Synthesis of Zerovalent Bis(η-arene) Compounds of Zirconium, Hafnium, Niobium, Tantalum, and Tungsten using the Metal Vapours

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Co-condensation of the vapours of the metals niobium, tantalum, and tungsten, derived from a positive hearth electron-gun furnace, with an excess of arenes gives the bis(η-arene) compounds $[M(\eta\text{-arene})_2]$ (M = Nb, Ta, or W). Similarly, zirconium and hafnium vapours with a mixture of arenes and trimethylphosphine give the bent bis(η-arene) compounds $[M(\eta\text{-arene})_2(PMe_3)]$ (M = Zr and Hf). The bis(η-arene)tungsten compounds protonate readily in dilute aqueous acids to form the bent bis(η-arene)hydrido-cations $[W(\eta\text{-arene})_2H][PF_6]$. Spectroscopic properties and other characterising data are presented for the new compounds.

CO-CONDENSATION of metal vapours generated from a furnace with unsaturated hydrocarbons is a well established route to organometallic compounds. Bis(η-benzene)chromium was the first example of an arene organometallic compound prepared in this manner.[1] The simplicity and directness of using metal atoms and a neutral hydrocarbon ligand to form the metal–ligand adduct is somewhat offset by the difficulty of generating the metal vapours, particularly those of the more refractory metals. Also, if it is wished to develop the chemistry of compounds prepared in this manner then it is desirable if they can be prepared in 1—10-g quantities within a reasonable period of time.

Previously, we described the synthesis of bis(η-arene)titanium derivatives where the titanium atoms were generated from an electrostatically focused electron-beam gun furnace with the water-cooled copper hearth operating at earth potential.[2] It was found that suitable evaporation rates for titanium were obtained when the molten sample of titanium was heated at *ca.* 1 900 °C. It seemed possible, therefore, that analogous unknown zerovalent bis(η-arene) derivatives of the metals Zr, Hf, Nb, and Ta might similarly be prepared. However, these metals require considerably higher temperatures to give comparable evaporation rates (typically, 2 600 °C for hafnium and 3 300 °C for tantalum). Tungsten requires a temperature of 3 500 °C.

The furnace employed for the vaporisation of titanium had a maximum power input of 200 mA at 7 kV, giving 1.4 kW. Under these conditions it was found possible to evaporate molybdenum slowly (2 600 °C) giving bis(η-arene)molybdenum derivatives in small quantities (*ca.* 0.3—0.5 g).[2]

At the higher accelerating potentials (4.5—7 kV) there was evidence for decomposition of the hydrocarbon ligands and presumably decomposition of the product could also occur.[3] One possible source of the decomposition was the presence of stray electrons which are known to be reflected from electron-beam furnaces which have their hearths at earth potential.

Therefore, we set out to design and construct an improved apparatus for synthesis using metal vapours which would have a more powerful electron-gun furnace and which would be suitable for the investigation of the nature and cause of product decomposition in the co-condensation experiment. The apparatus was also intended for use in the exploration of the chemistry of the atoms of the most refractory elements. Preliminary accounts of part of this work have been communicated.[4]

EXPERIMENTAL

Apparatus.—The new apparatus is shown in outline in Figure 1. For simplicity, a 5-l bell jar was used as the reaction vessel. The remainder of the apparatus was con-

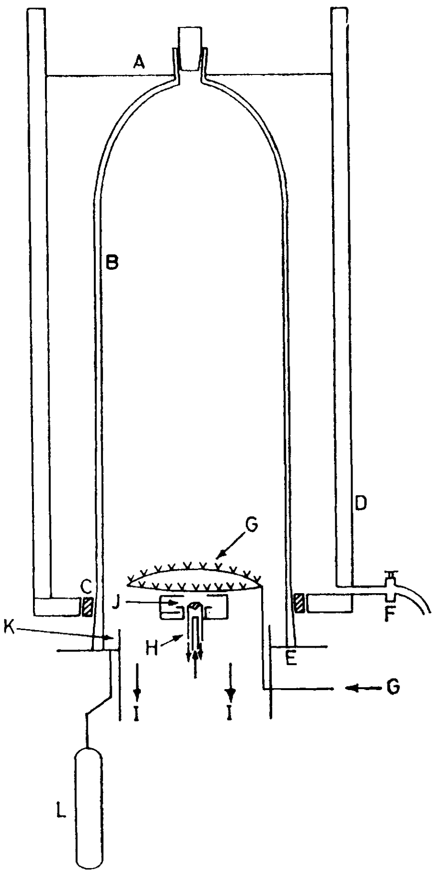

FIGURE 1 Apparatus for metal-vapour syntheses. A, Coolant level; B, 5-l glass reaction vessel; C, gasket; D, insulated container for coolant; E, ground flange seating for Viton O-ring; F, coolant drain; G, ligand vapour inlet, 'gas-ring;' H, electron-beam furnace; I, outlet to trap and diffusion pump (3-in diameter); J, metal sample; K, gutter for collection of products; L, vessel for product receipt

structed of brass and the vacuum seals were effected with Viton O-rings, or by brazing, as appropriate. The apparatus was pumped by a 3-in diffusion pump backed by a two-stage rotary pump. The diffusion pump was protected from noxious vapours, *e.g.* the ligands, by two liquid-nitrogen traps which were placed between the reaction vessel and the diffusion pump.

The new electron-beam furnace had a maximum power input of 3.5 kW and a capacity of 5 cm^3 of molten metal; it is shown in outline in Figure 2. The furnace was designed in essence by G. V. Planer Ltd. and constructed and modified in our laboratory.

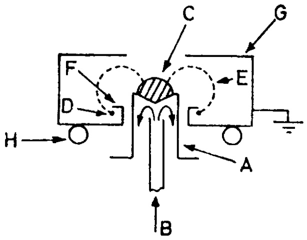

FIGURE 2 Electron-beam furnace. A, Water-cooled copper hearth maintained at a positive potential of 0—10 kV (in the earthed-hearth mode the filament and shield are held at high negative potential relative to the earthed hearth); B, cooling water flow; C, metal sample; D, tungsten emitter filament heated by *ca.* 45 A at *ca.* 5 V; E, electron path; F, electrostatic shield; G, focusing lid; H, auxiliary water cooling coil

The furnace was designed so that it was possible to operate it with the hearth, and therefore the metal sample, at either a positive or at earth potential. Thus it would be able to examine the consequences of the different modes of polarity on the performance of the furnace. The necessary insulation of the water supply for cooling the hearth was achieved by using the natural resistance (*ca.* 150 kΩ) of a long length of nylon water pipe. It was found by experiment that the water drain current from the furnace to earth was 7.0 mA per kilovolt of applied potential. The furnace was driven by a S10/50 power supply commercially available from G. V. Planer Ltd. The supply operated up to 500 mA and 10 kV. Some typical rates for the evaporation of metal atoms from the furnace are given in Table 1.

TABLE 1

Rates of evaporation of metals

Metal	Power input [a]/kW	Evaporation rate [b]/g h^{-1}
Titanium	1.0	1.3
Zirconium	2.2	0.5
Hafnium	1.8	1.5
Niobium	2.0	0.5
Tantalum	1.8	1.5
Molybdenum	1.2	1.0
Tungsten	1.8	1.5
Rhenium	1.8	1.5
Osmium	1.4	1.5
Uranium [c]	1.4	0.5

[a] Corrected for the water drain current. The power required reflects both the temperature required to achieve metal evaporation and the power lost by radiation and by conduction through the water-cooled copper hearth. These losses are a function of sample size. Typically about 0.5 cm^3 of metal sample was used. [b] The quantity given is that leaving the furnace through the hole in the lid. The proportion of metal that condenses onto the inside of the furnace lid depends on the sample size and typically is *ca.* 40% of the quantity evaporated from the initial sample. [c] Uranium forms a very mobile liquid which gives rise to excessive conduction through the copper hearth. Therefore, uranium was evaporated from a previously prepared U–Re alloy (40 : 60).

Experiments were carried out to measure the emission of secondary, reflected electrons from the furnace in both the positive and earthed hearth modes. A metal plate was suspended in the bell jar above the furnace and the current flowing from the plate to earth was measured during the operation of the furnace under a variety of conditions. The data are given in Table 2.

TABLE 2

Nature of charged particles reflected from the furnace

(*a*) Positive-hearth mode [a]

	Accelerating potential/kV				
Beam current/mA	1	2	3	4	5
100		−2.5	−2.5	−2.7	−2.5
150			−5.5	−6.0	−10.0
200			−4.5	−6.0	−10.0
250				−6.0	−13.0
300				−6.0	−25.0
350				−17.0	−40.0

(*b*) Earthed-hearth mode [b]

	Accelerating potential/kV				
Beam current/mA	1	2	3	4	5
100		+0.75	+0.85	+0.90	+0.90
150			+1.5	+1.5	+1.5
200				+2.0	+2.0
250				+2.2	+2.3
300					+2.9
350					+3.4

[a] Plate-to-earth currents given in microamps. [b] Currents in milliamps.

The data show that when the furnace is operating in the positive-hearth mode the current flowing to ground is only a very small positive-ion current. In contrast, in the earthed-hearth mode under the same conditions of power input, there is a much greater electron current which is *ca.* 1% of the applied electron-beam current. Unless stated otherwise, all the experiments described in the work were carried out with the hearth operating in the positive-hearth mode.

Volatile ligands were introduced into the reaction vessel from a reservoir *via* a stainless-steel needle valve into a heated glass manifold, and from there to a ' gas-ring ' (see Figure 1) and onto the cooled reactor walls. Figure 3 shows how involatile liquids and solutions of involatile solids were introduced as ' falling films '. These require that the solution has a vapour pressure of less than 10^{-4} mbar * at the chosen temperature of the reaction vessel walls (*e.g.* −78 °C). When 1,2-di-isopropylbenzene was used as a liquid film at −78 °C it was found necessary to provide differential pumping to maintain a suitable vacuum near the furnace. This was achieved by provision of a liquid-nitrogen cooled shroud surrounding the furnace.

The requirement for the low vapour pressure arises from the need for a suitable mean free path in the reaction vessel if the metal atoms are to reach the wall. Also, the electron-gun furnace will not work in a satisfactory manner if the pressure inside the vessel is greater than *ca.* 5×10^{-4} mbar.

The reaction vessel was provided with a gutter for the collection of product and the product and washings were collected in a receiving Schlenk vessel *via* a drain-pipe from the gutter (Figure 1).

* Throughout this paper: 1 mbar = 10^2 Pa; 1 eV ≈ 1.60×10^{-19} J.

All preparations and manipulations were carried out under argon, dinitrogen, or *in vacuo* using conventional Schlenk techniques and a Vacuum Atmospheres dry box containing argon (*ca.* 1 p.p.m. of oxygen and water). Solutions of the niobium, tantalum, hafnium, and zirconium compounds were handled exclusively under argon (dried by passage through 4A molecular sieves) since they decomposed slowly in a dinitrogen atmosphere. Solvents were dried by distillation under a dinitrogen atmosphere from liquid sodium, potassium, or sodium–potassium alloy, as appropriate. Samples for the various spectra were prepared by Schlenk-type techniques; the e.s.r. or n.m.r. tubes were then sealed *in vacuo*.

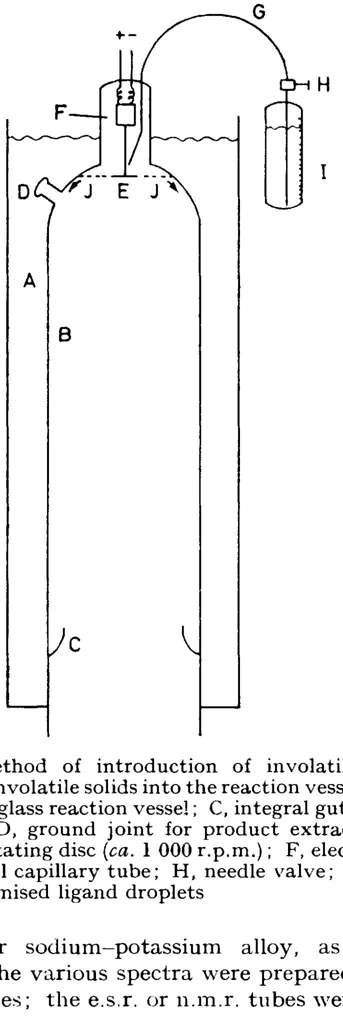

FIGURE 3 Method of introduction of involatile liquids and solutions of involatile solids into the reaction vessel. A, Coolant bath; B, 5-l glass reaction vessel; C, integral gutter for product collection; D, ground joint for product extraction (*via* cannula); E, rotating disc (*ca.* 1 000 r.p.m.); F, electric motor; G, stainless-steel capillary tube; H, needle valve; I, ligand reservoir; J, atomised ligand droplets

E.s.r. spectra were recorded on a JEOL-3BX instrument and were calibrated using 1,1-diphenyl-2-picrylhydrazyl. Infrared spectra were obtained as mulls using a Perkin-Elmer 457 instrument or as matrix-isolation spectra in argon at 8—20 K using a Perkin-Elmer 225 double-beam instrument.

Hydrogen-1 n.m.r. spectra were measured on JEOL C60HL or Perkin-Elmer R14 instruments and were calibrated using the solvents as internal standards. Mass spectra were measured using either A.E.I. MS9 or V.G. Micromass instruments. Photoelectron spectra were obtained using a Perkin-Elmer PS16017 instrument fitted with a Helectros lamp, capable of giving both He^{I} and He^{II} radiation.

Massive metal samples were supplied as follows: niobium rod (99.9%, 6.3 mm diameter) and hafnium rod (99.9%, 12.7 mm diameter) from Koch-Light Ltd.; tungsten slugs (99.9%, 11 × 9 mm diameter) from the Tungsten Manufacturing Co. Ltd.; tantalum rods (99.9%, 12.7 mm diameter) from Murex Metals Ltd.; zirconium rod (99.9%, 12.7 mm diameter) from Alfa Inorganics. The samples invariably contained occluded, non-condensable gases and it was normally essential to remove these volatile impurities in a pre-melt operation before the co-condensation experiment. The removal of most of the volatiles in the premelting step enhanced the conditions of the vacuum during the co-condensation experiments.

The general procedure for the outgassing of metal samples was as follows. The metal lump (0.5—1 cm^3) was placed on the hearth of the electron gun and a simple bell-jar cover was used to contain the vacuum. The jar was not cooled. When the vacuum was *ca.* 10^{-5} mbar the sample was heated and the input power of the gun was increased slowly until the vacuum had deteriorated to *ca.* 10^{-4} mbar. The sample was continuously pumped until the outgassing had decreased with consequent improvement of the vacuum. The power input and hence the sample temperature was then increased. This procedure was repeated until the sample had arrived at the temperature suitable for evaporation of the metal atoms; in most cases this meant that the metal sample had reached melting point or above. We note that at the point where the metal sample started to melt it was necessary to increase the power input slowly to avoid bumping and splattering of the metal sample from the hearth. When there is slightly too much power input for molten samples then small bright sparks of ejected metal can be seen; we call this the ' shooting star ' effect. The ' stars ' have only a very small mass and are not harmful to the reaction vessel.

Bis(η-arene)niobium Compounds.—A typical experiment is described. A premelted bead of niobium (*ca.* 7 g) was placed on the hearth of the electron-gun furnace, the apparatus was assembled and evacuated to better than 10^{-5} mbar, and the reaction vessel wall was cooled to −195 °C. The power input for the electron gun was slowly increased up to *ca.* 1.5 kW. Benzene was introduced at the rate of 30 $cm^3\ h^{-1}$. Under these conditions the vacuum, measured at the gauge near the furnace, was 10^{-5} mbar.

The experiment was continued for 3 h during which time niobium (*ca.* 1.0 g, 10 mmol) and benzene (90 cm^3, 920 mmol) were co-condensed. The electron gun was switched off and the reaction mixture was allowed to warm to room temperature (40 min) under argon. The resulting deep red-brown liquor was washed down to the gutter and *via* the drain-pipe into the receiving Schlenk vessel using benzene as the washing solvent. The reaction mixture was immediately filtered through dried Celite to remove metallic precipitates. The solvent was removed under reduced pressure at 50 °C. The red-purple semi-crystalline residue was extracted with light petroleum (150 cm^3, b.p. 40—60 °C). The extract was filtered off and concentrated under reduced pressure giving deep red needle crystals which were collected, cooled to −30 °C, washed with light petroleum (b.p. 30—40 °C), and finally dried *in vacuo*. The yield was *ca.* 1.0 g, 40% based on the niobium which left the furnace.

Bis(η-toluene)- and bis(η-mesitylene)-niobium were prepared similarly but required lower temperatures (−60 °C) for their crystallisation from light petroleum (b.p. 30—40 °C) since they were more soluble than the unsubstituted analogue.

Bis(η-arene)tungsten Compounds.—The experiments were carried out in essentially the same manner as is described above for the niobium compounds.

Tungsten beads (*ca.* 10 g) were used and the power input required for a suitable evaporation rate was 1.5 kW. This power input was less than was first anticipated by extrapolation from, for example, titanium, and reflects the fact that molten tungsten near its melting point is not very mobile and makes poor contact with the water-cooled copper hearth. Thus, energy losses due to conduction through the hearth are relatively small.

During the 3 h run *ca.* 2.5 g of tungsten metal were evaporated into 90 cm^3 of benzene (or other arenes). The resulting reaction mixture was green-brown and was filtered through Celite and the solvent was removed from the filtrate under reduced pressure. The residue was extracted with 1 mol dm^{-3} hydrochloric acid (2 × 100 cm^3) giving a bright orange aqueous phase. After separation from organic residues the aqueous phase was treated with an excess of aqueous sodium hydroxide and, as the solution became basic, bright green crystals separated. These were collected, washed with water, and recrystallised from benzene–light petroleum (b.p. 80—100 °C), yield 1.5 g, 30—40%.

Most of the other bis(η-arene) compounds were similarly prepared in comparable yields. Bis(*m*-di-isopropylbenzene)tungsten was prepared using the solution reactor as described below.

Bis(m-*di-isopropylbenzene*)*tungsten*.—This was prepared using the liquid reactor device shown in Figure 3. A mixture of *m*-di-isopropylbenzene (60 cm^3, 350 mmol) and 1,2-dimethylcyclohexane (10 cm^3) was allowed to fall as a thin film down the reactor wall at −78 °C. During this time tungsten was evaporated (*ca.* 1 g) into the film. The 1,2-dimethylcyclohexane was added to prevent the film freezing. The pressure measured at the gauge during the experiment was 2×10^{-5} mbar.

At the conclusion of the run the product was extracted from the gutter *via* a metal capillary tube using differential argon pressure. The reactor walls and gutter were washed with toluene (2 × 50 cm^3). The product was isolated as described for the other bis(η-arene)tungsten compounds giving green crystals of the pure compound, yield 0.80 g, 30%.

Bis(η-*arene*)*hydridotungsten Hexafluorophosphate*.—A typical experiment is described. Bis(η-toluene)tungsten (1.0 g, 3 mmol) was dissolved in hydrochloric acid (1 mol dm^{-3}, 100 cm^3) and the resulting orange solution was treated with an excess of aqueous [NH_4][PF_6] giving a yellow precipitate. This was collected, washed with water (2 × 20 cm^3), and then extracted with acetone. The orange extract was filtered and ethanol was added to the filtrate. Concentration of the resulting solution under reduced pressure gave orange crystals which were collected, washed with ethanol, and dried *in vacuo*, yield *ca.* 1.4 g, 90%.

Bis(η-*benzene*)*tantalum*.—In a typical experiment *ca.* 1.5 g of tantalum, from an ingot of *ca.* 9 g, were evaporated using a power input of 1.5 kW and the tantalum vapour was co-condensed with benzene vapour for 3 h. After warming, the reaction mixture was washed from the reaction vessel walls with benzene (500 cm^3). The resultant deep red-brown solution was filtered and pumped to dryness at 40 °C. Extraction with warm light petroleum (b.p. 40—60 °C, 3 × 100 cm^3) gave a deep red solution which was filtered. Concentration and cooling to 0 °C gave deep maroon crystals which were collected, washed with cold light petroleum (b.p. 30—40 °C), and dried *in vacuo*, yield *ca.* 0.80 g, 30%.

Bis(η-*toluene*)*trimethylphosphinehafnium*.—Typically, hafnium (*ca.* 1.5 g from an ingot of *ca.* 8 g at a power input of 1.5 kW) was co-condensed with a mixture of toluene (*ca.* 70 cm^3, 800 mmol) and PMe_3 (*ca.* 7 cm^3, 90 mmol) in a run lasting 3.5 h. After allowing to warm to room temperature (*ca.* 1 h) the reactor walls were washed with toluene (500 cm^3) and the resultant deep green-brown solution filtered and pumped to dryness at 60 °C. Extraction with light petroleum (b.p. 40—60 °C, 3 × 100 cm^3) gave a deep green solution which was filtered, concentrated, and cooled to −30 °C giving deep green-black crystals. These were collected, washed with light petroleum (b.p. 30—40 °C) at −30 °C, and dried *in vacuo*, yield *ca.* 1.3 g, 40%.

Bis(η-benzene)trimethylphosphinehafnium was prepared similarly and in similar yield.

Bis(η-*toluene*)*trimethylphosphinezirconium*.—Typically zirconium (*ca.* 0.75 g from an ingot of *ca.* 5 g at a power input of 1.8 kW) was co-condensed with a mixture of toluene (*ca.* 70 cm^3, 800 mmol) and PMe_3 (*ca.* 7 cm^3 90 mmol) in a run lasting 3 h. Extraction and isolation were essentially identical to that of the hafnium derivative. The yield was *ca.* 1.2 g, 40%.

Co-condensation of Toluene and Tungsten Atoms with the Furnace in the Earthed-hearth Mode.—The apparatus was assembled in the normal way except that the polarity of the furnace was changed so that the hearth was earthed (see Figure 2). The power input to the furnace was slowly raised to 1.5 kW during which time the pressure in the reaction vessel slowly fell back to the original value of *ca.* 10^{-6} mbar. This pressure change reflects a final outgassing of the filament and metal sample. Toluene was then introduced into the reaction vessel and this led to an immediate and sharp rise of pressure to 10^{-4} mbar, with occasional surges to 10^{-3} mbar. The maximum allowable rate for the toluene introduction which was compatible with smooth operation of the furnace was *ca.* 10 cm^3 h^{-1}. The run was continued for 2.5 h, during which time tungsten (*ca.* 1.7 g, 10 mmol) was co-condensed with toluene (*ca.* 25 cm^3, 250 mmol). At the conclusion of the run the reaction vessel was washed with toluene and the extracted reaction mixture was divided into two equal portions.

One half of the reaction product was concentrated under reduced pressure giving *ca.* 1 cm^3 of a dark brown oil. Analysis (g.l.c.) showed three major components in approximately equal amounts; gas chromatography–mass spectrometry showed these components to be bitolyls (*m/e* 182), dihydrobitolyls (*m/e* 184), and tetrahydrobitolyls (*m/e* 186). Analysis of the peak areas showed that *ca.* 6% of the initial toluene had been converted to these products. In contrast, g.l.c. analysis of the less volatile components from the positive-hearth co-condensation experiment showed <0.1% conversion of toluene to dimeric species.

The other half of the reaction product was treated in the same manner as for the isolation of bis(η-arene)tungsten compounds described above. The reaction product yielded 50 mg of bis(η-toluene)tungsten. Hence the total yield was *ca.* 100 mg, 3%. This yield is about a tenth that obtained from the positive hearth mode.

RESULTS

Synthesis of Bis(η-*arene*) *Derivatives of the Transition Metals*.—The positive-hearth furnace was able to melt a 12-g ingot of tungsten metal and to evaporate it at a rate of *ca.* 1.5 g h^{-1}. Co-condensation of the tungsten vapour with an excess of benzene, toluene, or mesitylene (1,3,5-trimethylbenzene) at 77 K gave, upon warming the reaction mixtures, deep green-brown solutions. After filtration to remove metallic particles, the filtrate was extracted with dilute hydrochloric acid giving a bright orange aqueous layer. Addition of aqueous ammonium hexafluorophosphate gave the orange hydrido-cations $[W(\eta\text{-}C_6H_3R_3)_2H][PF_6]$, where $R_3 = H_3$, H_2Me, or 1,3,5-Me_3. Addition of an excess of aqueous sodium hydroxide to the aqueous solutions precipitated green crystals of the neutral bis(η-arene) compounds $[W(\eta\text{-}C_6H_3R_3)_2]$. It was found possible to prepare 1—1.5 g of the neutral bis(η-arene) compounds in a single 3—4 h run.

TABLE 3

Analytical and spectroscopic data

Compound	Colour	Analytical data [a]/%		Mass spectrum [b]	I.r. data [c] (cm^{-1})	Hydrogen-1 n.m.r.,[d] e.s.r., and photoelectron spectral data
		C	H			
$[W(\eta\text{-}C_6H_6)_2]$	Green			340, P^+		5.25, *s*, (η-C_6H_6)
$[W(\eta\text{-}C_6H_5Me)_2]$	Green			368, P^+		4.95, **10**, *s*, (η-C_6H_5); 7.85, **6**, *s*, Me [e]
$[W(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2]$	Dark green	50.8 (50.9)	5.7 (5.7)	424, P^+		5.25, **6**, *s*, (η-C_6H_3); 7.97, **18**, *s*, Me [e]
$[W(\eta\text{-}C_6H_4Pr^i_2\text{-}m)_2]$	Dark green			508, P^+		5.10, **8**, *s(br)*, (η-C_6H_4); 7.55, **4**, *septet* [*J*(H–H) 7.0] CH; 8.63, **24**, *d* [*J*(H–H) 7.0] Me [e]
$[W(\eta\text{-}C_6H_6)_2H][PF_6]$	Orange	29.3 (29.3)	2.8 (2.7)		1 870	4.22, **12**, *d* [*J*(H–H) 2.0] (η-C_6H_6); 8.93, **1**, *s(br)*, WH [f]
$[W(\eta\text{-}C_6H_5Me)_2H][PF_6]$	Orange	32.5 (32.7)	3.2 (3.3)		1 859	4.33, **10**, *m*, (η-C_6H_5); 7.33, **6**, *s*, Me; 8.93 **1**, *s*, WH [f]
$[W(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2H]\text{-}[PF_6]$	Orange	38.0 (37.9)	4.3 (4.4)			4.44, **6**, *d* [*J*(H–H) 2.0] (η-C_6H_3); 7.38, **18**, *s*, Me; 10.41, **1**, *s*, WH [f]
$[W(\eta\text{-}C_6H_5OMe)_2H][PF_6]$	Orange	31.0 (30.8)	3.3 (3.1)			4.13, **8**, *m*, 5.60, **2**, *c*, (η-C_6H_5); 6.20, **6**, *s*, Me; 10.80, **1**, *s*, WH [f]
$[W(\eta\text{-}C_6H_5F)_2H][PF_6]$	Orange	27.1 (27.6)	2.1 (2.1)			3.50, **8**, *c*, 5.45, **2**, *c*, (η-C_6H_5); 10.55, **1**, *t* [*J*(F–H) 20], WH [f]
$[Nb(\eta\text{-}C_6H_6)_2]$	Claret red	[g]		249, P^+		Photoelectron spectrum: 1st i.p. at 5.57 eV
$[Nb(\eta\text{-}C_6H_5Me)_2]$	Claret red	[g]		277, P^+		E.s.r. data:[h] 10 lines, $A_{iso.} = 4.59$ mT; $\langle g \rangle = 1.992$
$[Nb(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)_2]$	Claret red	64.65 (64.8)	7.1 (7.1)	333, P^+		E.s.r. data:[h] 10 lines, $A_{iso.} = 7.74$ mT, $\langle g \rangle = 2.009$
$[Ta(\eta\text{-}C_6H_6)_2]$	Purple-red	[i]		337, P^+		E.s.r. data:[h] 8 lines, $A_{iso.} = 13.9$ mT, $\langle g \rangle = 1.943$
$[Zr(\eta\text{-}C_6H_5Me)_2(PMe_3)]$	Dark green			274, $P^+ - PMe_3$		4.45, **2**, *c*, 5.87, **8**, *c*, (η-C_6H_5); 7.80, **6**, *c*, Me; 9.15, **9**, *d* [*J*(P–H) 4.0] PMe_3 [e]
$[Hf(\eta\text{-}C_6H_6)_2(PMe_3)]$	Dark green			336, $P^+ - PMe_3$		5.65, **12**, *d* [*J*(P–H) 0.8] (η-C_6H_6); 9.15, **9**, *d* [*J*(P–H) 4] PMe_3 [e]
$[Hf(\eta\text{-}C_6H_5Me)_2(PMe_3)]$	Dark green	46.2 (46.5)	4.9 (4.9)	368, $P^+ - PMe_3$		4.70, **2**, *c*, 6.00, **8**, *c*, (η-C_6H_5); 8.00, **6**, *s*, Me; 9.10, **9**, *d* [*J*(P–H) 5] PMe_3 [e]

[a] Calculated values are given in parentheses. [b] P^+ Indicates the presence of a band assignable to the parent ion with the appropriate fragmentation pattern and, where applicable, the correct isotope pattern. [c] (W–H) Stretch. [d] Hydrogen-1 n.m.r. data given as: chemical shift (τ), **relative intensity,** *multiplicity* (*J* in Hz), assignment. [e] In C_6D_6. [f] In $(CD_3)_2CO$. [g] Not obtained; characterised by mass spectrum, the matrix isolation i.r. spectrum, and e.s.r. spectrum. [h] In light petroleum (b.p. 60—80 °C). [i] Not obtained due to thermal instability; characterised by the mass spectrum, i.r. spectrum, and e.s.r. spectrum.

In a similar manner, tungsten vapour was co-condensed with fluorobenzene or anisole giving, after acid extraction, the cations $[W(\eta\text{-}C_6H_5F)_2H][PF_6]$ and $[W(\eta\text{-}C_6H_5OMe)_2H][PF_6]$. As described above, the low volatility of *m*-diisopropylbenzene enabled the co-condensation experiment to be carried out using the falling-film technique at −78 °C.

The data characterising the bis(η-arene)tungsten compounds are given in the Table 3 and do not require further discussion.

Co-condensation of niobium vapour with excess of benzene, toluene, or mesitylene gave deep red-purple solutions from which volatile red-purple crystals of the compounds $[Nb(\eta\text{-}C_6H_3R_3)_2]$, where $R_2 = H_3$, H_2Me, or 1,3,5-Me_3, were isolated. Solutions of these compounds in light petroleum are instantly decomposed by oxygen but addition of water causes only a slow reaction. Both reactions give white niobium pentaoxide. The bis(η-arene)niobium compounds are volatile and sublime in vacuum with some decomposition at *ca.* 80 °C, 10^{-3} mbar. Their mass spectra and photoelectron spectra have been determined (Table 3). The low values for the first ionisation potentials, which lie in the range 5.18—5.57 eV, show the compounds to be 'high energy' (electron-rich) molecules. The e.s.r. spectra of solutions of the compounds in light petroleum (b.p. 60—80 °C) at room temperature show the ten-line spectrum expected for a paramagnetic, 17-electron, d^5 niobium compound with one unpaired electron. The i.r. spectra in dilute argon matrices at 8 K have been determined for the compounds $[Nb(\eta\text{-}C_6H_3R_3)_2]$ (R = H and Me). The data and assignment given in Table 4 show, by analogy with the i.r. matrix spectra of bis(η-benzene)molybdenum, that the niobium analogues also have a symmetrical sandwich structure.

Molten tantalum at *ca.* 3 300 °C vaporises readily and smoothly. Co-condensation of the vapour with an excess of benzene gave a deep red-brown solution from which deep red, well formed crystals could be isolated. They are soluble in light petroleum (b.p. 30—40 °C) and benzene; the solutions are exceptionally sensitive to oxygen and are thermally unstable above 50—60 °C. Attempts to sublime the tantalum compound resulted in substantial decomposition so that we were unable to obtain a matrix i.r. spectrum. However, it was found possible to observe a highest band in

TABLE 4

Infrared spectral data (cm^{-1}) for bis(η-arene)niobium compounds

[Nb(η-C_6H_6)$_2$]	[Nb(η-$C_6H_3Me_3$)$_2$]	[Mo(η-C_6H_6)$_2$]	Assignment
350	375	379	Antisymm. metal–ring stretch
412	410	438	Antisymm. ring tilt
732, 750, 950, 988	812, 910, 981, 1 007 1 035, 1 145	777, 809, 965, 1 000	Ligand deformation
Not seen		1 430	C–C stretch
3 079	2 865, 2 885, 2 920, 2 950 2 970, 3 022, 3 050	3 060	Symm. C–H stretch

the mass spectrum which corresponded to the parent ion expected for bis(η-benzene)tantalum. Further, solutions of the compound in light petroleum gave an e.s.r. spectrum consisting of eight lines as expected for an unpaired electron coupling with a ^{181}Ta nucleus (spin $\frac{7}{2}$). The i.r. spectrum in liquid paraffin mulls shows prominent bands at 303 cm^{-1} and 370 cm^{-1} which are assignable to the benzene–metal stretch and benzene–ring tilt respectively.

Following the successful synthesis of bis(η-arene)titanium compounds [2] we decided to react the vapours of zirconium and hafnium with an excess of benzene or toluene. Warming the resulting deep red reaction mixtures to above *ca.* -100 °C caused their decomposition giving black metallic material and some intractable brown substance.

The compounds [M(η-arene)$_2$] (M = Zr or Hf) are isoelectronic with the compounds [M(η-C_5H_5)$_2$] (M = Mo or W). The latter have been shown to insert readily into the C–H bonds of arenes [5] and to add to ligands such as CO and tertiary phosphines.[6] Therefore, we decided to attempt to trap any initially formed bis(η-arene)-zirconium, or -hafnium, by the addition of trimethylphosphine to the reaction mixture.

Treatment of the red co-condensation mixtures described above with trimethylphosphine caused no visible reaction. However, when the metal vapours were co-condensed with a mixture of benzene (or toluene) and trimethylphosphine (*ca.* 10% v/v), the resulting reaction mixtures were deep green and after removal of excess reactants and crystallisation from light petroleum ether deep green-black crystals of the compounds [Hf(η-C_6H_5R)$_2$(PMe_3)] (R = H and Me) and [Zr(η-C_6H_5R)$_2$(PMe_3)] were isolated.

The compounds are quite exceptionally sensitive both to oxygen and to traces of water but they appear to be stable indefinitely at room temperature. They have been characterised by the analytical data, mass and ^{1}H n.m.r. spectra given in Table 3.

DISCUSSION

At the outset of this work, of the compounds given in Table 3 only bis(η-benzene)tungsten had been previously described. It was prepared, in small yields, by the classic reducing Friedel-Craft procedure devised by Fischer.[7] During the course of this work Skell and coworkers [8] described the synthesis of bis(η-arene)tungsten compounds using tungsten vapour where the atoms were generated from a resistively heated tungsten wire. For practical reasons this method is limited to a small scale, *e.g.* 50—100 mg of metal atoms per filament. In this work we have shown that the positive-hearth electron-beam furnace provides a convenient and relatively large-scale source of tungsten atoms and that the vapour synthesis apparatus is suitable for the synthesis of bis(η-arene)-tungsten compounds on a scale of up to 3 g per day.

The bis(η-arene) derivatives of niobium, zirconium, and hafnium represent the first examples of zerovalent compounds of these elements. We have very recently described the synthesis using tantalum atoms of the compound [Ta($Me_2PCH_2CH_2PMe_2$)$_3$].[9] Thus it is now possible to state that zerovalent compounds are known for all the transition metals of Groups 4—6.

The first ionisation potentials of these compounds, where determined, clearly show that they may be classed as ' high-energy ' compounds. And the ease with which the bis(η-arene)tungsten compounds undergo protonation supports this conclusion. We note that the compounds [W(η-arene)$_2$H][PF_6] and [M(η-arene)$_2$(PMe_3)] (M = Zr or Hf) represent the first examples of bent bis(η-arene) derivatives and their stability suggests that more representatives of this class may exist.

Recently we have developed a larger-scale apparatus which is essentially similar to that described here and this provides, for example, bis(toluene)-tungsten or -titanium on a scale of 4—7 g or 15—21 g per run respectively.[10]

We are continuing to develop the chemistry of the heavier transition metals of Groups 4—6.

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