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Synthesis of η-arene derivatives of chromium and molybdenum containing Lewis-acid boron substituents*

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The compounds $Ph(CH_2)_3B(OH)_2$ **I**, $[Ph(CH_2)_3BO]_3$ **II**, $Ph(CH_2)_3B(1,2\text{-}O_2C_6H_4)$ **III**, $Ph(CH_2)_3BC_8H_{14}$ **IV** (BC_8H_{14} = 9-borabicyclo[3.3.1]nonan-9-yl), $[Cr\{\eta\text{-}Ph(CH_2)_3B(1,2\text{-}O_2C_6H_4)\}(CO)_3]$ **1**, $[Cr\{\eta\text{-}Ph(CH_2)_3BC_8H_{14}\}(CO)_3]$ **2**, $[Cr\{\eta\text{-}Ph(CH_2)_3BBr_2{\cdot}SMe_2\}(CO)_3]$ **3**, $[Cr\{\eta\text{-}Ph(CH_2)_4BC_8H_{14}\}(CO)_3]$ **4**, $[Cr(\eta\text{-}Ph(CH_2)_4BC_8H_{14}\}(CO)_2(PPh_3)]$ **5**, $[Cr\{\eta\text{-}PhCH_2CH{=}CH_2\}(CO)_3]$ **6**, $[Cr\{\eta\text{-}Ph(CH_2)_2CH{=}CH_2\}(CO)_3]$ **7**, $[Cr\{\eta\text{-}Ph(CH_2)_2\eta\text{-}CH{=}CH_2\}(CO)_2]$ **8**, $[Cr\{\eta\text{-}Ph(CH_2)_2CH{=}CH_2\}(CO)_2(PPh_3)]$ **9**, $[Li(Et_2O)_n][Cr\{\eta\text{-}PhCH_2CH{=}CH_2\}(CO)_2\{C(O)Ph\}]$ **10**, $[Li(Et_2O)_n][Cr\{\eta\text{-}Ph(CH_2)_2CH{=}CH_2\}(CO)_2\{C(O)Ph\}]$ **11**, $[Mo\{\eta\text{-}Ph(CH_2)_3BC_8H_{14}\}_2]$ **12** and $[Cr\{\eta\text{-}Ph(CH_2)_3BOC_8H_{14}\}(CO)_3]$ **13**, have been prepared and characterised. Compounds **1**–**5**, **12** and **13** have π-donor η-arene ligands which also bear a Lewis-acid σ-acceptor boron group. There was no evidence that these boron groups formed ground-state intra- or inter-molecular interactions with the Lewis base functions of the carbonyl oxygen atoms.

We were interested to develop the transition-metal coordination chemistry of molecules containing both donor and acceptor functionalities. Formal representations of compounds in which the donor or acceptor function may be described as either σ or π type are shown in Fig. 1. In this work we describe a study of synthetic strategies towards transition-metal compounds containing a ligand which combines both an η-arene π-donor group and a boron σ-acceptor (Lewis acid) group. It was hoped that the presence of the Lewis-acid group would lead to intramolecular donor–acceptor bonding, for example with carbon monoxide ligands in metal carbonyl derivatives, and thereby increase the electrophilicity of the carbonyl carbon atom and inducing interesting reactivity within the system.

Results and Discussion

The first strategy adopted was to prepare potential ligand molecules in which the π-donor function was an η-arene group and the σ-acceptor function was a BR_3 grouping, and then to bond the arene ring to a transition-metal centre. The compounds $Ph(CH_2)_3B(OH)_2$ **I**, $[Ph(CH_2)_3BO]_3$ **II**, $Ph(CH_2)_3B(1,2\text{-}O_2C_6H_4)$ **III** and $Ph(CH_2)_3BC_8H_{14}$ **IV** (BC_8H_{14} = 9-borabicyclo[3.3.1]nonane-9-yl) were prepared as potential ligands or ligand precursors by the reactions[1–3] shown in Scheme 1. The available characterising data for these compounds, and for all the other new compounds described, are given in Table 1. These data will not be further discussed unless interpretation is not straightforward. The reaction between **III** and $[Cr(CO)_6]$ gave yellow crystals of $[Cr\{\eta\text{-}Ph(CH_2)_3B(1,2\text{-}O_2C_6H_4)\}(CO)_3]$ **1**. The data show that the $Cr(CO)_3$ unit is exclusively at the phenyl ring and not at the catechol moiety, as shown in Scheme 2. However, in general the synthetic strategy used for **1** was not found to be successful. For example, treatment of $[Cr(CO)_6]$ with **IV** did not give the η-arene derivative $[Cr\{\eta\text{-}Ph(CH_2)_3BC_8H_{14}\}(CO)_3]$ **2** in an acceptable yield.

The second strategy, chosen for compounds **2**–**5**, was to coordinate to the metal centre a phenyl group which bears an olefinic side-chain [$Ph(CH_2)_xCH{=}CH_2$, x = 1 or 2]. Subsequently, the Lewis-acid boron moiety is attached to the resulting η-arene ligand system by employing hydroboration of the olefinic groups with HBR_2.[2–4] Thus treatment of the compound $[Cr(\eta\text{-}PhCH_2CH{=}CH_2)(CO)_3]$ **6** with HBC_8H_{14}[3] gives **2**, and with $HBBr_2{\cdot}SMe_2$[4] the complex $[Cr\{\eta\text{-}Ph(CH_2)_3BBr_2{\cdot}SMe_2\}(CO)_3]$ **3** is formed. Similarly, the η-4-phenylbut-1-ene derivative $[Cr\{\eta\text{-}Ph(CH_2)_2CH{=}CH_2\}(CO)_3]$ **7** reacts with HBC_8H_{14} to give $[Cr\{\eta\text{-}Ph(CH_2)_4BC_8H_{14}\}(CO)_3]$ **4** (Scheme 3). An attempt to prepare the catechol borane derivative **1** by this method gave a reaction mixture which contained several products from which **1** could not be separated completely. Thus the hydroboration reaction with $HB(1,2\text{-}O_2C_6H_4)$, which is less reactive than $HBBr_2{\cdot}SMe_2$[4] and HBC_8H_{14}, requires more drastic conditions (neat mixture of both components and a prolonged reaction time or elevated temperatures).[5] Therefore, it is preferable to prepare **1** as described earlier. Since $Cr(CO)_3$ in **1** is bonded to the most electron-rich aromatic ring, it may be inferred that the π-acceptor strength of the boron centre in **1** is sufficiently high to reduce the electron density of the catechol ring below the level of that of the C_6H_5 ring.

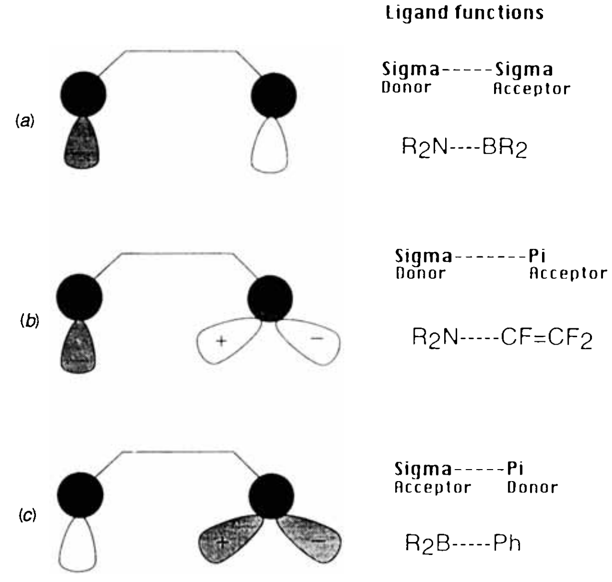

Fig. 1 Schematic representations of molecules which contain both a donor and an acceptor function: (*a*) showing σ-donor and -acceptor functions; (*b*) showing σ-donor and π-acceptor functions and (*c*) showing σ-acceptor and π-donor functions

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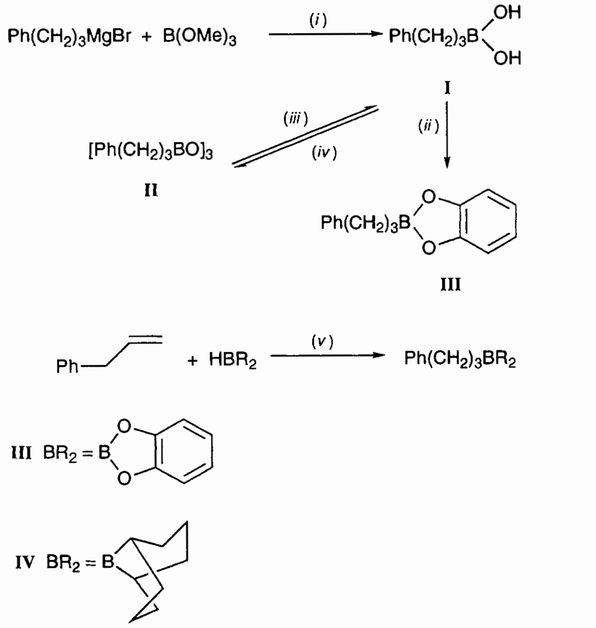
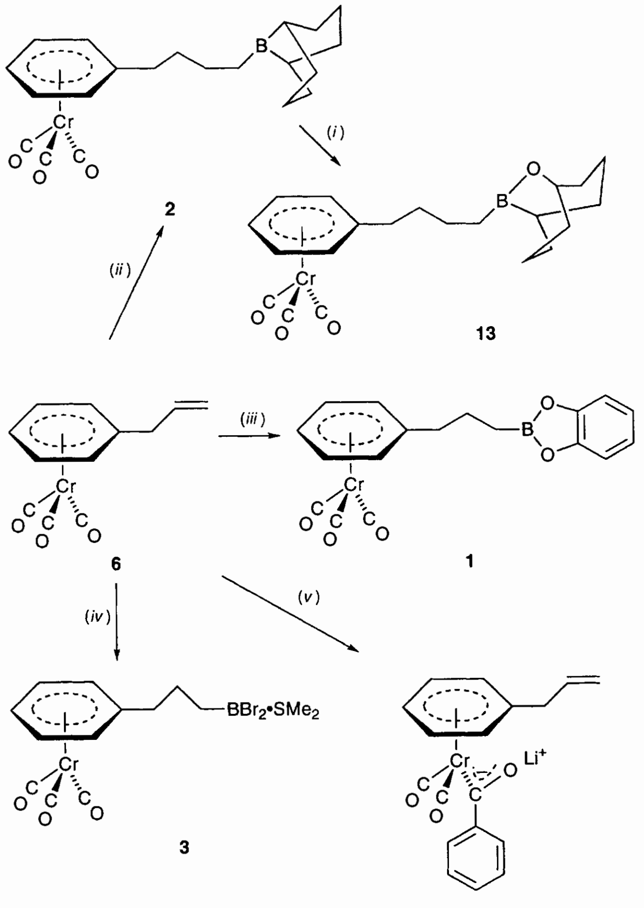
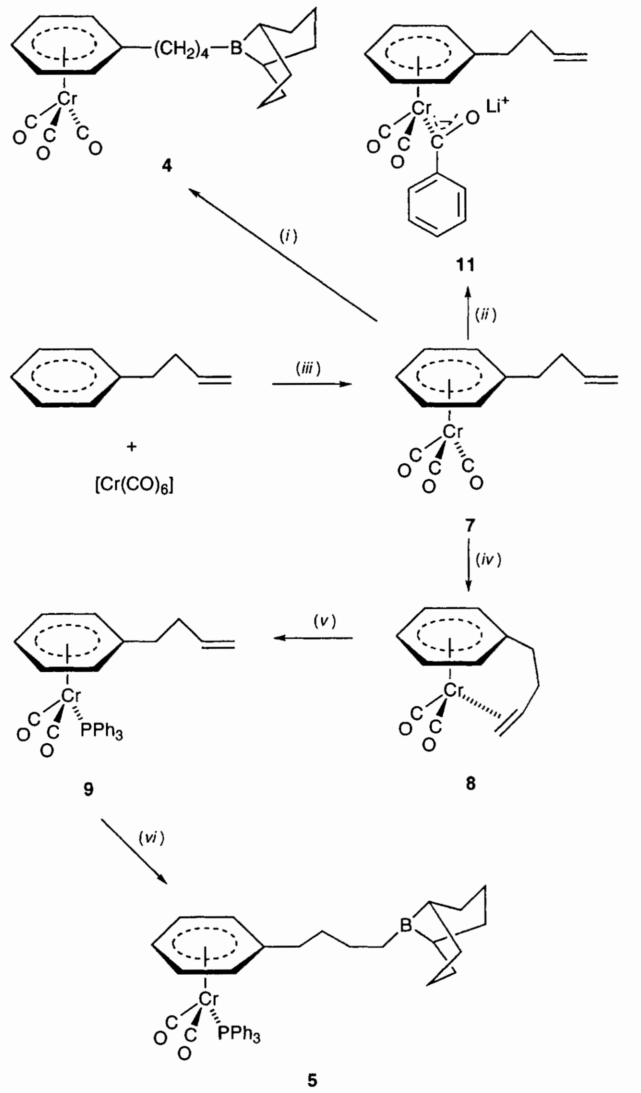
* *Non-SI unit employed:* Torr ≈ 133 Pa.



Scheme 1 (*i*) In Et_2O at 35 °C, then 1 mol dm^{-3} H_2SO_4; (*ii*) in toluene, benzene-1,2-diol, reflux in Dean–Stark apparatus; (*iii*) warming under reduced pressure; (*iv*) 1 mol dm^{-3} H_2SO_4; (*v*) at 100 °C (for **3**), at room temperature (r.t.) (for **4**)



Scheme 2 (*i*) 1 equivalent Me_3NO in tetrahydrofuran (thf) at r.t. for 24 h; (*ii*) HBC_8H_{14} in thf at r.t., then distillation; (*iii*) $HB(1,2\text{-}O_2C_6H_4)$ at 100 °C, volatiles removal; (*iv*) $HBBr_2{\cdot}SMe_2$ in CH_2Cl_2 at 0 °C; (*v*) LiPh in Et_2O at −78 °C, warming to r.t.



Scheme 3 (*i*) HBC_8H_{14} in thf at r.t.; (*ii*) LiPh in Et_2O at −78 °C, warming to r.t.; (*iii*) 4-phenylbut-1-ene in diglyme (2,5,8-trioxanonane)–thf at 130 °C at r.t.; (*iv*) photolysis in light petroleum (b.p. 40–60 °C) below 50 °C, medium-pressure mercury lamp; (*v*) PPh_3 in benzene, reflux for 12 h; (*vi*) HBC_8H_{14} in thf at r.t. for 12 h

We set out to replace one of the three carbonyl substituents of compound **7** by a PPh_3 ligand since this would increase the electron density on the chromium centre and the consequential greater Cr-to-CO back donation would augment the Lewis basicity of the remaining carbonyl oxygen atoms. Photolysis of **7** with a medium-pressure mercury lamp resulted in evolution of carbon monoxide and formation of the *ansa*-compound $[Cr\{\eta\text{-}Ph(CH_2)_2\text{-}\eta\text{-}CH{=}CH_2\}(CO)_2]$ **8** which, in turn, reacts with triphenylphosphine to give $[Cr\{\eta\text{-}Ph(CH_2)_2CH{=}CH_2\}(CO)_2(PPh_3)]$ **9**. Compounds **6**–**9** have been described previously[6,7] but less characterising data were given. Treatment of **9** with HBC_8H_{14} yields the desired $[Cr\{\eta\text{-}Ph(CH_2)_4BC_8H_{14}\}(CO)_2(PPh_3)]$ **5**. No abstraction of the PPh_3 ligand from the chromium centre and subsequent formation of a $Ph_3P{\cdot}HBC_8H_{14}$ adduct was observed.

The ^{11}B NMR resonances of compounds **1**, **2**, **4** and **5** are found in the usually observed range for trivalent boron nuclei.[8] Moreover, the signals in the carbonyl region of the infrared spectra [two absorptions (A_1, E)] do not change upon hydroboration, *i.e.* upon going from **6** and **7** to **1**, **2** and **4**. This is evidence for the absence of any significant CO-to-boron bonding in the borylated complexes, which would inevitably lead both to a better shielding of the boron nuclei and to a perturbation of the local symmetry of the $Cr(CO)_3$ fragment. A similar argument holds for **5**.

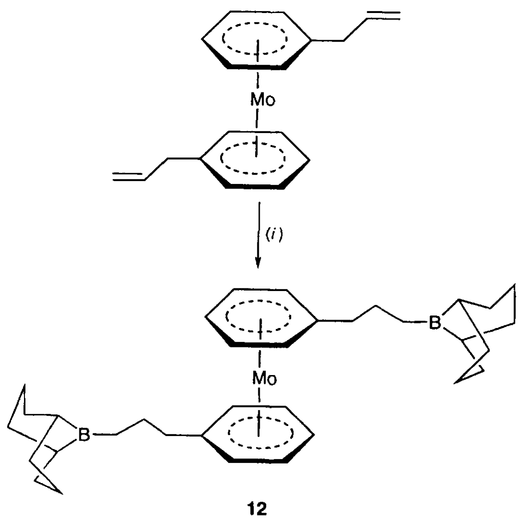
Compounds **6** and **7** were reacted with phenyllithium in order to generate the lithiated Fischer-carbene complexes **10** and **11**, which can be expected to possess oxygen atoms of higher Lewis basicity than that even of **9**, and also to be better located towards potential oxygen–boron bonding as shown, for example, in related cyclopentadienylrhenium complexes.[9]

Attempts to introduce boron substituents in the side-chains of compounds **10** and **11** by reaction with HBC_8H_{14} did not give isolable reaction products. However, ^1H NMR spectra of the crude reaction mixtures indicated the absence of olefinic protons. We believe that O–B adducts may be formed after the successful hydroboration of **10** and **11**, but the resulting compounds decompose possibly by carbon–oxygen bond cleavage. A similar reaction pathway is well known for the generation of Fischer carbynes.[10]

We were also interested in the possibility of formation of intermolecular donor–acceptor bonds between d-electron lone pairs on the transition-metal centres and the boron functionalities in the ligand sphere. Therefore, we prepared the bis(η-arene) compound $[Mo\{\eta\text{-}Ph(CH_2)_3BC_8H_{14}\}_2]$ **12** by treatment of the previously described compound bis(η-allylbenzene)molybdenum[11,12] with HBC_8H_{14} (Scheme 4). There was the possibility that one of the boron centres of **12** would bind to the molybdenum centre.[13] Direct metal-to-boron interactions have recently been shown to exist in (dibromoboryl)ferrocene.[14] Spectroscopic studies of **12** showed no evidence for intra- or inter-molecular Mo–B interactions.

The reaction between $[Cr\{\eta\text{-}Ph(CH_2)_3BC_8H_{14}\}(CO)_3]$ **2** and trimethylamine oxide (1 equivalent)) was investigated to explore whether carbon dioxide[15] was formed or if reaction occurred at the boron centre.[16] It was found that the latter reaction occurred giving the oxygen-insertion product $[Cr\{\eta\text{-}Ph(CH_2)_3BOC_8H_{14}\}(CO)_3]$ **13**. When **13** is treated with more trimethylamine oxide, or if an excess of this agent is present at the outset, the chromium complex is degraded with liberation of $Ph(CH_2)_3BOC_8H_{14}$. This suggests that the Lewis acidity of the carbonyl carbon atoms in **2** is higher than that of an R_2BOR (R = alkyl) group, but lower than that of a BR_3 moiety in the same molecule.

In conclusion, several pathways to the synthesis of low-valent (η-arene)transition-metal compounds also containing boron centres with varying degrees of Lewis acidity have been demonstrated. In these compounds there are no strong ground-state interactions between the Lewis-acid boron centre and 'lone pairs' on other systems in the molecule. This may reflect a low basicity, for example, of the metal-based 'lone pairs', poor acidity of the boron centres, or an insufficiently long hydrocarbon chain between the complexed phenyl ring and the boron centres.



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Scheme 4 (*i*) HBC_8H_{14} in thf at r.t. for 12 h

Experimental

All preparations and manipulations were carried out under an inert atmosphere of dinitrogen using either standard Schlenk techniques or an inert-atmosphere box, unless otherwise stated. All solvents were thoroughly deoxygenated before use either by repeated evacuation followed by admission of dinitrogen, or by bubbling dinitrogen through the solvent for approximately 15 min. Solvents were predried over activated 4 Å molecular sieves and then distilled over sodium (toluene), sodium–potassium alloy and benzophenone (benzene), sodium and benzophenone (diethyl ether, thf, diglyme), or calcium hydride [pentane, light petroleum (b.p. 40–60 °C), dichloromethane] under a slow continuous stream of dinitrogen. Perdeuteriated solvents for NMR spectroscopy were deoxygenated and then dried over calcium hydride (dichloromethane) or potassium (benzene and toluene). Activated, neutral, Brockmann I, standard grade, ≈150 mesh alumina (Al_2O_3) was used for chromatography and deoxygenated before use by repeated evacuation followed by admission of dinitrogen. Celite 545 filtration aid (Koch-Light) was predried at 140 °C and similarly deoxygenated before use.

Proton, ^{13}C and ^{31}P NMR spectra were recorded using a Bruker AM 300 spectrometer (^1H, 300; ^{13}C, 75.5; ^{31}P, 121.6 MHz). Spectra were referenced internally using residual protio solvent resonances (^1H and ^{13}C) relative to tetramethylsilane (δ 0) or externally using trimethyl phosphate in D_2O (^{31}P). Electron-impact mass spectra were recorded on an AEI MS 302 mass spectrometer updated by a data-handling system supplied by Mass Spectrometry Services Ltd. Infrared spectra were recorded on a Perkin-Elmer 1510 FT interferometer. Elemental analyses were performed by the Oxford Analytical Laboratory.

Syntheses

$Ph(CH_2)_3B(1,2\text{-}O_2C_6H_4)$ III. *Method A.* Magnesium turnings (4.00 g, 165 mmol) in dry diethy ether (20 cm^3) were treated with a solution of 1-bromo-3-phenylpropane (20.60 g, 103 mmol) in diethyl ether (80 cm^3) in a dropwise manner with stirring at a rate sufficient to keep the ether solution at reflux. When the addition was complete the reaction mixture was heated under reflux for 15 min. The resulting clear yellow solution was filtered from excess of magnesium. Standard titrations showed the solution contained 70 mmol of $Ph(CH_2)_3MgBr$.

The compound $B(OMe)_3$ (6.70 g, 64.5 mmol) in diethyl ether (20 cm^3) was cooled to −78 °C in a propan-2-ol–solid CO_2 bath. The solution of the Grignard $Ph(CH_2)_3MgBr$ was added dropwise with stirring over a period of 2 h. After addition was complete the reaction mixture was stirred for 2 h at −78 °C. During the course of the reaction a white powder precipitated. The mixture was allowed to reach room temperature. Then 1 mol dm^{-3} H_2SO_4 (42 cm^3) was added whereupon the precipitate gradually dissolved. The ether phase was separated and the water phase then extracted once with diethyl ether (40 cm^3). The solvent was removed from the combined ether extracts to yield a white, semi-solid product. Recrystallisation from $CHCl_3$ at 55 °C gave white colourless platelets of $Ph(CH_2)_3B(OH)_2$ **I**. Yield *ca.* 40%. The NMR spectra showed varying extents of water. Attempts to remove this crystal water resulted in the formation of the boroxine $[Ph(CH_2)_3BO]_3$ **II**. Therefore, no yield and no elemental analysis of **I** could be obtained. Addition of water and a few drops of sulfuric acid to the boroxine and then extraction with diethyl ether recovered **I**. In $CDCl_3$ **I** is oligomeric *via* hydrogen bridges whereas in Me_2SO it is a monomer.

A mixture of platelets of compound **I** (6.12 g, 37 mmol) and catechol (4.00 g, 37 mmol) was refluxed in toluene (100 cm^3) in a Dean–Stark apparatus to remove water. After 6 h no further water was formed and the reaction mixture was cooled to room

Table 1 Analytical and spectroscopic data

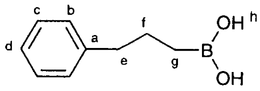
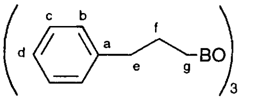
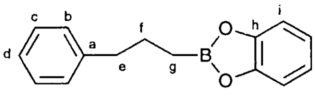
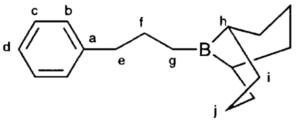
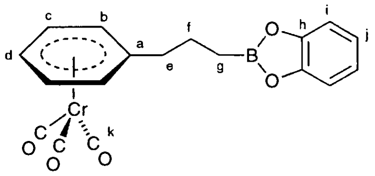
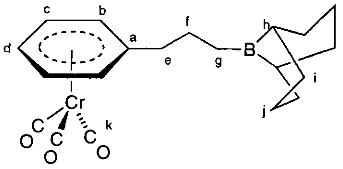
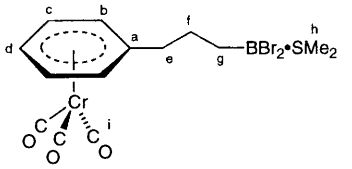
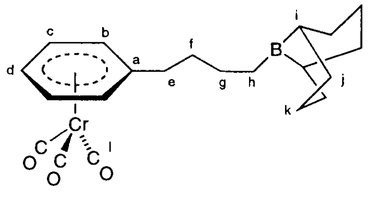
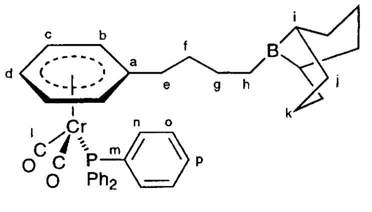
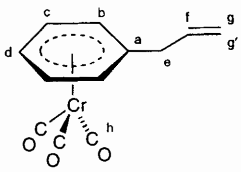
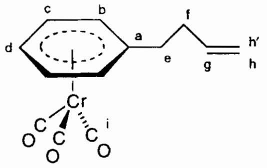
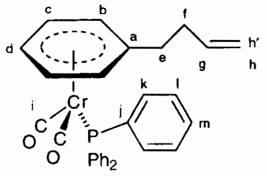
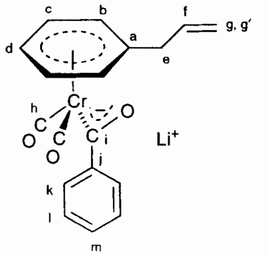
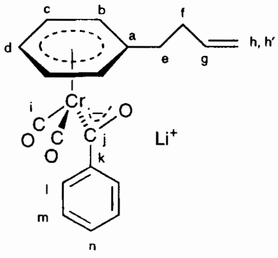
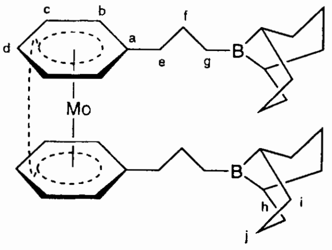
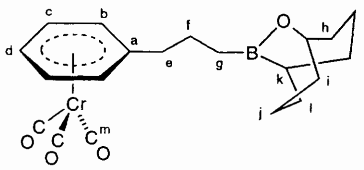
Compound and analysis (%)	Spectroscopic data^{a}
I Tends to liberate water (see text) 	^{1}H:^{b} 0.61 [t, J(HH) = 7.8, 2 H, H^{g}], 1.61 (q, 2 H, H^{f}), 2.51 [t, J(HH) = 7.1, 2 H, H^{e}], 7.12–7.28 (m, 5 H, H^{b-d}); (CDCl$_3$) 0.85, 0.95 [t, t, 1 H, 1 H, J(HH) = 7.8, 7.5, H^{g}], 1.80 (m, 2 H, H^{f}), 2.66 [t, J(HH) = 7.5, 2 H, H^{e}], 5.23 (br, 2 H, H^{h}), 7.21–7.34 (m, 5 H, H^{b-d}) ^{13}C:^{b} 15.1 (br, C^{g}), 26.3 (C^{e}), 38.1 (C^{f}), 125.4 (C^{d}), 128.1 (C^{b}), 128.3 (C^{c}), 142.6 (C^{a}) ^{11}B:^{c} 31.9
II C, 75.5 (74.0); H, 7.75 (7.6) 	^{1}H:^{d} 0.89 [t, J(HH) = 7.7, 6 H, H^{g}], 1.80 (q, 6 H, H^{f}), 2.55 [t, J(HH) = 7.4, 6 H, H^{e}], 7.07–7.17 (m, 15 H, H^{b-d}) ^{13}C:^{d} 15.4 (br, C^{g}), 25.7 (C^{e}), 38.6 (C^{f}), 128.1 (C^{d}), 128.7 (C^{b}), 129.0 (C^{c}), 142.6 (C^{a}) ^{11}B:^{d} 31.0
III^{e} 	^{1}H:^{d} 1.07 [t, J(HH) = 7.8, 2 H, H^{g}], 1.61 (q, 2 H, H^{f}), 2.50 [t, J(HH) = 7.6, 2 H, H^{e}], 6.80 [dd, J(HH) = 3.4, 5.8, 2 H, H^{i}], 7.03 [dd, J(HH) = 3.4, 5.8, 2 H, H^{j}], 7.18–7.30 (m, 5 H, H^{b-d}) ^{13}C:^{d} 11.2 (br, C^{g}), 25.8 (C^{e}), 38.4 (C^{f}), 112.4 (C^{i}), 122.7 (C^{j}), 126.0 (C^{d}), 128.5 (C^{b}), 128.6 (C^{c}), 142.2 (C^{a}), 148.7 (C^{h}) ^{11}B:^{d} 34.7 Mass: m/z 238 (M^{+})
IV^{e} 	^{1}H:^{d} 1.37 [t, J(HH) = 7.7, 2 H, H^{g}], 1.10–1.95 (m, 16 H, H$^{f,h-j}$), 2.58 [t, J(HH) 7.6, 2 H, H^{e}], 7.09–7.20 (m, 5 H, H^{b-d}) ^{13}C:^{d} 23.5 (C^{j}), 26.9 (C^{e}), 28.1 (br, C^{g}), 31.3 (br, C^{h}), 33.4 (C^{i}), 39.5 (C^{f}), 126.0 (C^{d}), 128.6 (C^{b}), 128.8 (C^{c}), 143.0 (C^{a}) ^{11}B:^{d} 86.0 Mass: m/z 241 (M^{+})
1 C, 57.7 (57.8); H, 4.2 (4.0) 	^{1}H:^{d} 0.89 [t, J(HH) = 7.7, 2 H, H^{g}], 1.43 [q, J(HH) = 7.7, 2 H, H^{f}], 1.92 [t, J(HH) = 7.7, 2 H, H^{e}], 4.25 [t, J(HH) 6.3, 1 H, H^{d}], 4.32 [d, J(HH) = 6.3, 2 H, H^{b}], 4.49 [t, J(HH) = 6.3, 2 H, H^{c}], 6.81 [dd, J(HH) = 3.3, 5.5, 2 H, H^{i}], 7.03 [dd, J(HH) = 3.3, 5.5, 2 H, H^{j}] ^{13}C:^{d} 25.3 (C^{e}), 37.1 (C^{f}), 89.9 (C^{d}), 92.3, 93.5 (C^{b,c}), 112.5 (C$^{i\text{ or }j}$), 113.5 (C^{a}), 122.9 (C$^{i\text{ or }j}$), 148.6 (C^{h}), 233.6 (C^{k}) ^{11}B:^{d} 36.0 Mass: m/z 374 (M^{+}) IR(Nujol): ṽ(CO) 1966, 1875 cm^{-1}
2 C, 64.0 (63.8); H, 6.8 (6.7) 	^{1}H:^{d} 1.1–1.9 (m, 14 H, H^{h-j}), 1.19 [t, J(HH) = 8.0, 2 H, H^{g}], 1.46 [q, J(HH) = 8.0, 2 H, H^{f}], 2.02 [t, J(HH) = 8.0, H^{e}], 4.31 [t, J(HH) = 6.0, 1 H, H^{d}], 4.45 [d, J(HH) = 6.0, 2 H, H^{b}], 4.55 [t, J(HH) = 6.0, 2 H, H^{c}] ^{13}C:^{d} 23.5 (C^{j}), 26.6 (C^{e}), 27.6 (br, C^{g}), 31.4 (br, C^{h}), 33.4 (C^{i}), 38.2 (C^{f}), 90.1 (C^{d}), 92.5 (C$^{b\text{ or }c}$), 93.6 (C$^{b\text{ or }c}$), 113.7 (C^{a}), 233.7 (C^{k}) ^{11}B:^{d} 88.1, 64.9 (thf) Mass: m/z 376 (M^{+}) IR(Nujol): ṽ(CO), 1975, 1906 cm^{-1}
3 C, 34.4 (34.4); H, 3.5 (3.5) 	^{1}H:^{d} 1.06 [t, J(HH) = 7.5, 2 H, H^{g}], 1.42 (s, 6 H, H^{h}), 1.80 [q, J(HH) = 7.5, 2 H, H^{f}], 2.10 [t, J(HH) = 7.5, 2 H, H^{e}], 4.25 [t, J(HH) = 5.9, 1 H, H^{d}], 4.41 [d, J(HH) = 5.9, 2 H, H^{b}], 4.49 [t, J(HH) = 5.9, 2 H, H^{c}] ^{13}C:^{d} 22.5 (C^{e}), 29.0 (C^{h}), 38.5 (C^{f}), 90.0 (C^{d}), 92.7 (C$^{b\text{ or }c}$), 94.0 (C$^{b\text{ or }c}$), 114.0 (C^{a}), 232.9 (C^{i}) ^{11}B:^{d} 3.0 IR(Nujol): ṽ(CO) 1975, 1876 cm^{-1}
4 C, 64.4 (64.7); H, 6.8 (6.9) 	^{1}H:^{d} 1.3, 1.7, 1.8, 2.0 (m, m, m, m, 22 H, H^{e-k}), 4.31 [t, J(HH) = 6, 1 H, H^{d}], 4.43 [d, J(HH) = 6, 2 H, H^{b}], 4.55 [t, J(HH) = 6, 2 H, H^{c}] ^{13}C:^{d} 23.5 (C^{k}), 24.2 (C^{e}), 28.0 (br, C^{h}), 31.4 (br, C^{i}), 33.4 (C^{j}), 34.4 (C$^{f\text{ or }g}$), 35.1 (C$^{f\text{ or }g}$), 90.1 (C^{d}), 92.4 (C$^{b\text{ or }c}$), 93.6 (C$^{b\text{ or }c}$), 113.8 (C^{a}), 233.7 (C^{l}) ^{11}B:^{d} 88.0 Mass: m/z 390 (M^{+}) IR(Nujol): ṽ(CO) 1976, 1929 cm^{-1}
5 	^{1}H:^{d} 1.0–2.0, 2.36 (m, 22 H, H^{e-k}), 4.20 (t, 1 H, H^{d}), 4.27 (d, 2 H, H^{b}), 4.46 (m, 2 H, H^{c}), 7.05 (m, 9 H, H^{n,p}), 7.68 (t, 6 H, H^{o}) ^{13}C:^{d} 23.5 (C^{k}), 24.5 (C^{e}), 28.1 (br, C^{h}), 31.4 (br, C^{i}), 33.4 (C^{j}), 35.0 (C$^{f\text{ or }g}$), 35.7 (C$^{f\text{ or }g}$), 88.3 (C$^{b\text{ or }c}$), 88.9 (C^{d}), 91.6 (C$^{b\text{ or }c}$), 108.3 (C^{a}), 128.1 (C^{o}), 129.0 (C^{p}), 133.3 [J(PC) = 10, C^{n}], 140.5 [^{1}J(PC) = 33, C^{j}], 240.9 [J(PC) = 20, C^{l}] ^{11}B:^{d} 88.0 ^{31}P:^{d} 89.4 IR(Nujol): ṽ(CO) 1903, 1852 cm^{-1}

Table 1 (*continued*)

Compound and analysis (%)	Spectroscopic data^{a}
6 C, 57.0 (56.7); H, 3.9 (3.9) 	^{1}H:^{d} 2.63 [d, *J*(HH) = 6.6, 2 H, H^{e}], 4.37 [t, *J*(HH) = 6.2, 1 H, H^{d}], 4.42 [d, *J*(HH) 6.2, 2 H, H^{b}], 4.56 (t, 2 H, H^{c}), 4.80 [dd, *J*(HH) = 1.2, 17.0, 1 H, H$^{g'}$], 4.91 [dd, *J*(HH) = not resolved, 10.0, 1 H, H^{g}], 5.57 [ddt, *J*(HH) = 6.6, 10.0, 17.0, 1 H, H^{f}] ^{13}C:^{d} 38.6 (C^{e}), 90.5 (C^{d}), 92.7, 93.8 (C^{b,c}), 111.3 (C^{a}), 117.9 (C^{g}), 134.9 (C^{f}), 233.6 (C^{h}) IR(Nujol): ṽ(CO) 1977, 1907 cm^{-1}
7 C, 57.7 (58.2); H, 4.3 (4.5) 	^{1}H:^{d} 1.86 [t, *J*(HH) = 6.6, 2 H, H^{e}], 1.92 (m, 2 H, H^{f}), 4.30 (m, 3 H, H^{b,d}), 4.52 [t, *J*(HH) = 6.5, 2 H, H^{c}], 4.86 (m, 2 H, H$^{h,h'}$), 5.49 [ddt, *J*(HH) = 6.6, 10.0, 17.0, 1 H, H^{f}] ^{13}C:^{d} 34.4, 35.1 (C^{e,f}), 90.3 (C^{d}), 92.7, 93.8 (C^{b,c}), 112.9 (C^{a}), 116.0 (C^{h}), 136.7 (C^{g}), 233.7 (C^{i}) IR(Nujol): ṽ(CO), 1977, 1908 cm^{-1}
9 C, 72.7 (71.7); H, 5.3 (5.4) 	^{1}H:^{d} 2.06 (dt, 2 H, H^{f}), 2.33 (t, 2 H, H^{e}), 4.16 [d, *J*(HH) = 5.7, 2 H, H^{b}], 4.41 (m, 3 H, H^{c,d}), 4.92 (m, 2 H, H$^{h,h'}$), 5.61 [ddt, *J*(HH) = 6.6, 10, 17, 1 H, H^{g}], 7.0, 7.7 (m, 15 H, H^{k-m}) ^{13}C:^{d} 35.3 (C$^{e \text{ or } f}$), 36.0 (C$^{e \text{ or } f}$), 88.3 (C$^{b \text{ or } c}$), 89.0 (C^{d}), 91.5 (C$^{b \text{ or } c}$), 107.0 (C^{a}), 115.5 (C^{h}), 128.1 (C^{l}), 129.0 (C^{m}), 133.3 [*J*(PC) = 11, C^{k}], 137.5 (C^{g}), 140.5 [*J*(PC) = 34, C^{j}], 241.0 [*J*(PC) = 21, C^{i}] ^{31}P:^{d} 89.2 IR(Nujol): ṽ(CO) 1904, 1853 cm^{-1}
10 	^{1}H:^{g} 3.00 [d, *J*(HH) = 7.0, 2 H, H^{e}], 4.40 (m, 3 H, H^{b,d}), 4.61 [t, *J*(HH) = 6.0, 2 H, H^{c}], 4.93 (m, 2 H, H$^{g,g'}$), 5.95 (m, 1 H, H^{f}) 7.00 [t, *J*(HH) = 7.1, 1 H, H^{m}], 7.15 [t, *J*(HH) = 7.1, 2 H, H^{l}], 7.52 [d, *J*(HH) = 7.1, 2 H, H^{k}] ^{13}C:^{g} 40.0 (C^{e}), 87.9 (C^{d}), 88.4 (C$^{b \text{ or } c}$), 91.5 (C$^{b \text{ or } c}$), 105.3 (C^{a}), 115.6 (C^{g}), 123.6 (C$^{k \text{ or } l}$), 126.4 (C^{m}), 126.6 (C$^{k \text{ or } l}$), 138.0 (C^{f}), 158.8 (C^{j}), 242.6 (C^{h}), 341.0 (C^{i}) IR(KBr): ṽ(CO) 1866, 1750 cm^{-1}
11 	^{1}H:^{g} 2.20 [dt, *J*(HH) = 6.8, 2 H, H^{f}], 2.31 [t, *J*(HH) = 6.8, 2 H, H^{e}], 4.38 [d, *J*(HH) = 6.0, 2 H, H^{b}], 4.40 [t, *J*(HH) = 6.0, 1 H, H^{d}], 4.61 [t, *J*(HH) = 6.0, 2 H, H^{c}], 4.88 (m, 2 H, H$^{h,h'}$), 5.73 (m, 1 H, H^{g}), 7.00 [t, *J*(HH) = 7.0, 1 H, H^{n}], 7.14 [t, *J*(HH) = 7.0, 2 H, H^{m}], 7.49 [d, *J*(HH) = 7.0, 2 H, H^{l}] ^{13}C:^{g} 35.6, 36.1 (C^{e,f}), 87.7 (C^{d}), 88.4, 91.4 (C^{b,c}), 107.3 (C^{a}), 114.6 (C^{h}), 123.6 (C$^{l \text{ or } m}$), 126.3 (C^{n}), 126.7 (C$^{l \text{ or } m}$), 138.4 (C^{g}), 158.7 (C^{k}), 242.7 (C^{i}), 340.0 (C^{j}) IR(KBr): ṽ(CO) 1870, 1747 cm^{-1}
12 C, 70.6 (70.8); H, 8.6 (8.7) 	^{1}H:^{d} 1.16–1.95 (m, 32 H, H$^{f,h-j}$), 1.48 [t, *J*(HH) = 7.7, 4 H, H^{g}], 2.24 [t, *J*(HH) = 7.0, 4 H, H^{e}], 4.70 (br, 10 H, H^{b-d}] ^{13}C:^{d} 23.6 (C^{j}), 28.0 (C^{e}), 28.3 (br, C^{g}), 31.5 (br, C^{h}), 33.5 (C^{i}), 40.0 (br, C^{f}), 75.2 (br, C^{b,c}), 76.3 (br, C^{d}), 78.3 (br, C^{b,c}), 95.6 (br, C^{a}) ^{11}B:^{d} 88.0 Mass: *m*/*z* 576 (*M*$^{+}$)
13 C, 61.2 (61.2); H, 6.6 (6.4) 	^{1}H:^{d} 0.85 [t, *J*(HH) = 7.7, 2 H, H^{g}], 1.2–1.7 (m, 16 H, H$^{f,h-l}$), 2.07 [t, *J*(HH) = 7.7, 2 H, H^{e}], 4.26 [t, *J*(HH) = 6.0, H^{d}], 4.45 [d, *J*(HH) = 6.0, 2 H, H^{b}], 4.53 [t, *J*(HH) = 6.0, 2 H, H^{c}] ^{13}C:^{d} 22.6 (C^{j}), 22.8 (br, C^{k}), 26.1 (C^{e}), 26.2 (C^{l}), 32.0 (C^{i}), 38.0 (C^{f}), 73.4 (C^{h}), 90.0 (C^{d}), 92.7 (C$^{b \text{ or } c}$), 93.8 (C$^{b \text{ or } c}$), 114.4 (C^{a}), 233.9 (C^{m}) ^{11}B:^{d} 54.0 Mass: *m*/*z* 392 (*M*$^{-}$) IR(Nujol): ṽ(CO) 1975, 1905 cm^{-1}

[a] Given as: chemical shift (δ) (multiplicity, *J* Hz, relative intensity, assignment), *etc.* [b] In $(CD_3)_2SO$. [c] In $CDCl_3$. [d] In C_6D_6. [e] Analysis unsatisfactory, too air sensitive. [f] No satisfactory elemental analysis obtained due to loss of diethyl ether. [g] In $[^2H_8]$thf.

temperature. The solvent was removed *in vacuo* to yield a slightly yellow oil. Traces of this oil when exposed to air become green-blue. The NMR spectra of the oil showed it to contain **III** (*ca.* 85%) and free catechol (*ca.* 15%). Attempts to achieve further purification by distillation failed. Yield *ca.* 40%.

Method B. A mixture of freshly distilled and degassed allylbenzene (3.30 g, 27.9 mmol) and $HB(1,2\text{-}O_2C_6H_4)$ (3.34 g, 27.9 mmol) was kept at 100 °C with stirring for 2 h. Distillation of the resulting dark yellow oil at 110–130 °C (10^{-1} Torr) gave pure compound **III**, as shown by NMR and mass spectra (yield 65%). Satisfactory elemental analysis could not be obtained due to the air sensitivity of the product. A derivative of **III**, namely the metal complex **1**, gave a satisfactory analysis (Table 1).

$Ph(CH_2)_3BC_8H_{14}$ IV. The compound HBC_8H_{14} (3.21 g, 27.1 mmol) in tetrahydrofuran (40 cm^3) was added to allylbenzene (3.31 g, 27.1 mmol) with stirring at room temperature. The mixture was kept at r.t. for 12 h; then the thf was removed under reduced pressure. Distillation of the residual yellow liquid gave pure **IV** (135–140 °C, 10^{-1} Torr; yield 83%). An elemental analysis could not be obtained due to the air sensitivity of the product. A derivative of **IV**, namely the metal complex **2**, gave a satisfactory analysis (Table 1).

$[Cr\{\eta\text{-}Ph(CH_2)_3B(1,2\text{-}O_2C_6H_4)\}(CO)_3]$ 1. *Method A.* Freshly sublimed $[Cr(CO)_6]$ (0.64 g, 2.9 mmol) in diglyme (70 cm^3) and thf (10 cm^3) was treated with compound **III** (0.70 g, 2.9 mmol) and the mixture stirred at 125 °C until evolution of CO ceased (overall reaction time 22 h). A green cloudy reaction mixture was obtained. After filtration through two layers of glass filter-paper the resulting yellow-green filtrate was evaporated under reduced pressure to yield a green powder. This was washed with light petroleum (b.p. 40–60 °C, 3 × 50 cm^3). The residue was extracted into toluene (50 cm^3) and the yellow solution filtered from small amounts of green residue. The filtrate was concentrated under reduced pressure and then cooled to −25 °C for 5 h and then to −80 °C for 24 h to give large yellow crystals of pure complex **1** (yield 58%).

Method B. A neat mixture of (0.64 g, 2.5 mmol) of complex **6** and $HB(1,2\text{-}O_2C_6H_4)$ (0.34 g, 2.8 mmol) was kept stirring at 100 °C for 2 h. The course of the reaction was monitored by ^1H NMR spectroscopy. Upon heating the mixture darkened continuously and became increasingly viscous to yield an almost black waxy solid. Toluene was added and the resulting orange solution was filtered from a black residue. The toluene filtrate was concentrated under reduced pressure giving an orange oil. Further volatiles were removed over a period of 3 h at 50 °C (10^1 Torr). The ^1H NMR spectrum showed the residual oil to contain *ca.* 80% of complex **1** together with some unknown impurity. All attempts to achieve further purification by recrystallising the crude product from toluene, ether and mixtures of those with light petroleum (b.p. 40–60 °C) failed. The reaction was also carried out at r.t. for 16 h but there was no significant improvement in the purity of the product.

$[Cr\{\eta\text{-}Ph(CH_2)_3BC_8H_{14}\}(CO)_3]$ 2. The compound HBC_8H_{14} (0.38 g, 3.15 mmol) in tetrahydrofuran (20 cm^3) was added dropwise with stirring at r.t. to a solution of complex **6** (0.80 g, 3.15 mmol) in thf (20 cm^3). After stirring for 12 h at r.t. the reaction mixture was still the initial orange. The solvent was removed under reduced pressure to yield an orange oil. The oil was extracted with light petroleum (b.p. 40–60 °C) to give a clear, orange solution and small amounts of a white insoluble residue. After filtration the solvent was removed under reduced pressure to give a green-yellow powder. The crude product was recrystallised from light petroleum as amber-coloured crystals of pure complex **2**. These crystals appeared to be too soft to be suitable for r.t. X-ray analysis (yield 90%).

$[Cr\{\eta\text{-}Ph(CH_2)_3BBr_2\cdot SMe_2\}(CO)_3]$ 3. Compound **6** (0.38 g, 1.5 mmol) in CH_2Cl_2 (30 cm^3) was treated dropwise with a 1 mol dm^{-3} solution (1.5 cm^3) of $HBBr_2\cdot SMe_2$ in CH_2Cl_2 with stirring at 0 °C. The mixture was allowed to warm up slowly, stirred at r.t. overnight and then refluxed for 2 h to yield a bright yellow solution. After evaporation of the CH_2Cl_2 a dark orange oil was left which fumed in air. This oil was extracted with toluene to give a yellow solution and a small amount of insoluble material. After filtration the residue was investigated by IR spectroscopy; no CO bands were found. The toluene solution was concentrated under reduced pressure. The solution was then transferred into a long and narrow Schlenk tube, layered with a little neat toluene and then a covering layer of light petroleum (b.p. 40–60 °C). This gave yellow crystals of pure complex **3** after 24 h (yield 43%).

$[Cr\{\eta\text{-}Ph(CH_2)_4BC_8H_{14}\}(CO)_3]$ 4. Compound **7** (0.94 g, 3.5 mmol) in thf (30 cm^3) was treated dropwise with a solution of HBC_8H_{14} (0.50 g, 4.1 mmol) in thf (15 cm^3) with stirring at r.t. No immediate colour change was observed. The reaction mixture was stirred at r.t. overnight. The solvent was removed under reduced pressure to give an orange oil which was kept at 60 °C (10^{-1} Torr) to sublime off the excess of HBC_8H_{14}. During this sublimation the oil gradually turned into an orange solid. This was dissolved in light petroleum (b.p. 40–60 °C) and the saturated solution kept at −25 °C to give orange platelets of pure complex **4** (yield 81%).

$[Cr\{\eta\text{-}Ph(CH_2)_4BC_8H_{14}\}(CO)_2(PPh_3)]$ 5. A solution of compound **9** (0.60 g, 1.2 mmol) in thf (30 cm^3) was added to a solution of HBC_8H_{14} (0.18 g, 1.45 mmol) in thf (15 cm^3) with stirring at room temperature. After stirring overnight the solvent was removed from the clear orange reaction mixture under reduced pressure. The residual orange oil was kept for 5 h at 50 °C (10^{-1} Torr) to remove the excess of HBC_8H_{14}. The waxy residue was dissolved in light petroleum (b.p. 40–60 °C, 100 cm^3) and kept at −80 °C for 24 h to give yellow microcrystalline complex **5** (yield 64%).

$[Cr(\eta\text{-}PhCH_2CH{=}CH_2)(CO)_3]$ 6.[6,7] The compound $[Cr(CO)_6]$ (2.20 g, 10.0 mmol) and allylbenzene (1.20 g, 10.0 mmol) in a mixture of diglyme (150 cm^3) and thf (20 cm^3) were stirred at 140 °C. The carbon monoxide evolved was trapped in a gas burette. After approximately 20 h the liberation of CO ceased. The IR spectrum of the green-brown reaction mixture showed no remaining $[Cr(CO)_6]$. The crude reaction mixture was filtered through Celite to give a clear orange solution from which the solvents were removed at 60 °C under reduced pressure. The residual orange oil was soluble in hexane and cooling this solution to −80 °C gave yellow-orange platelets of complex **6**. The crystals were collected at −80 °C and then dried *in vacuo* at −20 °C. They melt at r.t. (yield 78%).

$[Cr\{\eta\text{-}Ph(CH_2)_2CH{=}CH_2\}(CO)_3]$ 7.[6,7] The compound $[Cr(CO)_6]$ (3.00 g, 13.6 mmol) and 4-phenylbut-1-ene (1.90 g, 14.4 mmol) in a stirred mixture of diglyme (150 cm^3) and thf (20 cm^3) were kept at 130 °C. The carbon monoxide evolved was trapped in a gas burette. After approximately 24 h the liberation of CO ceased. The IR spectrum of the green-brown reaction mixture showed no remaining $[Cr(CO)_6]$. The crude mixture was filtered through Celite to give a clear orange solution from which the solvents were removed at 60 °C under reduced pressure. This yielded an orange oil which was recrystallised from hexane at −80 °C to give yellow-orange needles of pure complex **7**. The supernatant was cannulated off at −80 °C and the crystals were dried *in vacuo* at −20 °C. The melting point is below r.t. (yield 67%).

$[Cr\{\eta\text{-}Ph(CH_2)_2\text{-}\eta\text{-}CH{=}CH_2\}(CO)_2]$ 8.[6,7] Compound **7** (1.00 g, 3.7 mmol) in light petroleum (b.p. 40–60 °C) in a quartz glass vessel was irradiated with a medium-pressure UV lamp and the temperature strictly maintained below 50 °C to avoid decomposition. Evolution of CO was observed immediately after the photolysis started and the solution changed gradually from orange to deep red. After 24 h half of the starting material had reacted to give complex **8**. Owing to its lower solubility, some of the product precipitated as a red powder. After 3d the reaction was complete. The IR spectrum showed most of the starting material was cleanly transformed into **8**. The reaction mixture was filtered from a small amount of green precipitate and the red filtrate cooled to −80 °C giving **8** as a red microcrystalline powder (yield 91%).

$[Cr\{\eta\text{-}Ph(CH_2)_2CH{=}CH_2\}(CO)_2(PPh_3)]$ 9.[6,7] A mixture of complex **8** (0.35 g, 1.47 mmol) and PPh_3 (0.39 g, 1.47 mmol) in benzene (70 cm^3) was kept under reflux for 12 h. The reaction was monitored by IR spectroscopy. The benzene was removed under reduced pressure and the residue dissolved in light petroleum (b.p. 40–60 °C). After filtration from a small amount of insoluble material the filtrate was kept at −80 °C overnight to give a yellow precipitate of pure complex **9** (yield 83%).

$[Li(Et_2O)_n][Cr\{\eta\text{-}PhCH_2CH{=}CH_2\}(CO)_2\{C(O)Ph\}]$ 10. To a solution of complex **6** (1.15 g, 4.5 mmol) in ether (50 cm^3) was added with stirring at −78 °C a solution of LiPh (4.5 mmol in 10 cm^3 diethyl ether). No colour change was observed at that temperature. The mixture was allowed very slowly to warm to r.t. giving a red solution and a yellowish precipitate. The mixture was stirred at r.t. overnight and the precipitate was filtered off. The residue was a sandy powder of unknown composition. The red ether filtrate was stored at r.t. for several days to give a few crystals of pure complex **10**. This compound is stable at r.t. in the solid state as well as in thf solution, but it is essential to carry out the reaction at low temperature.

$[Li(Et_2O)_n][Cr\{\eta\text{-}Ph(CH_2)_2CH{=}CH_2\}(CO)_2\{C(O)Ph\}]$ 11. To compound **7** (1.0 g, 3.7 mmol) in diethyl ether (50 cm^3) was added a solution of phenyllithium (3.8 mmol) in diethyl ether (20 cm^3) dropwise with stirring, at −78 °C. No colour change was observed at this temperature. The yellow reaction mixture was very slowly warmed to room temperature. At −50 °C it had become orange, at −25 °C it was cherry red and at 0 °C very deeply red, almost black. After stirring at r.t. for 3 h the clear reaction mixture was cooled to −18 °C overnight to give red needles of pure complex **11** (yield, 38%). The compound is stable at r.t. in the solid state as well as in thf solution, but it is essential to carry out the reaction at low temperature.

$[Mo\{\eta\text{-}Ph(CH_2)_3BC_8H_{14}\}_2]$ 12. Bis(η-allylbenzene)molybdenum[12] (0.14 g, 0.4 mmol) in thf (20 cm^3) was treated with HBC_8H_{14} (0.12 g, 1.0 mmol) in thf (20 cm^3) at r.t. and the mixture was stirred overnight. No change of the initial green colour was observed. The solvent was evaporated under reduced pressure to give a green powder from which most of the excess of HBC_8H_{14} was then removed by sublimation (at 60 °C, 10^{-1} Torr). Addition of light petroleum (b.p. 40–60 °C) gave a clear green solution and some white residue. After filtration pure complex **12** crystallised at −25 °C from the filtrate (yield 55%).

$[Cr\{\eta\text{-}Ph(CH_2)_3BOC_8H_{14}\}(CO)_3]$ 13. The compound Me_3NO (0.03 g, 0.4 mmol) in thf (30 cm^3) was added with stirring at r.t. to a solution of **2** (0.16 g, 0.43 mmol) in thf (20 cm^3). After stirring at r.t. for 24 h the solvent was removed under reduced pressure to give a yellow-green semi-solid material. This was dissolved in light petroleum (b.p. 40–60 °C) and a yellow solution was filtered from a little white residue. The filtrate was kept at −25 °C for 5 h to give amber-coloured needles of pure complex **13** (yield 79%).

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References

1 P. A. McCusker, E. C. Ashby and H. S. Makowski, *J. Am. Chem. Soc.*, 1957, **79**, 5179.
2 H. C. Brown and S. K. Gupta, *J. Am. Chem. Soc.*, 1975, **97**, 5249.
3 H. C. Brown, E. F. Knights and C. G. Scouten, *J. Am. Chem. Soc.*, 1974, **96**, 7765.
4 H. C. Brown, N. Ravindran and S. U. Kulkarni, *J. Org. Chem.*, 1980, **45**, 384.
5 C. F. Lane and G. W. Kabalka, *Tetrahedron*, 1976, **32**, 981.
6 A. N. Nesmeyanov, M. I. Rybinskaya, V. V. Krivykh and V. S. Kaganovich, *J. Organomet. Chem.*, 1975, **93**, C8.
7 A. N. Nesmeyanov, V. V. Krivykh, P. V. Petrovskii, V. S. Kaganovich and M. I. Rybinskaya, *J. Organomet. Chem.*, 1978, **162**, 323.
8 H. Nöth and B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, Springer, Berlin, Heidelberg, New York, 1978.
9 E. O. Fischer and A. Riedel, *Chem. Ber.*, 1968, **101**, 156.
10 E. O. Fischer, *Adv. Organomet. Chem.*, 1976, **14**, 1.
11 P. R. Brown, D. Phil. Thesis, University of Oxford, 1982.
12 I. Treurnicht, D. Phil. Thesis, University of Oxford, 1984.
13 J. Kotz and D. Pedrotty, *Organomet. Chem. Rev. A*, 1969, **4**, 479.
14 A. Appel, F. Jäkle, T. Priermeier, R. Schmid and M. Wagner, *Organometallics*, 1996, **15**, 1188.
15 Y. Shvo and E. Hazum, *J. Chem. Soc., Chem. Commun.*, 1974, 336.
16 G. W. Kabalka and H. C. Hedgecock, *J. Org. Chem.*, 1975, **40**, 1776.

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