Naphthalene Complexes. Part 1. Metal Vapour Preparation of Bis(η^6-naphthalene)chromium(0) and its Arene Replacement Reactions

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Bis(η^6-naphthalene)chromium(0), formed in high yield from chromium atoms and naphthalene in solution at −80 °C, is a thermally stable but very reactive compound. Two-electron donor ligands displace one naphthalene ring [L = PF_3, $P(OMe)_3$, or PMe_3] or both naphthalene rings (L = CO, $CNBu^t$, or CNC_6H_{11}) in rapid reactions at room temperature. The product $[Cr(C_{10}H_8)(PMe_3)_3]$ is susceptible to further displacement of naphthalene by CO at 0 °C. The reaction of chromium atoms with 1,4-dimethylnaphthalene is stereospecific. More than 95% of the product is the isomer of $[Cr(C_{10}H_6Me_2)_2]$ in which the unsubstituted ring is bonded to the metal. Bis(1-methylnaphthalene)chromium exists as a mixture of 10 isomers which can be distinguished on the basis of their ^1H n.m.r. spectra.

UNTIL recently, naphthalene sandwich complexes containing the metal in a zerovalent state had been prepared only on a spectroscopic scale.[1] The reducing Friedel–Craft synthesis,[2] although successful in the preparation of the cationic bis(naphthalene)ruthenium(II) complex,[3] yields with chromium only partly hydrogenated naphthalene complexes with a composition approaching that of bis(η^6-tetralin)chromium.[3,4] The reaction of a metal halide with an arene radical anion failed to yield the elusive naphthalene sandwich complex,[5] although we have had more success using potassium vapour.[6] However, the metal-atom technique [7] provides an easy route to this class of compounds and two independent reports in 1977 described the synthesis of bis(η^6-naphthalene)chromium(0) by this method.[8,9]

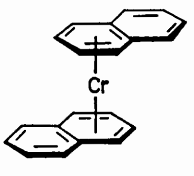
Our interest in these compounds stems from their potential lability towards ligand displacement. Benzene and substituted benzenes in compounds of the type $[Cr(arene)_2]$ or $[Cr(arene)L_3]$ (where L is a two-electron donor) are generally difficult to displace.[10,11] However, with $[Cr(naphthalene)(CO)_3]$ displacement of naphthalene is known to be fairly easy.[12,13] Similarly, there is a marked enhancement of ligand-exchange reactivity in some complexes when cyclopentadienyl is replaced by indenyl, *e.g.* $[Mo(\eta^5\text{-}C_5H_5)(CO)_3Br]$ compared with $[Mo(\eta^5\text{-}C_9H_7)(CO)_3Br]$.[14,15] Fused rings apparently share an ability to undergo ready slippage, freeing a co-ordination site for an incoming ligand. We set out to explore the area by preparing bis(naphthalene)chromium and studying its reactions with ligands. A preliminary account of some of this work has been given.[8]

RESULTS AND DISCUSSION

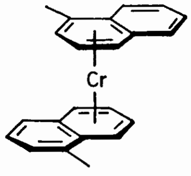
Condensation of Cr atoms into a solution of naphthalene in diglyme (−80 °C, 5 × 10^{-2} Torr †) yields a deep red-brown solution. Purification of the reaction products (see Experimental section) yields black crystals which elemental analysis and ^1H n.m.r. data (Table) show to be bis(η^6-naphthalene)chromium(0), (1). Compound (1) is sparingly soluble in diethyl ether and more soluble in tetrahydrofuran (thf), benzene, and toluene. Solutions as well as crystals of (1) are decomposed almost immediately on exposure to air. Attempted oxidation of (1) to the chromium(I) cationic complex by the usual means (air, H_2O_2, or I_2), which work for bis(benzene)chromium,[16] yielded only chromium(III) species.

In the absence of O_2, crystals of (1) are stable for months. They can be sublimed at 100 °C (10^{-3} Torr). Higher temperatures lead to concomitant decomposition on the hot wall of the sublimation vessel.

The ^1H n.m.r. spectrum of (1) (Table) consists of three signals at δ 4.34, 5.24, and 6.92 with an intensity ratio of 1 : 1 : 2. The two symmetrical multiplets of equal intensity form an AA′BB′ system and are assigned to the four protons of the ring co-ordinated to the metal. The protons of the unco-ordinated ring appear as a singlet shifted slightly upfield from the resonance of the free ligand. Assignment of the two AA′BB′ signals to the 5,8 or 6,7 protons is in accordance with the observations of stronger shielding for 2,3 and 6,7 protons compared to 1,4 and 5,8 protons in naphthalene systems.[17]

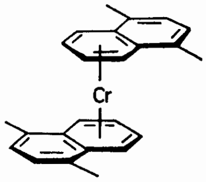


(1)



(2)

(10 isomers)



(3)

The 1-methyl- and 1,4-dimethyl-naphthalene analogues [(2) and (3) respectively] are readily prepared by the same route. The enhanced solubility of the substituted naphthalenes allows the reaction to be carried out in methylcyclohexane–thf solvent mixtures ‡ in very good yields.

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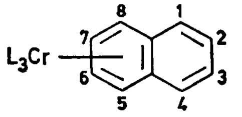
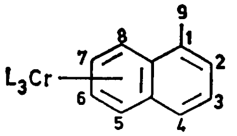
† Throughout this paper: 1 Torr = (101 325/760) Pa; 1 atm = 101 325 Pa.

‡ Control experiments with diglyme or methylcyclohexane–thf (3 : 1) and chromium vapour showed these solvents to be inert under the reaction conditions used in the experiments [*e.g.* no formation of chromium(III) oxide due to deoxygenation of the ethers was observed].

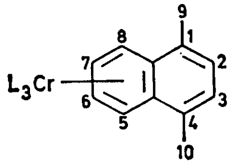
Hydrogen-1 n.m.r. data of chromium–naphthalene complexes [a]



Compound	H_L	$H^{6,7}$	$H^{5,8}$	$H^{2,3}$	$H^{1,4}$
$C_{10}H_8$		7.28	7.66	7.28	7.66
$[Cr(C_{10}H_8)_2]$		4.34	5.24	6.92 (s)	
$[Cr(C_{10}H_8)(CO)_3]$		4.75	5.37	6.88 (m)	
$[Cr(C_{10}H_8)(PF_3)_3]$		4.73	5.50	6.93 (m)	
$[Cr(C_{10}H_8)\{P(OMe)_3\}_3]$	3.45 (m)	4.70	5.35	7.00	7.50
$[Cr(C_{10}H_8)(PMe_3)_3]$	1.05	3.75	4.50	6.80	*b*



	H_L	$H^{6,7}$	$H^{5,8}$	$H^{2,3}$	H^4	H_{CH} (9)
$C_{10}H_7Me$			7.0—7.8			2.40
$[Cr(C_{10}H_7Me)_2]$ [c]		4.40	5.30	6.88		2.05, 2.35
$[Cr(C_{10}H_7Me)(PF_3)_3]$		4.65	5.48	6.72		2.06
$[Cr(C_{10}H_7Me)\{P(OMe)_3\}_3]$	3.42 (m)	4.76	5.42	6.93	7.40	2.57
$[Cr(C_{10}H_7Me)(PMe_3)_3]$	1.06	4.16	4.60	6.7	*b*	2.46



	H_L	$H^{6,7}$	$H^{5,8}$	$H^{2,3}$	H_{CH_3} (9, 10)
$C_{10}H_6Me_2$		7.32	7.85	7.04	2.44
$[Cr(C_{10}H_6Me_2)_2]$		4.45	5.33	6.70	2.15
$[Cr(C_{10}H_6Me_2)(CO)_3]$ [d]		5.52	6.18	7.11	2.54
$[Cr(C_{10}H_6Me_2\{P(OMe)_3\}_3]$	3.43	4.85	5.54	6.88	2.59

[a] In C_6D_6, position in p.p.m. downfield from $SiMe_4$ (δ scale). [b] Signal obscured by free naphthalene. [c] Mixture of isomers, see text. [d] Ref. 17, in $CDCl_3$.

Monosubstituted naphthalenes are expected to give rise to a number of isomeric complexes. Co-ordination to the metal can occur from the substituted or unsubstituted ring unit. Each of the resulting three co-ordination isomers exists as a mixture of diastereoisomers arising from random orientation of the substituted naphthalene on complex formation. In the case of 1-methylnaphthalene the ten isomers (four enantiomeric pairs and two *meso* compounds) thus expected should produce eight signals for magnetically distinct methyl groups in the ^1H n.m.r. spectrum.* Two complex groups of methyl signals are indeed observed in the 100 MHz spectrum. They are centred at δ 2.35 and 2.05, and have an intensity ratio of *ca.* 1 : 2. They are assigned to the methyl groups of the compounds containing the metal co-ordinated to the C_6H_3Me and C_6H_4 ring unit respectively. The assignment proceeds from an analysis of the intensity ratio of the complex signals assigned to protons in positions 2,3 (or 6,7) to those assigned to protons in positions 1,4 (or 5,8) of the co-ordinated ring unit. The ratio of 1.16 : 1 indicates that 70% of the 1-methylnaphthalenes are co-ordinated to the metal through the non-substituted ring unit. Within the limits of n.m.r. sensitivity (*ca.* 95%) bis(1,4-dimethylnaphthalene)chromium is found to be present in only one isomeric form. The metal is co-ordinated uniquely to the non-substituted ring unit. This co-ordination selectivity is remarkable, although preferred co-ordination of the unsubstituted ring unit in 1,4-disubstituted naphthalene has been observed previously in the reaction with $[Cr(CO)_6]$.[17]

Treatment of a solution of (1) in thf with CO yields $[Cr(CO)_6]$. Compounds (2) and (3) react likewise with substitution of both naphthalene rings. Possible reaction pathways include slippage of one η^6-naphthalene to a η^4-naphthalene followed by displacement of the first naphthalene to give the intermediate tricarbonyl(η^6-naphthalene)chromium [path (A)]; alternatively, a dicarbonylbis(η^4-naphthalene)chromium compound [path (B)] may be formed (Scheme 1). A somewhat similar compound bis(η^4-cyclohexa-1,3-diene)chromium bis(hexafluorophosphate) has recently been reported.[18]

To establish the reaction pathway, the displacement reaction was followed by i.r. spectroscopy. Carbon monoxide was passed through a solution of (1) in methyl-

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* Splitting of methyl resonances has been observed previously for several diasteroisomeric bis(arene) complexes: V. Graves and J. J. Lagowski, *J. Organometallic Chem.*, 1976, **120**, 397.

cyclohexane. At regular intervals samples were taken and the ν(CO) region was scanned. Bands due to $[Cr(C_{10}H_8)(CO)_3]$ [19] and $[Cr(CO)_6]$ were observed immediately after the start of the reaction. No other lines due to different intermediates were observed. The reaction thus proceeds by stepwise replacement of the co-ordinated naphthalenes. The lability of naphthalene in $[Cr(C_{10}H_8)(CO)_3]$ towards replacement by CO was confirmed independently in a reaction with a conventionally prepared sample of this complex.[17]

$$[Cr(\eta^6\text{-}C_{10}H_8)_2] \xrightarrow[C_{10}H_8]{CO} [Cr(\eta^6\text{-}C_{10}H_8)(CO)_3] \xrightarrow[-C_{10}H_8]{CO} [Cr(CO)_6] \quad (A)$$

$$[Cr(\eta^6\text{-}C_{10}H_8)_2] \xrightarrow{CO} [Cr(\eta^4\text{-}C_{10}H_8)_2(CO)_2] \xrightarrow[-2C_{10}H_8]{CO} [Cr(CO)_6] \quad (B)$$

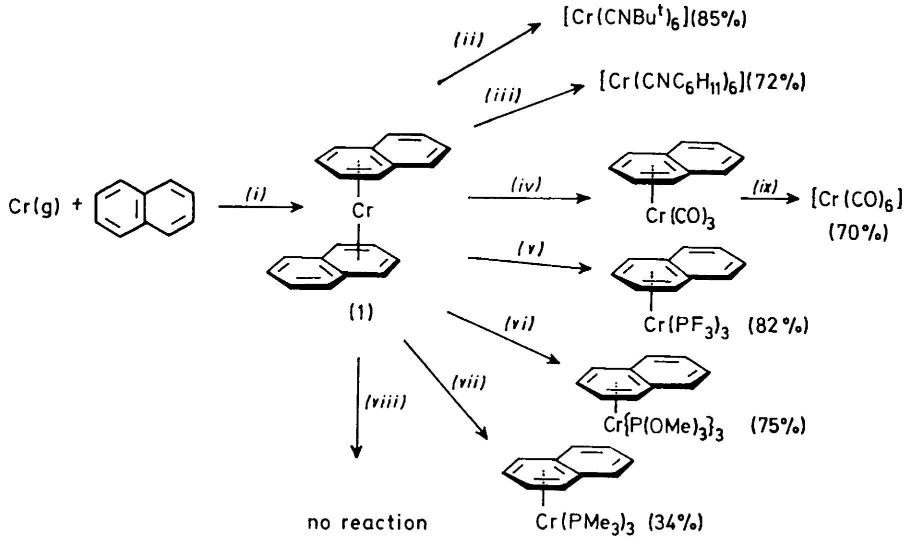
SCHEME 1

Likewise, treatment of (1) or (2) with alkyl isocyanides ($CNBu^t$ or CNC_6H_{11}) in diethyl ether or pentane causes smooth displacement of both naphthalenes to yield the corresponding hexakis(isocyanide)chromium(0) complexes (Scheme 2).[20,21] The ν(CNR) region of the i.r. spectrum displays very characteristic broad absorptions with maxima (in cyclohexane) at 1 880 cm^{-1} $[Cr(CNBu^t)_6]$ and 1 871 cm^{-1} $[Cr(CNC_6H_{11})_6]$. When a Nujol mull of $[Cr(CNBu^t)_6]$ is left in air for several minutes, bands at 2 028 and 2 070 cm^{-1} previously assigned to $[Cr(CNBu^t)_6]$ [20] grow in. This observation, coupled with the position of the bands, indicates that they are associated with a complex containing the metal in a higher oxidation state, presumably $[Cr^I(CNBu^t)_6]^+$.

Reaction of (1) with PF_3, $P(OMe)_3$, or PMe_3 in hexane or diethyl ether at 0 °C causes displacement of one naphthalene (Scheme 2). The complexes $[Cr(C_{10}H_8)L_3]$ are formed in good yield; their stoicheiometry is established by elemental analysis and ^1H n.m.r. spectroscopic data (Table). The compound $[Cr(C_{10}H_8)(PF_3)_3]$ forms bright orange air-stable crystals which melt at 153 °C without decomposition. The compounds $[Cr(C_{10}H_8)\{P(OMe)_3\}_3]$ and $[Cr(C_{10}H_8)(PMe_3)_3]$ form black crystals; the latter decomposes slowly in the absence of free PMe_3. They dissolve readily in non-polar organic solvents such as benzene and light petroleum to give dark brown-red and dark brown-green solutions respectively. The phosphine complex decomposes instantaneously on exposure to air, whereas the phosphite complex shows decomposition only after several minutes. Reaction of the mixture of isomers of $[Cr(C_{10}H_7Me)_2]$ with PR_3 ligands (R = OMe, Me, or F) yields exclusively the products (an enantiomeric pair) with the CrL_3 unit co-ordinated to the unsubstituted ring unit. Apparently, naphthalenes co-ordinated through the substituted ring are more labile than those co-ordinated through the unsubstituted ring unit.

The naphthalene in the $[Cr(C_{10}H_8)L_3]$ [$L = PF_3$, $P(OMe)_3$, or PMe_3] complexes shows marked changes in lability depending on the nature of L. With $L = PF_3$ no reaction with CO (methylcyclohexane, 25 °C) is observed. The naphthalene in this complex appears to form a more robust Cr–naphthalene bond than in the CO analogue. At the other extreme, the PMe_3 complex reacts readily with CO (methylcyclohexane, 0 °C). The products of the reaction are *fac*-$[Cr(PMe_3)_3(CO)_3]$ and *cis*-$[Cr(PMe_3)_2(CO)_4]$. The compounds were identified by their i.r. spectra.[22] No intermediate was observed; however, growth and disappearance of a strong band at 1 804 cm^{-1} in the initial phase of the analogous reaction with $[Cr(C_{10}H_7Me)(PMe_3)_3]$ points to the formation of $[Cr(C_{10}H_7Me)(PMe_3)_2(CO)]$ as the likely precursor of $[Cr(PMe_3)_2(CO)_4]$.

Apart from signals due to the ligands L, the ^1H n.m.r. spectra of the [Cr(naphthalene)L_3] complexes consist of an AA′BB′ system and two complex multiplets (Table). The former appears near the position of the protons of free naphthalene and is assigned to the protons of the unco-ordinated ring. The two multiplets, on broad-



SCHEME 2 (*i*) Diglyme, −80 °C; (*ii*) $CNBu^t$; (*iii*) CNC_6H_{11}; (*iv*) CO, 0 °C; (*v*) PF_3; (*vi*) $P(OMe)_3$; (*vii*) PMe_3; (*viii*) PPh_3; (*ix*) CO band ^{31}P decoupling, form a second AA'BB' system shifted upfield from the free-ligand resonances. They are accordingly assigned to the co-ordinated ring protons. These shifts appear to parallel the electron-withdrawing or -donating nature of the co-ligands. In the PF_3 and $P(OMe)_3$ complexes the co-ordinated ring protons appear close to those of $[Cr(C_{10}H_8)(CO)_3]$, downfield from the resonances of bis(naphthalene)chromium, whereas in the electron-rich PMe_3 complex these protons are shifted upfield from the parent compound. Naphthalene thus shows remarkable ability to adapt to the electronic nature of the CrL_3 fragment. Attempts to prepare analogous complexes with PPh_3, $P(OPh)_3$, and PMe_2Ph failed; with the former two reagents no reaction was observed, whereas the reaction with the latter resulted in decomposition even at 0 °C. Steric hindrance may account for this observation although the ' cone angle '[23] of $P(OPh)_3$ is only slightly larger than that of PMe_3.

Bis(naphthalene)chromium and its methyl-substituted analogues are the first examples of fused six-membered ring sandwich complexes with the metal in a zerovalent state. Although we expected a higher reactivity of bis(naphthalene)chromium compared to bis(benzene)-chromium, we are amazed at the lability of the metal–naphthalene bond. The mild reaction conditions for naphthalene replacement reactions (*e.g.* CO, 1 atm, 0 °C) compare with the stringent conditions necessary to replace the arene in the benzene analogue (CO, 320 atm, 200 °C).[10]

Kinetic studies of arene replacement by phosphine in $[Mo(arene)(CO)_3]$ complexes imply an associatively activated mechanism.[24] That is, as the phosphine approaches, the arene becomes a η^4-ligand, and then a η^2-ligand as the second phosphine approaches. In the naphthalene system, the first step in particular can be expected to occur more easily since the intermediate (or the transition state) is stabilized by the presence of the second ring which retains its full resonance energy, whereas in the arene complex this step leaves an isolated double bond in the six-membered ring.

EXPERIMENTAL

The design of the rotating solution reactor has been described previously.[7] Hydrogen-1 n.m.r. data were recorded on Varian T60A or XL 100 spectrometers. All chemical shifts are reported in p.p.m. downfield from $SiMe_4$. Infrared spectra were recorded on Perkin-Elmer 225 or Pye–Unicam SP 1100 spectrometers. All preparations and reactions were carried out in freshly distilled, dry, deoxygenated solvents in an atmosphere of dry nitrogen or argon.

Bis(η^6-*naphthalene*)*chromium*(0).—Chromium (0.98 g, 18.8 mmol) was evaporated over a period of 2.5 h from an alumina crucible (1 cm³) with imbedded molybdenum wire (diameter 1.2 mm), resistance heated using 31 A at 4.2 V. The crucible assembly was insulated by an alumina blanket (Saffil, I.C.I.). The chromium vapour was condensed into a cooled (−80 °C) solution of naphthalene (10 g, 78 mmol) in dry diglyme (150 cm³) in a rotating flask (2 dm³). The pressure in the reactor was kept below 10^{-2} Torr during the reaction. On evaporation of chromium, the solution quickly turned an intense reddish brown colour. After removal of the solvent *in vacuo*, the excess of naphthalene was sublimed onto a liquid N_2 cooled cold-finger (1 h, 40 °C, 10^{-3} Torr). The black residue was extracted with toluene (3 × 100 cm³), filtered, diluted with pentane (200 cm³), and cooled to −78 °C to give black crystals of (1) on standing for 48 h. The crystals were separated, washed with cold pentane, and dried *in vacuo* (2 h, 10^{-3} Torr). Yield 2.49 g, 43% based on chromium (Found: C, 77.75; H, 5.55. $C_{20}H_{16}Cr$ requires C, 77.9; H, 5.20%).

Bis(1-*methylnaphthalene*)*chromium and Bis*(1,4-*dimethylnaphthalene*)*chromium*.—These were prepared in the same manner as above except that the solvent used was methylcyclohexane–thf (3 : 1), the temperature of the cooling bath was −120 °C, and the products were extracted with diethyl ether and crystallized from pentane–diethyl ether. Yields in both reactions were 60—65% based on chromium {Found: C, 78.25; H, 5.80. $[Cr(C_{10}H_7Me)_2]$, $C_{22}H_{20}Cr$ requires C, 78.55; H, 5.95%. Found: C, 78.85; H, 6.50. $[Cr(C_{10}H_6Me_2)_2]$, $C_{24}H_{24}Cr$ requires C, 79.1; H, 6.60%}.

Chromium Hexacarbonyl.—Carbon monoxide gas was passed through a solution of (1) (0.34 g, 1.1 mmol) in thf (40 cm³) at 10 °C. After 4 h the initial brown-red solution had completely decolourized. The solvent was pumped off at 0 °C, the naphthalene was extracted with small portions of cold diethyl ether (6 × 5 cm³), and the $[Cr(CO)_6]$, identified by its i.r. spectrum, was sublimed at room temperature. Yield 170 mg (70%).

Hexakis(*t-butyl isocyanide*)*chromium*(0).—t-Butyl isocyanide (1 g, 12 mmol) was added to a solution of (2) (405 mg, 1.2 mmol) in diethyl ether (30 cm³). The mixture was stirred at 0 °C for 6 h. The solvent and the excess of $CNBu^t$ were removed *in vacuo* and the orange residue dissolved in pentane (130 cm³). The solution was filtered through a short column of degassed Kieselguhr, concentrated under vacuum, and cooled to −78 °C to give orange crystals of $[Cr(CNBu^t)_6]$[20] (0.56 g, 85%). Infrared spectrum (see text) in methylcyclohexane: $\nu(C\equiv NR)$ at 1 880s, br and 1 960m (sh) cm^{-1}.

Hexakis(*cyclohexyl isocyanide*)*chromium*(0).—This was prepared in the same manner as yellow-orange crystals[21] (72%). Infrared spectrum in methylcyclohexane: $\nu(C\equiv NR)$ at 1 871s, br (Found: C, 71.2; H, 9.40; N, 12.05. $C_{42}H_{66}CrN_6$ requires C, 71.4; H, 9.35; N, 11.9%).

(η^6-*Naphthalene*)*tris*(*trifluorophosphine*)*chromium*(0).—Gaseous PF_3 (200 cm³, 8.3 mmol) was condensed on a vacuum line into a Carius tube (150 cm³) fitted with an O-ring stopcock and containing a solution of (1) (0.38 g, 1.23 mmol) in thf (25 cm³). After 3 h at 0 °C the initially brown-red solution had turned to orange. Excess of PF_3, solvent, and finally naphthalene were pumped off on a high-vacuum line. The residue was extracted with toluene (20 cm³), filtered, concentrated to 10 cm³ under reduced pressure, diluted with hexane (40 cm³), and cooled to −78 °C. Yellow-orange crystals of $[Cr(\eta^6-C_{10}H_8)(PF_3)_3]$ were collected and dried under high vacuum; 0.45 g (82%), m.p. 153 ± 1 °C. An analytically pure sample was obtained by sublimation onto a water-cooled finger (90 °C, 10^{-3} Torr) (Found: C, 27.25; H, 1.90. $C_{10}H_8CrF_9P_3$ requires C, 27.05; H, 1.80%).

The methylnaphthalene analogue is made in the same way in 80% yield. It was extracted and crystallised from pentane: $[Cr(C_{10}H_7Me)(PF_3)_3]$, m.p. 115 ± 1 °C (Found: C, 29.05; H, 2.35. $C_{11}H_{10}CrF_9P_3$ requires C, 28.8; H, 2.20%).

(η^6-Naphthalene)tris(trimethyl phosphite)chromium(0) —A suspension of bis(naphthalene)chromium (0.65 g, 2.1 mmol) in diethyl ether (60 cm^3) was treated with trimethyl phosphite (1.5 cm^3) and stirred overnight at 0 °C. Solvent and excess of ligand were pumped off and free naphthalene sublimed. The residue was extracted with pentane (150 cm^3), filtered, and cooled to -78 °C. After standing for 48 h, black crystals of $[\mathrm{Cr(C_{10}H_8)\{P(OMe)_3\}_3}]$ were separated and dried *in vacuo* (*ca.* 0.87 g, 75%) (Found: C, 41.2; H, 6.30. $\mathrm{C_{19}H_{35}CrO_9P_3}$ requires C, 41.3; H, 6.35%). The 1-methyl- and 1,4-dimethyl-naphthalene analogues were prepared in the same manner. Yields *ca.* 70%.

(η^6-Naphthalene)tris(trimethylphosphine)chromium(0).—The compound $[\mathrm{AgI(PMe_3)}]$[25] (2.5 g, 8 mmol) was thermally decomposed in a vacuum line and the phosphine distilled into a Schlenk tube containing a suspension of bis(naphthalene)chromium (0.49 g, 1.6 mmol) in diethyl ether (20 cm^3). The reaction mixture was stirred overnight at 0 °C under argon. Excess of phosphine and solvent were removed *in vacuo* and naphthalene was sublimed under high vacuum. The residue was extracted with pentane (50 cm^3) and filtered. The extremely air-sensitive green-brown solution was concentrated under reduced pressure to 20 cm^3 and cooled to -78 °C to produce black crystals of $[\mathrm{Cr(C_{10}H_8)(PMe_3)_3}]$ (0.22 g, 34%). The 1-methylnaphthalene analogue was similarly prepared but attempts to crystallize the compound from pentane or arene–alkane mixtures were not successful due to the high solubility of $[\mathrm{Cr(C_{10}H_7Me)(PMe_3)_3}]$. Attempts to chromatograph the trimethylphosphine compounds on degassed basic $\mathrm{Al_2O_3}$ or silica gel led to immediate decomposition.

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