Preparation of Zerovalent Di(η-arene)titanium Compounds using Titanium Vapour

By **Martin T. Anthony, Malcolm L. H. Green,*** and **Dennis Young,** Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

An apparatus for generation of metal vapours and their reactions with potential ligand precursors are described. Co-condensation of titanium atoms with benzene, toluene, or mesitylene gives the compounds $[(H_6C_6)_2Ti]$, $[(MeC_6H_5)_2Ti]$, and $[(mes)_2Ti]$, respectively. Symmetrical sandwich structures are proposed for these compounds on the basis of ^1H n.m.r., i.r., mass, and photoelectron spectroscopy.

THE use of atoms of less volatile elements such as carbon [1] or the transition metals [2] as synthetic intermediates is a quite recent but rapidly developing technique. A normal practice is to co-condense the atoms produced from a high-temperature source with the desired ligand molecules at liquid-nitrogen temperatures. Clearly, more reactive molecules have enhanced opportunity to survive under these relatively clean and low-temperature conditions.

It has been our objective to isolate and study electron-rich transition-metal compounds, namely those which have an unusually high electron density about the metal and a correspondingly low ionisation potential for electrons primarily associated with the metal. Such compounds are likely to catalyse the reactions of hydrocarbons. The transition metals of Groups 4—6 are the more electropositive and they are more likely to give rise to electron-rich compounds than Group 8 transition metals. For these reasons we set out to isolate zerovalent compounds of the earlier transition metals, such as titanium, using metal-vapour synthesis techniques, as described below. A brief communication of this work has been made.[3]

---

[1] P. S. Skell, J. J. Havel, and M. J. McClinchey, *Accounts Chem. Res.*, 1973, **6**, 97.

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

[3] F. W. S. Benfield, M. L. H. Green, J. S. Ogden, and D. Young, *J.C.S. Chem. Comm.*, 1973, 866.

RESULTS

Chemical Studies.—The apparatus described in the Experimental section and discussed below was used. Massive titanium metal was evaporated at a temperature of *ca.* 1 750 °C *in vacuo* (*p ca.* 5×10^{-5} Torr) * at a rate of *ca.* 400 mg h^{-1} and the titanium atoms were co-condensed with excess of benzene vapour on the walls of the reaction vessel which were cooled to 77 K. The deep red co-condensate gave burgundy-red crystals which the data below show to be di(η-benzene)titanium, (I). Compound (I) is moderately soluble in light petroleum or tetramethylsilane and more soluble in benzene, toluene, and acetone. Pure solutions in light petroleum *in vacuo* or argon have been stable for *ca.* 1 year at room temperature and in daylight. However, concentrated solutions in benzene are prone to spontaneous decomposition giving a black residue, presumed to be the metal. We are unable to decide on the cause of decomposition but suspect that it arises from autocatalytic decomposition initiated by traces of impurities, arising in turn from oxidation. It was observed that when the original co-condensate was allowed to stand at room temperature in the presence of the excess of unchanged metal then the deep red colour was discharged within a few minutes. As would be expected, all solutions of (I) were instantly decomposed by oxygen. Surprisingly, benzene and light petroleum solutions of (I) are stable in the presence of water for at least several hours. Indeed, the compound could be chromatographed rapidly on an alumina column in benzene–light petroleum. Crystals of (I) are stable for several months at room temperature. They are volatile and can be sublimed *in vacuo* at 80 °C (10^{-3} Torr) with concomitant slow decomposition on the hot glass walls of the sublimation vessel.

TABLE 1

Analytical and spectroscopic data

Compound	$[(H_6C_6)_2Ti]$, (I)	$[(MeC_6H_5)_2Ti]$, (II)	$[(mes)_2Ti]$, (III)
Colour	Burgundy-red	Burgundy-red	Burgundy-red
Analysis[a]/%	Ti 24.1(23.5)		
^1H N.m.r. spectra[b]	4.96, **s** ($2\ C_6H_6$);[c] 4.87, **s** ($2\ C_6H_6$)[d]	5.11, *10*, **c** ($2\ C_6H_5$); 7.85, *6*, **s** ($CH_3C_6H_5$)[e]	5.31, *6*, **s** (2 *sym*-C_6H_3); 8.04, *18*, **s** [2 *sym*-$(CH_3)_3C_6H_3$][e]
Mass spectra[f]	204(20), $[(H_{12}C_{12})^{48}Ti]^+$; 126(43), $[(H_6C_6)Ti]^+$; 48(100), $^{48}Ti^+$	232(66), $[(H_{16}C_{14})^{48}Ti]^+$; 140(100), $[(H_8C_7)^{48}Ti]^+$; 138(40), $[(H_6C_7)^{48}Ti]^+$; 116(15), $[(H_{16}C_{14})^{48}Ti]^{2+}$; 70(3), $[(H_8C_7)^{48}Ti]^{2+}$; 48(29), $^{48}Ti^+$	
I.r. spectra/cm^{-1}	411vs, 452m, 946s, 979s	411.5s, 786m, 968m, 986m	421m
P.e. spectra[g]	5.5—6.0 (e_{2g})	5.4 (e_{2g}), 9.0 and 9.3 ($e_{1u} + e_{1g}$), 11.3, 12.9, and 13.8 (ligand)	

[a] The calculated value is given in parentheses. [b] Position in τ, *integration*, **multiplicity**, (assignment). [c] In C_6D_6. [d] In $(CD_3)_2CO$. [e] In $SiMe_4$. [f] *m/e* (Relative intensity), assignment. [g] Vertical ionisation energy in eV (assignment).

The mass spectrum of (I) was reproducible and showed a strong highest band at *m/e* 204 assignable to the parent ion, $[(H_{12}C_{12})^{48}Ti]^+$. Lower bands occurred at *m/e* 126 $\{[(H_6C_6){}^{48}Ti]^+\}$, 78 ($C_6H_6^+$), and 48 ($^{48}Ti^+$), suggesting the fragmentation pattern $[(H_{12}C_{12})Ti]^+ \longrightarrow [(H_6C_6)Ti]^+ \longrightarrow Ti^+$. The mass spectrum of the crude reaction mixture also showed traces of bands assignable to biphenyl. The ^1H n.m.r. spectrum showed only a sharp single band at τ 4.96 in C_6D_6 [τ 4.87 in $(CD_3)_2CO$]. This was in the region associated with η-bonded benzene ligands. The normality of the position and half-width of this band suggested (I) to be diamagnetic. The i.r. spectrum of (I) was determined at 20 K in an argon matrix. The data (Table 1) were entirely consistent with a symmetrical mononuclear sandwich structure. In particular, comparison of this spectrum with that[4] of the known sandwich molecule di(η-benzene)chromium in an argon matrix at 14 K showed a clear correspondence. Since an independent detailed study of the vibration spectrum of (I) is in progress[5] further discussion here is not warranted.

The photoelectron (p.e.) spectrum of di(η-toluene)titanium, (II), was reproducible and is shown in Figure 1. However, attempts to directly calibrate this spectrum by use of a mixture of noble gases, as described elsewhere,[6] were not totally successful. On introduction of a sample of noble gases, the sharp bands attributable to noble-gas ionisations appeared anomalously low and a small broad band between the first and second lowest-energy bands of the spectrum of (II) increased in intensity. This band was in the region normally associated with the first ionisation potential of free toluene. The most likely cause of such an effect is that the inert gases induced decomposition of (II) by a collisional process to produce free arene, while concomitant deposition of metallic titanium could have caused the calibration shift. The spectrum of (II) was therefore indirectly calibrated by first calibrating the bands relative to the position-shifted noble-gas bands; then, assuming the highest ionisation-energy band was equal in energy to the corresponding band in the spectra of $[(MeC_6H_5)_2Cr]$ and $[(MeC_6H_5)_2Mo]$,[7] the

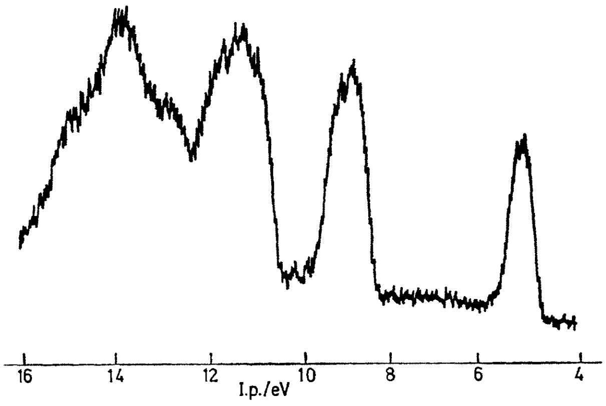

FIGURE 1 P.e. spectrum of $[(MeC_6H_5)_2Ti]$

---

* 1 Torr = (101 325/760) Pa, 1 eV ≈ 1.60×10^{-19} J.

[4] J. W. Boyd, J. M. Lavoie, and D. M. Gruen, *J. Chem. Phys.*, 1974, **60**, 4088.

[5] F. W. S. Benfield and A. J. Downs, to be submitted for publication.

[6] A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc.* (*B*), 1968, 22.

[7] S. Evans J. C. Green, S. E. Jackson, and B. Higginson, *J.C.S. Dalton*, 1974, 304.

spectrum of (II) was calibrated relative to this energy (Table 2). The basis for such a calibration was the observation that the three ionisation bands between 13.5 and 16.5 eV in the spectrum of [$(MeC_6H_5)_2Cr$] [7] were identical in energy to corresponding bands in the spectrum of [$(MeC_6H_5)_2Mo$] [7] (± 0.05 eV). This was not surprising as these bands were due to ionisations from molecular orbitals almost exclusively ligand in character and composition. The principal bands of the spectrum of toluene [8] are also given in Table 2 for comparison.

TABLE 2

Vertical ionisation energies (eV)

[$(MeC_6H_5)_2Ti$] [a]					
b	*c*	[$(MeC_6H_5)_2Cr$] [d]	[$(MeC_6H_5)_2Mo$] [d]	PhMe [e]	Assignment
		5.24	5.13		a_{1g}
7.2	5.4	6.19	6.03		e_{2g}
10.8	9.0	9.16	8.63	8.82	$e_{1u} + e_{1g}$ [f]
11.1	9.3	9.53	9.31		
13.1	11.3	11.1	11.2	11.2	Ligand
		11.6	11.8		Ligand
14.7	12.9				Ligand
15.6	13.8	13.8	13.8		Ligand
		14.7	14.7		Ligand
		16.2	16.2	16.4	Ligand

[a] Probe temperature 60 °C. [b] Calibrated with respect to position-shifted noble-gas bands. [c] Calibrated with respect to highest-energy band scanned being equal to corresponding bands in spectra of [$(MeC_6H_5)_2Cr$] and [$(MeC_6H_5)_2Mo$], *i.e.* 13.8 eV. [d] Ref. 7. [e] Ref. 8. [f] Mainly ligand in character.

Attempts to scan the p.e. spectrum of (I) were less successful. A probe temperature of 85 °C was required to give a spectrum, and at this temperature the compound decomposed sufficiently rapidly to prevent a full spectrum being scanned. However, the band attributable to the first ionisation potential (e_{2g}) was observed in the region 5.5—6.0 eV. It was approximately calibrated by a band at 4.98 eV due to ionisation of He atoms by radiation from a small amount of He^+ in the light source.[7]

Although the exact magnitudes of the ionisation energies of (I) and (II) were in doubt, the ordering of bands in the spectrum of (II) was the same as in di(η-arene)-chromium and -molybdenum compounds and was hence consistent with a sandwich structure. Furthermore, in the case of (II), splitting of the ($e_{1u} + e_{1g}$) band, analogous to those in [$(MeC_6H_5)_2Cr$] and [$(MeC_6H_5)_2Mo$],[7] was observed.

The Metal-vapour Synthesis Apparatus.—A vapour pressure of *ca.* 10^{-2}—10^{-1} Torr is convenient for use in metal-vapour synthesis techniques. The earlier transition metals require unusually high temperatures, including the highest (3 500 °C for W and 3 200 °C for Re), to achieve this vapour pressure. Crucible furnaces using electrical-resistance heating are restricted to below *ca.* 1 600—1 700 °C and evaporation from hot filaments of metal is limited to those metals which have a suitably high vapour pressure below their m.p.s. Therefore, we chose to use an electron-beam gun for the high-temperature source. The general design of the apparatus is shown in Figure 2. A basic feature of the apparatus is the rotation of the glass reaction vessel. This allows the metal-vapour source and the ligand inlet to be well separated which reduces contamination of the hot furnace by decomposed ligand vapours. Also, the furnace vapour may be directed upwards yet the whole vessel is continuously cooled in liquid nitrogen. A spiral-screw device may be placed inside the vessel and, on rotation of the flask, this causes liquid to be dispersed from the bottom of the flask to provide a renewable film over the reaction surface. Rotation also facilitates removal of solid products from the reaction vessel since they rapidly collect into the lowest point, namely a receiver attached to the exit.[9]

The inlet device enables introduction of gases and vapours, and especially liquids of low volatility or solutions of involatile substances. The adequate dispersion of the latter two phases is achieved by a rapidly rotating metal disc which causes the initially introduced liquid to break up into fine droplets. These are directed onto the wall of the reaction vessel and simultaneous rotation of the vessel sweeps the deposit into a continuous band around the reaction surface of the vessel. The water-cooled copper hearth provides the advantage that normally no crucible is required so that reaction with or contamination by crucible materials is avoided.

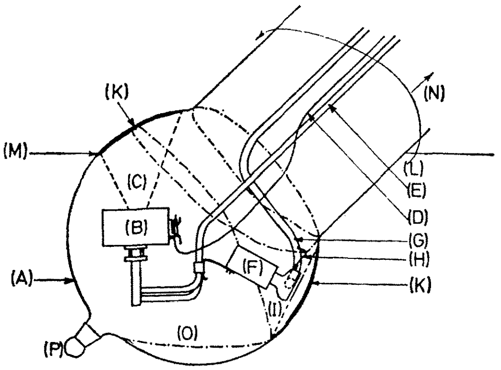

FIGURE 2 The reaction vessel: (A), glass reaction vessel; (B), electron-beam evaporation source EBS1 (supplied by G. V. Planer Ltd.), 0—1.4 kW input; (C), metal-vapour beam; (D), one of two insulated electrical leads to (B); (E), one of two water pipes to (B); (F), spinning dispersion device powered by 12 W electric motor;[9] (G), co-reactant vapour inlet;[9] (H), co-reactant solution inlet;[9] (I), beam of vapour and microdroplets of solution; (K), co-condensate layer; (L), rotation; (M), level of liquid-nitrogen coolant; (N), to stationary vacuum manifold containing vacuum lead throughs for (C)—(H), pressure gauges, and 3 in pumping system (connected to reaction vessel by rotating Wilson seal driven by adapted Büchi unit); (O), tubing placed on the flask wall along the line (— · — · —) allowing dispersion of liquid or solution co-reactant samples *via* Archimedes' screw action; and (P), product outlet (stoppered)

DISCUSSION

It is proposed that the compounds (I), (II), and [(mes)$_2$-Ti], (III; mes = η-mesitylene), have a symmetrical

---

[8] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy,' Interscience, 1970.

[9] See V. M. Akhmedov, M. T. Anthony, M. L. H. Green, and D. Young, *J.C.S. Dalton*, preceding paper.

sandwich structure analogous to that of di(η-arene)-chromium compounds.[10] The p.e. spectral data are consistent with an electron structure for compounds (I)—(III) in terms of the molecular-orbital (m.o.) configuration $(a_{1g})^2\,(a_{2u})^2\,(e_{1g})^4\,(e_{1u})^4\,(e_{2g})^4\,2(a_{1g})^0$, which is the same m.o. ordering as in the isostructural group of compounds [(η-arene)$_2$M] (M = V or Cr).[7] This is totally consistent with the observation that the isostructural series [(cht)(cp)M] (M = Ti, V, or Cr; cht = η-cycloheptatrienyl, cp = η-cyclopentadienyl) have the same ordering of electron energy levels.[7] The ^{1}H n.m.r. data suggest that compounds (I)—(III) are diamagnetic. In support, the p.e. spectral data are consistent with a diamagnetic electron configuration. Had the compounds been paramagnetic, the low ionisation-energy region would have been expected to contain additional bands analogous to the isoelectronic paramagnetic compound [(cp)$_2$Cr].[8] No such bands were observed within the limits of resolution of the p.e. spectrometer ($\pm$0.05 eV). The first ionisation potentials of (I) and (II), 5.5—6.0 and 5.4 eV respectively, show the compounds to be electron rich. Although the exact magnitudes of these energies are in doubt (*see above*), the values are consistent with observed trends. As would be expected, the ionisation energy from the e_2 orbital (7.19 eV) in the formally bivalent molecule [(cht)(cp)Cr] is higher than that (6.19 eV) from the e_{2g} orbital in the isoelectronic zerovalent molecule [(MeC$_6$H$_5$)$_2$Cr].[7] Similarly, the ionisation energy from the e_2 orbital (8.93 eV) of [(cht)(cp)Ti] [7] is higher than that (5.4 eV) from the e_{2g} orbital in the isoelectronic (II).

To conclude, the assigned structure and electron configuration classifies (I)—(III) as zerovalent d^4 titanium species, analogous to zerovalent d^6 chromium compounds, [(arene)$_2$Cr], and as electron-rich compounds.

EXPERIMENTAL

Titanium metal was obtained as a rod (12.5 mm diameter) of 99.6 % purity from Alfa Products Ltd. All solvents were distilled from calcium hydride immediately before use. All manipulations were made either *in vacuo* or under an atmosphere of argon (B.O.C., >99.99%). Mass spectra were determined on a Varian CH7 instrument, the samples being introduced with an inert-atmosphere-protected inlet. I.r. spectra were measured using an apparatus described elsewhere,[11] ^{1}H n.m.r. spectra on a J.E.O.L. C6OHL instrument at probe temperature, and p.e. spectra on a Perkin-Elmer P.S.16/18 instrument. The apparatus for metal-vapour synthesis will be described in detail elsewhere but the essential details are given in Figure 2. A discussion of various features of the apparatus is given in the text.

Di(η-benzene)titanium.—Massive titanium (*ca.* 20 g, as a 1 cm length of 12.5 mm diameter rod) was placed on the copper hearth of the furnace. The reaction vessel was positioned and the whole apparatus was evacuated to better than 5×10^{-5} Torr. The vessel was immersed in a liquid-nitrogen bath and rotated (60 revolutions min^{-1}). Benzene was introduced, as vapour, into the vessel at an average rate of 45 cm^3 h^{-1}. The electron gun was switched on and the accelerating voltage was slowly adjusted upwards until the power input was 300 W. It was found by trial and error that the rate of evaporation of titanium under these conditions was *ca.* 400 mg h^{-1} and that this rate gave optimum yields. With faster rates of metal evaporation more massive metal was formed in the product. Since di(η-benzene)titanium is decomposed at room temperature by the insoluble residues in the reaction mixture it was thought desirable to keep excess of titanium in the reaction mixture to a minimum.

In a typical run *ca.* 800 mg of titanium was co-condensed with *ca.* 90 cm^3 of benzene over 2 h. The co-condensate was allowed to warm to room temperature under argon and, following extraction from the flask using a stainless-steel capillary, the mixture was immediately filtered to remove insoluble matter. Normally the filtrate was then concentrated and addition of light petroleum resulted in separation of fine red crystals. These were washed with light petroleum and dried *in vacuo*. Yields were typically *ca.* 1 g, 30% based on titanium leaving the furnace. Di(η-toluene)- and di(η-mesitylene)-titanium were prepared in an essentially identical manner giving the same yield.

We thank the S.R.C. and the Petroleum Research Fund administered by the American Chemical Society for support.

[5/021 *Received, 6th January,* 1975]

---

[10] F. A. Cotton, W. A. Dollase, and J. S. Wood, *J. Amer. Chem. Soc.*, 1963, **85**, 1543.

[11] M. J. Rix, D.Phil. Thesis, Oxford, 1970.