are bent furthest away from the α-position that the strongest α-preference is observed, and this is corroborated by the observed preference of bulky nucleophiles for the β-position in complexes **3** and **4**.

Financial support of this work by the *Swiss National Science Foundation* (grant No. 27.940.89) is gratefully acknowledged. We thank Mr. *J. P. Saulnier*, Mr. *A. Pinto*, and Mrs. *D. Clément* for NMR and MS measurements, Mr. *P. Romanens* for technical assistance and Dr. *P.-Y. Morgantini* for help with the calculations.

Experimental Part

General. All manipulations involving Cr complexes or carbanions were carried out under an inert atmosphere of purified N_2 and using standard *Schlenk* techniques [32]. THF, Et_2O, and Bu_2O were distilled from sodium-benzophenone-ketyl immediately prior to use. Toluene was refluxed 4 h over Na before distillation. Pentane, hexane, 2-methylpropionitrile, and *trans*-decaline were distilled from CaH_2. Hexamethylphosphortriamide (HMPA) was stirred for 15 h at 60° with CaH_2 before distillation under a reduced atmosphere of N_2 (10 Torr). $(i\text{-}Pr)_2NH$ was distilled from KOH pellets. $Cr(CO)_6$ (*Pressure Chemical Co.* or *Strem Chemicals*) was used as received. BuLi (*Fluka*) was titrated before use according the method of *Gilman* and *Cartledge* [33]. GLC was performed on a *Perkin-Elmer 900* spectrometer by using a 2 m × 6 mm column packed with *Chromosorb/OV 225* (10%) or a *Hewlett-Packard 5890A* spectrometer by using a 15 m × 0.25 mm cap. column *OV-31*. For quant. GLC, *trans*-decaline was added as internal standard. Anal. and TLC were carried out with silica gel plates *Merck 60* F_{254}. Column chromatography was carried out by the flash method described by *Still et al.* [34]. ^1H- and ^{13}C-NMR spectra: M.p.: on a *Büchi 510* apparatus; not corrected. IR spectra: with NaCl cells on a *Perkin-Elmer 681* or a *Mattson Polaris* (FT) spectrometer. Either a *Bruker WM-360* (^1H at 360 MHz and ^{13}C at 90.6 MHz), a *Varian XL-200* (^1H at 200 MHz and ^{13}C at 50.3 MHz), or a *Bruker AMX 400* spectrometer (^1H at 400 MHz), the chemical shifts δ are given in ppm relative to TMS and the coupling constants J in Hz. Attribution of ^{13}C-resonances was made *via* the APT pulse sequence. MS: *Varian CH 4* or a *SM 1* instrument; relative intensities are given in parentheses. The HR-MS were measured on an anal. *VG 7070-E* instrument (data system 11250, resolution 7000).

Complexes. The complexes $[Cr(CO)_3$(1,2-dihydrocyclobutabenzene)] (**1**) [16] [35], $[Cr(CO)_3$(indane)] (**2**) [9] [11b] [35a], $[Cr(CO)_3$(1,2,3,4-tetrahydronaphthalene)] (**3**) [36] [37], and $[Cr(CO)_3$(*o*-xylene)] (**4**) [36–38] were prepared *via* literature procedures either by thermolysis of $Cr(CO)_6$ [39] or by arene exchange in $[Cr(CO)_3$(naphthalene)] [40].

[Cr(CO)$_3$(4a, 5–8, 8a-η)-Tetrahydronaphthalene)] (**3**): IR (hexane): 1973vs, 1903vs. ^1H-NMR (200 MHz, $CDCl_3$): 5.22 (*s*, H–C(5–8)); 2.68–2.57 (*m*, H–C(1,4)); 1.85–1.68 (*m*, H–C(2,3)). MS: 268 (12, M^+), 184 (100), 52 (84).

*[Cr(CO)$_3$(*ortho*-Xylene)]* (**4**): IR ($CHCl_3$): 3020*w*, 1970vs, 1890vs. ^1H-NMR (360 MHz, $CDCl_3$): 5.34–5.27 (*m*, H–C(3,6)); 5.27–5.22 (*m*, H–C(4,5)); 2.20 (*s*, 2 CH_3). MS: 242 (3, M^+), 158 (14), 91 (4), 77 (3), 53 (12), 52 (100).

Preparation of C-Nucleophiles. THF solns. (0.1M) of $LiC(Me)_2CN$ (**A**), $LiCH_2CN$ (**B**), $LiC(Me)(CN)OCH(Me)OCH_2CH_3$ (**C**), $LiCHS(CH_2)_3S$ (**D**), $LiC(Me)S(CH_2)_3S$ (**E**), $LiC(Me)_2CO_2Me$ (**F**), and $LiCH_2CO_2(t\text{-}Bu)$ (**G**) were prepared as described in [3b].

General Procedure for the Nucleophilic Additions to Complexes **1–4**. The $[Cr(arene)(CO)_3]$ complex (1.0 mmol) was added in one portion, either as a solid or in soln. (THF, −78°), to the soln. of the nucleophile (1–1.1 mmol in THF, 10 ml, −78 or −90°). If required, HMPA was added dropwise at this stage. The mixture was then stirred for the time and at the temp. indicated in the *Tables*. After recooling to −78°, a cold (−78°) soln. of I_2 (5–6 mmol) in THF (10 ml) was added rapidly *via* transfer tube. After a few min, the cooling bath was removed, and the temp. of the mixture was slowly (1 h) raised to 20° and stirred at this temp. for 4 h. The mixture was diluted with Et_2O (40 ml) and washed with aq. $NaHSO_3$ (10%, 3 × 30 ml), aq. HCl (1N, 3 × 30 ml; if HMPA was used), sat. $NaHCO_3$ (30 ml), H_2O (2 × 30 ml), and brine (30 ml). The org. layer was dried ($MgSO_4$) and Et_2O removed in a rotavapor to give the crude product.

Reaction of LiCMe$_2$CN (**A**) *with* **1**: *Formation of* **5**. Following the *General Procedure*, a soln. of **1** (0.240 g, 1 mmol) and *trans*-decaline (1 mmol) in dry THF (4 ml) was added to a soln. of **A** (1.05 mmol) in THF at −90° (6 ml). After 5 min, half of the mixture was transferred *via* a precooled *Teflon* transfer tube to another *Schlenk* flask (soln. **B**). The first half of the mixture (soln. A) was immediately treated with I_2 and worked up as described. Soln. B was warmed to 0° and stirred at this temp. for 2 h followed by recooling, oxidation, and workup. ^1H-NMR and GLC of the crude products indicated in both cases the presence of a single regioisomer (**5**) in yields of 76% (reaction A) and 67% (reaction **B**).

2-(Bicyclo[4.2.0]octa-1,3,5-trien-2-yl)-2-methylpropionitrile (**5**): IR (hexane): 2240*w*, 1602*w*, 1420*s*, 1196*w*, 1112*m*, 785*s*, 780*s*, 706*s*. ^1H-NMR (360 MHz, $CDCl_3$): 7.28–7.23 (*m*, 2 H); 7.05–7.00 (*m*, 1 H); 3.40–3.35 (*m*, 2 H–C(8)); 3.25–3.21 (*m*, 2 H–C(7)); 1.70 (*s*, $C(CH_3)_2CN$). MS: 171 (65, M^+), 156 (26), 144 (47), 129 (100).

Reaction of LiCH$_2$CN (**B**) *with* **1**: *Formation of* **6**. Following the *General Procedure*, **1** (0.272 g, 1.13 mmol) in THF (5 ml) was added to a soln. of **B** (1.13 mmol) in THF/HMPA (5:1 ml) at −78°. The mixture was stirred for 30 min at −20° followed by oxidation and workup as described. Purification by prep. TLC (toluene/hexane 1:1) yielded **6** in 65% yield.

(Bicyclo[4.2.0]octa-1,3,5-trien-2-yl)acetonitrile (**6**): IR (hexane): 3030*w*, 2250*w*, 1610*w*, 1430*m*, 1418*m*, 907*w*, 780*s*, 735*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.22 (*t*, *J* = 7.5, H–C(4)); 7.11 (*d*, *J* = 7.5, 1 arom. H); 7.04 (*d*, *J* = 7.5, 1 arom. H); 3.63 (*s*, CH_2CN); 3.27 (*AB*(*m*), 2 H–C(8)); 3.25 (*AB*(*m*), 2 H–C(7)). MS: 143 (100 M^+), 116 (43).

Reaction of LiC(Me)(CN)OCH(Me)OCH$_2$CH$_3$ (**3**) *with* **1**: *Formation of* **7**. Following the *General Procedure*, the carbanion was prepared at −78° from the cyanohydrine [41] (0.154 g, 1.1 mmol) and LDA (1.1 mmol) in THF/HMPA (10:1 ml). Complex **1** (0.258 g, 1.1 mmol) was added in soln. in THF (5 ml), and the mixture was stirred for 30 min at −20°. Oxidation and workup as described was followed stirring the Et_2O soln. for 3 h with H_2SO_4 (10%, 30 ml) and for 20 min with NaOH (15%, 20 ml) to yield a colorless solid which was recrystallized from pentane to give **7** (0.143 g, 91%).

Bicyclo[4.2.0]octa-1,3,5-trien-2-yl Acetate (**7**): IR (hexane): 1695*s*. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.75 (*d*, *J* = 7, 1 arom. H); 7.31 (*t*, *J* = 7, H–C(4)); 7.23 (*d*, *J* = 7, 1 arom. H); 3.45 (*AB*(*m*), 2 H–C(8)); 3.27 (*AB*(*m*), 2 H–C(7)); 2.50 (*s*, CH_3). MS: 146 (100, M^+), 131 (51), 103 (65).

Reaction of 2-Lithio-1,3-dithiane (**D**) *with* **1**: *Formation of* **8**. Following the *General Procedure*, **1** (0.292 g, 1.22 mmol) in THF (7 ml) was added to a soln. of **D** (1.22 mmol) in THF (5 ml) at −78°. After stirring for 30 min at 0°, the soln. recooled, treated with I_2, and worked up as described. The crude product was purified by chromatography on silica (hexane/Et_2O 1:1) to give **8** (0.187 g, 69%).

2-(Bicyclo[4.2.0]octa-1,3,5-trien-2-yl)-1,3-dithiane (**8**): IR (hexane): 1420*s*, 1270*m*, 1170*m*, 1166*s*. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.25 (*d*, *J* = 8, 1 arom. H); 7.17 (*t*, *J* = 8, H–C(4′)); 6.96 (*d*, *J* = 8, 1 arom. H); 5.16 (*s*, H–C(2)); 3.32 (*dd*, *J* = 4,4, 2 H–C(8′)); 3.17 (*dd*, *J* = 4, H–C(7′)); 3.05 (*ddd*, *J* = 13,13,3, H–C(4,6)); 2.90 (*dt*, *J* = 13,3, H–C(4,6)); 2.20–2.10 (*m*, H–C(5)); 2.01–1.87 (*m*, H–C(5)). MS: 222 (2, M^+), 143 (100), 115 (45), 103 (7).

Transformation of **8** *into Aldehyde* **11**. To a suspension of *N*-chlorsuccinimide (0.736 g, 5.38 mmol) and $AgNO_3$ (1.09 g, 6.4 mmol) in MeCN/H_2O 4:1 (25 ml) were added collidine (1.28 ml, 9.6 mmol) and **8** (0.300 g, 1.35 mmol). After stirring for 2 min, aq. Na_2SO_3 was added (10%, 25 ml) followed by sat. $NaHCO_3$ (25 ml). The mixture was extracted with CH_2Cl_2 and the org. layer washed with HCl (1N), sat. $NaHCO_3$, H_2O, and brine. After filtration through a silica-gel column (Et_2O) 0.142 g of **11** was isolated in 80% yield. ^{1}H-NMR and IR of **11** matched those published earlier for this compound [16].

Reaction of LiC(Me)S(CH$_2$)$_3$S (**E**) with **1**: *Formation of* **9**. Following the *General Procedure*, **1** (0.24 g, 1 mmol) and HMPA (2.5 ml) were added to a soln. of 2-lithio-2-methyl-1,3-dithiane (1.1 mmol) [42] in THF (10 ml) at −78°. The mixture was stirred at 0° for 4 h. Oxidation with I_2 and workup followed by prep. TLC (CH_2Cl_2/hexane 1:2) gave **9** (0.149 g, 63%).

2-(Bicyclo[4.2.0]octa-1,3,5-trien-2-yl)-2-methyl-1,3-dithiane (**9**): ^{1}H-NMR (360 MHz, $CDCl_3$): 7.64 (*dd*, *J* = 7,1, 1 arom. H); 7.24 (*t*, *J* = 7, H–C(4′)); 6.99 (*d*, *J* = 7, 1 arom. H); 3.39 (*t*, *J* = 4, 2 H–C(8′)); 3.15 (*t*, *J* = 4, 2 H–C(7′)); 2.86–2.73 (*m*, 2 H–C(4,6)); 2.01–1.93 (*m*, 2 H–C(5)); 1.81 (*s*, CH_3). MS: 236 (60, M^+), 221 (5), 162 (100), 147 (65), 128 (32), 115 (20), 59 (18).

Reaction of LiCMe$_2$CO$_2$Me (**F**) with **1**: *Formation of* **10**: The carbanion **F** was formed as described by reacting $CHMe_2CO_2Me$ (1.1 mmol) with LDA (1.1 mmol) for 40 min in THF (10 ml) at −10°. After cooling to −78°, **1** (0.240 g, 1 mmol) was added as a solid and the mixture stirred for 20 min at −30°. Oxidation with I_2, workup, and chromatography on silica gave **10** (0.145 g, 71%).

Methyl 2-(Bicyclo[4.2.0]octa-1,3,5-trien-2-yl)-2-methylpropionate (**10**): ^{1}H-NMR (360 MHz, $CDCl_3$): 7.17 (*t*, *J* = 7.5, H–C(4′)); 7.09 (*d*, *J* = 7.5, H–C(3′) or H–C(5′)); 6.94 (*d*, *J* = 7.5, H–C(3′) or H–C(5′)); 3.67 (*s*, CH_3); 3.24–3.21 (*AB*(*m*), 2 H–C(8)); 3.16–3.12 (*AB*(*m*), 2 H–C(7)); 1.57 (*s*, 2 CH_3). MS: 204 (20, M^+), 146 (14), 145 (100), 130 (11), 129 (11), 128 (9).

Reaction of LiCH$_2$CN (**B**) *with* **2**: *Formation of* **13a**. A soln. of **B** (1.1 mmol) in THF (10 ml) was prepared as described. At −78°, **2** (0.254 g, 1 mmol) was added as a solid and the mixture stirred for 2 h at −20°. Oxidation and workup gave a crude product which, by GLC and ^{1}H-NMR, was found to consist of a single regioisomer. Chromatography yielded crystalline **13a** (0.140 g, 89%). A separate experiment which was carried out in THF/HMPA 3:1 at −40° again gave exclusively **13a** (95% yield).

(Indan-4-yl)acetonitrile (**13a**): M.p. 38–39° (hexane). IR ($CHCl_3$): 3025*s*, 3010*m*, 2955*s*, 2850*m*, 2255*m*, 1596*m*, 1474*m*, 1455*m*, 1437*m*, 1415*m*, 1234*m*, 1066*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.24–7.12 (*m*, 3 H); 3.64 (*s*, CH_2CN); 2.96 (*t*, *J* = 7.5, 2 H–C(3′)); 2.90 (*t*, *J* = 7.5, 2 H–C(1′)); 2.15 (*quint.*, *J* = 7.5, 2 H–C(2′)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 145.2; 142.6; 127.1; 125.8; 125.8; 124.3; 117.6; 33.0; 31.1; 24.8; 21.8. MS: 157 (23, M^+), 131 (11), 130 (100), 129 (27), 117 (47), 115 (44), 77 (12), 64 (15), 63 (18), 51 (25).

Reaction of LiC(Me)(CN)OCH(Me)OCH$_2$CH$_3$ (**C**) *with* **2**: *Formation of* **14** *and* **14b**. Following the *General Procedure*, **2** (0.381 g, 1.5 mmol) and HMPA (1 ml) were added to a soln. of **C** (1.5 mmol) in THF (10 ml) at −78°. After stirring for 30 min at 20°, recooling, oxidation, and hydrolysis as described for **7**, column chromatography furnished **14a** and **14b** as a 9:1 mixture (determined by ^{1}H-NMR) in 95% yield.

Indan-4-yl Acetate (**14a**): M.p. 37–39°. IR ($CHCl_3$): 2930*s*, 2900*s*, 2850*m*, 1740*s*, 1595*m*, 1580*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.67 (*d*, *J* = 7, 1 arom. H); 7.42 (*d*, *J* = 7, 1 arom. H); 7.24 (*t*, *J* = 7, H–C(6)); 3.27 (*t*, *J* = 7, 2 H–C(3)); 2.97 (*t*, *J* = 7, 2 H–C(1)); 2.60 (*s*, CH_3); 2.09 (*quint.*, *J* = 7, 2 H–C(2)). MS: 160 (59, M^+), 145 (100), 117 (55), 115 (37), 91 (13).

Indan-4-yl Acetate (**14b**): ^{1}H-NMR (360 MHz, $CDCl_3$): 7.83 (*s*, H–C(4)); 7.77 (*d*, *J* = 7, H–C(6)); 7.31 (*d*, *J* = 7, H–C(7)); 2.94 (*t*, *J* = 7.5, 2 H–C(1,3)); 2.59 (*s*, CH_3); 2.11 (*quint.*, *J* = 7.5, 2 H–C(2)).

Reaction of **D** *with* **2**: *Formation of* **15a**. Following the *General Procedure*, **2** (0.381 g, 1.5 mmol) was added as a solid to a soln. of **D** (1.55 mmol) in THF (10 ml) at −78°. After 10 min, HMPA (1 ml) was added and the mixture stirred at −10° for 1 h. After oxidation and workup, the crude solid product was recrystallized from hexane to yield **15a** (0.314 g, 89%).

2-(Indan-4-yl)-1,3-dithiane (**15a**): M.p. 112–114°. IR ($CHCl_3$): 3003*m*, 2955*s*, 2900*s*, 2845*m*, 1595*w*, 1470*m*, 1452*m*, 1423*s*, 1277*s*, 1175*m*, 908*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.41–7.35 (*m*, 1 arom. H); 7.22–7.15 (*m*, 2 arom. H); 5.27 (*s*, H–C(2)); 3.17–3.05 (*m*, H–C(4,6)); 3.05 (*t*, *J* = 7.5, 2 H–C(3′)); 3.00–2.89 (*m*, 4 H, H–C(1′,4,6)); 2.23–2.13 (*m*, H–C(5)); 2.12 (*quint.*, *J* = 7.5, 2 H–C(2′)); 2.03–1.89 (*m*, H–C(5)). MS: 236 (87, M^+), 162 (100), 161 (98), 147 (32), 130 (77), 115 (31), 45 (33).

Transformation of **15a** *into Aldehyde* **17**. Aldehyde **17** was obtained quantitatively *via* the same procedure described for the preparation of **11**.

Indane-4-carbaldehyde (**17**) [43]: ^{1}H-NMR (360 MHz, $CDCl_3$): 10.16 (*s*, CH=O); 7.64 (*dd*, *J* = 7.5, 1, 1 arom. H); 7.48 (*dd*, *J* = 7.5, 1, 1 arom. H); 7.33 (*t*, *J* = 7.5, H–C(6)); 3.30 (*t*, *J* = 7.5, 2 H–C(3)); 2.95 (*t*, *J* = 7.5, 2 H–C(1)); 2.16 (*quint.*, *J* = 7.5, 2 H–C(2)). MS: 146 (82, M^+), 145 (26), 131 (8), 128 (9), 118 (16), 117 (100), 116 (24), 115 (49), 91 (16).

Reaction of **E** *with* **2**: *Formation of* **16a**. Following the *General Procedure*, **2** (0.381 g, 1.5 mmol) and HMPA (1 ml) were added to a soln. of **E** (1.6 mmol) in THF (10 ml) at −78°. The mixture was stirred at 0° for 16 h, then quenched, and worked up as described. Chromatography gave **16a** (0.336 g, 89%) as colorless crystals.

2-(Indan-4-yl)-2-methyl-1,3-dithiane (**16a**): M.p. 55–56° (hexane). IR ($CHCl_3$): 3010*m*, 2965*s*, 2915*m*, 2850*w*, 1462*m*, 1444*m*, 1424*s*, 1369*w*, 1278*w*, 1087*m*, 1064*m*, 910*w*, 867*w*. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.75 (*d*, *J* = 7, 1 arom. H); 7.22–7.15 (*m*, 2 arom. H); 3.35 (*t*, *J* = 7, 2 H–C(3′)); 2.90 (*t*, *J* = 7, 2 H–C(1′)); 2.88–2.75 (*m*, 2 H–C(4,6)); 2.10–1.96 (*m*, 2 H–C(2′,5)); 1.96 (*s*, CH_3). MS: 250 (28, M^+), 176 (100), 175 (88), 161 (28), 144 (25), 128 (28), 115 (35).

Reaction of **A** *with* **3**: *Formation of* **18a** *and* **18b**. The reaction was carried out in THF/HMPA 3:1 on a 1.5-mmol scale by using the *General Procedure*. The mixture was stirred at −50° for 1 h, before quenching and workup. Chromatography on silica (hexane/Et_2O 10:1) gave **18a** and **18b** (0.210 g, 70%) as a 1:2 mixture (determined by ^{1}H-NMR).

2-Methyl-2-(1,2,3,4-tetrahydronaphth-5-yl)propionitrile (**18a**): ^{1}H-NMR (360 MHz, $CDCl_3$): 7.25–7.07 (*m*, 3 arom. H); 3.08 (*t*, *J* = 6, 2 H–C(4′)); 2.83 (*m*, 2 H–C(1′)); 1.88–1.79 (*m*, 2 H–C(2′,3′)); 1.73 (*s*, $C(CH_3)_2CN$).

2-Methyl-2-(1,2,3,4-tetrahydronaphth-6-yl)propionitrile (**18b**): IR ($CHCl_3$): 2980*m*, 2925*s*, 2865*m*, 2240*w*, 1503*m*, 1460*m*, 1435*m*, 712*s*, 672*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.22–7.17 (*m*, 2 arom. H); 7.10 (*d*, *J* = 8, 1 arom. H); 2.85–2.75 (*m*, 2 H–C(1′,4′)); 1.88–1.80 (*m*, 2 H–C(2′,3′)); 1.72 (*s*, $C(CH_3)_2CN$). MS: 199 (38, M^+), 185 (100), 156 (11), 142 (12), 131 (75), 115 (16), 104 (12), 91 (15), 77 (10).

Reaction of **C** *with* **3**: *Formation of* **20a** *and* **20b**. The reaction was carried out on a 1-mmol scale using the identical procedure as fore the synthesis of **7**. Chromatography of the crude reaction product on silica yielded **20a** and **20b** (0.101 g, 58%) as a 2:1 mixture of regioisomers.

1,2,3,4-Tetrahydronaphth-5-yl Acetate (**20a**): IR ($CHCl_3$): 3040*m*, 3010*m*, 2940*s*, 2870*s*, 1680*vs*, 1580*w*, 1452*m*, 1432*m*, 1352*m*, 1230*s*, 1129*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.45 (*dd*, *J* = 7, 1.5, 1 arom. H); 7.24–7.13 (*m*, 2 arom. H); 3.00–2.94 (*m*, 2 H–C(4)); 2.87–2.80 (*m*, 2 H–C(1)); 2.56 (*s*, CH_3); 1.85–1.75 (*m*, 2 H–C(2,3)). MS: 174 (71, M^+), 159 (100), 131 (56), 91 (32), 77 (12).

1,2,3,4-Tetrahydronaphth-6-yl Acetate (**20b**): ^{1}H-NMR (360 MHz, $CDCl_3$): 7.68 (*m*, 2 H–C(5,7)); 7.15 (*d*, *J* = 8.5, H–C(8)); 2.83 (*m*, 2 H–C(1,4)); 2.58 (*s*, CH_3); 1.83 (*m*, 2 H–C(2,3)).

Reaction of **E** *with* **4**: *Formation of* **20a**, **21a**, *and* **22**. Following the *General Procedure*, **3** (0.381 g. 1.5 mmol) was added as a solid to a soln. of **E** (1.6 mmol) in THF (10 ml) at −78°. After 15 h at −30°, the soln. was cooled, oxidized, and treated as described. The hydrolyzed α-product **20a** (0.040 g) was isolated by prep. TLC (hexane/Et_2O 12:1) in 24% yield. In these additions, the secondary product **22** was often observed with maximum 30% yield.

2-[(1,2,3,4-Tetrahydronaphth-5-yl)methylidene]-1,3-dithiane (**22**): IR ($CHCl_3$): 2930*s*, 2860*m*, 2840*w*, 1580*w*, 1560*w*, 1450*m*, 1420*m*, 1305*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.11–6.95 (*m*, 3 arom. H); 5.79 (*s*, C=CH); 3.68–3.54 (*m*, 2 H–C(4,6)); decoupling at 2.23 gives a *d*; 2.92–2.83 (*m*, 2 H–C(4′)); decoupling at 1.78 gives a *s*; 2.83–2.74 (*m*, 2 H–C(1′)); decoupling at 1.78 gives a *s*; 2.23 (*quint.*, *J* = 6, 2 H–C(5)); 1.79 (*quint.*, *J* = 3, 2 H–C(2′,3′)).

^{13}C-NMR (50.3 MHz, $CHCl_3$): 141.2 (C(2 or 5')); 137.6 (C(2 or 5')); 135.3 (C(4a' or 8a')); 135.2 (C(4a' or 8a')); 129.1 (CH); 126.8 (CH); 125.1 (CH); 118.7 (CH); 32.7 (CH_2); 31.8 (CH_2); 31.1 (CH_2); 29.9 (CH_2); 26.8 (CH_2); 23.3 (CH_2); 22.9 (CH_2). MS: 262 (55, M^+), 220 (11), 219 (17), 201 (24), 188 (63), 187 (52), 160 (76), 155 (66), 153 (30), 141 (37), 128 (57), 115 (74), 106 (44), 77 (31), 45 (100).

Reaction of **A** *with* **4**: *Formation of* **23a** *and* **23b**. The addition/oxidation sequence was carried out on a 1.5-mmol scale in THF and the mixture was stirred at 0° for 1.5 h before oxidation. Chromatography on silica (hexane/Et_2O 10:1) gave **23b** (0.227 g, 87%). GLC indicated the presence of *ca.* 1% of **23a**. The reaction was repeated by rapidly mixing a cold (−90°) THF soln. of **4** with the soln. of the nucleophile at the same temp. The reaction was quenched with I_2 after 2 min to give, after workup and chromatography, **23a** and **23b** as a 1:4 mixture in 85% yield. Analogous reactions in THF/HMPA (2.5:1; HMPA added before the complex) gave **23a** and **23b** in the yields and ratios indicated in *Table 4* (*Entries 3* and *4*).

2-(2,3-Dimethylphenyl)-2-methylpropionitrile (**23a**): IR (hexane): 2230*w*, 1480*m*, 780*s*, 722*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.20–7.10 (*m*, 3 arom. H); 2.52 (*s*, CH_3–C(3')); 2.30 (*s*, CH_3–C(2')); 1.80 (*s*, $C(CH_3)_2CN$). MS: 173 (30, M^+), 158 (100), 143 (8), 131 (24), 115 (8), 105 (7), 91 (8), 77 (7).

2-(3,4-Dimethylphenyl)-2-methylpropionitrile (**23b**): IR (hexane): 2250*w*, 1510*m*, 1260*m*, 885*w*, 875*w*, 820*m*, 815*m*, 715*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.30–7.10 (*m*, 3 arom. H); 2.30 (*s*, CH_3–C(4)); 2.27 (*s*, CH_3–C(3)); 1.72 (*s*, $C(CH_3)_2CN$). MS: 173 (24, M^+), 158 (100), 131 (11), 115 (6), 91 (6), 77 (5).

Reaction of **B** *with* **4**: *Formation of* **24a** *and* **24b**. The reactions were carried out on a 1-mmol scale as detailed in the *General Procedure* and in *Table 4* (*Entries 5–7*). Product mixtures were analyzed by GLC and NMR.

(2,3-Dimethylphenyl)acetonitrile (**24a**): M.p. 51–52°. IR ($CHCl_3$): 3030*m*, 3007*m*, 2948*m*, 2922*m*, 2858*w*, 2252*m*, 1586*w*, 1465*s*, 1419*m*, 1389*m*, 1232*m*, 1095*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.22 (*d*, J = 7.5, 1 arom. H); 7.18 (*d*, J = 7.5, 1 arom. H); 7.13 (*t*, J = 7.5, H–C(5)); 3.69 (*s*, CH_2CN); 2.33 (*s*, CH_3–C(2)); 2.26 (*s*, CH_3–C(3)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 137.6 (C); 134,7 (C); 130.1 (CH); 128.5 (C); 126.6 (CH); 126.2 (CH); 117.9 (C); 22.5 (CH_2); 20.5 (CH_3); 15.3 (CH_3). MS. 145 (47, M^+), 130 (35), 119 (13), 118 (100), 117 (28), 115 (14), 105 (70), 103 (28), 91 (15), 79 (13), 78 (12), 77 (34), 65 (19), 63 (21), 51 (38).

(3,4-Dimethylphenyl)acetonitrile (**24b**): ^{1}H-NMR (200 MHz, $CDCl_3$): 7.23–6.95 (*m*, 3 arom. H); 3.69 (*s*, CH_2CN); 2.27 (*s*, CH_3–C(3)); 2.26 (*s*, CH_3–C(4)).

Reaction of **C** *with* **4**: *Formation of* **25a** *and* **25b**. The reaction was carried out on a 1-mmol scale using the identical procedure as for 7. Chromatography of the crude reaction product on silica (hexane/Et_2O 8:1) yielded **25a** and **25b** (0.096 g, 65%) as a 1:2 mixture of regioisomers.

2,3-Dimethylacetophenone (**25a**) [44]: IR ($CHCl_3$): 3010*m*, 1685*s*, 1356*w*, 1291*w*, 1263*m*, 1133*w*. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.40 (*d*, J = 7.5, 1 arom. H); 7.26 (*d*, J = 7.5, 1 arom. H); 7.15 (*t*, J = 7.5, H–C(5)); 2.58 (*s*, $COCH_3$); 2.37 (*s*, CH_3–C(2)); 2.33 (*s*, CH_3–C(3)). MS: 148 (48, M^+), 133 (100), 105 (65), 77 (16), 51 (7).

3,4-Dimethylacetophenone (**25b**): IR ($CHCl_3$): 3010*s*, 2975*m*, 2950*m*, 2925*m*, 2870*w*, 1677*vs*, 1607*m*, 1360*m*, 1263*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 7.75 (*d*, J = 1.5, H–C(2)); 7.70 (*dd*, J = 7.5, 1.5, H–C(6)); 7.23 (*d*, J = 7.5, H–C(5)); 2.59 (*s*, $COCH_3$); 2.33 (*s*, 2 CH_3). MS: 148 (40, M^+), 133 (100), 105 (54), 77 (17).

Reaction of tert-*Butyl 2-Lithioacetate* (**G**) *with* **4**: *Formation of* **26a** *and* **26b**. Following the *General Procedure*, **4** (0.245 g, 1 mmol) was added as a solid to a soln. of **G** (1.1 mmol) in THF (9 ml) at −78°. HMPA (3 ml) was added dropwise and the mixture stirred for 1.5 h at −55°. Oxidation, workup, and purification by prep. TLC (hexane/Et_2O 6:1) gave **26a** and **26b** (as a 4:1 mixture (by ^{1}H-NMR) 57%). A separate experiment, carried out at 0°, gave a 7:3 mixture of the same products in 44% yield.

tert-*Butyl 2-(2,3-Dimethylphenyl)acetate* (**26a**): ^{1}H-NMR (200 MHz, $CDCl_3$): 7.10–7.00 (*m*, 3 arom. H); 3.58 (*s*, CH_2); 2.29 (*s*, CH_3–C(3)); 2.20 (*s*, CH_3–C(2)); 1.43 (*s*, *t*-Bu).

tert-*Butyl 2-(3,4-Dimethylphenyl)acetate* (**26b**): ^{1}H-NMR (200 MHz, $CDCl_3$): 7.10–7.00 (*m*, 3 arom. H); 3.46 (*s*, CH_2); 2.24 (*s*, CH_3–C(3)); 2.23 (*s*, CH_3–C(2)); 1.43 (*s*, *t*-Bu).

X-Ray Crystal-Structure Determinations. Complex **1**. M = 240.18, orthorhombic $P2_12_12_1$, Z = 4, a = 11.418(1), b = 12.688(1), c = 7.035(1) Å from 28 reflections ($22 \leq 2\theta \leq 46°$), $d_{obs.}$ = 1.56(2), $d_{calc.}$ = 1.57 g·cm^3. Crystal: yellow prism 0.24 × 0.13 × 0.13 mm obtained from octane soln. and sealed in a glass capillary. *Data Collection: Philips PW1100*, $\lambda(MoK_\alpha)$ = 0.71069 Å, r.t., $\omega - 2\theta$ scan, width 1.2 + 0.3 tan(θ)°, speed 0.02°/s; $6 < 2\theta < 60°$; $0 \leq h \leq 16$, $0 \leq k \leq 17$, $0 \leq l \leq 9$; standard reflections measured every 120 min, variation $< 2.5\sigma(I)$. Reflections measured: 1724, observed ($I \geq 3\sigma(I)$): 885. Corrections made for *Lorentz* and polarization effects, and for anomalous dispersion, but not for absorption. Structure solved by *Patterson* and *Fourier* synthesis methods. *Refinement:* function minimized $\Sigma(w(F_o - F_c))^2$, with unit weights. All non H-atoms refined with anisotropic atomic displacement parameters, H-atoms refined with a fixed isotropic atomic displacement parameter. Final blocked matrix (2 blocks) refinement with 162 variables and 885 reflections gave R = 0.038. The final *Fourier*-difference synthesis gave a minimum of −0.22 and a maximum of +0.31 e·Å^{-3}. All calculations used a

local version of the XRAY76 system [45] with scattering factors for neutral atoms from *Cromer* and *Mann* [46] and anomalous dispersion corrections from the international tables [47].

Complex **4**. $M = 242.2$, orthorhombic $P2_12_12_1$, $Z = 4$, $a = 7.37(2)$, $b = 11.693(2)$, $c = 12.824(1)$ Å from 22 reflections ($23 \leq 2\theta \leq 32°$), $d_{calc.} = 1.46$ g·cm^3. Crystal: yellow prism 0.09 × 0.20 × 0.30 mm obtained from octane soln. and mounted on a quartz fibre. *Data Collection: Nonius CAD4*, $\lambda(MoK_\alpha) = 0.71069$ Å, r.t., $\omega - 2\theta$ scan, width $1.2 + 0.2 \tan(\theta)°$, speed 0.02–0.14°/s; $4 < 2\theta < 46°$; $0 \leq h \leq 8$, $0 \leq k \leq 12$, $0 \leq l \leq 14$ with all antireflexions of these; standard reflections measured every 100 reflections, variation $< 3.2\sigma(I)$. Reflections measured: 1816, observed ($|F_o| \geq 4\sigma(F_o)$): 1374. Corrections made for *Lorentz* and polarization effects, and for anomalous dispersion, but not for absorption. Structure solved by direct methods [48]. *Refinement:* function minimized $\Sigma(w(F_o - F_c))^2$, with $w = 1/\sigma^2(F_o)$. All non H-atoms refined with anisotropic atomic displacement parameters, H-atoms in calculated positions. Final full-matrix refinement with 137 variables and 1374 reflections gave $R = 0.047$, $wR = 0.044$. The final *Fourier*-difference synthesis gave a minimum of −0.28 and a maximum of +0.27 e·Å^{-3}. The chirality/polarity of the structure was refined and the absolute structure parameter [49] converges to $x = -0.02$ (6). All calculations used XTAL 3.0 [50].

Calculations. Calculations using the extented *Hückel* method [27] with the modified *Wolfsberg-Helmholtz* formula [51] were made using the parameters given below (ζ_n exponent of nth component of orbital; c_n contraction coefficient of the nth component of double ζ expansion):

Atom	Orbital	H_{ii} [eV]	ζ_1	c_1	ζ_2	c_2
H	1s	−13.6	1.3			
C	2s	−21.4	1.625			
	2p	−11.4	1.625			
O	2s	−32.3	2.275			
	2p	−14.8	2.275			
Cr	4s	− 9.33	1.70			
	4p	− 5.23	1.70			
	3d	−11.17	4.95	0.4876	1.60	0.7205

The following bond distances in [Å] were used for calculations: C–H(aliphatic) 1.09, C–H(aromatic) 1.08, C–C(aromatic) 1.40, C(aromatic)–C(aliphatic) 1.514, C(aliphatic)–C(aliphatic) in the cyclobutane ring 1.532, Cr–C 1.83, C–O 1.152. The Cr-atom was placed 1.72 Å below the centre of the aromatic ring. OC–M–CO angles were taken to be 90°. For calculations on the η^5 intermediate, the sp^3-C-atoms was placed 0.56 Å above the aromatic ring, and bond lengths from this C-atom to the aromatic C-atoms were taken to be 1.505 Å. The calculations of interaction energies were performed as described in [31].

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