Synthesis of Zerovalent Bis-areneniobium Compounds Using Niobium Vapour

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Summary Co-condensation of niobium atoms from an electron gun furnace with benzene, toluene, or mesitylene gives good yields of the crystalline paramagnetic sandwich compounds [Nb(η-arene)$_2$].

We have recently developed an apparatus for synthesis using metal atoms which is convenient for use with the most refractory metals such as tungsten.[1] Here we report that niobium is readily volatised from an electron-gun furnace (*ca.* 3000 °C, *ca.* 10^{-5} Torr) and that co-condensation at 77 K of the niobium atoms with benzene, toluene or mesitylene gives the bis-arene compounds [Nb(C_6H_6)$_2$] (**1**), [Nb(MeC_6H_5)$_2$] (**2**), and [Nb($C_6H_3Me_3$)$_2$] (**3**),† respectively. In a typical experiment 0·75 g of niobium were condensed into 60 cm^3 of mesitylene during a 2 h run giving 1·0 g of pure compound after recrystallisation from light petroleum-ether (yield *ca.* 40%, based on niobium).

The compounds (**1**)—(**3**) form deep red-purple highly air-sensitive crystals. They are volatile and compound (**3**) may be readily sublimed at 80 °C and 10^{-3} Torr without decomposition. Compounds (**1**) and (**2**) decompose slowly during sublimation (80 °C) leaving a niobium mirror. The mass spectra of all three compounds show the expected peaks for the parent ions [^{93}Nb(arene)$_2$]$^+$. Compound (**1**), for example, also shows a peak at *m/e* 171 corresponding to the ion [$C_6H_6{}^{93}Nb^+$].

The e.s.r. spectra of compounds (**2**) and (**3**) dissolved in the parent arene show the expected ten line spectrum [(**2**); $<g> = 1{\cdot}992$, $A = 45{\cdot}9$ G; (**3**); $<g> = 2{\cdot}009$, $A = 77{\cdot}4$ G relative to diphenyl picrylhydrazyl as external standard] arising from coupling of the unpaired electron in these 17 electron paramagnetic compounds with the nuclear spin of the niobium (I ^{93}Nb = 9/2).

The He I photoelectron spectral data of the compounds (**1**)-(**3**) are given in the Table and the assignments therein are wholly consistent with a d^5 bis-areneniobium system with a $^2A_{1g}$ ground state. The $^1A_{1g}$ bands were very sharp and were relatively more intense in the corresponding He II spectra than the E_{2g} bands indicating non-bonding metal localised character for the a_{1g} M.O. The Table shows that the energy order of the ion states $^1A > {}^3E > {}^1E$ differs from that found for bis-arenevanadium compounds ($^3E > {}^1A > {}^1E$)[2] which may be interpreted as arising from a greater ligand field splitting for the second row metal.

Table

Ionisation energy data (eV) and assignment for bis-areneniobium compounds

	$^1A_{1g}$	$^3E_{2g}$	$^1E_{2g}$	av.E_{2g}[b]
(C_6H_6)$_2$Nb[a]	5·57	6·17	6·67	6·30
(C_6H_5Me)$_2$Nb	5·49	6·01	6·62	6·16
($C_6H_3Me_3$)$_2$Nb	5·18	5·59	6·15	5·73

[a] The spectrum also shows bands arising from free benzene.
[b] Average weighted by degeneracy of states.

A sample of compound (**1**) sublimed on to a cooled (8 K) caesium iodide window with an excess of argon gives an i.r. spectrum showing prominent bands at 350, 412, 732, 750, 950, and 988 cm^{-1} which by analogy with the i.r. spectrum of [(C_6H_6)$_2$Mo] may be assigned to a similar [(C_6H_6)$_2$Nb] sandwich molecule. Similarly the i.r. spectrum of the matrix isolated compound (**3**) closely resembles that of [($C_6H_3Me_3$)$_2$W]. Previously a matrix isolated i.r. study has given evidence for the existence of bis-benzeneniobium obtained from reaction of sputtered niobium atoms with benzene in an argon matrix at 30 K.[3]

The above studies emphasise that vapour produced from suitable e-gun furnaces are entirely convenient for synthesis even for very reactive and fragile molecules.

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† Compound (**3**) gave satisfactory microanalysis.

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