Preparation of Diarenemetal Complexes by Potassium Atom Reduction

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Summary Diarenemetal complexes, including bistoluenetitanium and bis(1-methylnaphthalene)molybdenum, are prepared by condensing potassium atoms into solutions containing metal halides and arenes in tetrahydrofuran at -100 °C.

KNOWN methods of preparing diarenemetal sandwich complexes are broadly of two types: direct reaction of metal atoms with arenes at low temperature[1,2] or reduction of metal salts in the presence of arene[3] or cyclohexadiene[4] ligands. The atom method permits formation of the complexes under exceptionally mild conditions so that a wider range of complexes can be made by this procedure than by existing reductive methods. We now report a new reductive synthesis which can be carried out under conditions as mild as those used in the direct metal atom synthesis.

Potassium atoms are condensed at -100 °C into a well stirred solution of a metal halide (5 mmol) and an arene (200 mmol) in tetrahydrofuran (THF) (3 mol) as solvent. The reaction is carried out in a rotating 2000 ml flask[5] under reduced pressure ($<10^{-2}$ Torr) and the potassium is evaporated at a rate of *ca.* 1 mmol min^{-1} from a stainless steel crucible heated electrically to 300 °C. Halide starting materials with sufficient solubility at -100 °C may be pre-formed THF adducts, *e.g.* $VCl_3\cdot 3THF$, or pure halides, *e.g.* $MoCl_5$. The extent of reduction of the dissolved metal halide by condensing potassium atoms is indicated by the colour changes which occur in the solution. We have determined experimentally the colour of each solution which gives an optimum yield of the desired product and the condensation is continued until the 'end-point' colour is very intense (see Table). The solution is then evaporated and the residue extracted with fresh THF and filtered.

TABLE

Starting materials	Initial solution colour	'End-point' colour	Product isolated	Approximate yield[e]/%
$CrCl_3 \cdot 3THF$ + 1-Methylnaphthalene	Purple	Red-brown	$Cr(\eta^6\text{-}C_{10}H_7Me)_2$[a]	40
$MoCl_5$ + Toluene	Red-brown	Red-brown[b]	$Mo(\eta^6\text{-}PhMe)_2$	40
$MoCl_5$ + 1-Methylnaphthalene	Red-brown	Red-brown[b]	$Mo(\eta^6\text{-}C_{10}H_7Me)_2$[a]	45
$VCl_3 \cdot 3THF$ + Toluene	Pink	Black[c]	$V(\eta^6\text{-}PhMe)_2$	30
$VCl_3 \cdot 3THF$ + 1-Methylnaphthalene	Pink	Black[c]	$V(\eta^6\text{-}C_{10}H_7Me)_2$[a]	35
$TiCl_3 \cdot 3THF$ + Toluene	Blue	Brown-black[c]	$Ti(\eta^6\text{-}PhMe)_2$[d]	20
$TiCl_3 \cdot 3THF$ + Mesitylene	Blue	Brown-black[c]	$Ti(\eta^6\text{-}C_6H_3Me_3)_2$[d]	15

[a] See refs. 6 and 7. [b] Several intermediate colours were observed. [c] Excess potassium atoms used. [d] See ref. 2. [e] Yield based on the transition metal halide.

In most cases, the diarenemetal product can be isolated by evaporating this filtrate, extracting with pentane, and crystallizing. However, preparation of diarenetitanium compounds requires the use of an excess of potassium. The THF extract then appears to contain the complexed titanium in a very low oxidation state, but this can be converted into the desired zerovalent state by passing the solution through a short column of degassed chromatographic grade alumina.

The products have been identified by mass spectrometry, ^1H n.m.r. or e.s.r. spectroscopy, chemical analysis, and by comparison with authentic samples made by the direct metal atom method. The diarenetitanium[2] and bis(1-methylnaphthalene)metal[6,7] complexes prepared in this work have only previously been isolated using the transition metal atoms as reagents. The potassium atom method is experimentally simpler and more readily scaled-up than the direct atom method. This is because potassium is much more volatile than transition metals and its evaporation is accompanied by liberation of relatively tiny amounts of radiant heat compared with the heat radiated when transition metals are vaporised.

We have not attempted to determine the mechanism of reduction by potassium atoms although it seems likely that the arenes are activated by conversion into radical anions. Sodium can be used in place of potassium but the work-up of products is more difficult.

We thank the S.R.C. for research support and for a studentship to one of us (P.N.H.).

(*Received*, 26*th April* 1978; *Com.* 438.)

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