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THE USE OF ATOMS OF THE GROUP IV, V AND VI TRANSITION METALS FOR THE SYNTHESIS OF ZEROVALENT ARENE COMPOUNDS AND RELATED STUDIES

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I. Introduction

It was the report by Allen and Senoff that the cation $[Ru(NH_3)_5H_2O]^{2+}$ in aqueous solution would react at room temperature and atmospheric pressure with dinitrogen giving $[Ru(NH_3)_5(N_2)]^{2+}$ [1] that eventually led to our present work on, for example, zerovalent arenehafnium derivatives. At the time of the Allen and Senoff paper, dinitrogen had in my view no right to bond to a cationic transition metal centre. The only reasonable explanation that I could envisage was that the d^6 electrons of the ruthenium were much higher in energy than my intuition had led me to believe. I held a discussion with several members of my research group, namely Dr. Taro Saito, Colin Campbell and Michael Swanwick, and we agreed that for two months we would work exclusively on the problem of trying to understand the $[Ru(NH_3)_5N_2]^{2+}$ cation and also try to make other dinitrogen compounds. A rather scrappy note describing this work has appeared [2] in which there was one fact of interest to me. We had prepared the carbonyl $[Ru(NH_3)_5CO]^{2+}$ and the CO stretching frequency at 1955 cm^{-1} was much lower than would be reasonably expected for a "cation". Clearly there was, indeed, very strong back donation arising from high energy of the d^6 orbitals. This was a relief. I decided that a general condition that would allow a metal centre to react with dinitrogen was that there must be an available site on the metal where the metal *d*-orbitals were unusually high in energy, i.e. the electrons in the *d*-orbitals would have low ionisation energies. These conditions would be achieved by a transition metal centre with a 16-electron (or less) environment where the ligands gave rise to a substantial build-up of electron density on the metal. Suitable ligands were thought to include arenes, η-cyclopentadienyl and tertiary phosphines. At this time we referred to compounds with the desired electronic properties as being "electron rich" although nowadays I prefer the expression "high energy".

Since molybdenum occurs in the enzyme nitrogenase this was chosen to be the metal centre. Bill Silverthorn arrived from the Bell Telephone Laboratory as a post-doctoral fellow, and on the basis of arguments given above it was decided to synthesize and explore the chemistry of arene-molybdenum deriva-

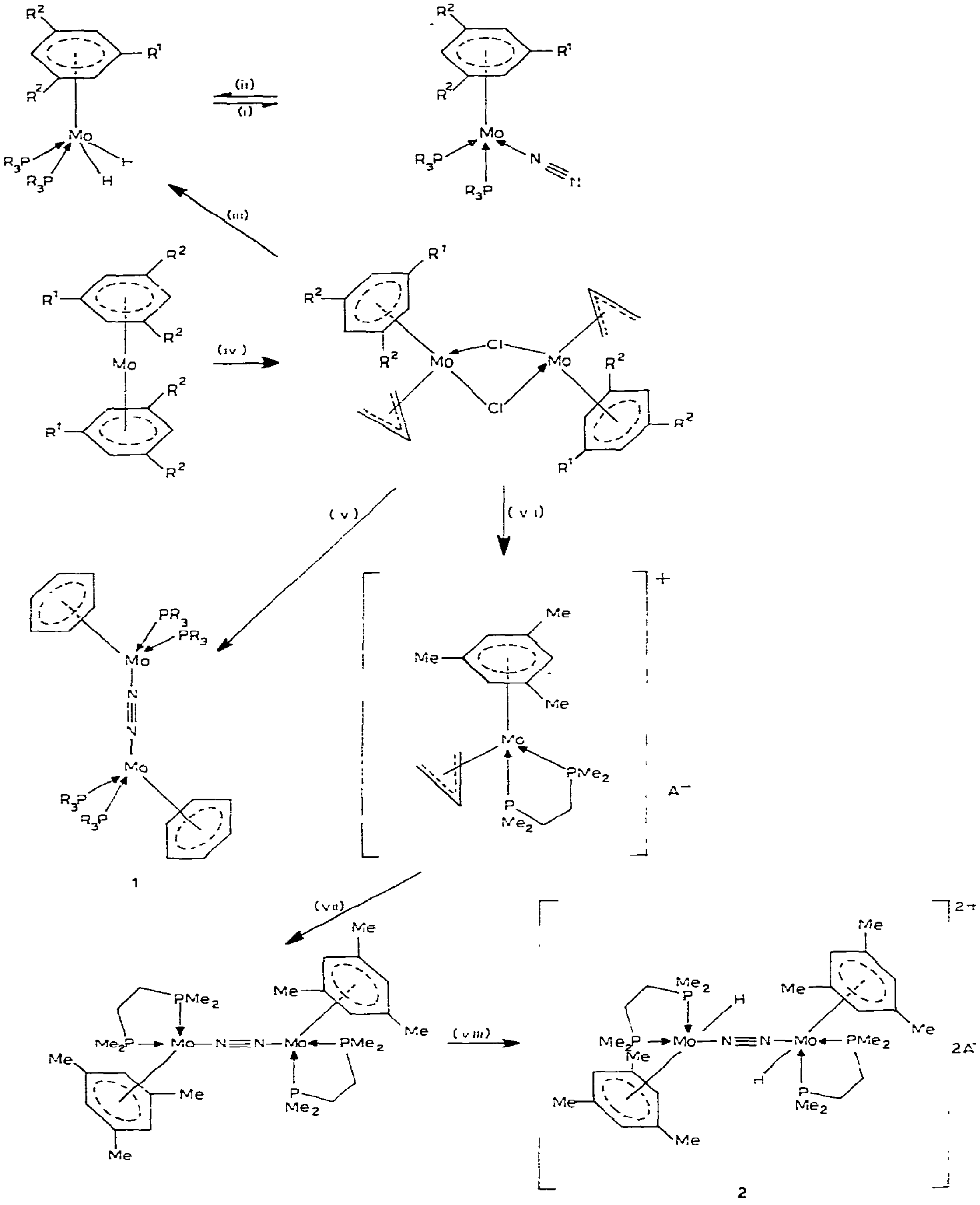


Fig. 1. Synthesis and reactions of arene-molybdenum dinitrogen compounds [5,6]. (i) $R_1 = R_2 = H$; $R_1 = H$, $R_2 = Me$; N_2 at 1 atm. $R_3 = Ph_3$. (ii) H_2 at r.t. (iii) $NaBH_4$ and excess R_3P. (iv) $CH_2{=}CHCH_2Cl$ excess in toluene at r.t. (v) $LiBu^n$ and Ph_3P under N_2 (1 atm). (vi) dmpe in ethanol, reflux 6 h, $R_1 = R_2 =$ Me only. (vii) Na/Hg in THF under N_2, 1 atm. (viii) HBF_4 in Et_2O at −79°C.

tives but to avoid carbon monoxide as a ligand since it is such a strong π-acceptor (π-acid) that it removes electron density from the metal thus preventing formation of high energy metal centres. A possible route to new arene-molybdenum compounds was to start with bis-arene molybdenum compounds. Bill proved to be a fearless experimenter and within a short time was preparing bis(toluene) (or -benzene)molybdenum in 60—80 gram/week quantities. The ability of benzene to build up electron density of the ligand compared to carbon monoxide is illustrated by the observation that the first ionisation potential of $(\eta\text{-}C_6H_6)_2Mo$ is 5.01 eV [3] and for $Mo(CO)_6$ it is 4.22 eV higher at 9.23 eV [4]. Bill Silverthorn, later assisted by Len Mitchard and John Knight, established much new chemistry of the arene-molybdenum system, including new compounds of dinitrogen (see Figure 1) [5,6].

Parshall and Hardy [7] had speculated that a system such as "Mo—N≡N—Mo" would be suitable for the reduction of the N≡N system to hydrazine or ammonia. In this respect our unusual binuclear dinitrogen systems shown in compounds 1 and 2 in Figure 1 seemed specially promising. Disappointingly, however, we were unable to persuade the dinitrogen in these compounds to add hydrogen in any form.

A possible development from this impasse was to compare the chemistry of the arenemolybdenum system with that of related tungsten derivatives. However, bis-arenetungsten, though long known from the work of Professor E.O. Fischer [8] was very difficult to prepare, using the "reducing Friedel-Crafts procedure". Typically a yield of 2% was obtainable after about 2—3 weeks of hard and exacting work by John Knight.

II. Development of metal vapour synthesis using electron-gun furnaces

At about this time Dr. Peter Timms gave a seminar in Oxford where he described his most elegant synthesis of bis-benzenechromium by co-condensation of chromium atoms with an excess of benzene [9]. The chromium atoms were generated from a resistance heated furnace operating at about 1500°C. I resolved there and then to try to synthesise bis-arenetungsten compounds using tungsten atoms.

In order to evaporate tungsten a temperature of around 3600°C is required; further the molten tungsten needs to be contained. After making enquiries it seemed that a possible solution to these technical problems lay with electron gun furnaces where the metal sample would be supported on a water-cooled copper hearth. An electrostatically focussed electron gun driven by a 1.4 kW power supply was purchased from G.V. Planer Ltd., using monies provided by an S.R.C. grant. In order to strengthen my application for this grant a postdoctoral assistant, Dr. Adam Hart-Davies, had previously constructed a small rotating glass reactor using a Buchi rotating evaporator and a molybdenum resistance heater. This apparatus was successfully employed to co-condense chromium with cycloheptatriene at —195°C giving $Cr(\eta\text{-}C_7H_7)(\eta\text{-}C_7H_9)$.

Dennis Young built a new and larger rotating apparatus designed to contain electron-gun furnace and the outline of the apparatus is shown in Figure 2 [10]. The electron gun itself is a very simple device and the essential details of the design are illustrated in Figure 3.

The apparatus built by Dennis Young worked quite well and was used, for example, in the synthesis of bis-arenechromium and molybdenum and the zero valent titanium compounds e.g. bis-arenetitanium [10]. Also, all of the 3*d* and 4*d* transition metals were evaporated in a study of their catalytic properties with butadiene [11]. However, the apparatus was limited and it was possible to evaporate tungsten only with great difficulty and on a rather small scale (10—100 mg/hour). Also, at the higher accelerating potentials used for maximum power input (1.4 kW), there was evidence of deterioration of introduced arene ligand. Attempts to co-condense toluene with tungsten gave rise to bitolyls as side products. These side products could arise from several factors. At high power input the hot sample radiates more heat and thus the reaction walls are warmer so cryogenic pumping of toluene would be less effective. The resulting increase of vapour pressure could give rise to thermolysis of toluene molecules at the hot tungsten surface. Dihydrogen would be a non-condensable product causing a further deterioration of the vacuum. Plasma discharge conditions occur when the vacuum is poor ($<10^{-4}$ torr) and/or when the accelerating potential is high. Plasma discharge will generate organic fragments and more dihydrogen. Of course there is a dynamic situation in the reaction chamber and the greater the speed of the evacuating pump system the

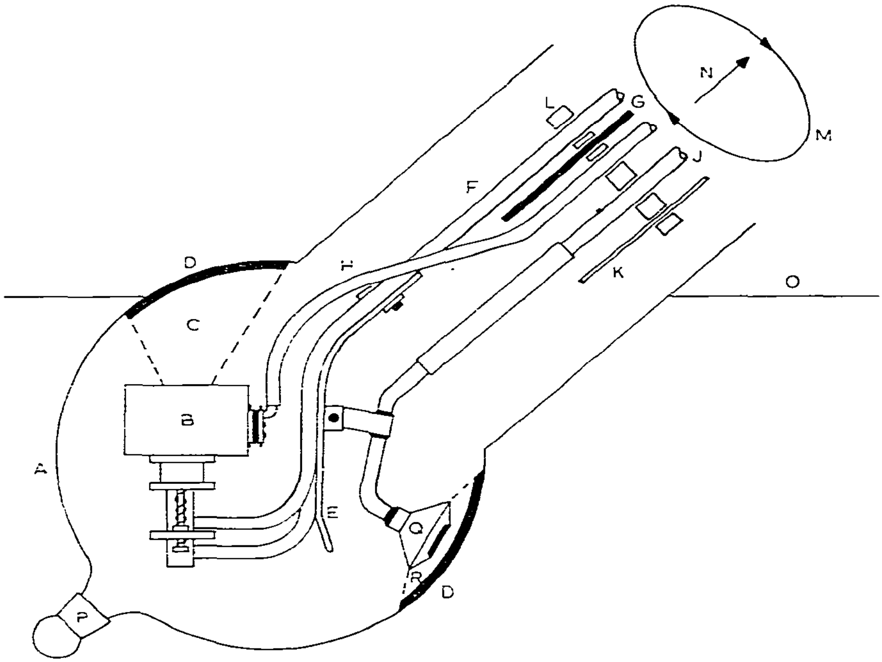


Fig. 2. A: Glass reaction vessel. B: Electron beam furnace, model EBS1, G.V. Planer Ltd. C: Vapour beam of metal atoms. D: co-condensate of metal and substrate vapours. E: Heat shield. F: Furnace cooling water pipes. G: Electrical lead for substrate solution dispersion device. H: Furnace electrical leads. J: Substrate inlet pipe (vapour). K: Substrate inlet pipes (solution). M: rotation of reaction vessel. N: to vacuum rotating seal, service vacuum lead throughs and pumping systems. O: Level of coolant (usually liquid nitrogen). P: Capped joint for product extraction. Q: Substrate vapour dispersion device. R: Substrate vapour beam.

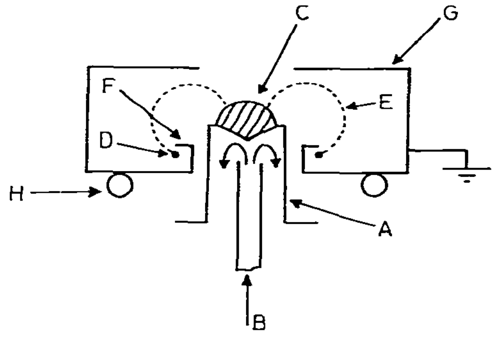


Fig. 3. Line diagram of cross-section of an electrostatically focussed electron gun. A: Water-cooled hearth, maintained at a positive potential of 0—10 kV (in the earth hearth mode the filament and shield are held at negative potential relative to the earthed hearth). B: Cooling water flow. C: Metal sample. D: Tungsten emitter filament, heated by ca. 45 A at 5 V. E: Electron path. F: Electrostatic shield. G: Focussing lid. H: Subsidiary water cooling coil.

sooner stable conditions are restored. Another source of product and ligand damage could be electron damage. The electrons accelerated onto the metal sample could reflect and travel to the walls. The higher accelerating potentials result in greater energies of the reflected electrons. It is probable that all these factors operate to some extent.

It was clear that to evaporate tungsten effectively a more powerful electron gun would be required and also that it would be desirable to study the effect of reversing the potential of the electron-gun as a possible means of reducing product damage. Also, improved pumping speeds were considered to be desirable.

The reverse potential mode for the gun would have the water cooled hearth together with its metal sample at a high positive potential whilst the focussing walls would be maintained at earth potential. It was anticipated that electrons would reflect less readily from a sample at high positive potential.

G.V. Planer Ltd. had available the designs of a suitable electron-gun which could be operated in a positive hearth mode up to 3.5 kW (compared to 1.4 kW for the first gun). Geoff Cloke constructed an electron-gun based on the Planer design and housed it in a simple bell-jar apparatus. The apparatus is shown in outline in Figure 4. It can be seen to be very simple in design which, as it turned out, had many advantages for our purposes. The apparatus was capable of evaporating tungsten metal at 1—2 g/h and was used to compare the effect of changes of polarity on emission from the gun and on the yield of bis-toluenetungsten from co-condensation of toluene with tungsten atoms.

Table 1 shows that there is indeed a considerable difference in the nature of the emission from electron gun hearth depending on the polarity. In summary a positive hearth emits only a very small positive ion current whilst the neutral hearth emits a substantial negative (electron) current at higher applied accelerating potentials. Further, Table 2 shows that the yield of bis-arene tungsten is ten times greater in the positive hearth mode.

Thus the positive hearth apparatus had at last achieved the goal of synthesis of bis-arenetungsten on a substantial laboratory scale (1—2 gram/day) [12].

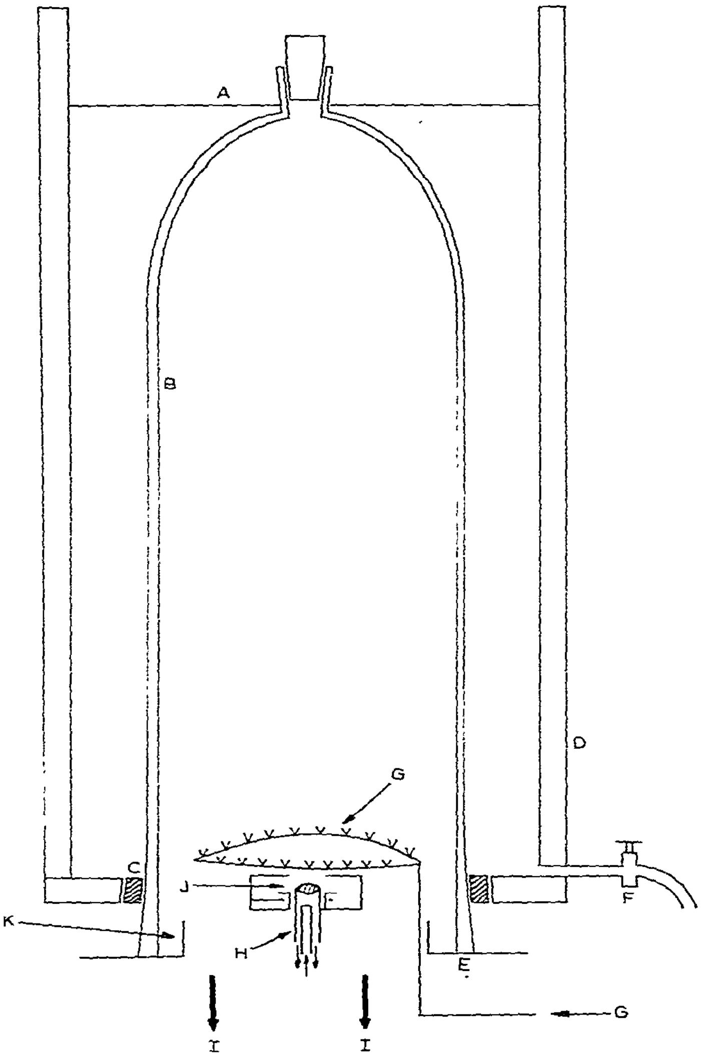


Fig. 4. Simple bell-jar apparatus. A: Coolant level. B: 10 l glass vessel, reaction well. C: Gasket. D: Dewar vessel, E: Ground flange. F: Coolant drain. G: Ligand vapour inlet, "gas-ring". H: Positive hearth electron gun, maximum capacity 2.5 cm^3 (see Fig. 3). I: To trap and diffusion pump (4"). J: Metal sample. K: Gutter for collection of reactants.

Just prior to this Skell had reported that bis-arene-tungsten could be prepared (on 100—300 milligram scale) by evaporation from a tungsten filament [13].

I have now become a highly enthusiastic proponent for synthesis using atoms derived from positive hearth electron gun furnaces. We have very recently built a much larger version of the Cloke apparatus incorporating some modifications. Thus we have separated the reaction surface from the glass outside wall, which alleviates problems of cold vacuum seals. The new apparatus is shown in Figure 5. It works very well and we routinely synthesise 20 gram/day of bis-toluenetitanium or 5 gram/day of bis-arenetungsten compounds.

TABLE 1

ELECTRON CURRENTS REFLECTED FROM 3.5 kW FURNACE AS A FUNCTION OF A VARYING POWER INPUT

(i) Positive Hearth Mode

Electron-beam current input (mA)	Accelerating Voltage Input (kV)					
	1	2	3	4	5	
100	—	−2.5	−2.5	−2.7	−2.5	Emitted current in microamps [a]
150	—	—	−5.5	−6.0	−6.0	
200	—	—	−4.5	−6.0	−10.0	
250	—	—	—	−6.0	−13.0	
300	—	—	—	−6.0	−25.0	
350	—	—	—	−17.0	−40.0	

(ii) Earthed Hearth Mode

Electron-beam current input (mA)	Accelerating Voltage Input (kV)					
	1	2	3	4	5	
100	—	+0.75	+0.85	+0.90	+0.90	Emitted current in milliamps [b]
150	—	—	+1.5	+1.5	+1.5	
200	—	—	—	+2.0	+2.0	
250	—	—	—	+2.2	+2.3	
300	—	—	—	—	+2.9	
350	—	—	—	—	+3.4	

[a] In fact, a small positive ion current. [b] A substantial flow of electrons.

III. Synthesis of compounds of the Group IV, V and VI transition metals using metal atoms

We now feel that most of the technical problems for carrying out synthesis using metal atoms on a laboratory scale have been overcome up to the level of ligand limitations. By the latter comment I mean, for example, that factors such as the volatility or solubility of the co-condensate (ligand) can limit the convenience or effectiveness of the experiment. The operation of the apparatus is straightforward and reproducible and requires only the normal precautions

TABLE 2

EFFECT OF HEARTH POLARITY ON THE SYNTHESIS OF $(\eta\text{-}C_6H_5Me)_2W$

	Positive hearth mode	Earthed hearth mode
Vacuum near e-gun (torr)	10^{-5} torr	$>10^{-4}$ torr
Power input (kW)	1.8	1.8
Ligand inlet rate ($cm^3\ h^{-1}$) [a]	30	10 [b]
Duration of run (h)	2	2
% conversion of toluene to bitolyls (GLC/MS)	<0.01	6
Yield of $(\eta\text{-}C_6H_5Me)_2W$ [c]	0.50 g (30%)	50 mg (3%)

[a] Typically, 340 milliamp at 5.5 kV. [b] Maximum rate compatible with maintenance of vacuum $<10^{-3}$ torr. [c] Isolated and crystallised.

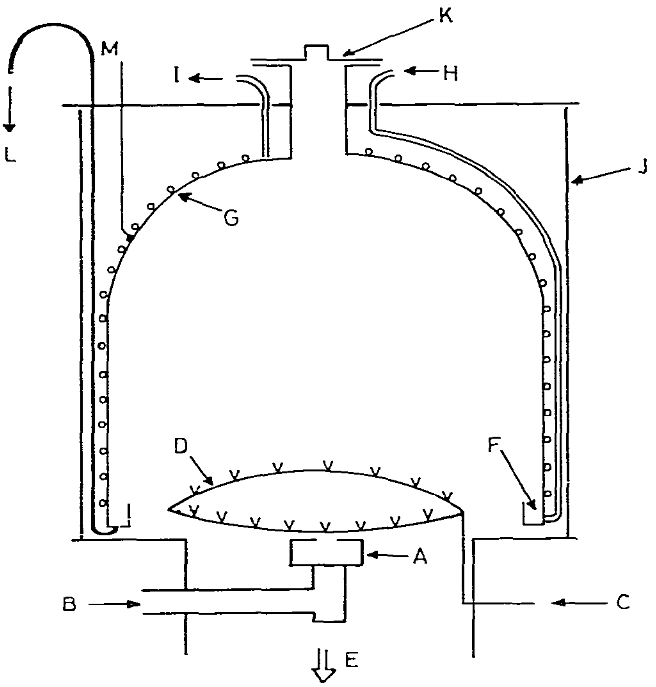


Fig. 5. The large scale metal atom reactor. A: 10 kW positive hearth electron beam furnace, maximum capacity 10 cm^3 of molten metal (ca. 50 gr of titanium). B: Cooling water and power input for furnace. C: Ligand vapour inlet (ca. 50—100 cm^3/hour). D: Gas ring for ligand vapour dispersion. E: To cryogenic pumping system. F: Product collection gutter. G: Copper reaction chamber with cooling coil (co-condensation surface area: 10^4 cm^2): H: Liquid nitrogen in. I: Liquid nitrogen out. J: Glass vacuum vessel (diameter 450 cm, height 600 cm). K: Port for washing products off chamber walls. L: Product extraction. M: Thermocouple to monitor co-condensation surface temperature.

associated with work requiring a reliable vacuum in the region of 10^{-4}—10^{-5} torr.

Over the last eighteen months we have set out to demonstrate that synthesis using metal atoms is no longer a matter for devoted specialists but, with suitable equipment, is a technique available to any synthetic chemist. Further, we wished to demonstrate that the method can provide on a viable laboratory scale 1—20 grams/day of very many known or new compounds which are not only of intrinsic interest but many of which can be seen to be precursors for unexplored areas of chemistry and for catalysis.

In effect we can now say that the transition metals atoms are available as starting materials in gram quantities. Pure metals are often amongst the cheapest sources of the element.

Using the apparatus described above we have surveyed the reactions of many of the transition metals with potential hydrocarbon ligands, and some of our results are summarised below.

(a) Zerovalent bis-η-arene derivatives

In Table 3 we give a brief description of new zerovalent compounds of the elements titanium, zirconium, hafnium, niobium and tantalum which have been prepared via the metal atoms. Some reactions are shown in Figure 6.

TABLE 3

ZERO-VALENT BIS-ARENE COMPOUNDS OF TITANIUM, ZIRCONIUM, HAFNIUM, NIOBIUM AND TANTALUM

Compound [a]	Colour	Comments	I.P. (eV) [b]
$Ti(\eta\text{-}C_6H_6)_2$ [c]	Burgundy red	Diamagnetic	5.5
$Ti(\eta\text{-}C_6H_5Me)_2$ [c]	Burgundy red	Diamagnetic	5.4
$Ti(\eta\text{-}C_6HMe_3)_2$ [c]	Burgundy red	Diamagnetic	—
$Zr(\eta\text{-}C_6H_5Me)_2PMe_3$ [d]	Dark green black	Diamagnetic	decomp. 80°C/10^{-3} torr
$Hf(\eta\text{-}C_6H_6)_2PMe_3$ [d]	Dark green-black	Diamagnetic	decomp. 80°C/10^{-3} torr
$Hf(\eta\text{-}C_6H_5Me)_2PMe_3$ [d]	Dark-green black	Diamagnetic	decomp. 80°C/10^{-3} torr
$Nb(\eta\text{-}C_6H_6)_2$ [e]	Maroon	Paramagnetic	5.57
$Nb(\eta\text{-}C_6H_5Me)_2$ [e]	Maroon	Paramagnetic	5.49
$Nb(\eta\text{-}C_6H_3Me_3)_2$ [e]	Maroon	Paramagnetic	5.18
$Ta(\eta\text{-}C_6H_6)_2$ [f]	Maroon	Paramagnetic	decomp. ~70°C/10^{-3} torr

[a] Satisfactory microanalyses for all compounds and mass spectra all show parent ion bands. [b] Lowest energy band in the photoelectron spectrum of the vapour, the electron arises from an orbital which is largely of *d*-character. [c] Ref. 10. [d] Ref. 15. [e] Ref. 14. [f] Ref. 16.

(b) Bis- and mono-arenetungsten chemistry

We have, for reasons given earlier, developed the chemistry of the arene-tungsten systems. It has taken about five years to put two arene rings on the tungsten atom and it was about a year before we found a good method of cleaving one of them off! At present the best route to the system W(η-arene)-(η-allyl) is via the reaction between the bis-arenetungsten compounds and allylacetate giving W(η-arene)(η-allyl)(acetate). This and many other reactions of the mono-arenetungsten system are shown in Figure 7.

Some reactions of bis-η-arenetungsten compounds are shown in Figure 8 including the first examples of bent bis-arene derivatives. The crystal structures of the compounds 3 and 4 have been determined [21]. The methyl group in 4 adopt a position consistent with minimum steric interactions within the molecule. In contrast in 3 the fluorines adopt an eclipsed configuration and lie in a plane in

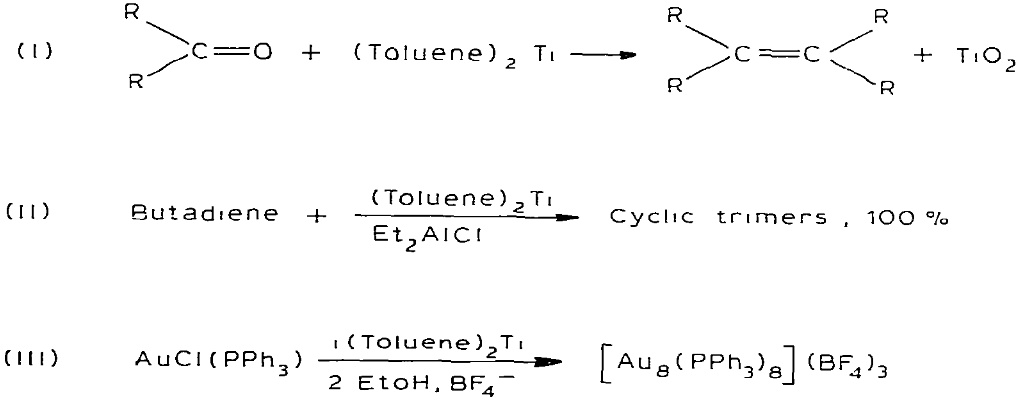


Fig. 6. Some reactions of bis-toluenetitanium. (i) Synthesis of olefins from aldehydes and ketones [17]. (ii) Cyclooligomerisation of butadiene [11]. (iii) As a reducing agent giving a variety of gold clusters [18].

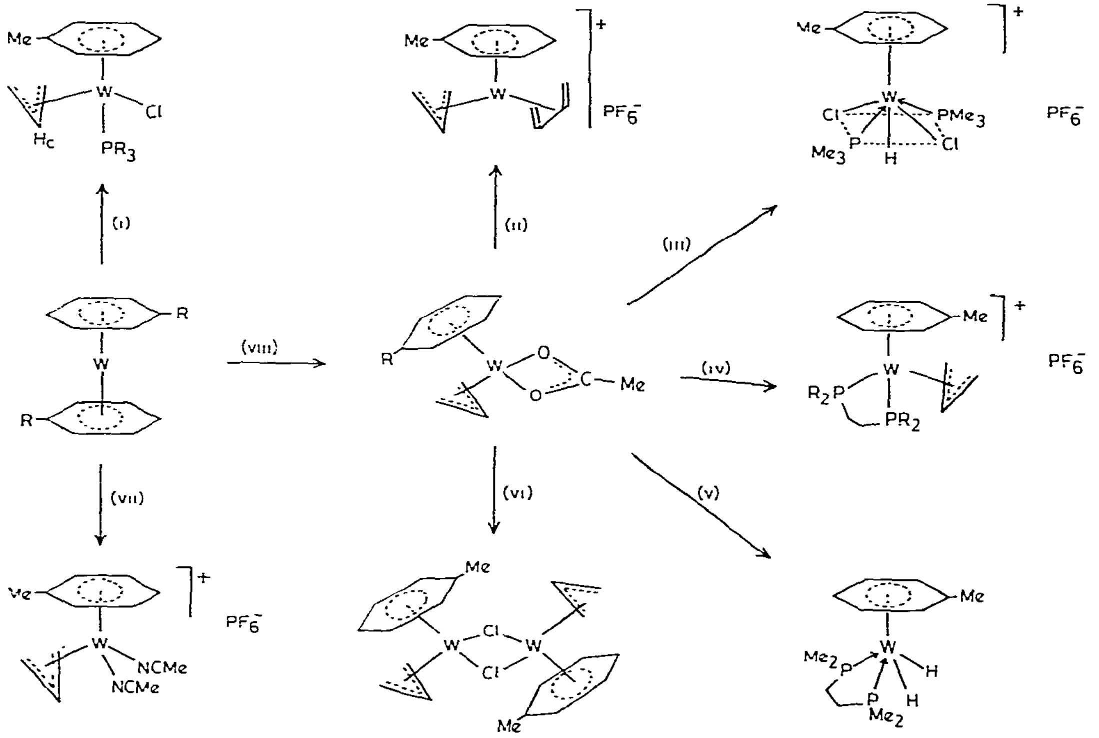


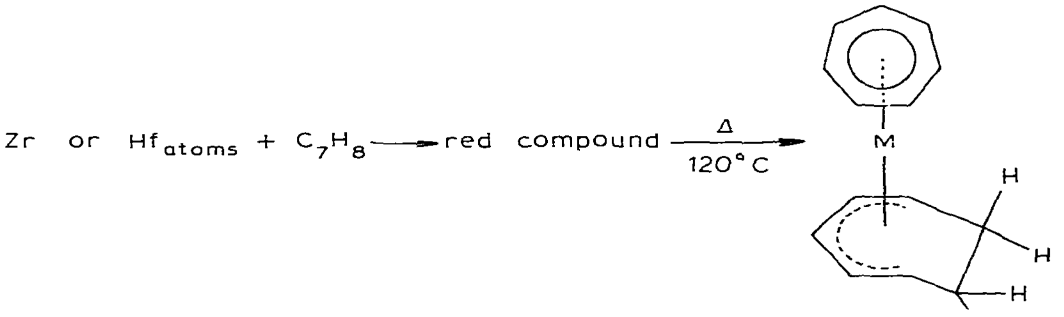
Fig. 7. Some mono-η-arenetungsten chemistry. (i) R_3 = Me_3, Me_2Ph, $MePh_2$; allylchloride in MeCN, then R_3P. (ii) $EtAlCl_2$ in toluene, then butadiene, PF_6^- aq. (iii) $NaAlH_2(OCH_2CH_2OMe)_2$ and Me_3P, then HCl aq., PF_6^- aq. (X-ray structure) [19].(iv) R_2 = Ph_2 or Me_2; dppe (or dmpe) in EtOH, PF_6^- in MeOH. (v) dmpe and Li[BEt_3H] in toluene. (vi) $EtAlCl_2$ in toluene. (vii) Allylacetate in acetonitrile at 70°C, 5% (X-ray structure) [20]; R = H, Me. (viii) Allylacetate in acetonitrile at 70°C, 70%, R = H.

which also contains the W—H system. This suggests there may be a bonding interaction between the W-hydrogen and the fluorine atoms. However, the tungsten—hydrogen stretching frequencies for 3 and 4 are quite closely similar, being at 1862 and 1859 cm^{-1} respectively so that there seems not to be a more than weak fluorine—hydrogen interaction.

Some data characterising the arenetungsten compounds are given in Table 4.

(c) *η-Cycloheptatrienyl-zirconium and -hafnium compounds*

Co-condensation of zirconium and hafnium with cycloheptatriene gives a red oil which, after vacuum pyrolysis, yields the red, volatile crystalline compounds M(η-C_7H_7)(η-C_7H_9), M = Zr or Hf, viz. [22]:



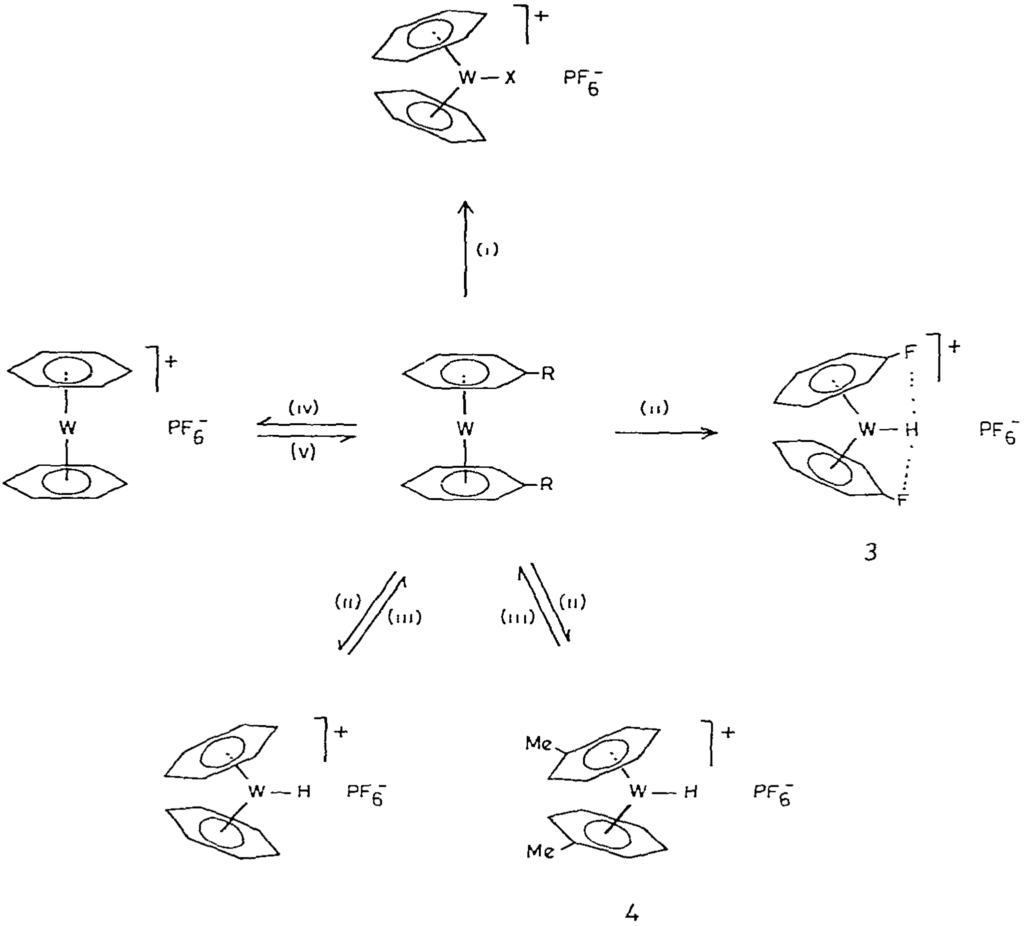


Fig. 8. Some reactions of bis-η-arenetungsten, R = H, F, Me (i) FeX_3aq then PF_6^- aq, (ii) HCl aq then PF_6^-, (iii) NaOH aq, (iv) allylchloride, (v) KOH aq at 70°C, disproportionation.

(d) 1,1′-Disubstituted bis-arenemolybdenum compounds

The reactions between the metal atoms and the ligands occurs in the matrix of the co-condensate. Normally this will be held at —195°C, thus the reactions of the metals in effect take place under very mild conditions. This enables the synthesis of compounds where the ligand would not survive more vigorous reaction conditions. We have taken advantage of this situation to prepare bis-η-chlorobenzenemolybdenum in order to develop the chemistry of the bis-arenemolybdenum system with functionalised groups attached to the arene rings. Some of our preliminary findings are shown in Figure 9.

(e) Bis(σ-butyl-η-cyclopentadienyl)molybdenum

An approach to functionalised bend bis-η-cyclopentadienyl derivatives is illustrated by the co-condensation of atoms of molybdenum with spiro[4.4]-nona-1,3-diene giving good yields of the chiral compound 5; M = Mo [24].

TABLE 4

REPRESENTATIVE DATA FOR SOME BIS-η-ARENETUNGSTEN COMPOUNDS

Compound [a]	Colour	^1H NMR data [b]
$W(\eta\text{-}C_6H_3Me_3)_2$	dark green	5.25 (6, s, 2 C_6H_3); 7.97 (18, s, Me_6) [c]
$[W(\eta\text{-}C_6H_6)_2H]PF_6$	orange	4.22 (12, s, 2 C_6H_6); 8.93 (s, 1, WH) [d]
$[W(\eta\text{-}C_6H_5Me)_2H]PF_6$	orange	4.33 (10, c, 2 C_6H_5); 7.33 (6, s, Me_2); 9.20 (1, s, WH) [d]
$[W(\eta\text{-}C_6H_5F)_2H]PF_6$		3.50 (10, c, 2 C_6H_5); 10.55 (1, s, WH) [d]
$[W(\eta\text{-}C_6H_6)_2Cl]PF_6$	red-brown	4.48 (s, 2 C_6H_5) [d]
$[W(\eta\text{-}C_6H_6)_2Br]PF_6$	red-brown	4.37 (s, 2 C_6H_6) [d]
$[W(\eta\text{-}C_6H_5Me)_2Br]PF_6$	red	4.25, 5.70 (10, c, 2 C_6H_5); 7.30 (6, s, 2 Me) [d]
$[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(MeCN)_2]PF_6$	red	4.75—5.35 (5, c, Ph); 6.35 (1,5 lines, (J = 7 Hz) $H_{central}$); 7.35 (6, s, 2 MeCN); 7.65 (2, d, J = 4 Hz, H_{syn}); 8.1 (3, s, Me); 8.15 (s, d, J = 8 Hz), H_{anti}) [d]
$[W(\eta\text{-}C_6H_5Me)(\eta\text{-}C_3H_5)(\bar{\mu}\text{-}Cl)]_2$	violet	5.76—6.15 (6, c, Ph and $H_{central}$ of $\eta\text{-}C_3H_5$); 6.94, 6.95 (2, d, J = 5.7, 2 H_{syn}); 7.67, 7.69 (2, d, J = 5.5, 2 H_{anti}); 8.29 (s, 2, Me) [c]
$W(\eta\text{-}C_6H_5Me)(dmpe)H_2$	red	5.3—5.6 (5, c, Ph); 7.63, 7.69 (4, c, 2 CH_2); 8.11, 8.2, 8.4, 8.5, 16.8 (Me_4 and Me of toluene); 17.45 (2, t, J(P,H) = 99 Hz WH_2) [c]

[a] Satisfactory microanalyses and (where relevant) mass spectra were obtained for all compounds. [b] Given as: chemical shift (τ) (rel. intensity, multiplicity, J in Hz, assignment, etc. [c] In C_6D_6. [d] In $(CD_3)_2CO$.

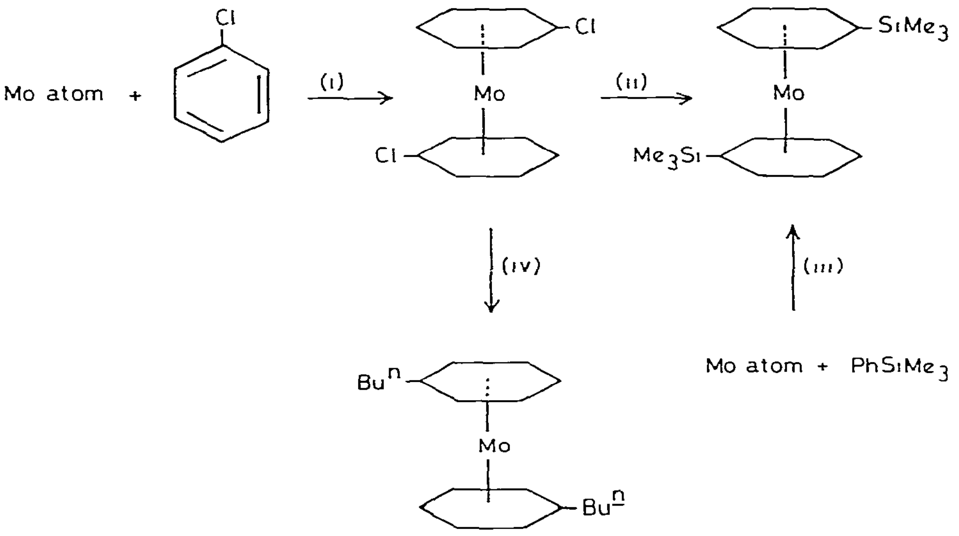
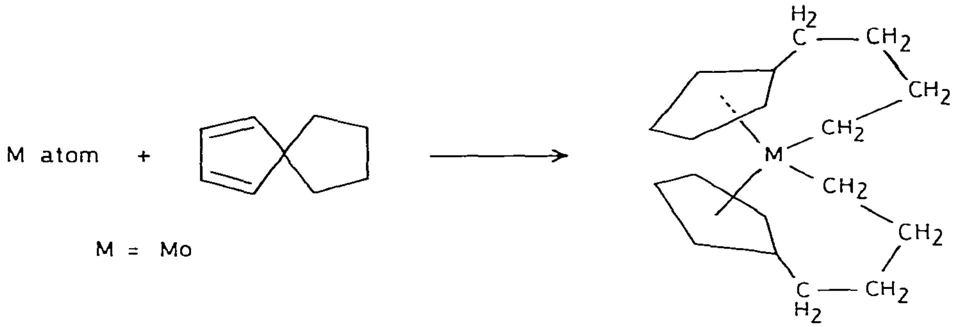


Fig. 9. Synthesis and reactions of 1,1'-disubstituted bis-η-arenemolybdenum derivatives [23]. (i) Molybdenum atoms (1.5 g) from a molten ingot (8 g at 2600°C) were co-condensed at —195°C with excess of chlorobenzene (80 cm^3) during 4 h, yield 2.0 g, ca. 50%. (ii) $LiBu^t$ in toluene at —78°C, then Me_3SiCl and warm to r.t., ca. 40%. (iii) $PhSiMe_3$ (25 cm^3) in THF (75 cm^3) and Mo atoms (1.5 g), yield 0.75 g, ca. 30%. (iv) Excess $LiBu^n$ at room temperature.

The ability of spiro[4.4]non-1,3-diene to add to metals giving σ-butyl-η-cyclopentadienyl derivatives has been previously and clearly demonstrated by Eilbracht [25].

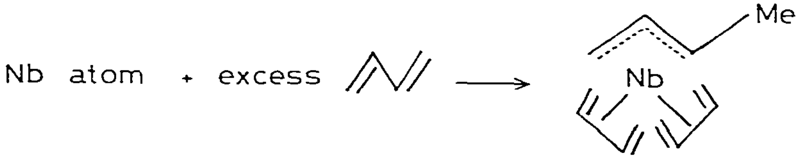


20 - 40%

5

(f) *η-Methylallylbis(η-butadiene)niobium*

Finally, Skell showed that co-condensation of butadiene with molybdenum or tungsten from filaments gave the tris-butadiene compounds $M(\eta\text{-}C_4H_6)_3$ [26]. These compounds can also be made in reasonable yields using molybdenum or tungsten atoms generated from the positive hearth *e*-gun furnace. Further, when niobium atoms are co-condensed into butadiene then one obtains a good yield of a purple, diamagnetic compound which the analytical and spectroscopic data show to be the compound 6 or a closely related isomer [23], (i.e. the butadienes may be up or down with respect to the η-methylallyl group).



6

In conclusion, I have presented a historical account of an exploratory synthetic study. We are still pursuing our initial objective concerning functionalisation of dinitrogen, and we are now investigating the chemistry of the new, highly reactive and high energy covalent compounds of transition metals of Groups IV, V and VI. This account illustrates the difficulty that arises in predicting the outcome of a research project and the freedom to follow up interesting observations which is a characteristic of fundamental academic research.

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