Reactions of Metal Atoms with Poly(methylphenylsiloxanes) and Other Polymers and Compounds of Low Volatility

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Liquid poly(methylphenylsiloxanes) react at 0 °C with Ti, V, Cr, Mo, and W atoms to give high yields of bis(η^6-arene)metal complexes [arene = $-\overset{|}{\text{Si}}(\text{Ph})\text{O}-$ groups]. The coloured complexes are very thermally stable but all are sensitive to air or moisture. Condensation of Fe, Co, or Ni atoms into the poly(methylphenylsiloxanes) at 0 °C gives only metal slurries, although at low temperatures we observe the formation of an unstable arene–iron complex. Liquid poly(phenyl ethers) give stable bis(η^6-arene)metal complexes with V or Cr atoms at 30 °C. Polystyrene in solution in diethylene glycol dibutyl ether at −50 °C, reacts with Cr atoms to yield a complex in which 55% of the available phenyl groups are co-ordinated to the metal.

CONDENSING the vapours of transition metals with organic ligands under vacuum is recognised as a useful one-step synthesis of organometallic compounds.[1,2] Most of the reported experiments have been with volatile ligands and the atom reactions have been carried out below −100 °C so that a vacuum can be maintained in the presence of the reactants. In 1974, we demonstrated the possibility of reacting metal atoms with solutions of ligands cooled to a temperature from −130 °C to 0 °C depending on the volatility of the reactants.[3] We have now exploited this idea to carry out reactions of metal atoms to form complexes with a range of large molecules and polymers at temperatures up to 20 °C. The work is of special importance as a new way of making complexes of polymers since few alternative methods are known.[4,5] A preliminary account of our work with poly(methylphenylsiloxanes) has been published.[6]

EXPERIMENTAL

Atom reactions were performed using a rotary reactor of a type which has been described previously.[3,7] Metals were evaporated by resistance heating methods as indicated in Table 1. All reaction products were maintained under an inert atmosphere and deoxygenated, dry solvents were used.

Hydrogen-1 n.m.r. spectra were recorded using either a Varian Associates HA 100 or a JEOL PS 100 spectrometer. Spectra were calibrated relative to tetramethylsilane in many cases, but some of the polysiloxane spectra were calibrated relative to the peak due to the Si–CH_3 group in the polysiloxane. Carbon-13 and ^{31}P n.m.r. spectra were recorded on a JEOL PFT 100, Fourier-transform n.m.r. spectrometer; ^{13}C spectra were calibrated by means of internal $SiMe_4$ and ^{31}P spectra were calibrated from external H_3PO_4.

Infrared spectra were obtained on Perkin-Elmer 257 or 457 spectrometers and ultraviolet–visible spectra were obtained using a Varian Techtron 634 spectrometer.

Electron spin resonance spectra were run on a Varian Associates V-4502 spectrometer, operating in the X-band region and spectra were calibrated relative to 1,1-diphenyl-2-picrylhydrazyl (dpph), $g = 2.0036$. Finally, mass spectra were measured using an A.E.I. MS9 mass spectrometer.

The Reactions between Metal Atoms and Poly(methylphenylsiloxanes).—Metal atoms were treated with liquid poly(methylphenylsiloxanes) made by Dow Corning. The designation, the viscosity at 20 °C, and other relevant characteristics of the fluids were as follows: DC 510: viscosity 0.40 poise, number average molecular weight 3 300, corresponding to *ca.* 40 $-R_2SiO-$ units per molecule; ratio Ph : Me 1 : 17; DC 550: viscosity 1.15 poise, ratio Ph : Me 1 : 3; DC 556: viscosity 0.22 poise, contains OH substituents in addition to methyl and phenyl, ratio OH : Ph : Me 1 : 6 : 27; DC 704: viscosity 0.39 poise, a trisiloxane, $Ph_2MeSiOSiMe_2OSiMePh_2$.

1. *Reactions with* DC 510 *as the Ligand.*—Experimental details and spectroscopic measurements are summarised in Table 1. The method for carrying out these reactions is exemplified by the reaction of molybdenum vapour with the poly(methylphenylsiloxane). Molybdenum vapour (0.6 g, 6.3 mmol), was sublimed for 4 h from a molybdenum filament and condensed into 150 cm³ of DC 510 at −10 °C to give a gold-brown liquid plus a small amount of brown resinous material. At the end of the reaction, the resulting liquid was filtered under nitrogen through a No. 3 glass sinter to remove small amounts of metal particles. For products from other reactions which contained considerable excess of metal, a short column of alumina (Brockman II) was used as a filter.

Viscosity measurements. A series of reactions was carried out between chromium atoms and DC 510 to give liquid products containing different ratios of co-ordinated and unco-ordinated phenyl groups. The ratio was measured for each liquid by comparison of the intensity of the peaks in the ^1H n.m.r. for co-ordinated and unco-ordinated phenyl groups. The viscosities of the liquids were measured using an Ostwald viscometer at 25 °C. The results were as shown.

% Co-ordination of phenyl groups	0	10	20	30
Viscosity (poise)	0.40	0.46	0.66	1.19

The viscosity rose very rapidly when more than 35% of the phenyl groups were co-ordinated making further measurements difficult.

Air oxidation. Air was bubbled through a few cm³ of the red-brown liquid product from a chromium atom–DC 510 reaction. The liquid turned yellow after *ca.* 10 min. The e.s.r. spectrum of the yellow liquid diluted in n-hexane, showed that it contained the ion $[Cr(arene)_2]^+$ (single line centred at $g = 1.988$ with hyperfine coupling $a_H = 3.45$ G, 10 H). Further air oxidation over 3 h resulted in a yellow suspension which separated and the solid material reacted with an aqueous solution of $[NH_4][PF_6]$ to yield $[Cr(C_6H_6)_2][PF_6]$. This was identified by comparison of its i.r. spectrum with that of a known sample.[15]

Bubbling air through the pink liquid product from the titanium atom–DC 510 reaction, caused immediate decolorisation and precipitation of TiO_2 as a white solid. Dark-coloured, metal-containing precipitates were obtained by air oxidation of the corresponding V, Mo, and W containing liquids. Controlled oxidation of the W atom–DC 510 product with iodine at 60 °C gave a paramagnetic solution. The e.s.r. spectrum showed a broad, single line, centred at $g = 1.943$ with $a_W = 380$ G.

TABLE 1

Reactions of metal atoms with poly(methylphenylsiloxanes)

Polysiloxane	Metal	Wt. metal/ vol. fluid (g cm^{-3})	Mode of evap.[a]	Colour of product	Nature of product[b]	Spectroscopic details[c]
DC 510	Ti	0.1/150	C	Pink	Ti(arene)$_2$	^{1}H n.m.r.: δ 5.39 (m)[d] U.v.–vis.: 355 nm
	V	0.2/100	A	Brown	V(arene)$_2$	E.s.r.: $g = 1.987$, $a_v = 63.5$ G ($I = \frac{7}{2}$)[e] U.v.–vis.: 330 nm
	Cr	1.5/150	B	Red-brown	Cr(arene)$_2$	^{1}H n.m.r.: δ 4.59 (m)[f] ^{13}C n.m.r.[g]: -74.3 (C^1), -74.9 (C^4), -78.2 (C^{2,6}), -76.4 (C^{3,5}) p.p.m. U.v.–vis.: 318 nm I.r.: 488, 458 cm^{-1}[h]
	Mo	0.6/150	C	Gold-brown	Mo(arene)$_2$	^{1}H n.m.r.: δ 4.85 (m)[i] U.v.–vis.: 320 nm
	W	1.0/100	C	Yellow-brown	W(arene)$_2$	^{1}H n.m.r.: δ 4.96 (m)[j] U.v.–vis.: 314 nm
	Fe	0.9/100	B	Dark brown	Metal slurry	E.s.r.: $g \approx 2.1$ (broad)[k]
	Co	0.7/25	B	Dark brown	Metal slurry	E.s.r.: $g \approx 2.1$ (broad)[k]
	Ni	2.0/100	B	Dark brown	Metal slurry	
DC 550	Cr	0.2/25	B	Red-brown	Cr(arene)$_2$	^{1}H n.m.r.: δ 4.80 (m)
DC 556	Cr	0.5/3.0	B	Red-brown	Cr(arene)$_2$	^{1}H n.m.r.: δ 4.35 (m) U.v.–vis.: 316 nm I.r.: 485, 453 cm^{-1}[h]
DC 704	Cr	1.25/20	B	Red-brown	Cr(arene)$_2$	^{1}H n.m.r.: δ 4.55 (m) ^{13}C n.m.r.[g]: -74.4, -74.1 (C^1) -74.8, -74.8 (C^4) -76.2, -75.6 (C^{3,5}) -78.5, -78.3 (C^{2,6}) p.p.m. U.v.–vis.: 328 nm I.r.: 483, 449 cm^{-1}[h]
	V	0.2/20	A	Red	V(arene)$_2$	E.s.r.: $g = 1.986$, $a_v = 63.0$ G ($I = \frac{7}{2}$)[e]

[a] Mode of evaporation (see ref. 7): A, open spiral of Mo or W wire; B, alumina crucible; C, filament of evaporant. [b] Nature of product; arene = $>$Si(Ph)O–. [c] Most spectra contain additional bands due to unco-ordinated parts of the polysiloxanes. [d] Compare dibenzenetitanium (ref. 8). [e] Dibenzenevanadium shows an e.s.r. spectrum consisting of eight lines at $g = 1.987$ with $a_r = 63.5 \pm 1.0$ G (see ref. 9). [f] Compare $[Cr(\eta^6\text{-}C_6H_5SiMe_3)_2]$ ref. 10. [g] See ref. 11; negative values for the chemical shifts are equivalent to a downfield shift in p.p.m. from $SiMe_4$, using C_6D_6 as solvent. [h] Dibenzenechromium shows an i.r. spectrum with strong bands at 492 and 466 cm^{-1} (ref. 12). [i] Compare dibenzenemolybdenum (ref. 13). [j] Compare dibenzenetungsten (ref. 14). [k] Compare with the g factor measured using highly polished metal discs; $g_{Fe} = 2.904$, $g_{Co} = 2.190$ (ref. 15).

Reaction with methanol. Addition of methanol (2 cm^3 in 10 cm^3 of toluene) to the chromium product, followed by stirring at room temperature for 24 h resulted in the formation of a brown-green solution. Removal of solvent *in vacuo* and insertion of a sublimation probe resulted in a yellow sublimate being obtained. Washing with n-hexane, followed by pumping to dryness yielded a dark brown solid, the mass spectrum of which showed it to be $[Cr(C_6H_6)_2]$.[16] Washing the residual liquid with n-hexane and centrifuging, removed all traces of chromium-containing species. The ^{1}H n.m.r. spectrum of the liquid showed an additional single peak at δ 3.69 ascribed to a methoxy-group attached to silicon.

Reaction with tcnq. A portion (10 cm^3) of the chromium product (42% Ph co-ordination) was treated with a tetrahydrofuran (thf) solution containing 0.57 g of 7,7,8,8-tetracyanoquinodimethane (tcnq) at 50 °C to give a dark green solution. After filtration and removal of the solvent a clear viscous liquid remained. This was shown to contain the complex salt $[Cr(arene)_2(tcnq)_2]_2$. The e.s.r. spectrum consisted of two signals centred at $g_1 = 1.986$ $[Cr(arene)_2]^+$ and $g_2 = 2.000$ $(tcnq)_2^-$.[17] Infrared spectrum ν(CN): 2 153w and 2 120m cm^{-1}.[18] Ultraviolet–visible spectrum: 233, 272 nm (unco-ordinated phenyl); 280, 335, 411 nm $[Cr(arene)_2]^+$; 394, 423, 440, 672, 687 nm $(tcnq)_2^-$.[19]

The electrical conductivity of the fluid was measured at 22 °C using platinum electrodes. Both a.c. (1 kHz) and d.c. gave the same results indicating a specific conductivity of 1.87×10^{-5} ohm^{-1} cm^{-1}. For comparison, a sample of the original chromium–DC 510 product was oxidised with allyl bromide to give a fluid containing equal proportions of co-ordinated Cr^0 and Cr^I, and its electrical conductivity was measured in the same way. The specific conductivity was 9×10^{-8} ohm^{-1} cm^{-1} at 22 °C.

Catalytic reactions. On heating a sample of the titanium–DC 510 product to 180 °C for 2 h in the presence of 1 atm * of butadiene no change was observed in the colour of the fluid, and the mass spectrum of volatile material present was that of C_4H_6 with no peaks of higher m/e attributable to oligomers. A small amount of polybutadiene (<10%) however, was obtained.

Slurries were made by condensing 1 g each of nickel or

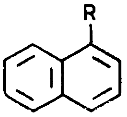
* Throughout this paper: 1 atm = 101 325 Pa; 1 mmHg ≈ 13.6 × 9.8 Pa.

cobalt vapours into DC 510 (150 cm^3) at 0 °C over 1 h. Portions (10 cm^3) of each slurry were mixed with toluene (5 cm^3) and subjected to a pressure of 100 atm hydrogen at 50 °C for 3 h. The nickel and cobalt slurries respectively caused 22% and 15% conversion of toluene to methylcyclohexane. A portion (10 cm^3) of the cobalt slurry was mixed with 1,3-butadiene (20 cm^3) and warmed to 35 °C for 4 h in a Carius tube. About 10% of the butadiene was converted to a mixture of 5-methylhepta-1,3,6-triene and octa-1,3,6-triene in a ratio of 11 : 2.

2. *Reactions of Chromium Vapour with Mixtures of* DC 510 *and* 1-*Alkylnaphthalenes*.—Chromium (1 g, 19 mmol) was evaporated over 1.5 h and condensed into a mixture of DC 510 (100 cm^3, 140 mmol of Ph group) and 1-methylnaphthalene (20 cm^3, 140 mmol) at -20 °C, giving a deep red liquid. Filtration and evaporation of unchanged methylnaphthalene yielded a red liquid containing the three complexes: $[Cr(arene)_2]$, $[Cr(C_{10}H_7Me)_2]$, and $[Cr(arene)(C_{10}H_7Me)]$ where arene = DC 510. Hydrogen-1 n.m.r. data are given in Table 2.

TABLE 2

^1H n.m.r. spectrum of product from Cr + DC 510 +



Chemical shift (δ)		
R = CH_3	R = C_6H_{13}	Assignment
2.04s		$-CH_3$
2.46s		$-CH_3$
4.47m	4.48m	*a*
4.66m	4.59m	*b*
4.78m	4.78m	*c*
5.13m	5.13m	*d*
5.28m	5.43m	*a*
5.77m	5.89m	*d*

[a] Bis(alkylnaphthalene)chromium (ref. 20). [b] Bis(DC 510)-chromium. [c] (DC 510)Chromium moiety of mixed complex. [d] (Alkylnaphthalene)chromium moiety of mixed complex.

Reaction of the above red liquid product with 1 atm of CO at 25 °C for 12 h brought about a colour change to a pale orange-red. It was possible to sublime $[Cr(CO)_6]$ and $[Cr(CO)_3(C_{10}H_7Me)]$ [20] from this solution leaving a yellow viscous liquid identified as containing $[Cr(arene)(CO)_3]$; i.r. spectrum in n-hexane ν(CO) 1 967, 1 895 cm^{-1} (compare with ref. 5). Addition of $CNBu^t$ (2 cm^3) to the red product solution (25 cm^3), followed by stirring at 25 °C for 12 h resulted in the colour changing to orange. Removal of unreacted $CNBu^t$ yielded a solution containing $[Cr(CNBu^t)_6]$ [20] in addition to a product identified as $[Cr(arene)(CNBu^t)_3]$; i.r. in n-hexane: ν(CN) at 2 050, 1 999, and 1 949 cm^{-1}, ^1H n.m.r. (C_6D_6) at δ 4.81(m) (η^6-C_6H_5) and δ 1.52(s) $[CNC(CH_3)_3]$.

Similarly, evaporation of chromium (1 g, 19 mmol) into a mixture of DC 510 (100 cm^3, 140 mmol of Ph group) and 1-hexylnaphthalene (5 cm^3, 20 mmol) over 1 h at 0 °C yielded a red-brown liquid containing $[Cr(arene)_2]$ and $[Cr(arene)(C_{20}H_7C_6H_{13})]$ in appreciable amounts plus a trace of $[Cr(C_{10}H_7C_6H_{13})_2]$ (Table 2). The mixed sandwich complex was also found to lose hexylnaphthalene on addition of CO in a manner analogous to the methylnaphthalene case.

3. *Reactions involving* DC 550, DC 556, *and* DC 704.—Experimental details and results for the reactions, involving DC 550, DC 556, and DC 704 are shown in Table 1.

When chromium vapour was condensed into the DC 550 fluid in a rotating reaction flask cooled to 0 °C, much aggregation of atoms to form a suspension of metal was observed; on filtration, the fluid was yellow and its ^1H n.m.r. spectrum indicated only a little co-ordination to chromium. However, raising the temperature of the cooling bath to 10 °C seemed to allow much more efficient reaction with the chromium atoms as the fluid, after filtration, was deep red and showed a strong signal for co-ordinated arene protons in its n.m.r. spectrum.

Evaporation of chromium atoms into the DC 556 fluid in a rotating flask cooled to -30 °C, gave a red-brown solution with no excess of metal visible. The ^1H n.m.r. spectrum of the fluid showed a strong resonance for co-ordinated arene protons but it also showed that the ratio of Si–OH to Si–CH_3 protons in the fluid was the same as before reaction with the chromium atoms.

At 0 °C, DC 704 reacted efficiently with chromium atoms to give a red-brown liquid. The ^1H n.m.r. spectrum showed the expected multiplet due to co-ordinated arene protons, but the ^{13}C n.m.r. was more complicated than had been observed for the DC 510–chromium product. The red-brown liquid was chromatographed on alumina (Brockman II) which had been pretreated with hexamethyldisilazane. Elution with n-hexane afforded a pale yellow solution. Recrystallisation at -78 °C yielded a small amount of a yellow crystalline material. The mass spectrum possessed an ion of highest *m/e* occurring at 536, corresponding to $C_{28}H_{32}Si_3O_2Cr^+$. The envelope of peaks was consistent with the isotope ratios of the atoms contained in the above formula. The rest of the spectrum was dominated by fragmentation of the ligand. A red-brown band remained on the chromatography column indicating the presence of higher molecular weight products.

Iron (0.9 g, 16 mmol) was condensed into a solution containing DC 704 (20 cm^3) in methylcyclohexane (180 cm^3) at -120 °C over 1 h to give a clear brown solution. Portions of this product were treated at low temperatures as follows.

(a) Allyl bromide (2.5 cm^3, 20 mmol) was added to the reaction product (100 cm^3) and the flask allowed to warm to room temperature. Removal and collection of volatiles under vacuum, followed by fractional distillation at 1 atm allowed the separation of a colourless liquid shown to be hexa-1,5-diene from its ^1H n.m.r. spectrum.

(b) Exposure of the product to 1 atm of hydrogen as it was warmed from -120 °C to room temperature, brought about a decrease in the ratio of Ph : Me groups in the DC 704 (normally 1 : 1) as shown by the ^1H n.m.r. spectrum. This was confirmed by the appearance of a multiplet at δ 1.25 attributed to protons in a cyclohexyl group.

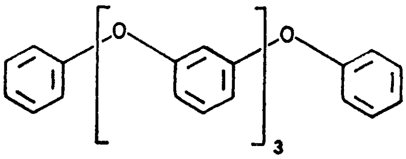
(c) Addition of 1 atm of carbon monoxide to the product prior to warming to -10 °C resulted in a reddening of the solution. The i.r. spectrum of the solution at this temperature showed a complex pattern of peaks attributed to ν(CO). However, on warming to room temperature only two bands at 2 013 and 1 989 cm^{-1}, assigned to $[Fe(CO)_5]$, were present. In a control experiment, iron atoms were condensed into a solution of the poly(methylsiloxane), DC 200, in methylcyclohexane at -120 °C. The resulting iron slurry was far less chemically reactive than the product formed under the same conditions from DC 704.

Reactions of Chromium Vapour with other Phenylsilanes.—(a) *Preparation of* $[Cr(\eta^6\text{-}C_6H_5SiMeCl_2)_2]$. Chromium (0.8 g, 15 mmol) was evaporated over 1.5 h and condensed into a solution of methylphenyldichlorosilane (25 cm^3, 130 mmol) in methylcyclohexane (180 cm^3) at -130 °C. At the end of the reaction methylcyclohexane was removed *in vacuo*, and the product dissolved in toluene and filtered. Unchanged silane was removed on a high vacuum line, and the product recrystallised from toluene–pentane (2 : 1) at -80 °C to give exceedingly air sensitive gold-brown needles of $[Cr(\eta^6\text{-}C_6H_5SiMeCl_2)_2]$ (4.0 g, 60% based on chromium evaporated) (Found: C, 39.85; H, 3.85. Calc.: C, 38.9; H, 3.70%). Mass spectral data: *m/e* 432, $C_{14}H_{16}Si_2Cl_4Cr^+$ (11); 242, $C_7H_8SiCl_2Cr^+$ (91); 190, $C_7H_8SiCl_2^+$ (13); 175, $C_6H_5SiCl_2^+$ (49); 155, $C_7H_8SiCl^+$ (45); 91, $C_7H_7^+$ (39); 77, $C_6H_5^+$ (14); 63, $SiCl^+$ (27); 52, Cr^+ (100). ^{1}H n.m.r. (C_6D_6): δ 0.97 (s, 3 H), δ 4.53 (m, 5 H). Infrared (Nujol–hexachlorobutadiene): in addition to bands characteristic of the ligand, bands attributable to a bis(arene)chromium complexes were present at 1 137, 1 007, 984, 485, and 465 cm^{-1}.[12]

Attempts to hydrolyse $[Cr(\eta^6\text{-}C_6H_5SiMeCl_2)_2]$ in the absence of air to give a polysiloxane with phenyl substituents co-ordinated to zero-valent chromium, were not successful. A polymer was formed but it appeared to contain bis(arene)chromium(I). It is thought that the HCl liberated in the hydrolysis may have caused this oxidation.

(b) *Preparation of* $[Cr\{\eta^6\text{-}C_6H_5Si(OEt)_3\}_2]$. Chromium (0.3 g, 6 mmol) was evaporated over a period of 1 h into a solution containing phenyltriethoxysilane (10 cm^3, 40 mmol) in methylcyclohexane (80 cm^3) at -130 °C. At the end of the reaction, the methylcyclohexane was removed *in vacuo*. The product was dissolved in toluene, filtered, and the unchanged silane sublimed from the product. Recrystallisation from pentane at -80 °C yielded a brown crystalline material, identified as $[Cr\{\eta^6\text{-}C_6H_5Si(OEt)_3\}_2]$ (1.3 g, 41% based on chromium evaporated) (Found: C, 55.25; H, 7.90. Calc.: C, 54.15; H, 7.50%). Mass spectral data: *m/e* 532, $C_{24}H_{40}Si_2O_6Cr^+$ (42); 458, $C_{20}H_{30}Si_2O_5Cr^+$ (9); 426, $C_{20}H_{30}Si_2O_3Cr^+$ (10); 292, $C_{12}H_{20}SiO_3Cr^+$ (100); 240, $C_{12}H_{20}SiO_3^+$ (4); 219, $C_9H_{11}O_3Cr^+$ (21); 175, $C_7H_7O_2Cr^+$ (19); 78, $C_6H_6^+$ (33); 52, Cr^+ (18). Hydrogen-1 n.m.r. (C_6H_6): δ 1.22 (t, 9 H), δ 3.92 (q, 6 H), δ 4.67 (m, 5 H). Infrared (Nujol–hexachlorobutadiene): in addition to bands characteristic of the ligand, bands attributable to a bis(arene)chromium complex were present at 1 005, 980, 468, and 450 cm^{-1}.[12]

Reaction of Metal Vapours with the Poly(phenyl ether), Santovac 5.—Santovac 5, made by Monsanto, is a liquid pentaphenyl ether (1) normally used as a diffusion pump oil.



(1)

Chromium (0.5 g, 10 mmol) was evaporated over 3 h and condensed into Santovac 5 (20 cm^3, 220 mmol arene) at 30 °C. The resulting viscous liquid was diluted in ether and filtered giving a red-brown liquid containing bis(arene)chromium. Yield = 30%, based on metal evaporated. Hydrogen-1 n.m.r. spectrum (C_6H_6): δ 4.31 and 4.81 (multiplets of equal intensity). Ultraviolet–visible spectrum: 327 nm.

Evaporation of vanadium (0.2 g, 4 mmol) over 1.5 h into 20 cm^3 of Santovac 5 at 30 °C, afforded a red-brown liquid. Addition of thf and filtration yielded a clear red liquid, which was shown to contain $V(arene)_2$ from its e.s.r. spectrum (n-hexane) which consisted of an eight-line pattern centred at $g = 1.984$ with $a_V = 61.7$ G. On exposure to air the colour was discharged.

Interaction of Chromium Vapour with Polystyrene.—The polystyrene used (supplied by Aldrich) was a crystalline polymer, *M ca.* 25 000.

Evaporation of chromium (0.2 g, 4 mmol) into a solution containing polystyrene (2 g) in diethylene glycol dibutyl ether (70 cm^3) at -50 °C over 2 h, produced a brown solution plus a small amount of insoluble material. Addition of thf, followed by filtration, yielded a brown solution. A small amount of methanol (20 cm^3) was added and the solution cooled to -80 °C to give a brown-green precipitate. This was separated and washed with methanol to give a brown-green solid. Ultraviolet–visible spectrum: 222, 263 nm (unco-ordinated arene), 318 nm (co-ordinated arene). Infrared (thin film): bands characteristic of polystyrene (comparison with authentic sample), plus bands at 3 000—2 900 and 1 110 cm^{-1} (weak) due to traces of diethylene glycol dibutyl ether which were occluded in the polymer lattice and bands at 483, 453 cm^{-1}, $[Cr(arene)_2]$ (Found: Cr, 11.1. Calc. for 100% Cr co-ordination: 20.0%). Therefore 55% of available phenyl groups are co-ordinated.

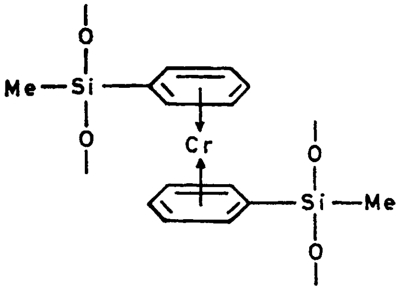
Poly(η-Bu^t-styrene) (supplied by Aldrich) was reacted under similar conditions but the i.r. spectrum showed that the yield of $[Cr(arene)_2]$ was small by the low intensity of the two characteristic bands in the 400—500 cm^{-1} region.

Reactions involving Triphenyl Phosphite.—Nickel (0.2 g, 3 mmol) was evaporated over a period of 30 min into redistilled $P(OPh)_3$ (20 cm^3) (b.p. 180 °C at 1 mmHg) at -10 °C. This formed a white suspension plus some unchanged metal. The product was dissolved in toluene and passed through a short column of alumina to remove metal. Removal of some of the toluene and addition of methanol to induce crystallisation was followed by cooling to 0 °C. The resulting white crystals were washed with methanol and dried *in vacuo* to give 0.8 g of $[Ni\{P(OPh)_3\}]$ (yield = 18% based on Ni evaporated) (Found: C, 66.4; H, 4.85. Calc.: C, 66.55; H, 4.65%). ^{1}H n.m.r. spectrum ($CDCl_3$): δ 6.80 (m). ^{31}P n.m.r. spectrum (C_6D_6): -130.52 p.p.m. from external H_3PO_4, in agreement with the literature spectrum.[21]

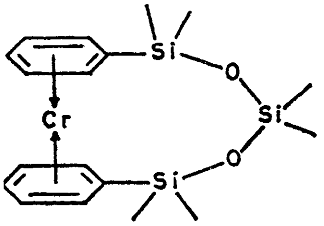
Chromium (0.3 g, 6 mmol) was condensed into triphenylphosphite (25 cm^3, 95 mmol) at -10 °C over a period of 1 h to give a dark red liquid. Separation of the product from the excess of starting material was attempted by a number of methods, *e.g.* preferential recrystallisation from pentane, oxidation, vacuum distillation, and column chromatography, but all proved unsuccessful. The crude product was studied by ^{1}H and ^{31}P n.m.r. spectroscopy. ^{1}H n.m.r. spectrum: δ 7.00 [m, free $P(OPh)_3$], δ 3.47 (m, co-ordinated arene). ^{31}P n.m.r. spectrum: -128.89 p.p.m. [s, free $P(OPh)_3$], -200.19 p.p.m. (d, 2 P), -140.26 p.p.m. (t, 1 P), ^2J(PP) 99 Hz.

RESULTS AND DISCUSSION

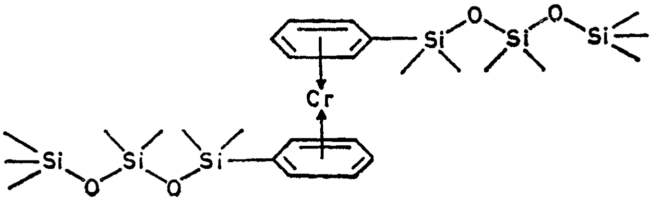
Metal Atoms and Poly(methylphenylsiloxanes).—There is little doubt from the results summarised in Table 1 that reaction of Ti, V, Cr, Mo, and W atoms with poly(methylphenylsiloxanes) yields complexes like (2) with co-ordination of the metal to the pendant phenyl groups on the siloxane chain. The ^{1}H n.m.r. chemical shifts for the co-ordinated phenyl groups are closely comparable to those for known bis(arene) complexes of the metals. Many of the reactions are exceptionally efficient compared with other reactions of metal atoms. The products are generally clear, coloured solutions with only small amounts of metal particles. Two factors may be contributing to the high yields. First, the reaction temperature is higher than in most other reported work with metal atoms. Higher temperatures will tend to make the rate of reaction of an atom with a ligand more comparable with the aggregation reaction of metal atoms which is fast at any temperature above 4 K. Second, it is possible that the polymeric nature of the ligand is helpful in promoting the co-ordination of a second phenyl group to a metal atom which has already become co-ordinated to one phenyl group. A potent side reaction in the interaction of simple arenes like benzene with metal atoms, is the formation of metal aggregates co-ordinated to phenyl groups. These may arise by reaction of metal atoms with an initially formed mono(arene)metal complex. In the course of our work, we prepared the new compounds $[Cr(\eta^6\text{-}C_6H_5SiMeCl_2)_2]$ and $[Cr\{\eta^6\text{-}C_6H_5Si(OEt)_3\}_2]$ by treating chromium atoms with solutions of the arenes in methylcyclohexane at −130 °C. The yields in these reactions were 60% and 40% respectively, typical of the yields observed with other simple arenes and lower than we obtained with the poly(methylphenylsiloxanes) at *ca.* 0 °C. These results show that the existence of the phenyl–silicon bond is not the factor giving exceptional yields.



(2)



(3)



(4)

Viscosity also seems to be an important factor in determining yields when metal atoms react with liquids. This is suggested by the results with DC 550 compared with DC 510. The former is more viscous and, although it is richer in phenyl groups, it reacts much less efficiently with chromium atoms at 0 °C than does DC 510. Raising the temperature to reduce the viscosity of the DC 550 gives a marked improvement in yield. Addition of chromium atoms to DC 510 causes a gradual increase in viscosity until *ca.* 30% of the available phenyl groups are co-ordinated. Above this the viscosity rises sharply, perhaps because intermolecular cross-linking reactions are occurring to an increasing extent. We have not succeeded in making a product with more than 43% of the phenyl groups co-ordinated. Presumably, as the viscosity of the liquid increases, the rate of diffusion of metal atoms away from the surface approaches the rate of condensation of atoms on the surface. The result is an increased chance of atom–atom interactions.

The reaction of chromium atoms with DC 704 provides evidence that co-ordination of metal to the phenyl groups of siloxane chains can be either intra- or intermolecular. The crude reaction product had a complicated ^{13}C n.m.r. spectrum suggesting a mixture of bis(arene)metal compounds and it gave red and yellow bands on an alumina column. The mass spectrum of the easily eluted yellow fraction indicated that it was the intramolecular product (3). The strongly absorbed red band is likely to be the intermolecular product (4).

The thermal stability of some of the bis(arene)metal complexes derived from the poly(methylphenylsiloxanes) seems higher than that of the analogous complexes with simpler arene ligands, but in many respects the properties of the two groups of complexes are closely comparable. For example, we found that the titanium–DC 510 product is stable to 200 °C whereas dibenzenetitanium is reported to decompose below 100 °C. However, the titanium–DC 510 product is as easily oxidised and shows the same low level of catalytic activity towards polymerisation of butadiene, as dibenzenetitanium.

We have observed that there is a clear trend in reactivity of the phenyl–silicon bond going from the free poly(methylphenylsiloxanes) to their bis(arene)chromium complexes in the zero and +1 oxidation states. The bond is very resistant to hydrolysis in the free poly(methylphenylsiloxanes), yet in the chromium–DC 510 complex it can be slowly cleaved by methanol at 25 °C. Elschenbroich. reported this same effect for bis(trimethylsilylbenzene)chromium.[10] After partial oxidation of our compounds, the carbon–silicon bonds became even more labile. Thus, the ultimate product of treating the chromium–DC 510 complex with air was dibenzenechromium(I) hydroxide. Oxidation of the complex was followed by rapid hydrolytic cleavage of the phenyl–

silicon bond. Similarly, oxidation of the chromium–DC 510 product with allyl bromide gave a solution containing the bis(arene)chromium(I) bromide, which could then be hydrolysed by cold water to give the dibenzenechromium cation.

On oxidation of a chromium–DC 510 product with 7,7,8,8-tetracyanodiquinomethane (tcnq), we obtained a green liquid containing the 1 : 2 complex [Cr(arene)$_2$][(tcnq)$_2$] at a concentration of one mole per 40 moles of $-\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{O}-$. The electrical conductivity of *ca.* 10^{-5} ohm^{-1} cm^{-1} of this liquid is lower by a factor of 10^3 than the conductivity of some crystalline, polymeric tcnq adducts.[22] This may be due in part to the comparative lack of order in the structure of our liquid polymer and in part to the low concentration of complexed sites.

By reacting a mixture of DC 510 and 1-methylnaphthalene with chromium atoms, a mixed complex, Cr(DC 510)(1-methylnaphthalene) was formed as indicated by the ^{1}H n.m.r. spectrum (see Table 2). Like other (η^6-naphthalene)metal complexes,[20] this product reacted quickly with CO or CNBu^t with displacement of the 1-methylnaphthalene. This may be a general approach for forming complexes of type M(η^6-arene)L$_3$ where the arene is a poly(methylphenylsiloxane).

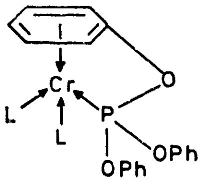
Reactions of Mn, Fe, Co, or Ni atoms with DC 510 or DC 704 at 0 °C gave metal slurries which were not very active as catalysts for hydrogenation of toluene or for oligomerisation of butadiene. However, reaction of DC 704 with iron atoms at −120 °C appears to give an organometallic product which is thermally unstable and reactive towards ligand displacement like the product of reacting iron atoms with simpler arenes at low temperatures.[23]

Reactions of Metal Atoms with Other Polymers and Compounds of Low Volatility.—The reaction of chromium and vanadium atoms with the liquid poly(phenyl ether), Santovac 5 diffusion pump oil, at 30 °C yielded clear coloured fluids. It was apparent from the ^{1}H n.m.r. spectrum of the chromium product that a bis(arene)-chromium complex of the ether was formed, although the complexity of the spectrum suggested co-ordination to both mono- and di-substituted aryl groups. The formation of a bis(arene)vanadium complex of the ether was indicated by the e.s.r. spectrum of the product. Both chromium and vanadium atoms attack the ether linkages of some aliphatic ethers, but there was no evidence that the poly(phenyl ether) caused any oxidation of the metal atoms.

There have been a number of attempts in the past to make metal complexes of polystyrene because such products have potential uses as catalysts. Two routes to these complexes have been studied, either using polystyrene as a ligand [24] or by simultaneous polymerisation and complexation of styrene.[25] With the former approach, it was only possible to form ' half-sandwich ' complexes with carbonyl and other ligands, while using the latter approach a liquid mixture of low molecular weight polymers was obtained.

Our approach to synthesis of complexes of polystyrene was by direct reaction of chromium atoms with a solution of the crystalline polymer. The product we obtained was a solid with 55% of the available phenyl groups co-ordinated to chromium as indicated by the ^{1}H n.m.r. spectrum. This result suggests that the metal-atom method is superior to the other known methods of forming such complexes. However, it is very improbable that we could achieve 100% co-ordination of the available phenyl groups because reaction of atoms with phenyl groups must occur initially in a random pattern which will create steric problems in the later stages of metal addition.

Triphenyl phosphite is a liquid of low enough volatility to be used as a neat ligand in reactions with metal atoms. Reacting the liquid with nickel atoms gave the well known [Ni{P(OPh)$_3$}$_4$] in good yield but a similar reaction with chromium atoms was more complex. In the latter case, we could not separate the red product from unreacted triphenyl phosphite. The ^{1}H n.m.r. spectrum of the crude product showed that there was η^6-arene co-ordination to chromium and the ^{31}P n.m.r. showed a doublet (area 2) and a triplet (area 1) in addition to the singlet of the free ligand. This spectral data is consistent with a product having the structure (5).



L = P(OPh)$_3$

(5)

In conclusion, our results show that metal atoms can be used for the direct preparation of metal complexes of polymers. The method is likely to prove of general use for any polymer-containing ligand groups, provided that the polymer is a neat liquid or it can be dissolved to form a solution of low vapour pressure. Cooling costs are low and the yields of products good for these reactions of polymers with metal atoms carried out at temperatures much higher than those traditionally associated with metal-atom chemistry.[7,*]

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* *Note added at proof:* Some of the reactions of metal atoms with poly(methylphenylsiloxanes) described in this paper have now been investigated spectroscopically.[26,27] The results show that the poly(methylphenylsiloxanes) have a remarkable ability to stabilise small metal clusters.

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