Reactions of Transition-metal Vapours with Cycloheptatriene and Cyclooctatetraene

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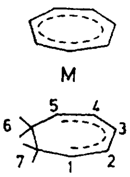
The co-ordination of cycloheptatriene in reactions with transition-metal atoms in the condensed phase at low temperature is accompanied by extensive hydrogen migration. Thus, condensation of C_7H_8 with the vapours of Ti, V, Cr, Fe, and Co affords $[Ti(\eta\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$, $V(C_{14}H_{16})$, $[Cr(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_{10})]$, $[Fe(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$ or $FeC_{14}H_{18}$, and $CoC_{14}H_n$(n = 15, 17, or 19) respectively. No organometallic products have been isolated from vapours of Mn, Ni, or Pd. Condensation of a PF_3–C_7H_8 mixture with vapours of Cr or Co affords $[Cr(C_7H_8)(PF_3)_3]$ or $[Co(C_7H_7)(PF_3)_3]$ respectively. Condensation of C_8H_8 with vapours of Ti, Fe, and Co gives intractable polymers, but with chromium vapour $[Cr_2(C_8H_8)_3]$ is obtained. The use of metal atoms in the preparation of olefinic metal complexes is compared with conventional reductive methods.

A NUMBER of papers have been published describing the reactions of transition-metal atoms with arenes or cyclopentadiene to give organometallic complexes. With arenes, simple systems such as $[M(\eta\text{-arene})_2]$ (M = Ti,[1] V,[2] Cr,[3] Mo,[4] W,[4] and Fe[5]) are obtained, but in the case of cyclopentadiene more complex reactions occur with metal atoms, involving extensive transfer of hydrogen atoms {in the formation of $[M(\eta\text{-}C_5H_5)_2]$ (M = Cr or Fe), $[Co(\eta\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)]$, $[Ni(\eta\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)]$,[6] or $[MH_2(\eta\text{-}C_5H_5)_2]$ (M = Mo or W)[7]}. Herein we report the reactions of cyclohepta-1,3,5-triene (C_7H_8) and cyclo-octa-1,3,5,7-tetraene (C_8H_8) with metal vapours as part of a continuing study into the scope and mechanism of atom reactions. The ligand C_7H_8 could co-ordinate in a position similar to an arene by acting as a six-electron donor or undergo hydrogen-transfer reactions as does cyclopentadiene in its interaction with metal atoms. Some reactions of C_7H_8 were reported while this work was in progress. Co-condensation of this ligand with Mo or W vapours affords $[M(\eta\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$,[8] and iron vapour (generated by laser evaporation) gives $[Fe(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$.[9]

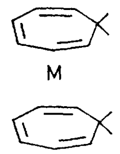
RESULTS AND DISCUSSION

From the condensation of titanium vapour and C_7H_8 at −196 °C it was possible to isolate the thermally stable complex $[Ti(\eta\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$ (1a) as diamagnetic green needles in 46% yield. This complex can be prepared conventionally by the reduction of $TiCl_3$ with $MgBrPr^i$ in the presence of C_7H_8.[10] In the metal-atom reaction, an intermediate species such as $[Ti(\eta^6\text{-}C_7H_8)_2]$ (1b) was not detectable, the characteristic green colour of (1a) being present at low temperature. An attempt to isolate the mixed-ligand system $[Ti(\eta^6\text{-}C_7H_8)(\eta\text{-}C_6H_6)]$ by co-condensation of titanium vapour with an equimolar mixture of C_7H_8 and C_6H_6 produced only (1a) and $[Ti(\eta\text{-}C_6H_6)_2]$ in approximately equal amounts {C_6H_6 is known to react with Ti atoms to afford $[Ti(\eta\text{-}C_6H_6)_2]$[1]}.

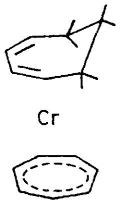
Vanadium vapour, condensed with C_7H_8 at −196 °C, afforded a yellow-brown material of composition $V_{14}H_{16}$ (2) (from elemental analysis and mass spectroscopy), obtained in 48% yield on work-up. This formula is consistent with either $[V(\eta\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$ (2a) or $[V(\eta^6\text{-}C_7H_8)_2]$ (2b). The complex is paramagnetic, exhibiting an eight-line e.s.r. spectrum (^{51}V, $I = \frac{7}{2}$) with a splitting of 82 G centred at g = 1.989.* A complex of the same composition as (2) has been synthesised by the reduction of VCl_4 with $MgBrPr^i$ in the presence of C_7H_8 and it exhibits a very similar eight-line e.s.r. (g 1.992, splitting 80 G) and mass spectrum to (2).[11,12] However, (2) appears to be much more thermally stable (decomp. > 300 °C) than the previously reported complex and indeed they may be the two isomers (2a) and (2b). In view of the close similarity between the two structures we believe that it is not possible to distinguish



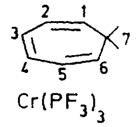
(1a) M=Ti
(2a) M=V



(1b) M = Ti
(2b) M = V
(3b) M = Cr



(3a)



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* 1 G = 10^{-4} T, 1 atm = 101 325 Pa, 1 mmHg ≈ 13.6 × 9.8 Pa, 1 Torr = (101 325/760) Pa.

[1] M. T. Anthony, M. L. H. Green, and D. Young, *J.C.S. Dalton*, 1975, 1419.

[2] K. J. Klabunde and H. F. Efner, *Inorg. Chem.*, 1975, **14**, 789.

[3] P. L. Timms, *Chem. Comm.*, 1969, 1033.

[4] M. P. Silvon, E. M. van Dam, and P. S. Skell, *J. Amer. Chem. Soc.*, 1973, **95**, 1945.

[5] G. Leach and P. L. Timms, unpublished work.

[6] P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, 1972, **14**, 121.

[7] M. S. D'Annello and E. K. Barefield, *J. Organometallic Chem.*, 1974, **76**, C50.

[8] E. M. van Dam, W. N. Brent, M. P. Silvon, and P. S. Skell, *J. Amer. Chem. Soc.*, 1975, **97**, 465.

[9] J. R. Blackborow, K. Hildenbrand, E. K. von Gustorf, A. Scrivanti, C. R. Eady, D. Entholt, and C. Krüger, *J.C.S. Chem. Comm.*, 1976, 17.

[10] H. O. van Oven and H. S. De Liefde Meijer, *J. Organometallic Chem.*, 1971, **31**, 71.

[11] S. Müller and B. Mertschenk, *J. Organometallic Chem.*, 1973, **34**, C41.

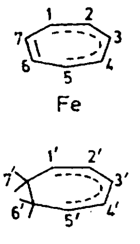
[12] J. Müller and B. Mertschenk, *Chem. Ber.*, 1972, **105**, 3346.

between them on spectroscopic evidence alone (an *X*-ray structure determination is being undertaken).

Chromium vapour was treated with a solution of C_7H_8 (10%) in the inert solvent methylcyclohexane at −130 °C to afford the paramagnetic pyrophoric complex $[Cr(\eta\text{-}C_7H_7)(\eta^4\text{-}C_7H_{10})]$ (3a) on work-up as brown needles in 17% yield. The i.r., m.s., and e.s.r. spectroscopic data were identical to that of the complex obtained by reduction of $CrCl_3$–C_7H_8 with $MgBrPr^i$.[13] There have been reports of an unstable complex, presumably $[Cr(\eta^6\text{-}C_7H_8)_2]$ (3b), obtained by deposition of chromium vapour with C_7H_8, but the assignment was only tentative.[14,15] Low-temperature (−20 °C) work-up of the methylcyclohexane solution failed to produce such a complex in our hands. Condensation of a mixture of PF_3 and C_7H_8 with chromium vapour at −196 °C afforded air-stable yellow $[Cr(\eta^6\text{-}C_7H_8)(PF_3)_3]$ (4) in 8% yield together with $[Cr(PF_3)_6]$ (ubiquitous in reactions of chromium vapour in the presence of PF_3). From the ^{19}F n.m.r. spectra at ambient temperature the PF_3 groups are undergoing a rapid chemical exchange. The exchange is intramolecular as the ^{13}C n.m.r. spectrum showed a quartet due to P–C coupling. At −90 °C this process slows down to afford two different environments for the PF_3 groups (ratio 1 : 2), consistent with the $Cr(PF_3)_3$ moiety lying on a mirror plane as expected.

Methylcyclohexane solutions of C_7H_8 (10%) reacted with Mn vapour at −130 °C to give golden-yellow solutions containing no free bulk metal. On warming extensive decomposition occurred resulting in the precipitation of bulk metal and leaving only trace amounts of a manganese containing yellow oil, which was not further characterised. Presumably at low temperatures these yellow solutions consist of metal atoms or small clusters of Mn in a weak association with the ligand. Such highly unstable but observable interactions are not uncommon in the reactions of metal atoms with organic molecules (*cf.* ' nickel–toluene ' at −90 °C) and have been termed ' solvated metal atoms '.[16] Condensation of Mn with a mixture of PF_3 and C_7H_8 gave no volatile products even though the carbonyl $[Mn(\eta^5\text{-}C_7H_7)(CO)_3]$ is a stable complex.[17]

Iron atoms reacted with C_7H_8 in methylcyclohexane to yield mainly a red-brown air-sensitive product of composition $FeC_{14}H_{16}$ (by elemental analysis and mass spectroscopy) and trace amounts of $FeC_{14}H_{18}$ (observed in the mass spectrum only). The structure of the major product (15% yield) was established by ^1H and ^{13}C n.m.r. spectroscopy to be $[Fe(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$ (5a). At 30 °C both the ^1H and ^{13}C n.m.r. spectra showed resonances due to a stereochemically rigid η^5-C_7H_7 moiety superimposed on those expected for η^5-C_7H_9. On warming the η^5-C_7H_7 resonances broadened and coalesced at 80 °C to a single signal at *ca.* δ 4 p.p.m. in the ^1H n.m.r. The corresponding resonances in the ^{13}C n.m.r. spectrum disappeared on warming to 90 °C. This rapid exchange in the η^5-C_7H_7 unit at elevated temperatures facilitates assignment of the spectra and eliminates the tautomeric structure $[Fe(\eta\text{-}C_7H_7)(\eta^3\text{-}C_7H_9)]$ (5b) as an alternative. Other systems containing a fluxional η^5-C_7H_7 ligand are known {*e.g.* $[Fe(\eta^5\text{-}C_7H_7)(CO)_3]^+$,[17,18] and $[Mn(\eta^5\text{-}C_7H_7)(CO)_3]$[17]}. The signals due to the η^5-C_7H_9 ring did not radically change on warming above room temperature.* The structure of (5a) is analogous to that of $[Ru(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]$, prepared by Müller *et al.*,[19] by reduction of $[\{Ru(C_7H_8)Cl_2\}_n]$–C_7H_8 with $MgBrPr^i$. The reduction of $FeCl_3$–C_7H_8 with $MgBrPr^i$ has been reported to afford $[Fe(\eta^5\text{-}C_7H_9)_2]$ rather than (5a).[12] However, (5a) is the major product of this reduction under certain conditions, together with a small amount of $[Fe(\eta^5\text{-}C_7H_9)_2]$.[20] It is probable that the minor product, $FeC_{14}H_{18}$, observed in the mass spectrum of the metal-atom reaction is also $[Fe(\eta^5\text{-}C_7H_9)_2]$. No $[Fe(\eta^4\text{-}C_7H_8)(PF_3)_3]$, analogous to the known carbonyl $[Fe(\eta^4\text{-}C_7H_8)(CO)_3]$,[18] could be detected in the co-condensation of Fe atoms with a mixture of PF_3 and C_7H_8.



(5a)

The reaction of Co atoms with a solution of C_7H_8 (10%) in methylcyclohexane gave an inseparable mixture of products, isolated as a very air-sensitive orange oil in poor yield. The mass spectrum of this material showed it to contain complexes of the composition $CoC_{14}H_n$ (n = 15, 17, or 19). A mixture of three complexes of the same composition has been reported as the product of the reduction of $CoCl_2$–C_7H_8 with $MgBrPr^i$.[12] In that study the structure of one component, $CoC_{14}H_{17}$, was shown to be $[Co(\eta^5\text{-}C_7H_9)(\eta^4\text{-}C_7H_{10})]$. When a mixture of PF_3 and C_7H_8 was condensed with Co atoms, a very air-sensitive orange oil, $[Co(\eta^3\text{-}C_7H_7)(PF_3)_3]$ (6), was formed, together with the more volatile, $[CoH(PF_3)_4]$.

Both Ni and Pd atoms interact weakly with C_7H_8 in solution at −130 °C (see above for Mn). Even in the

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* Complex (5a) has also been characterised [9] as a product in laser co-condensation experiments between Fe atoms and C_7H_8 where an exchange process occurring in the η^5-C_7H_9 ring was also noted at low temperatures.

[13] E. O. Fischer, A. Reckziegel, J. Müller, and P. Göser, *J. Organometallic Chem.*, 1968, **11**, P13.

[14] P. S. Skell, D. L. Williams-Smith, and M. J. McGlinchey, *J. Amer. Chem. Soc.*, 1973, **95**, 3337.

[15] E. A. K. von Gustorf, O. Jaenicke, O. Wolfbeis, and C. R. Eady, *Angew. Chem. Internat. Edn.*, 1975, **14**, 278.

[16] K. S. Klabunde, *Proc. 170th Amer. Chem. Soc. Meeting*, INOR 70, Chicago, 1975.

[17] S. H. Whitesides and R. A. Budnick, *Chem. Comm.*, 1971, 1514.

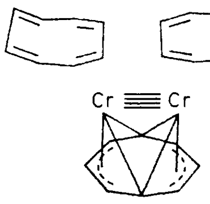
[18] J. E. Mahler, D. A. K. Jones, and R. Pettit, *J. Amer. Chem. Soc.*, 1964, **86**, 3589; H. J. Dauben, jun., and D. J. Bertelli, *ibid.*, 1961, **83**, 498.

[19] J. Müller, C. G. Kreiter, B. Mertschenk, and S. Schmitt, *Chem. Ber.*, 1975, **108**, 273.

[20] R. Burt, M. Green, and T. W. Turney, unpublished work.

case of Ni, where only part of the metal was recovered as a bulk solid, no complex could be isolated from the reaction. Similarly only [Ni(PF_3)$_4$] was produced by condensing nickel vapour with a PF_3–C_7H_8 mixture.

In contrast to the reactions of C_7H_8 with metal atoms, C_8H_8 generally did not produce definite complexes. Co-condensation of Ti, Fe, and Co atoms yielded only polymeric products in spite of the fact that C_8H_8 complexes of these metals are well established, *i.e.* [Ti(C_8H_8)$_2$], [Ti_2(C_8H_8)$_3$], [Fe(C_8H_8)$_2$], and [Co(C_8H_8)(C_8H_9)].[21–23] The reaction of Mn atoms with C_8H_8 afforded a trace amount of an air-stable purple complex whose composition has not yet been adequately determined. Condensation of C_8H_8 with chromium vapour gave a black deposit, soluble in aromatic solvents. A complex of the composition $Cr_2C_{24}H_{24}$ was isolated as moderately air-stable black crystals in 43% yield. Both the ^1H and ^{13}C n.m.r. spectra of this complex each contained only a single resonance, indicating apparent chemical equivalence of all the CH environments at room temperature. Addition of free C_8H_8 gave separate ^1H and ^{13}C n.m.r. resonances demonstrating that the system was undergoing fast intramolecular exchange. A unit-cell determination by *X*-ray diffraction gave identical results to those obtained by Brauer and Krüger[24] for [Cr_2(C_8H_8)$_3$] (7). Brief mention has been made of this complex, prepared conventionally by reduction of $CrCl_3$–C_8H_8 mixtures with either Na_2(C_8H_8) or MgBrPr^i.[25,26] In a preliminary study of the chemistry of (7), it was found unreactive towards CO and PF_3 (1 atm) in solution, but rapidly reacted with Bu^{t}NC in refluxing n-hexane to afford [Cr(CNBu^t)$_6$] (8).



(7)

The reaction of metal atoms with C_7H_8 is characterised by products in which the seven-membered ring is retained, but with extensive hydrogen migration occurring. In some cases intermolecular hydrogen migration must be invoked to explain the formation of the complex {*e.g.* [Cr(η-C_7H_7)(η^4-C_7H_{10})] and $CoC_{14}H_n$(n = 15, 17, or 19)}. In others the structure of the product can be explained in terms of intramolecular migration of hydrogen {*e.g.* [M(C_7H_7)(C_7H_9)] (M = Ti, Fe, Mo,[8] or W[8])}, but in the absence of any isolated or trapped intermediates there is no compelling evidence that this is the case. Generally, whatever the initial product, the ultimate isolated product reflects the tendency of the metal to attain a stable electronic configuration. In this respect the reactions of metal atoms with C_7H_8 resemble those with C_5H_6.[6] The synthesis of the 17-electron complex (2) with V atoms is not unexpected {*cf.* the stability of [V(CO)$_6$]} but the formation of the stable paramagnetic complex (3a) rather than [Cr(C_7H_8)$_2$] (3b) is inexplicable {*cf.* the stability of [Cr(arene)$_2$] complexes}. Low-temperature trapping experiments are in progress to determine if the initial products of reactions of metal atoms with C_7H_8 and C_5H_6 are different from those actually isolated.

In some cases the final isolated product can be altered by the simultaneous condensation of the metal vapour with PF_3 as well as C_7H_8. Thus vapours of Cr and Co afford (4) and (6) respectively. It is possible that the complex [Cr(C_7H_8)$_2$] does exist at low temperature as has been tentatively suggested,[14,15] and that this subsequently reacts with PF_3 to afford (4). However, as [Cr(PF_3)$_6$] is also a product of this reaction, co-ordinatively unsaturated species [Cr(PF_3)$_n$] must be intermediates and could react with C_7H_8 to afford (4). The mode of formation of (6) is also uncertain. It is known that [Co_2(CO)$_8$] gives [Co(η^3-C_7H_7)(CO)$_3$] with C_7H_8.[27] Thus, if [Co_2(PF_3)$_8$] is formed initially, subsequent reaction with C_7H_8 should afford a mixture of (6) and [CoH(PF_3)$_4$] as is observed.

Although a quantitative comparison between the energetics of metal-atom reactions and conventional reductive methods is not possible, the products from both of these techniques are probably endothermic with respect to the bulk metal and free ligand. The usable energy supplied to the system on metal vaporisation far exceeds any endothermicity of the products, and certainly provides much more energy to the system than is obtainable by conventional reductions. For this reason the metal-atom technique in principle allows access to systems which are far too endothermic to be prepared conventionally, the method ultimately being limited by the reactivity and thermal instability of the products under the conditions of work-up. Nevertheless, in the present study there is a remarkable similarity between the products of the reactions of metal atoms with the analogous conventional reductions. The most striking example of this is the formation of apparently the same mixture of products, $CoC_{14}H_n$ (n = 15, 17, or 19) with C_7H_8 by both the metal-atom technique and by MgBrPr^i reduction. This is of significance to conventional organometallic synthesis as it suggests that reductive methods should be re-examined for some of those compounds which are presently only obtainable by metal-atom techniques, *e.g.* [M(C_4H_6)$_3$] (M = Mo or W),[28]

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[21] H. Breil and G. Wilke, *Angew. Chem. Internat. Edn.*, 1966, **10**, 898.

[22] A. Carbonaro, A. Greco, and G. Dall'Asta, *Tetrahedron Letters*, 1967, **22**, 2037.

[23] A. Greco, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 285.

[24] D. S. Brauer and C. Krüger, unpublished work.

[25] Studiengesellschaft m.b.h., B.P. 1,128,128 (*Chem. Abs.*, 1972, **70**, 96963k).

[26] S. Müller, W. Holzinger, and M. Menig, *Proc. VIIIth Internat. Conf. Organometallic Chem.*, Venice, 1975.

[27] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1964, **3**, 785.

[28] E. M. van Dam, N. N. Brent, M. P. Silvon, and P. S. Skell, *J. Amer. Chem. Soc.*, 1975, **97**, 465.

$[Nb(C_6H_6)_2]$,[29] [Ti(arene)$_2$],[1] and $[M(1,5\text{-}C_8H_{12})_2]$ (M = Fe or Co).[30]

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on Varian Associates T60 or HA 100 spectrometers. Fluorine-19, ^{31}P, and proton-decoupled ^{13}C n.m.r. spectra were obtained on a JEOL JNM-PFT 100 spectrometer. All chemical shifts are reported in p.p.m., positive downfield from the reference ($SiMe_4$, $CFCl_3$, or 85% H_3PO_4). Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer and mass spectra on a A.E.I. MS 902 double-focusing mass spectrometer. The design of the co-condensation reactor and the rotating reactor have been described previously.[30,31] All manipulations were either *in vacuo* or in an atmosphere of oxygen-free nitrogen in deoxygenated dry solvents. E.s.r. spectra were recorded on a Varian V4560 spectrometer with diphenylpicrylhydrazyl (dpph) as reference.

(1—5-η-*Cycloheptadienyl*)(η-*cycloheptatrienyl*)*titanium*(0), (1a).—Cycloheptatriene vapour (37.3 g, 405 mmol) was condensed with titanium vapour (91 mg, 1.96 mmol), obtained by the resistance heating of a 85% Ti–15% Mo alloy wire, at −196 °C over a period of 2 h. On warming the yellow-brown co-condensate to room temperature the colour changed to deep green and a small amount of non-condensible gas was evolved. The unchanged ligand was removed *in vacuo* and the resulting green solid extracted with n-hexane (30 cm^3). On cooling the filtered extract to −78 °C, air-sensitive dark green needles of (1a) were obtained (202 mg, 0.82 mmol, 46% based on Ti vaporised) (Found: C, 73.05; H, 7.45. $C_{14}H_{16}Ti$ requires C, 72.4; H, 6.95%), *M* 232 (mass spectrum). Hydrogen-1 n.m.r. in CS_2: 1.49(br) (m, 4 H, H^6 and H^7), 4.44 [tt, 1, H, H^3, $^4J(H^1H^3)$ 2 Hz, ^3J (H^2H^3) 9 Hz], 5.16 (m, 2 H, H^1 and H^5), 5.43 (s, 7 H, η-C_7H_7), and 5.79 p.p.m. [dd, 2 H, H^2 and H^4, $^3J(H^1H^2)$ 11 Hz]. Carbon-13 resonances in CS_2: 37.5 (C^6 and C^7), 88.7 (η-C_7H_7), 101.6 (C^1 and C^5), 102.5 (C^3), and 113.3 p.p.m. (C^2 and C^4).

Condensation of a 1 : 1 mixture of cycloheptatriene and benzene vapours (10 g) with titanium vapour (65.8 mg) gave a yellow-orange co-condensate, which on work-up as above afforded black-brown crystals. These were shown by ^1H n.m.r. to consist of (1a) and $[Ti(\eta\text{-}C_6H_6)_2]$ in the ratio of 1.2 : 1.0.

Interaction of Vanadium Vapour with Cycloheptatriene, (2).—Vanadium (0.20 g, 3.9 mmol), vaporised from a resistance-heated tungsten boat, was condensed with cycloheptatriene vapour (20 cm^3, 220 mmol) at −196 °C over 1 h to afford a yellow condensate. As the reaction mixture warmed to room temperature the excess of cycloheptatriene was pumped away *in vacuo*. Extraction with n-hexane (100 cm^3), filtration, and subsequent evaporation to dryness afforded yellow-brown crystals of (2). An analytically pure sample was obtained by recrystallisation from n-hexane at −78 °C (0.42 g, 1.9 mmol, 48%), m.p. 179—181 °C (decomp. 300 °C) (Found: C, 71.85; H, 7.10. $C_{14}H_{16}V$ requires C, 71.5; H, 6.85%), *M* 235 (mass spectrum).

(1—4-η-*Cyclohepta*-1,3-*diene*)(η-*cycloheptatrienyl*)-*chromium*(−I), (3a).—Chromium vapour (0.61 g, 11.7 mmol) was condensed into a mixture of cycloheptatriene (13 g, 141 mmol) and methylcyclohexane (140 cm^3) in a rotatory reactor at −130 °C over 1 h. The red-brown solution was warmed to room temperature and evaporated to dryness. The residue was extracted with n-hexane (70 cm^3) and filtered through Al_2O_3 (5 cm, Brockman II) to afford a golden-brown solution. On evaporation to dryness, pyrophoric brown crystals of (3a) were obtained (0.48 g, 2.03 mmol, 17% based on Cr evaporated), m.p. 87 °C (decomp.) (lit.,[12] 90 °C) (Found: C, 71.1; H, 6.90. $C_{14}H_{17}Cr$ requires C, 70.85; H, 7.20%), e.s.r. $g = 1.99$ (hexane), *M* 237 (mass spectrum).

Evaporation of the reaction mixture at −15 °C and extraction with n-hexane at −20 °C yielded (3a) as the only isolable product. The presence of (3b) could not be detected.

(1—6-η-*Cyclohepta*-1,3,5-*triene*)*tris*(*trifluorophosphine*)-*chromium*(0), (4).—Chromium vapour (0.4 g, 7.7 mmol) was co-condensed with a mixture of cycloheptatriene (7 g, 76 mmol) and PF_3 (710 cm^3 at s.t.p.) at −196 °C. On warming to 50 °C all the volatile materials were removed *in vacuo*. Separation of the PF_3 and cycloheptatriene left a yellow crystalline mixture of $[Cr(PF_3)_6]$ and (4). This was fractionally sublimed to remove the more volatile $[Cr(PF_3)_6]$ leaving behind orange-yellow air-stable (4) (0.22 g, 0.54 mmol, 8% based on Cr vaporised), m.p. 223 °C (partial decomp.), sublimes at 150 °C (760 mmHg), *M* 408 (mass spectrum). I.r. spectrum in Nujol: ν(P–F) at 901 s, br, 850 m, br, 817s; σ(P–F) 541m, 529m,br, and 523m, br cm^{-1}. Hydrogen-1 n.m.r. in C_6D_6: 0.84 and 2.1 (br) (m, 2 H, H^7), 2.60 (m, 2 H, H^1 and N^6), 4.09 (m, 2 H, H^2 and H^5), and 5.47 p,p.m. (m, 2 H, H^3 and H^4). At 30 °C, ^{19}F n.m.r. in $CFCl_3$: −7.3 (‘ J_{PF} ’ 1 264 Hz); at −90 °C, −7.26 (3F, ‘ J_{PF} ’ 1 264 Hz) and −12.49 p.p.m. (6F, ‘ J_{PF} ’ 1 245 Hz). At −90 °C, ^{31}P n.m.r. in toluene: 178.6 (d, 2 P, $^2J_{PP}$ 95 Hz) and 206.7 p.p.m. (t, 1P). At 30 °C, ^{13}C n.m.r. in C_6D_6: 23.4 (C^7), 49.1 (q, C^1 and C^6, $^3J_{PC}$ 3.6 Hz), 96.1 (C^2 and C^5), and 97.1 p.p.m. (C^3 and C^4).

Interaction of Manganese Vapour with Cycloheptatriene.—Manganese vapour (3 g, 67 mmol) was condensed into a solution of cycloheptatriene (28 g, 302 mmol) in methylcyclohexane (200 cm^3) at −130 °C to give a yellow-brown slurry containing very little powdered metal. Evaporation of the mixture at −20 °C to a small volume (*ca.* 10 cm^3) resulted in the deposition of much metal. This was extracted with n-hexane (60 cm^3) and filtered through Al_2O_3 (4 cm, Brockman II) to afford a pale yellow solution. Evaporation to dryness produced a trace amount (*ca.* 5 mg) of a yellow oil containing a manganese complex (Na[BiO$_3$] test). There was insufficient quantity to characterise.

(1—5-η-*Cycloheptadienyl*)(1—5-η-*cycloheptatrienyl*)-*iron*(0), (5a).—Iron vapour (0.66 g, 11.8 mmol) was condensed into a solution of cycloheptatriene (14.5 g, 157 mmol) in methylcyclohexane (180 cm^3) at −130 °C in a rotatory reactor over 1 h. The orange slurry was warmed to room temperature and evaporated to dryness. Extraction with n-hexane (2 × 60 cm^3) and filtration through Al_2O_3 (10 cm, Brockman II) gave an orange-red solution and an orange solid on evaporation to dryness. An analytically pure sample was obtained by recrystallising twice from i-pentane (10 cm^3) (0.43 g, 1.78 mmol, 15% yield based on Fe vaporised) (Found: C, 69.35; H, 7.20. $C_{14}H_{16}Fe$ requires C, 70.05; H, 6.70%), *M* 240 (mass spectrum) with a peak at *m*/*e* 242 apparently due to the parent molecular ion of a more volatile minor component, $FeC_{14}H_{18}$. At 30 °C, ^1H n.m.r. in [$^2H_8$]toluene: 1.20 and 2.49 (m, 4 H, $H^{6'}$ and $H^{7'}$), 3.22 (m, 2 H, H^1 and H^5), *ca.*

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[29] G. M. Gruen, personal communication.

[30] R. E. Mackenzie and P. L. Timms, *J.C.S. Chem. Comm.*, 1974, 650; R. M. Atkins, P. L. Timms, and T. W. Turney, unpublished work.

[31] P. L. Timms, *J. Chem. Educ.*, 1972, **49**, 782.

4.15 ($H^{1'}$ and $H^{5'}$), 4.23 ($H^{2'}$ and $H^{4'}$), *ca.* 4.40 [t, H^2 and H^4, $^3J(H^2H^3)$ 6.5 Hz), *ca.* 4.50 ($H^{3'}$), 4.98 [t, 2 H, H^6 and H^7, $^3J(H^1H^7)$ 2 Hz], and 5.79 [tt, 1 H, H^3, ^4J (H^1H^3) 1 Hz]; ^{13}C n.m.r. in [$^2H_8$]toluene 34.7 ($C^{6'}$ and $C^{7'}$), 68.7 (C^1 and C^5), 73.0 ($C^{1'}$ and $C^{5'}$), 89.3 ($C^{2'}$ and $C^{4'}$), 91.1 ($C^{3'}$), 94.3 (C^2 and C^4), 95.4 (C^3), and 133.2 p.p.m. (C^6 and C^7). At 85 °C the ^1H n.m.r. resonances originally at 3.22, *ca.* 4.40, 4.98, and 5.79 p.p.m. collapsed to a very broad singlet at *ca.* 4.0 p.p.m., whilst at 100 °C the ^{13}C resonances originally at 68.7, 94.3, 95.4, and 133.2 p.p.m. disappeared (intermediate-exchange region).

Interaction of Cobalt Vapour with Cycloheptatriene.—The experiment was performed as with the preparation of (5a) to afford an orange oil purified as above. This was further purified by sublimation (55 °C, 10^{-3} Torr) to give a semi-crystalline oily sublimate still contaminated with organic polymers (Found: C, 74.9; H, 9.05. $C_{14}H_{15}Co$ requires C, 69.4; H, 6.25%). Mass spectrum, *m/e* (intensity): $[Co(C_{14}H_{19})]^+$ 246 (100); $[Co(C_{14}H_{17})]^+$ 244 (41); $[Co(C_{14}H_{15})]^+$ (28).

(1—3-η-*Cycloheptatrienyl*)*tris*(*trifluorophosphine*)-*cobalt*(−I), (6).—Cobalt vapour (0.20 g, 3.4 mmol) was condensed with a mixture of cycloheptatriene vapour (5 g, 54 mmol) and PF_3 (510 cm^3 at s.t.p.) at −196 °C over 0.5 h. Removal of the excess of PF_3 and cycloheptatriene left a volatile orange oil (6) (0.13 g, 0.31 mmol, 9%) which was exceedingly air sensitive, *M* 414 (mass spectrum), ^1H n.m.r. resonance in $CFCl_3$ at 5.54(s) p.p.m., ^{19}F n.m.r. resonance in $CFCl_3$ at −13.6 p.p.m. (m, 'J_{PF}' 1 316 Hz).

Interaction of Vapours of Ni *and* Pd *with Cycloheptatriene.*—These experiments were performed as with the interaction of Mn with cycloheptatriene (see above). In both cases black-brown slurries were obtained which on work-up afforded very pale yellow n-hexane solutions. The yellow oils obtained on evaporation of the solvent contained no metal. Similarly the reaction of nickel vapour with a mixture of cycloheptatriene and PF_3 (performed as with cobalt above) afforded only $[Ni(PF_3)_4]$ (determined by i.r. and m.s.).

Tris(η-*cyclo-octatetraene*)*dichromium*(0), (7).—A mixture of cyclo-octatetraene (18.4 g, 177 mmol) and i-pentane (15 cm^3) vapours was condensed with chromium vapour (751 mg, 14.5 mmol) at −196 °C over a period of 1.5 h. The resulting red co-condensate was warmed to room temperature turning black-brown. After removal of the unchanged ligand and i-pentane *in vacuo* the residue was extracted with warm (50 °C) toluene (6 × 50 cm^3). The combined extracts were filtered and evaporated to dryness to afford a black solid. These were washed with n-hexane (5 × 30 cm^3) until the washings were colourless and dried *in vacuo* to afford 1.28 g (43% based on chromium vaporised) of (7) as moderately air-stable black crystals, m.p. *ca.* 185 °C (decomp.) (Found: C, 68.7; H, 5.50. $C_{24}H_{24}Cr_2$ requires, C, 69.2; H, 5.80%). Unit cell $P2_1$, a = 10.46(8), b = 11.79(4), c = 7.59(3) Å, β = 100.0(5)° [lit.,[24] a = 10.485(3), b = 11.819(4), c = 7.571(2) Å, β = 99.64(2)°]. Hydrogen-1 n.m.r. resonance in CS_2 at 5.27 (s), ^{13}C n.m.r. resonance in CS_2 at 105.2 p.p.m.

Hexakis(*t-butyl isocyanide*)*chromium*(0), (8).—A solution of (7) (0.21 g, 0.51 mmol) in tetrahydrofuran (20 cm^3) was heated under reflux with Bu^{t}NC (1.0 g, 12 mmol) for 1 h. After evaporation to dryness *in vacuo* the mixture was extracted with i-pentane (30 cm^3), filtered, and cooled to −78 °C to give orange prisms of (8) on standing (0.19 g, 0.35 mmol, 68%) (Found: C, 64.85; H, 9.30; N, 14.7. $C_{30}H_{54}CrN_6$ requires C, 65.4; H, 9.90; N, 15.25%), *M* 551 (mass spectrum), with the ions $[Cr(CNBu^t)_x]^+$ (x = 0—6) present. I.r. spectrum in Nujol: ν(C≡N) at 2 028m and 2 070m cm^{-1}. Hydrogen-1 n.m.r. resonance in C_6H_6 at 1.51(s) and ^{13}C n.m.r. resonances in C_6H_6 at 33.3 (CH_3) and 55.2 p.p.m. (C–CH_3).

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