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NAPHTHALENE COMPLEXES

V*. ARENE EXCHANGE REACTIONS IN NAPHTHALENECHROMIUM COMPLEXES

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Summary

Di-η^6-naphthalenechromium(0) (**1**) reacts at 150°C with benzene to yield (η^6-naphthalene)(η^6-benzene)chromium(0) (**3**) in 76% yield. In the presence of THF, **1** undergoes Lewis base catalyzed arene exchange at 80°C. Reactions of **1** with substituted arenes yield the mixed sandwich complexes **4** and **6–10** (arene = 1,4-$C_6H_4Me_2$, 1,3,5-$C_6H_3Me_3$, C_6Me_6, 1,4-$C_6H_4(OMe)_2$, 1,4-$C_6H_4F_2$ and 1,4-$C_{10}H_6Me_2$). In all but one case (with 1,4-dimethylnaphthalene) exchange of a single naphthalene ligand is observed. In marked contrast to the lability of **1**, dimesitylenechromium(0) (**5**) is inert to arene displacement in benzene up to 240°C. The molecular structure of **3** has been determined by X-ray crystallography. The crystal data are as follows: *a* 7.784(1), *b* 13.411(2), *c* 22.772(5) Å, $Z = 8$, space group *Pbca*. The structure was refined to a R_w value of 0.043. The naphthalene ligand in **3** is nearly planar and parallel to the approximately eclipsed benzene ring. Metal atom–ring distances are 1.631(9) and 1.611(4) Å for naphthalene and benzene, respectively. Catalyzed and uncatalyzed naphthalene exchanges in the sandwich complex are compared to the analogous reactions with the $Cr(CO)_3$ complex **2**. Naphthalene exchange in **2** in benzene is 10^3 to 10^4 times faster than arene exchange in other arenetricarbonylchromium compounds. The mild conditions for Lewis base catalyzed naphthalene exchange make **2** a good precursor of other arenetricarbonylchromium compounds. Examples include the $Cr(CO)_3$ complexes of styrene, benzocyclobutene, 1-ethoxybenzocyclobutene, 1,8-dimethoxy-9,10-dihydroanthracene and 1,4-dimethylnaphthalene.

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* For part IV see ref. 52.

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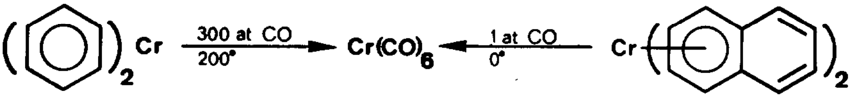
Introduction

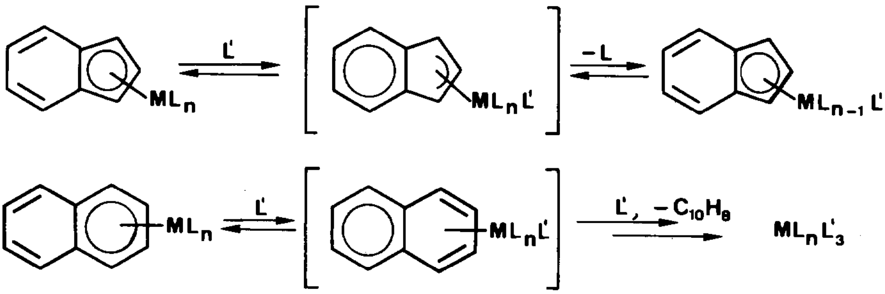
Arenechromium sandwich complexes are relatively inert to thermal or photochemical arene displacement reactions [1,2]. Di-η^6-benzenechromium, for example, reacts with CO only at high pressures (300 atm) and temperature (> 200°C), to yield $Cr(CO)_6$ (eq. 1) [3]. However, di-η^6-naphthalenechromium [4,5] (**1**) is a notable exception in this class of compounds. We have previously shown that this complex undergoes reactions with two electron donor ligands L, resulting in displacement of either one (L = $P(OR)_3$, PR_3) or both (L = CO, CNR) naphthalene ligands, under very mild conditions [5]. The striking difference in the reactivities of the naphthalene and the benzene complexes probably reflects a kinetic effect analogous to that observed with indenyl compounds [6–8].



(1)

The tremendous rate enhancement (10^3 to 10^8) observed for indenyl compounds compared to cyclopentadienyl compounds has been attributed to the re-aromatization of benzene in the transition state, which stabilizes the ene fragment of the allyl-ene transition state. The cyclopentadienyl ligand, which has no such stabilization, requires more energy to achieve this transition state. This argument can be used analogously to rationalize the increased reactivity of the metal-naphthalene compared with the metal–benzene bond. An associative mechanism is assumed which involves an initial approach of the ligand (or donor solvent) and a slippage of the η^6-arene– to a η^4-arene–metal bond as was suggested for arene displacement from arenetricarbonylmolybdenum complexes [2,9].

Although the origins of the indenyl and naphthalene effects are similar, the reactions of the indenyl and naphthalene compounds take different courses (Scheme 1). In the former the slippage $\eta^5 \rightleftarrows \eta^3$ is readily reversible, with η^5-coordination favoured [10]. The indenyl ligand effect manifests itself in a labilization of the coligands via the temporary provision of a coordination site, thus favouring an associative pathway to coligand displacement. On the other hand, the naphthalene ligand effect leads to the displacement of the arene ligand, thereby creating three free coordination sites. Naphthalenetricarbonylchromium is a good precursor for the $Cr(CO)_3$ fragment and, dinaphthalenechromium(0) is a source of an arenechromium fragment or of a "naked" Cr atom. The role played by the sandwich complex in



SCHEME 1. Comparison of the indenyl and of the naphthalene ligand effect in displacement reactions.

chromium chemistry is therefore analogous to that of di-1,5-cyclooctadienenickel in nickel chemistry [11].

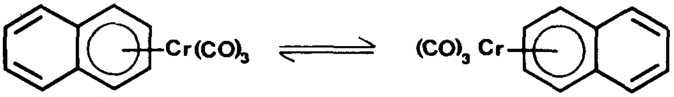
In this paper we describe our investigation into naphthalene displacement by other arene ligands.

Results and discussion

1. Intramolecular exchange

The ^{1}H [4,5] and ^{13}C NMR [12,13] spectra of the sandwich complex **1** (in C_6D_6, ambient temperature) are consistent with the presence of Cr bound to one ring of the condensed aromatic system. When a benzene solution of **1** was heated to 130°C in the NMR spectrometer probe neither line broadening nor coalescence of the NMR signals was observed. This indicates that under these conditions migration of the Cr atom from one ring to the other either does not occur or is too slow to be observed by NMR techniques. The behaviour of the sandwich complex **1** parallels that of the $Cr(CO)_3$ complex **2**, which has been investigated (albeit in coordinating solvents) by Nicholas, Kerber and Stiefel [14]. We found that the two AA'BB' multiplets for the hydrogens of the coordinated and uncoordinated rings of **2** in decane remained unchanged upon heating to 140°C in the NMR spectrometer probe. Above this temperature rapid decomposition of the complex occurred, as previously reported [15]. However, preliminary studies in this laboratory with a selectively deuterated naphthalenetricarbonylchromium complex indicate that ring exchange in **2** occurs in benzene much faster than intermolecular arene exchange of naphthalene for benzene (see below for an analysis of the latter reaction) (eq. 6). This result strongly implies an intramolecular pathway for the isomerisation shown in eq. 2. The rearrangement of 2,3-dimethylnaphthalenetricarbonylchromium in decane, studied by Deubzer [17], probably provides an additional, and much earlier, example of intramolecular rearrangement in this class of compounds.

The absence of rapid interring movement in **2** under mild conditions is not surprising. The degenerate reaction (eq. 2) has been the subject of a thorough theoretical analysis which shows that the pathway of least motion is symmetry forbidden, and that all bonding interaction is lost in the transition state [18]. Interring movement, if it does occur, is predicted to pass through an exocyclic allyl



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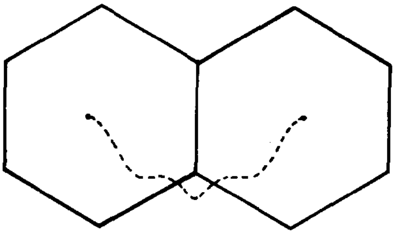


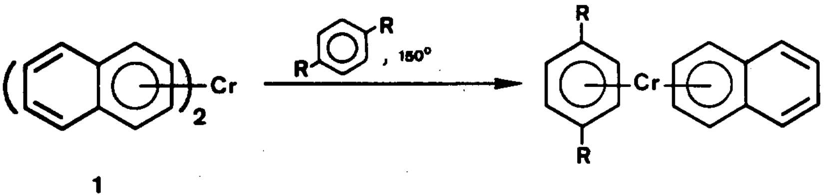
SCHEME 2. Calculated minimum energy path ($E_{\text{Act.}}$ 27.4 kcal/mol) for shifting the $Cr(CO)_3$ group in **2** (taken from ref. 18).

intermediate (Scheme 2). As the two fragments $Cr(CO)_3$ and Cr(arene) are isolobal [19] the features of this process should be the same, at least qualitatively, for **1** and **2**.

2. *Intermolecular exchange*

(a) Di-η⁶-naphthalenechromium (1)

Although no intra- or inter-molecular exchange of naphthalene in **1** was observed (by NMR) in benzene solution at temperatures up to 130°C, exchange of one naphthalene ligand for benzene occurred upon heating to 150°C (15 h). The reaction yielded the new mixed sandwich complex (η^6-naphthalene)(η^6-benzene)chromium(0) (**3**) (eq. 3). Likewise, reactions of **1** with *p*-xylene and mesitylene yielded complexes **4** and **6**.



(3)

1

3 R = H 76%
4 R = Me 80%

Exchange of both naphthalene ligands for benzene was not observed, either under these conditions, or in the THF-catalyzed reactions described below. Double exchange took place, however, with 1,4-dimethylnaphthalene (eq. 4). In reactions of **1** with 1,4-dimethylnaphthalene only the products with the metal bonded to the unsubstituted ring were obtained.

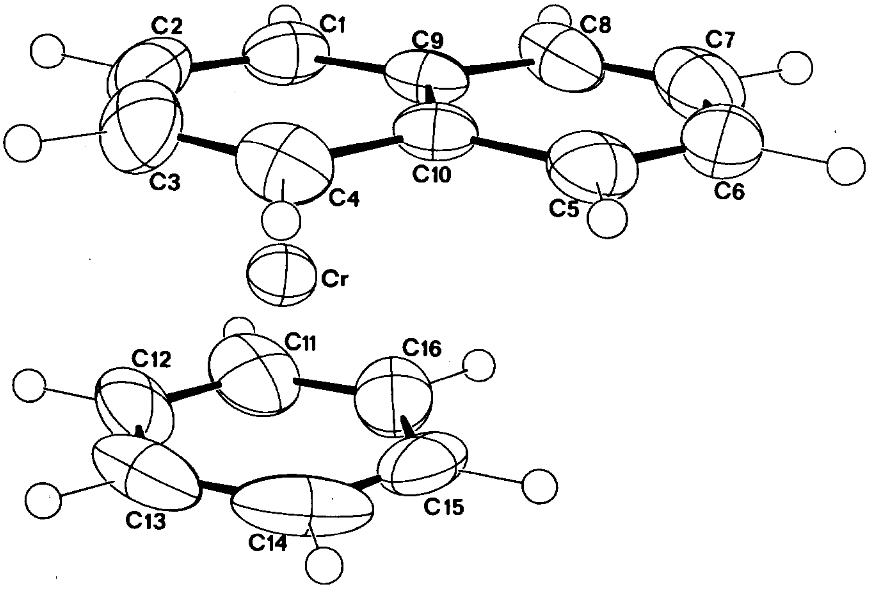
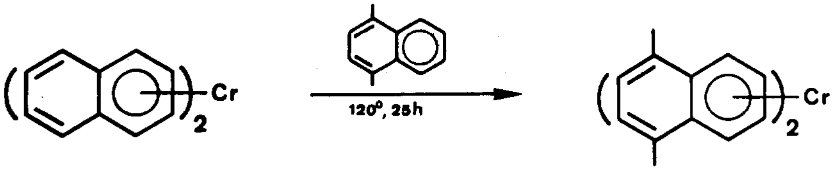


Fig. 1. The ORTEP diagram and atom numbering scheme for (η^6-$C_{10}H_8$)(η^6-C_6H_6)Cr^0 (3).



(4)

X-Ray crystallographic analysis of (η^6-benzene)(η^6-naphthalene)chromium (3)

Figure 1 shows an ORTEP diagram of complex **3** with the atom numbering scheme. Relevant bond lengths and angles are listed in Table 1. Final positional parameters and equivalent isotropic temperature factors are given in Table 5 *. The crystal structure of **3** reveals the naphthalene to be nearly planar (standard deviation of the atoms from the C(1)–C(10) plane 0.017 Å; max. dev. 0.030 Å) and parallel (0.9°) to the approximately eclipsed (9°) benzene ring. The distance between the Cr atom and the coordinated C_6 ring planes of naphthalene and benzene are 1.631(9) and 1.611(4) Å, respectively. The latter value is identical within experimental error to that in $Cr(C_6H_6)_2$ (1.609 Å) [20]. The Cr–C distances for naphthalene show a set of 4 shorter (Cr–C(1) to Cr–C(4) av. 2.142 Å) and 2 longer (Cr–C(9), Cr–C(10) av. 2.198 Å) bonds [21]. This results in a displacement of the projection of the Cr atom on the C_6 plane of naphthalene from the centre of gravity of the ring by 0.030(1) Å. This slippage away from the ring junction carbon atoms is a characteristic feature in complexes of condensed aromatic systems with Group VI metals [1a,13,22], and has been suggested to reflect the vastly different energies required for moving the metal towards (high energy) or away (low energy) from the central C–C bond [18]. Unexpectedly, however, a displacement of similar magnitude (0.035 Å) is observed

TABLE 1

INTERATOMIC DISTANCES (Å) AND ANGLES (Deg) FOR $(C_{10}H_8)(C_6H_6)Cr$ (3)

Bond distances					
Cr–C(1)	2.143(5)	Cr–C(15)	2.130(6)	C(7)–C(8)	1.345(9)
Cr–C(2)	2.145(6)	Cr–C(16)	2.134(6)	C(8)–C(9)	1.432(8)
Cr–C(3)	2.150(6)	C(1)–C(2)	1.398(8)	C(9)–C(10)	1.435(6)
Cr–C(4)	2.131(5)	C(1)–C(9)	1.432(8)	C(11)–C(12)	1.389(9)
Cr–C(9)	2.189(5)	C(2)–C(3)	1.392(9)	C(11)–C(16)	1.396(9)
Cr–C(10)	2.207(5)	C(3)–C(4)	1.407(8)	C(12)–C(13)	1.386(9)
Cr–C(11)	2.159(5)	C(4)–C(10)	1.441(8)	C(13)–C(14)	1.469(12)
Cr–C(12)	2.147(6)	C(5)–C(6)	1.344(9)	C(14)–C(15)	1.411(10)
Cr–C(13)	2.127(6)	C(5)–C(10)	1.431(8)	C(15)–C(16)	1.382(9)
Cr–C(14)	2.133(7)	C(6)–C(7)	1.429(9)		
Bond angles					
C(2)–C(1)–C(9)	120.1(5)	C(7)–C(8)–C(9)	121.0(5)	C(12)–C(11)–C(16)	121.2(6)
C(1)–C(2)–C(3)	120.9(5)	C(1)–C(9)–C(8)	122.3(4)	C(11)–C(12)–C(13)	120.6(6)
C(2)–C(3)–C(4)	120.3(5)	C(1)–C(9)–C(10)	119.9(4)	C(12)–C(13)–C(14)	119.0(6)
C(3)–C(4)–C(10)	120.9(5)	C(8)–C(9)–C(10)	117.7(5)	C(13)–C(14)–C(15)	118.1(6)
C(6)–C(5)–C(10)	121.0(5)	C(4)–C(10)–C(5)	123.0(4)	C(14)–C(15)–C(16)	121.1(6)
C(5)–C(6)–C(7)	120.0(6)	C(4)–C(10)–C(9)	117.7(5)	C(11)–C(16)–C(15)	119.9(6)
C(6)–C(7)–C(8)	121.2(6)	C(5)–C(10)–C(9)	119.1(5)		

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* Observed and calculated structure factors may be obtained on request from G.B.

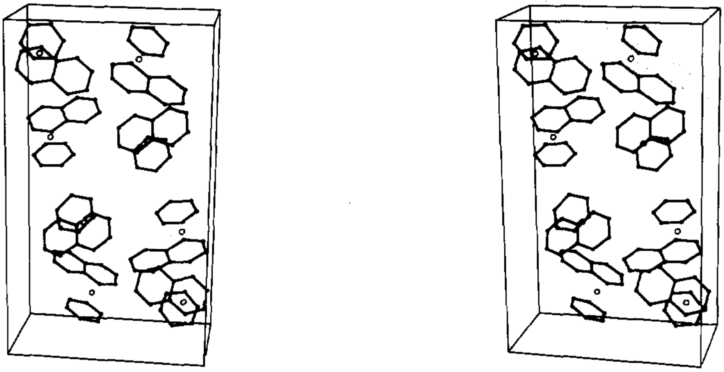
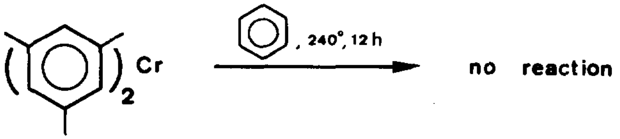


Fig. 2. A stereoview of the packing of **3** in the unit cell.

for the benzene ring in **3**. The Cr–C(11), Cr–C(12) bonds (av. 2.153 Å) are significantly longer than the other four Cr–C bonds (av. 2.131 Å). The C–C distances in the coordinated part of naphthalene average 1.417(21) Å, those in the non-coordinated part 1.403(45) Å, and those in the benzene ring 1.405(32) Å (1.412(32) Å when corrected for riding motion [23]). The large standard deviation in the mean C–C bond length in benzene can be traced to a significant lengthening of the C(13)–C(14) bond. This bond lengthening is significant, but its extent must be viewed with caution since C(13) and particularly C(14) are strongly affected by thermal motion (see Fig. 1).

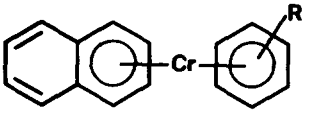
The high temperature required for this reaction and the observation of displacement of only one naphthalene ligand in **1** contrasts with the earlier report that di-η^6-mesitylenechromium(0) (**5**) yields di-η^6-benzenechromium(0) on refluxing in benzene [24] (1 h). Kinetic (see Introduction) as well as thermodynamic [24] considerations would predict an easier displacement of naphthalene than of mesitylene by benzene. On the basis of the results of our reinvestigation of this reaction we are unable to confirm this report of arene exchange in a chromium(0) sandwich complex; we recovered di-η^6-mesitylenechromium(0) (**5**) unchanged after reflux in benzene, and furthermore, no arene exchange was observed when a sealed NMR tube containing **5** in benzene was heated at temperatures up to 240°C (eq. 5). Above 250°C a slow gas phase decomposition gave rise to a Cr mirror in the upper portion of the tube.

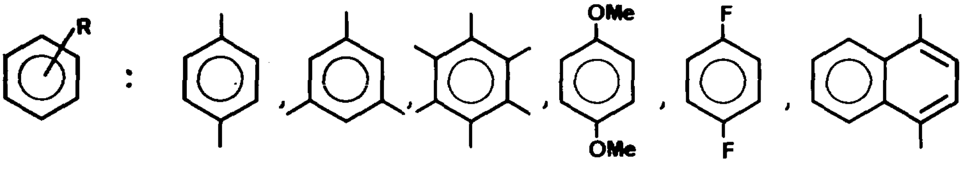


(5)

Partial oxidation of **5** to the cationic complex, followed by reflux in benzene and reduction, again yielded the starting complex. However exchange under these conditions, in the presence of $AlCl_3/AlCl_4^-$ is well documented [25]. The presence of a strong Lewis acid as well as a Cr^I oxidation state thus appear to be essential requirements in arene exchange of Cr sandwich complexes. Complex **1** is an exception, and its reaction with benzene is, to our knowledge, the first example of an uncatalyzed thermal arene exchange in this class of compounds.

Addition of tetrahydrofuran to the reaction mixture lowers the temperature of exchange from 150 to 80°C. Acceleration by Lewis base solvents lends support to the proposed slippage mechanism via an associative pathway. Exchange reactions with substituted arenes yield the series of mixed sandwich complexes (**4**, **6**–**10**) ^{1}H and ^{13}C NMR data are listed in Table 2.



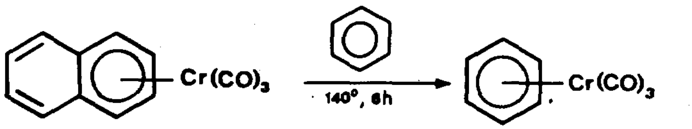


4 6 7 8 9 10

Lower yields in solvent assisted reactions occur due to metal agglomeration and ensuing autocatalytic decomposition reactions. Hexamethyl benzene represents an extreme case, since substantial amounts of solvent are required to dissolve the arene. Reaction of **1** with difluorobenzene gives a mixture of **9** and **3** in low yield; the latter product presumably arises from fluorine abstraction by the metal [26].

(b) Naphthalenetricarbonylchromium

Arene displacement in arenetricarbonylchromium complexes proceeds more readily than in the sandwich compounds [1,2], thermal arene exchange has found some limited application in the synthesis of new complexes. Reaction conditions in neat arene solvents are severe, however, with typical temperatures being in the 160–200°C range. Again, naphthalene was found to be an exception. The reaction shown in eq. 6 was complete after 6 h at 140°C.



(6)

The progress of the exchange was monitored by ^{1}H NMR spectroscopy. The data are listed in Table 3.

The activation energy for the uncatalyzed arene exchange is 22.5 kcal/mole. In this context, it is interesting to compare this value with the computed binding energy of naphthalene to Cr(CO)$_3$ (47 kcal/mol) and with calculated energies for the shifting of the Cr(CO)$_3$ group away from the central carbon–carbon bond in naphthalene: 24 kcal/mole for the most stable η^2-geometry and 17 kcal/mol for a η^3-geometry [18].

TABLE 2

^{1}H AND ^{13}C NMR DATA [a] FOR (η^6-NAPHTHALENE)(η^6-ARENE)CHROMIUM(0) COMPLEXES [b]

Compound	Naphthalene				Arene					
	H(1,4)	H(2,3)	H(6,7)	H(5.8)	H(2′,3′)	H(6′,7′)	H(5′,8′)	H′	Me	OMe
$Cr(C_{10}H_8)_2$ **(1)**	5.24	4.34	6.92							
$Cr(C_{10}H_8)(C_6H_6)$ **(3)**	5.54	4.38	6.92	7.60				4.05		
$Cr(C_{10}H_8)(C_6H_4Me_2)$ **(4)**	5.40	4.30	7.02	7.60				4.12	1.85	
$Cr(C_{10}H_8)(C_6H_3Me_3)$ **(6)**	5.24	4.24	7.05	7.58				4.02	1.95	
$Cr(C_{10}H_8)(C_6Me_6)$ **(7)**	4.83	3.98	7.11	7.50					2.00	
$Cr(C_{10}H_8)(C_6H_4(OMe)_2)$ **(8)**	5.41	4.45	6.98	7.60				4.19		3.27
$Cr(C_{10}H_8)(C_6H_4F_2)$ **(9)**	5.45	4.48	6.93	7.44				4.26		
$Cr(C_{10}H_8)(C_{10}H_6Me_2)$ **(10)**	5.30 [c]	4.44 [c]	6.87		6.77	4.50 [c]	5.36 [c]		2.07	

Compound	C(1,4)	C(2,3)	C(6,7)	C(5,8)	(C4a,8a)	C_{arene}		Me	OMe
						subst.	nonsubst.		
$Cr(C_{10}H_8)_2$ **(1)**	75.0 [d]	77.8 [d]	123.1 [d]	133.9 [d]	89.3				
$Cr(C_{10}H_8)(C_6H_6)$ **(3)**	73.5	76.7	123.8	136.5	90.9		77.3		
$Cr(C_{10}H_8)(C_6H_4Me_2)$ **(4)**	74.5	78.4	123.9	136.6	90.8	87.8	79.3	19.5	
$Cr(C_{10}H_8)(C_6H_3Me_3)$ **(6)**	74.9	78.8	123.3	135.9	90.1	88.2	80.6	19.6	
$Cr(C_{10}H_8)(C_6Me_6)$ **(7)**	76.0	81.4	123.2	135.4	89.9	88.8		16.6	
$Cr(C_{10}H_8)(C_6H_4(OMe)_2)$ **(8)**	74.4	78.1	124.2	135.8	93.1	131.5	64.9		55.5

[a] In C_6D_6. [b] See Fig. 1. for numbering. [c] Band assignment H, H′ is undetermined. [d] See ref. 12 for unambiguous band assignment.

The observed rate of exchange is 6.4 × 10^3 times as great as that of xylenetricarbonylchromium [27]. The naphthalene ligand effect is thus of the same order of magnitude as the more intensively studied indenyl ligand effect. Confirming an

TABLE 3

KINETIC DATA FOR THE REACTION OF BENZENE-d_6 WITH NAPHTHALENETRICARBONYLCHROMIUM (0.08 *M*)

T(°C)	$10^4\,K_{obsd}$ (s^{-1})	Activation data [a]
120	0.44±0.04	E_A = 22.5±1.5 kcal/mol
140	1.73±0.14	$\Delta H^{\neq}$ = 21.7±1.5 kcal/mol
150	3.93±0.22	$\Delta S^{\neq}$ = −24±3.6 cal/°mol
160	5.96±0.47	$\Delta G^{\neq}$ = 31.7±3 kcal/mol

[a] First order kinetics.

earlier report by Strohmeier [28], naphthalene exchange was found to be first order in complex, and so different from reactions of monocyclic arenes for which the rate law includes a term second order in the complex. Strohmeier's mechanistic conclusions from these kinetic studies have been challenged, however, and some chemically more plausible mechanisms have been proposed [2,27,29–31]. A very recent study [27] on xylenetricarbonylchromium demonstrated that the second order term is not a true bimolecular term but involves all the carbonyl compounds in the reaction mixture; this catalysis by carbonyl compounds may be compared to that by other Lewis bases (e.g. donor solvents). Naphthalene displacement in **2** by donor solvents is well documented [29–32], and so it is surprising that the above carbonyl catalysis should not also be effective in this system. However, in accord with the kinetic data and in contrast to Traylor's [27] observations on xylenetricarbonylchromium, we found naphthalene exchange to be unaffected by added arenetricarbonylchromium (in our study, benzene $Cr(CO)_3$). Steric effects may be the cause of this behaviour, particularly since naphthalene displacement occurs under relatively mild conditions. In an associative pathway slippage of the naphthalene ligand ($\eta^6 \rightarrow \eta^4$) requires the incoming ligand to approach from the side of the uncomplexed ring of the naphthalene [1a]. This makes the reaction very sensitive to the size of the attacking group (as has been noted previously for **1**) [5]. Alternatively, carbonyl catalysis may only become significant under the much severer conditions of exchange in monocyclic arenetricarbonylchromium complexes. Naphthalene heads a list of arenes assembled according to their ease of displacement by other arenes. These equilibria, reported by Mahaffy and Pauson [30], were established in THF at 142°C. Displacement of naphthalene must be exceedingly fast under these conditions since solvolysis of **2** in THF was reported to occur at room temperature [32b]. We found that the addition of 10% THF to a benzene solution of **2** accelerated the exchange to the extent that it proceeded at 60°C at roughly the same rate (time for 50% reaction ca. 1 h) as at 140°C in the non-catalyzed reaction. For preparative purposes the addition of small amounts of THF (rather than its use as the solvent) resulted in better yields. The conditions and results of some exchange reactions are listed in Table 4. Naphthalene exchange for another arene thus offers a mild synthetic route to arenetricarbonylchromium complexes, outperforming, in some reactions [33] other $Cr(CO)_3$ precursors such as $(CH_3CN)_3Cr(CO)_3$ [35] and $(NH_3)_3Cr(CO)_3$ [36].

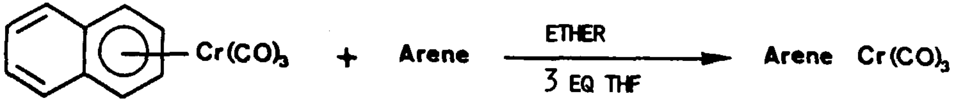
Conclusion

Naphthalenemetal complexes occupy a special place among arenemetal compounds. In marked contrast to the very inert benzene–chromium bond for example, the naphthalene–chromium bond, although thermally stable, is labile. The lability appears to be a consequence of the ability of the naphthalene ligand to undergo facile slippage freeing a coordination site for an incoming ligand. This is demonstrated in this study by the synthesis of a series of mixed arenechromium sandwich complexes via naphthalene exchange. The naphthalene sandwich complex is a source of a arenechromium fragment or of a naked Cr atom. Likewise the naphthalenetricarbonylchromium complex is a good starting material for the mild synthesis of other arenetricarbonylchromium compounds via $Cr(CO)_3$ fragment transfer. Further studies aimed at exploiting this lability in the chemistry of low valent metals of the Ti, V and Cr triad are in progress in this laboratory.

(Continued on p. 194)

TABLE 4

SYNTHESIS OF ARENETRICARBONYLCHROMIUM COMPLEXES VIA ARENE EXCHANGE IN NAPHTHALENETRICARBONYLCHROMIUM



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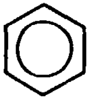
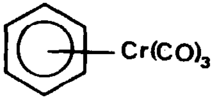
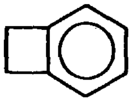
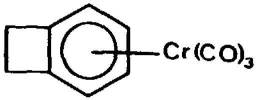
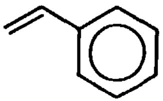
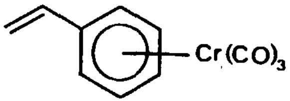
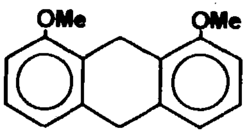
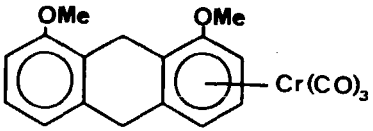
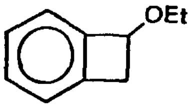
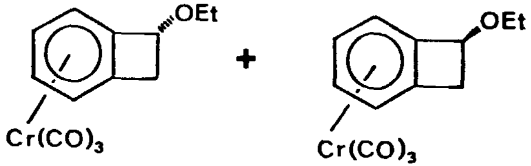
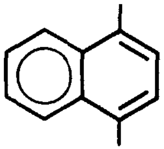
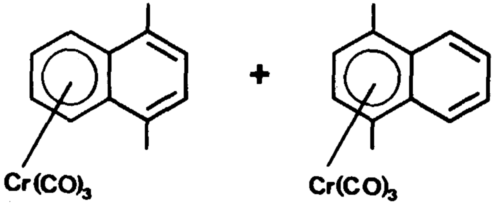
1.		16	70		94
2.		16	70		96
3.		19	70		90
4.		18	70		81 [b]

5.		22	70	 2 : 3	70
6.		26	75	 7 : 3 [c]	94

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[a] To accelerate the exchange 2 equiv. of arene were added (3 equiv. in entry 6). [b] The complex containing 2 $Cr(CO)_3$ units is formed in ca. 1% yield.
[c] Equilibrium mixture of the two regioisomers [17,51].

Experimental

All manipulations were carried out under nitrogen or argon or under vacuum, using standard Schlenk techniques or a stainless steel glovebox (Mecaplex GB 80) equipped with a dry-train. Solvents and reagents were dried with CaH_2 (alkanes, difluorobenzene), sodium-benzophenoneketyl (ethers) or sodium (benzene, toluene, *p*-xylene, mesitylene, 1,4-dimethylnaphthalene) and distilled under N_2 or in vacuo. Hexamethylbenzene (Fluka) was recrystallized from ethanol. *p*-Dimethoxybenzene was passed through a short column of Al_2O_3 (pentane solution).

^1H and ^{13}C NMR spectra were recorded on Varian XL-100 or Bruker WH-360 spectrometers. All chemical shifts are reported in ppm downfield from TMS. NMR measurements at elevated temperatures were carried out with tubes heat-sealed in vacuo. IR spectra were recorded on a Perkin–Elmer 681 spectrometer. Mass spectra were measured on a Varian CH-4 or SM-1 spectrometer at 70 eV. Melting points were obtained in sealed capillaries on a Büchi-510 apparatus and are not corrected. Elemental analyses were performed by F. Pascher, Microanalytical Laboratory, Bonn, and E. Thommen, Microanalytical Laboratory, University of Basel.

$(\eta^6\text{-}C_{10}H_8)_2Cr$ (**1**) was prepared via metal evaporation as described previously [5]. By the same route and using methylcyclohexane as solvent $(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2Cr$ (**5**) [37] was obtained in 56% yield after recrystallization from pentane. Both syntheses were carried out in a rotating solution reactor described earlier [38] and based on a design by Timms [39]. $(C_{10}H_8)Cr(CO)_3$ and $(C_6H_6)Cr(CO)_3$ were synthesized by standard methods [12,40].

$(\eta^6\text{-}C_6H_6)Cr(\eta^6\text{-}C_{10}H_8)$ (3)

(a) $(C_{10}H_8)_2Cr$ (**1**) (150 mg, 0.49 mmol) and benzene (10 ml) were placed in a Carius tube (equipped with an 8 mm 0-ring tap; Young, UK). The solution in the sealed system was stirred magnetically and heated to 150°C for 24 h. Volatiles were removed in vacuo, naphthalene was sublimed out, and the residue taken up in hexane and filtered through Celite. The dark brown solution was concentrated to 15 ml and kept at $-78°C$ overnight. Brown black crystals of **3** were isolated and dried at 10^{-2} mbar/20°C. Yield: 96 mg (76%). Anal. Found: C, 73.94; H, 5.50. $C_{16}H_{14}Cr$ calcd.: C, 74.42, H, 5.43%.

(b) $(C_{10}H_8)_2Cr$ (**1**) (220 mg, 0.71 mmol); benzene (5 ml) and THF (0.2 ml) were heated to 100°C for 20 h to give, after work-up as described above, **3** (62 mg, 34%). Yields varying between 20 and 30% of **3** were obtained on reflux of **1** (1 mmol) in benzene/THF 1/1 (30 ml) for 12 h.

$(\eta^6\text{-}1,4\text{-}C_6H_4Me_2)Cr(\eta^6\text{-}C_{10}H_8)$ (4)

The procedure was analogous to that described for **3** (method a), using **1** (123 mg, 0.40 mmol), *p*-xylene (10 ml); 140°C/16 h. Yield 92 mg (80%) brown black crystals. Anal. Found: C, 75,27; H, 6.38. $C_{18}H_{18}Cr$ calcd.: C, 75.52; H, 6.29%.

$(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)Cr(\eta^6\text{-}C_{10}H_8)$ (6)

(a) The procedure was analogous to that described for **3** (method a) using **1** (97 mg, 0.31 mmol), mesitylene (8 ml); 140°C/16 h. Yield 52 mg (55%) crystalline **6** (from hexane). Ca. 20 mg **6** (20%) remained in the mother liquor.

(b) Heating **1** (630 mg, 2.05 mmol) in a mixture of mesitylene (10 ml) and THF

(15 ml) to 60°C for 12 h yielded, after filtration and crystallization (hexane), **6** (100 mg, 16%). Anal. $C_{19}H_{20}Cr$ calcd.: C, 76.00; H, 6.67. Found: C, 75.51; H, 6.77%.

(η^6-C_6Me_6)Cr(η^6-$C_{10}H_8$) (7)

1 (250 mg, 0.81 mmol), hexamethylbenzene (1.4 g, 8.6 mmol), diethyl ether (8 ml) and THF (0.5 ml) were heated to 80°C for 16 h in a closed system (Carius tube) with magnetic stirring. Filtration (with added toluene present) followed by removal of solvents in vacuo, sublimation (60°C, 10^{-2} mbar) of $C_{10}H_8$ and C_6Me_6, and recrystallization of the residue from hexane yielded brown crystals of **7** (ca. 20 mg, 7%) identified by ^1H and ^{13}C NMR spectroscopy.

(η^6-1,4-$C_6H_4(OMe)_2$)Cr(η^6-$C_{10}H_8$) (8)

A solution of **1** (400 mg, 1.30 mmol) and 1,4-dimethoxybenzene (4.0 g) in THF (8 ml) was heated to 60°C for 4 days. Filtration followed by sublimation of the dimethoxybenzene and naphthalene and recrystallization of the residue from ether at -78°C yielded **8** as brown crystals. Yield 85 mg (21%). Anal. Found: C, 68.28; H, 5.72. $C_{18}H_{18}CrO_2$ calcd.: C, 67.92; H, 5.66%.

(η^6-1,4-$C_6H_4F_2$)Cr(η^6-$C_{10}H_8$) (9)

1 (134 mg, 0.44 mmol), *p*-difluorobenzene (3 ml) and THF (0.2 ml) were placed in a Carius tube and heated to 95°C for 12 h. Volatiles were removed in vacuo, naphthalene was sublimed out, and the residue taken up in toluene. The solution was filtered through Celite and taken to dryness, and the residue was extracted with hexane to leave a new residue which was identified (^1H NMR) as the starting complex **1** (68 mg). The hexane extract was kept at -78°C to give **9** contaminated by ca. 5% of the benzene complex **3**. Recrystallization yielded pure **9** (20 mg, 15%, 32% based on reacted **1**).

(η^6-$C_{10}H_8Me_2$)Cr(η^6-$C_{10}H_8$) (10) and (η^6-$C_{10}H_8Me_2$)$_2$Cr (11)

(a) The procedure was analogous to that described for **3** (method a), using **1** (92 mg, 0.30 mmol), 1,4-dimethylnaphthalene (8 ml); 120°C/25 h. Crystallization from hexane yielded 27 mg of a mixture of **10** and **11** [5] in a ratio of 1/6 (ratio determined by ^1H NMR).

(b) Heating **1** (336 mg, 1.09 mmol) in a mixture of 1,4-dimethylnaphthalene (3.4 ml) and THF (8 ml) to 45°C for 15 h yielded a mixture of **10** and starting material **1** (yield in **10** ca. 11%). A 95% pure sample of **10** for NMR analysis was obtained by two recrystallizations from hexane.

X-ray crystallographic analysis of 3

Dark brown crystals of **3** were obtained by recrystallization from hexane. A suitable crystal of average dimensions 0.15 × 0.23 × 0.35 mm was sealed in a Lindemann capillary under Ar. The lattice parameters and intensities were measured at room temperature on a Philips PW-1100 diffractometer with a graphite monochromated Mo-K_α radiation. Orthorhombic, *Pbca*, *a* 7.784(1), *b* 13.411(2), *c* 22.772(5) Å; *U* 2377 Å^3; $Z = 8$; μ 9.11 cm^{-1}; $F(000) = 1072$; D_c 1.443 g cm^{-3}. 2571 independent reflections were recorded (ω–2θscan) of which 1619 had $|F_0| > 3\sigma(F_0)$ and $|F_0| > 8$. Slight crystal degradation was observed causing a loss of about 4% of the diffracted intensities. All the intensities were corrected for this drift. The structure was solved by direct methods (MULTAN 80) [41] and refined by full matrix least-squares (XRAY 76) [42]. The atomic scattering factors for neutral isolated atoms and f' and f'' (for Cr atom) are from Cromer and Waber [43]. The final R factor, based on the 1619 observed reflections, was 0.071 ($R_w = 0.043$ with $w = (|F_0|/48)^2$ for $|F_0| < 48$ and $w = (48/|F_0|)^2$ for $|F_0| > 48$).

Attempted exchange reactions with (1,3,5-$C_6H_3Me_3$)$_2$Cr (5)

(a) NMR experiment. A solution of $(C_6H_3Me_3)_2Cr$ (15 mg) in C_6H_6 (0.5 ml) was filled into a 5 mm NMR tube provided with a potassium film in its upper portion. The tube was then heat sealed in vacuo and inverted. After 30 min contact time of the solution with the potassium film the ^1H NMR spectrum showed two sharp singlets for the arene (3.98 ppm) and methyl (2.08 ppm) protons of **5** [44]. The potassium-containing portion of the tube was removed (by heat sealing) and the tube immersed in an oil bath and heated first to 100°C then in increments of 20 to 30°C to 240°C. After periods of 1 to 2 h (12 h at 240°C) at each temperature, the ^1H NMR spectrum was recorded at ambient temperature. No change in the spectrum was observed and, in particular, no sign of a signal attributable to $(C_6H_6)_2Cr$, $(C_6H_6)Cr(C_6H_3Me_3)$ or the methyl group of exchanged mesitylene was detected. Heating overnight to 260°C led to chromium coating of the upper portion of the tube.

(b) Preparative scale. $(C_6H_3Me_3)_2Cr$ (292 mg, 1 mmol) in C_6H_6 (10 ml) was heated to reflux for 2 h. The solution was filtered through Celite, and taken to dryness, and a sample of the crude product (260 mg) was analyzed by ^1H NMR in C_6D_6. (Before the recording of the spectrum the solution was exposed to a potassium film as described below) and found to consist of starting material only.

In a separate experiment air was bubbled through the solution for 30 sec before reflux under N_2. Subsequent treatment of the mixture with an alkaline aqueous solution of $Na_2S_2O_4$ followed by extraction with benzene yielded a single product, which was shown to be the starting complex **5** (215 mg, 74%).

TABLE 5

FRACTIONAL COORDINATES WITH ESTIMATED STANDARD DEVIATIONS

	x	y	z	$U_{eq.}$ [a]
Cr	0.31288(10)	0.36176(6)	0.39123(3)	35.84(20)
C(1)	0.3505(6)	0.4079(4)	0.30208(22)	48.0(18)
C(2)	0.3912(7)	0.4873(4)	0.3393(3)	58.2(21)
C(3)	0.5075(7)	0.4750(4)	0.3852(3)	59.6(20)
C(4)	0.5843(6)	0.3816(4)	0.3953(3)	50.8(19)
C(5)	0.6291(6)	0.2027(4)	0.36454(23)	50.2(18)
C(6)	0.5914(8)	0.1267(5)	0.3283(3)	63.4(22)
C(7)	0.4724(8)	0.1410(5)	0.2813(3)	69.1(23)
C(8)	0.3966(7)	0.2298(5)	0.27223(22)	53.6(19)
C(9)	0.4336(6)	0.3134(4)	0.30925(20)	39.6(16)
C(10)	0.5541(6)	0.2991(4)	0.35618(20)	37.6(16)
C(11)	0.0356(6)	0.3578(6)	0.3915(3)	67.2(22)
C(12)	0.0919(8)	0.4283(5)	0.4318(3)	61.8(22)
C(13)	0.2114(9)	0.4031(6)	0.47446(24)	73(3)
C(14)	0.2767(7)	0.3004(8)	0.4768(3)	82(3)
C(15)	0.2171(9)	0.2321(4)	0.4343(3)	69.3(25)
C(16)	0.1009(7)	0.2609(4)	0.3916(3)	62.7(21)

[a] Equivalent isotropic temperature factors. U_{eq} ($Å^2 \times 10^3$). U_{eq} is the average of the eigenvalues of U.

Uncatalyzed arene exchange in $C_{10}H_8Cr(CO)_3$

$C_{10}H_8Cr(CO)_3$ (**2**) (600 mg, 2.27 mmol) and C_6H_6 (5 ml) were placed in a 10 ml Carius tube (equipped with an 8 mm 0-ring tap; Young, UK). The sealed system was heated to 140°C for 6 h to yield, after filtration and crystallization (toluene/hexane), $C_6H_6Cr(CO)_3$ (460 mg, 95%).

Rate constant determination

NMR tubes were silylated (5% etheral solution of *N*,*O*-bis(trimethylsilyl)-acetamide) before being charged with 0.5 ml of a 8×10^{-2} molar solution of **2** in C_6D_6 (Ciba Geigy, 99.8% D). After 3 freeze/pump/thaw cycles to degas the solution the tubes were heat sealed under vacuum (10^{-2} mbar), protected from light by aluminium foil, and immersed in an oil bath. Periodically the tubes were removed from the hot bath and rapidly cooled to ambient temperature. The ^1H NMR spectrum was recorded and the signals of H(1,4,5,8) of free naphthalene (centered at 7.66 ppm) and of H(1)–H(4) of coordinated naphthalene (4.75 and 5.37 ppm) carefully integrated. Reactions were followed to a half life at 120°C, 2 half lives at 140 and 160 and 3 half lives at 150°C. All reactions showed good first order kinetics. Rate constants were calculated using all (at least 10) data points. The correlation coefficient of the least squares analysis was > 0.99. Kinetic results in non-silylated but thoroughly dried (150°C/10^{-2} mbar) tubes gave good first order kinetic plots with respect to complex, but the rate constants varied from tube to tube, and considerably faster reactions were generally observed. This, together with the observation of rate dependence on change of concentration of **2**, suggested to us that there was catalysis by the OH groups on the glass surface.

THF catalyzed arene exchange in $C_{10}H_8Cr(CO)_3$ (2)

$C_6H_6Cr(CO)_3$. (a) $C_{10}H_8Cr(CO)_3$ (**2**) (600 mg, 2.27 mmol), benzene (5 ml) and THF (0.6 ml) were heated to 60°C for 6 h to yield, after filtration and crystallization (toluene/hexane), $C_6H_6Cr(CO)_3$ (432 mg, 89%). After 1 h of reaction a sample showed ca. 50% conversion (by IR).

(b) **2** (121 mg, 0.458 mmol), benzene (81 μl, 0.91 mmol) and THF (2 ml) were heated for 9.5 h at 50°C. The brown black mixture yielded after work-up $C_6H_6Cr(CO)_3$ (67 mg, 68%).

(c) **2** (164 mg, 1 mmol); benzene (178 μl, 2 mmol); THF (243 μl, 2 mmol) and ether (1 ml) were placed in a Carius tube with 0 ring tap and heated for 16 h at 70°C to give $C_6H_6Cr(CO)_3$ (201 mg, 94%).

Benzocyclobutenetricarbonylchromium [45]. The procedure of method (c) using 1 mmol of **2**, gave, after crystallization from octane, $C_8H_8Cr(CO)_3$ 230 mg (96%). The complex was also synthesized from $Cr(CO)_6$ using Pauson's method [40] in 73% yield and from $(NH_3)_3Cr(CO)_3$ (3 h reflux in dioxane) in 80% yield. Benzocyclobutene was prepared as described by Radlick and Brown [46].

Styrenetricarbonylchromium [36]. A procedure analogous to method (c), using 1 mmol of **2**, gave after crystallization, $C_8H_8Cr(CO)_3$ (216 mg, 90%).

$C_{14}H_{10}(OMe)_2Cr(CO)_3$ and $C_{14}H_{10}(OMe)_2(Cr(CO)_3)_2$. A procedure analogous to method (c) was used with 1,8-dimethoxy-9,10-dihydroanthracene [47] (120 mg, 0.5 mmol) and **2** (66 mg, 0.25 mmol), reaction time 18 h at 70°C. The crude product was chromatographed on Al_2O_3 (Merck, neutral, activity III) using toluene/hexane to yield, after recrystallization from toluene/hexane, $C_{14}H_{10}(OMe)_2Cr(CO)_3$ (76 mg,

81%); ^{1}H NMR (in C_6D_6 at 360 MHz) 7.16 (t, 1H, *J* 8 Hz, H(6)); 6.85 (d, 1H, *J* 8 Hz, H(7)); 6.50 (d, 1H, *J* 8 Hz, H(5)); 4.78 (t, 1H, *J* 7 Hz, H(3)); 4.60 (part of AB system, 1H, H(9) or H(10)); 4.30 (d, 1H, *J* 7 Hz, H(2) or H(4)); 4.16 (d, 1H, *J* 7 Hz, H(4) or H(2)); 3.53 (broad s, 2H, H(9) or H(10)); 3.42 (part of AB system, 1H, H(10) or H(9)); 3.35 (s, 3H, C(8)-OMe); 3.04 (s, 3H, C(1)-OMe). Anal. Found: C, 60.50; H, 4.43. $C_{19}H_{16}O_5Cr$ calcd.: C, 60.64; H, 4.26%. And $C_{14}H_{10}(OMe)_2(Cr(CO)_3)_2$ (1 mg, 1%) ^{1}H NMR (in C_6D_6 at 360 MHz): 4.75 (t, 2H, H(3) and H(6)), 4.34 (d, 2H, H(2) and H(7) or H(4) and H(5)); 4.08 (d, 2H, H(4) and H(5) or H(2) and H(7)), 3.80 (broad s, 2H, H(9) or H(10)); 3.45 (broad s, 2H, H(10) or H(9)); 2.96 (s, 6H, OMe).

1,8-Dimethoxy-9,10-dihydroanthracene [47] was synthesized in 67% yield by reduction of 1,8-dimethoxy-9,10-anthraquinone with $LiAlH_4/AlCl_3$ as described by Brown and White [48].

$C_6H_4CH_2CH(OEt)Cr(CO)_3$. The procedure of method (c) was used, with 1-ethoxybenzocyclobutene [49] (592 mg, 4 mmol); **2** (528 mg, 2 mmol), THF (0.488 ml) and ether (2 ml). 70°C/21 h. Crystallization from hexane gave ${}_6H_4CH_2$CH(OEt)Cr(CO)$_3$ (398 mg, 70%) as a 2/3 mixture of *syn* and *anti* isomer [50]. Anal. Found: C, 54.72, H, 4.46. $C_{13}H_{12}O_4Cr$ calcd.: C, 54.93, H, 4.23%.

1,4-$C_{10}H_6Me_2Cr(CO)_3$ [13,51]. The procedure of method (c) was used, with 1,4-dimethylnaphthalene (480 mg, 3.08 mmol), **2** (270 mg, 1.02 mmol), THF (0.25 ml) and ether (1 ml). 75°C/26 h. Yield: 279 mg, 94%. The product was a 7/3 mixture of the two isomers, the major product being that with the Cr coordinated to the unsubstituted ring. This has been observed previously [13].

Acknowledgments

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