Synthesis of Bis-π-benzene-titanium and -molybdenum using Metal Vapours

By FRANK W. S. BENFIELD, MALCOLM L. H. GREEN,* J. STEVEN OGDEN, and DENNIS YOUNG
(*Inorganic Chemistry Laboratory, South Parks Road, Oxford* OX1 3QR)

Summary Bis-π-benzene-titanium and -molybdenum are formed by co-condensation of benzene vapour with the metal vapours at 77K.

THE pioneering work of Timms demonstrated the synthesis of organo-transition metal compounds using metal vapours.[1] Following our interest in highly reactive compounds of the earlier transition metals we have built an apparatus for synthesis using metal vapours and, as many of the Group IV—VI transition metals are highly refractory, we choose electron beam evaporation methods as the source of metal vapour. A schematic diagram of the apparatus is shown in the Figure. Condensation of molybdenum vapour with benzene, toluene, or mesitylene gives the known bis-arenemolybdenum derivatives in *ca.* 10—20% yields.[2] For example, a molten bead of molybdenum (2600—2700°) weighing *ca.* 2·0 g, decreases in weight by 100 ± 20 mg in 1½ h and the vapour forms a dark brown cocondensate with toluene at 77 K. Sublimation of the less volatile component of the reaction mixture at 80°/10^{-3} mmHg gave green crystals (186 mg) which were shown to be bis-π-toluene-molybdenum by converting them into the derivative $[C_6H_5MeMo(\pi\text{-}C_3H_5)Cl]_2$[2] which was identified by its i.r. spectrum.

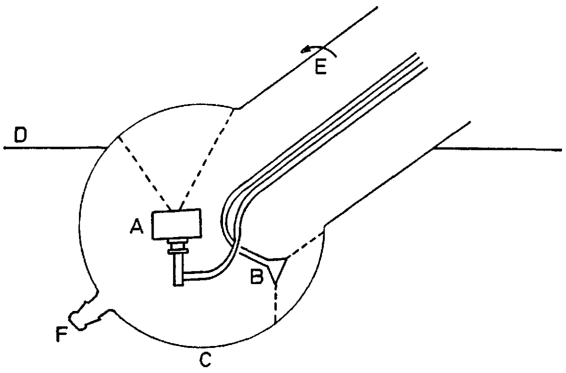

FIGURE. A. Electron beam evaporation source (Model EBS1), supplied by G. V. Planar Ltd., operates up to 7KV 200mA; water-cooled. B. Benzene vapour inlet. C. 7 l glass vessel, at *ca.* 10^{-5} Torr. D. Level of liquid nitrogen. E. Rotation at 20 r.p.m. of vessel about stationary furnace. F. Product outlet.

Similarly, titanium vapour and benzene react in a co-condensate to give extremely air-sensitive, red-orange crystals. Under optimal conditions 0·83 ± 0·08 g of titanium gave 0·797 g of $(C_6H_6)_2Ti$ in 5 h. The titanium compound is moderately soluble in light petroleum and acetone but more soluble in benzene. These solutions appear thermally unstable at room temperature and there is evidence that decomposition is auto-catalysed. Nonetheless, the compound may be chromatographed on an alumina column in benzene: light petroleum mixtures. The compound is readily volatile (80°/10^{-3} mmHg) with slight decomposition and the clean mass spectrum shows a highest parent ion peak of the correct isotope pattern for the ion $(C_6H_6)_2{}^{48}Ti^+$(*m/e* 204). The spectrum also shows bands corresponding to the ions $C_6H_2{}^{48}Ti^+$ (*m/e* 126), $C_6H_6^+$ (*m/e* 78), and $^{48}Ti^+$ (*m/e* 48), and the relative proportions of the ions $C_6H_6Ti^+$ and $C_6H_6^+$ vary so as to show that slow decomposition occurs at 80°. The ^1H n.m.r. spectrum shows a single sharp band assignable to typical arene π-C_6H_6 hydrogens [+2·29 rel. to Me_2CO in $(CD_3)_2CO$, and −2·23 rel. to C_6H_6 in C_6D_6]. The sharpness of the spectrum and the absence of shifts of the reference solvent bands with respect to external calibration suggests the titanium compound to be diamagnetic. This would be expected by analogy with the isoelectronic π-C_7H_7Ti-π-C_5H_5 which is also diamagnetic.[3]

When a sample of the compound was sublimed onto a cooled (20 K) caesium iodide window with an excess of argon, the i.r. spectrum of the deposit shows bands at *ca.* 680, 1040, and 1480 cm^{-1} due to molecular benzene, and in addition, four prominent bands at 411, 452, 946, and 979 cm^{-1} which by analogy with the i.r. spectra of $(C_6H_6)_2$-M, M=Cr or V[4] may be assigned to a similar $(C_6H_6)_2Ti$ molecule.[1]

Essentially the same i.r. absorptions were also observed after co-condensing titanium vapour with an excess of benzene directly onto a caesium iodide window at 77 K and warming the deposit to room temperature under vacuum to remove unchanged benzene. Preliminary isotopic labelling experiments using 1 : 1 mixtures of benzene and deuteriobenzene as the condensate with titanium vapour show the splitting pattern expected for a symmetrical sandwich structure.[5]

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