Reductive Preparation of Bis(arene)metal Complexes from Metal Halides in Solution using Potassium Atoms†

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Some known bis(arene) complexes of zerovalent Ti, V, Cr, and Mo have been synthesised in a new way by stepwise reduction of solutions of the metal chlorides in tetrahydrofuran and arene, using K atoms condensed into the solutions at −110 °C under vacuum in a rotary reactor. The extent of reduction was followed by observing colour changes in the solutions. With Ti and V, the initial products were anionic forms of the bis(arene) complexes, which were oxidised to give the zerovalent compounds. The method is a useful way of making 0.1—1 g samples of some bis(arene)titanium complexes and bis(naphthalene) complexes of V, Cr, and Mo which are otherwise accessible only by using the transition-metal atoms as reagents.

Many organo-transition metal complexes are conveniently made by reduction of metal halides in the presence of organic ligands. A wide range of reducing agents is available, among the most powerful of which are the alkali metals. These are used as free metals, amalgams, or intercalates in various solvents which may enhance or moderate the reducing effect.[1–4] We are studying the use of alkali metal atoms as reducing agents in the synthesis of organo-transition metal complexes and herein we report our work on the preparation of bis(arene)metal complexes. Preliminary accounts of this and related work with alkali metal atoms have been published elsewhere.[5,6]

Results and Discussion

The procedure for preparing bis(arene)metal complexes was broadly as follows. A metal chloride or its preformed tetrahydrofuran (thf) adduct was dissolved in a mixture of thf and an arene. Potassium atoms were condensed under vacuum into the solution cooled to −110 °C in a rotary metal-atom reactor. Reduction of the halide occurred stepwise, and the solution changed colour several times before reduction was complete and the product could be isolated. The results are summarised in the Table.

The best yield of titanium and vanadium compounds was obtained if an excess of potassium was used for the reduction. We believe the primary product to be a reduced, anionic form of the bis(arene)metal, which had to be oxidised to give the zerovalent compound. In the preparation of $[Ti(C_6H_5Me)_2]$, $[Ti(C_6H_3Me_3)_2]$, and $[V(C_{10}H_7Me)_2]$, this oxidation was conveniently achieved using chromatographic alumina, the surface $^-$OH groups of which act as the oxidant.

$$K^+[M(arene)_2]^- + {>}Al\text{–}OH \longrightarrow [M(arene)_2] + {>}Al\text{–}OK + \tfrac{1}{2}H_2$$

Henrici-Olivé and Olivé[7] demonstrated electrochemically that $17e^-$ $[V(C_{10}H_8)_2]$ can be reversibly reduced to $[V(C_{10}H_8)_2]^-$. We studied the titanium system and found that red, pentane-soluble $[Ti(C_6H_5Me)_2]$ was reduced by an equimolar amount of K atoms at −110 °C in thf solution to a green, thf-soluble species which we believe to be $[Ti(C_6H_5Me)_2]^-$. This species could be reconverted into $[Ti(C_6H_5Me)_2]$ using alumina or propan-2-ol, although an excess of propan-2-ol caused destructive oxidation of the zerovalent compound.

An excess of K was also used in the preparation of $[V(C_6H_5Me)_2]$, but in this case when the resulting yellow-green solution was warmed to 0 °C, it suddenly gave the desired product in solution without addition of an oxidising agent. The process is not fully understood, but it seems possible that reduction of V^{III} by K gave a sparingly soluble intermediate, of which part was reduced to V^{-I} by an excess of K atoms and part, in suspension at low temperatures, became soluble enough to react with V^{-I} to give V^0 on warming.

In the preparation of Cr and Mo complexes an excess of K atoms seemed to decompose the product, so a roughly stoicheiometric amount of K was used (*i.e. ca.* 3 mol K with $CrCl_3$ or 5 mol K with $MoCl_5$). After trial runs using more or less K, it was found easiest to add K until the solution assumed the particular colour which corresponded to the best yield of product (the 'end-point' colour in the Table). The process was like titrating with K atoms. The yield of $[Cr(C_{10}H_8)_2]$ seemed to be almost independent of the molar ratio of Cr to $C_{10}H_8$ in the initial solution over the range 1 : 2.5 to 1 : 20. As an excess of naphthalene was difficult to separate from the product, the lowest effective Cr : $C_{10}H_8$ ratio was used. Reducing the amount of ligand in most of the other preparations caused more significant reductions in yields.

We failed to prepare $[Cr(C_6H_5Me)_2]$ by K atom reduction. The problem seemed to be the formation of an insoluble intermediate reduction product which could not be effectively reduced further by K {see foregoing comments on $[V(C_6H_5Me)_2]$}. Even in the preparation of $[Ti(C_6H_5Me)_2]$, we found that the formation of insoluble intermediates could be troublesome if the initial concentration of Ti in thf was above 0.05 mol dm^{-3}. Using a greater concentration of the more soluble TiI_4 in place of $TiCl_3$, we observed the precipitation of a brown solid during the reduction with K atoms and the final yield of $[Ti(C_6H_5Me)_2]$ was very poor; at lower concentrations, TiI_4 was a satisfactory replacement for $TiCl_3$ in the preparation. We also failed to make either bis(arene)-niobium or -tungsten complexes using K atoms, despite trying a variety of starting materials and amounts of added K. The problem in these cases did not seem to be insoluble intermediates, but perhaps soluble cluster intermediates, resistant to complete reduction under the experimental conditions, were formed.

We considered using other ethers or amines as solvents for this work, but it seems that thf has a number of advantages which make it especially suitable. First, it has a low vapour pressure at its melting point (−111 °C) so that a vacuum could be maintained over cold thf sufficient to allow evaporation and condensation of K atoms, but it is volatile enough to be pumped away quickly below room temperature. Secondly, it is a fairly good solvent for metal halides, for many of the reaction intermediates, and for the products in zerovalent or anionic form. Thirdly, potassium is moderately soluble in thf

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† *Non-S.I. unit employed:* 1 G = 10^{-4} T.

Table. Preparation of bis(arene) metal complexes

Starting materials	Amount of K atoms	' End-point ' colour	Product isolated	Typical yield (%)
$[TiCl_3(thf)_3]$ + toluene	Excess	Green-black	$[Ti(C_6H_5Me)_2]$	19
$[TiCl_3(thf)_3]$ + mesitylene	Excess	Black	$[Ti(C_6H_3Me_3)_2]$	15
$[VCl_3(thf)_3]$ + toluene	Excess	Green-black	$[V(C_6H_5Me)_2]$	15
$[VCl_3(thf)_3]$ + 1-methylnaphthalene	Excess	Black	$[V(C_{10}H_7Me)_2]$	25
$[CrCl_3(thf)_3]$ + naphthalene	Stoicheiometric	Red-brown	$[Cr(C_{10}H_8)_2]$	36
$[CrCl_3(thf)_3]$ + 1-methylnaphthalene	Stoicheiometric	Red-brown	$[Cr(C_{10}H_7Me)_2]$	40
$MoCl_5$ + toluene	Stoicheiometric	Muddy brown	$[Mo(C_6H_5Me)_2]$	10
$MoCl_5$ + 1-methylnaphthalene	Stoicheiometric	Black	$[Mo(C_{10}H_7Me)_2]$	42

at low temperatures to give blue solutions, believed by Dainton *et al.*[8] to contain collodial metal and ion–electron pairs; they measured the solubility of K in thf at -78 °C as 30 mg dm^{-3}. We condensed K atoms into pure thf at -110 °C and prepared clear blue solutions containing 200—300 mg dm^{-3}, although these solutions were not stable and slowly deposited metal.

The yields of products we obtained were much higher when naphthalene or 1-methylnaphthalene was used as ligand than with toluene or mesitylene. This is in spite of the greater experimental difficulties in purifying the naphthalene products; the result must be a reflection of the greater ease of formation of a radical anion from the naphthalenes than from toluene or mesitylene.

We have experimented with a simpler form of apparatus, in which potassium atoms were directed downwards into a magnetically stirred, cold solution of the metal halide in thf–arene under vacuum. The main problem with this apparatus was that it was not as easy to observe the progress of the reduction as in the rotary flask apparatus. We also suspect that the mixing of K atoms into the bulk of the solution was less efficient than in the rotary apparatus, as yields of products were poorer.

In conclusion, our method of making bis(arene)metal complexes by K atom reduction has most obvious practical importance for bis(arene)titanium complexes and bis(naphthalene) complexes of V, Cr, and Mo which otherwise have to be made by using the transition metal atoms.[9,10] A less sophisticated vacuum and evaporation system is required to generate K atoms at 250 °C than Mo atoms at 2 500 °C. However, our procedure is also experimentally demanding because fairly dilute solutions of very air-sensitive materials have to be handled.

Experimental

The general form of our rotary apparatus for reaction of metal atoms with cold solutions has been described elsewhere.[11] The reaction vessel in this work was a 2-dm^3 Pyrex flask with a B45 socket neck joint and a 4-mm O-ring stopcock joined at 90 °C to the neck to allow admission of inert gas.

Potassium was evaporated inside the flask under vacuum from a 5-cm^3 quartz or stainless steel crucible supported within a resistively heated coil of 1-mm Mo wire attached to water-cooled electrodes; a power input of 30 W gave an evaporation rate of 1 mmol min^{-1} (40 mg min^{-1}) which was adequate for most experiments. The crucible was charged with potassium in an auxiliary device which allowed the metal to be melted and poured into the crucible under vacuum (10^{-3} Pa). When the filled crucible was cold, it was transferred quickly in air to the evaporation coil immediately before it was to be used. In this way, the metal did not bump out of the crucible during the evaporation.

Adducts of $TiCl_3$, VCl_3, and $CrCl_3$ with thf were made by Soxhlet extraction of the solid trichlorides with refluxing thf. All solvents used in the preparation of the bis(arene) complexes were rigorously dried and carefully degassed before use.

Typically, the metal chloride or its thf adduct was dissolved in 150—200 cm^3 of a mixture of thf and the arene (10—15% by volume) at room temperature. The solution was transferred to the reaction flask, which was then attached to the B45 cone on the rotary system and was cooled on a bath at -110 °C and evacuated. The flask was rotated at about 80 revolutions min^{-1} in the cooling bath until the pressure in the flask was $<10^{-5}$ Pa, and then heating and evaporation of the metal were commenced. Evaporation initially caused the development of a blue colouration on parts of the flask not continuously wetted by the rotating solution. As the evaporation progressed, these poorly wetted parts became black and the bulk of the solution changed colour. Liquid nitrogen was added periodically to the light petroleum bath to keep it cold enough to prevent any pressure rise within the flask. Evaporation of K was stopped when an excess had been added, or when the colour in the flask indicated that reaction was complete (see Table).

Details for isolating the individual products are discussed below. The most general problem was filtration of solutions containing suspended K. It was frequently necessary to evaporate such solutions to dryness to coagulate the metal and then to redissolve the residue in thf before filtering.

Proton n.m.r. spectra were recorded using a JEOL PS100 spectrometer, e.s.r. spectra using a Varian V-4500 spectrometer, and mass spectra with an A.E.I. MS902 spectrometer. Analysis for C and H were carried out by the School of Chemistry Microanalytical Laboratory.

Preparation of Bis(arene)titanium Complexes.—(a) *Toluene.* $[TiCl_3(thf)_3]$ (2.5 g, 6.75 mmol) was dissolved in thf (180 cm^3) and toluene (40 cm^3) and the pale blue solution was treated with an excess (2.0 g, 50 mmol) of potassium vapour condensed into the solution at -110 °C in 50 min. As K atoms condensed into it, the solution turned pale green, then a cloudy pale brown, and finally a dark, yellowish green solution containing suspended metal was obtained. The flask was rotated for 15 min at -100 °C after the metal had ceased evaporating. The solvent was then pumped off and the residual black solid taken up in thf (150 cm^3). This solution/suspension was filtered, first through glass wool and then on to a 8-cm column of alumina (B.D.H., Brockmann Activity II, degassed for 12 h at 100 °C under high vacuum before use) above a frit. The solution changed in contact with the alumina and a pink solution passed through. The thf was removed under vacuum and the red residue recrystallized from pentane to give $[Ti(C_6H_5Me)_2]$ (300 mg, 1.28 mmol, 19% yield) (Found: C, 73.5; H, 6.9. $C_{14}H_{16}Ti$ requires C, 72.4; H, 6.9%); ^{1}H n.m.r. (C_6D_6) δ 4.85 (m) and 2.03 (s) (lit.,[9] δ 4.89 and 2.15).

(b) *Mesitylene.* The experiment was carried out as with toluene but using [$TiCl_3(thf)_3$] (2.5 g, 6.75 mmol) dissolved in thf (120 cm^3) and mesitylene (40 cm^3). Addition of K atoms caused the pale blue solution to become intensely purple and then almost black as an excess of K atoms (50 mmol) was added. The solution was evaporated to dryness and then the contents of the flask were extracted with thf (75 cm^3 and 5 × 20 cm^3) until the extract ceased to be an intense green-brown. The solution became pink on passing through an alumina column. The solvent was removed and the residue recrystallised from pentane to give dark red needles of [$Ti(C_6H_3Me_3)_2$] (280 mg, 1.01 mmol, 15%) with properties (n.m.r., mass spectra) as described in ref. 9.

(c) *Ditoluenetitanium + potassium atoms.* [$Ti(C_6H_5Me)_2$] (520 mg, 2.25 mmol) was dissolved in thf (50 cm^3) and the solution was put in a 500 cm^3 reaction flask on the rotary system. Liquid K (117 mg, 3.0 mmol) was evaporated during 30 min. An estimated 75% of the K atoms condensed into the solution at −110 °C, the remainder condensing on the unwetted portions of the flask and on the water-cooled electrodes. During condensation of K atoms, the solution turned brown and finally clear green. The thf was pumped away and the green residue in the flask was found to be insoluble in pentane. The solid was redissolved and the solution removed from the reaction flask. It was found possible to convert the green solution into red ditoluenetitanium either by passing it through an alumina column or by dropwise addition of propan-2-ol; an excess of propan-2-ol caused decomposition.

Preparation of Bis(arene)vanadium Complexes.—(a) *Toluene.* [$VCl_3(thf)_3$] (1.5 g, 4.0 mmol) was dissolved in thf (175 cm^3) and toluene (25 cm^3) to give a pink-red solution. This became green and finally yellowish green with black metal in suspension as K atoms (1.5 g, 38 mmol) were condensed into the solution at −110 °C. The contents of the flask were then stirred under argon at −80 °C for 30 min and allowed to warm slowly to room temperature. At about −30 °C, the solution turned from yellow-green to a grey metallic suspension, but above 0 °C a reddish brown colour developed which persisted. The solution was filtered through a short alumina column to give a clear, brick-red solution. Evaporation, and recrystallisation of the residue from pentane gave fine black needles of [$V(C_6H_5Me)_2$] (140 mg, 0.6 mmol, 15%) (Found: C, 72.3; H, 7.0. $C_{14}H_{16}V$ requires C, 71.5; H, 6.8%); e.s.r., 8-line spectrum, $g = 1.997$, $A = 60.1$ G.[12]

(b) 1-*Methylnaphthalene.* [$VCl_3(thf)_3$] (2.5 g, 6.7 mmol) was dissolved in thf (150 cm^3) and 1-methylnaphthalene (20 cm^3) and the solution was reduced with potassium atoms at −110 °C through purple and green stages until the liquid appeared black and *ca.* 1.8 g (46 mmol) of K had been added. The flask was warmed to −10 °C with pumping to remove thf. The oily black residue in the flask was redissolved in thf (150 cm^3) to give a yellowish green solution; this was transferred to a clean flask where it was shaken with degassed, chromatographic alumina (20 g). The solution became red. After extraction and filtration, the red solution was evaporated to dryness under high vacuum using short-path distillation to remove the 1-methylnaphthalene. Recrystallization from pentane gave black needles of [$V(C_{10}H_7Me)_2$] (560 mg, 1.67 mmol, 25%) (Found: C, 78.2; H, 5.8. $C_{22}H_{20}V$ requires C, 78.8; H, 5.95%); m/z 335 ($VC_{22}H_{20}^+$, 4%), 193 ($VC_{11}H_{10}^+$, 2%), and 142 ($C_{11}H_{10}^+$, 100%); e.s.r., 8-line spectrum, $g = 1.995$, $A = 59.3$ G.

Preparation of Bis(arene)chromium Complexes.—(a) *Naphthalene.* [$CrCl_3(thf)_3$], (2.0 g, 5.3 mmol) was dissolved in thf (150 cm^3) containing naphthalene (2.0 g, 14.1 mmol). Potassium atoms were condensed into the solution at −110 °C; the colour changed from mauve to yellow-brown to green to red-brown and when this last colour was very intense, evaporation of K was stopped and the solution was stirred at −80 °C under argon for 15 min. Tetrahydrofuran was then pumped off on the rotary system as the flask warmed to room temperature; the excess of naphthalene was removed by vacuum sublimation at 30 °C with a cold finger inserted into the flask. The contents of the flask were extracted with thf and the extract was filtered, evaporated to dryness, and recrystallized from toluene to give dark needles of [$Cr(C_{10}H_8)_2$] (620 mg, 2.02 mmol, 36%); ^1H n.m.r. δ 4.34, 5.24, and 6.92 (as ref. 10).

(b) 1-*Methylnaphthalene.* [$CrCl_3(thf)_3$] (2.0 g, 5.3 mmol) was dissolved in thf (140 cm^3) and 1-methylnaphthalene (25 cm^3), and K atoms were condensed into this solution at −110 °C. The solution changed colour from mauve to yellow-brown to brown to green to a red-brown end-point. Then the solution was allowed to rotate in the flask at −80 °C under argon for 15 min before thf was pumped off as the flask warmed to room temperature; 1-methylnaphthalene was removed by short-path distillation under high vacuum. The black residue was extracted with thf; the solution was filtered, then evaporated, and the product recrystallized from pentane to give black needles of [$Cr(C_{10}H_7Me)_2$] (710 mg, 2.11 mmol, 40%) (Found: C, 78.6; H, 6.2. $C_{22}H_{20}Cr$ requires C, 78.55; H, 5.95%); ^1H n.m.r., five multiplets as ref. 10, area ratio of CH_3 multiplets at δ 2.04 and 2.34, 2.4 : 1.

Preparation of Bis(arene)molybdenum Complexes.—$MoCl_5$ (Koch-Light) was a convenient starting material for the preparations but it slowly attacked thf at room temperature and solutions had to be used immediately after they were made.

(a) 1-*Methylnaphthalene.* $MoCl_5$ (1.5 g, 5.5 mmol) was dissolved in thf (140 cm^3) and 1-methylnaphthalene (20 cm^3), and K atoms were condensed into the solution at −110 °C. The colour changed from red-brown to green to red-brown to black; evaporation was stopped when this black colour appeared. The flask was rotated for 15 min at −80 °C under argon before thf and 1-methylnaphthalene were pumped off, the latter under high vacuum on to a cold finger. The residual flaky black solid was extracted with thf (3 × 100 cm^3), and the solution filtered and evaporated. The new residue was recrystallized from pentane to give black needles of [$Mo(C_{10}H_7Me)_2$] (880 mg, 2.32 mmol, 42%) (Found: C, 70.2; H, 5.4. $C_{22}H_{20}Mo$ requires C, 69.45; H, 5.25%); ^1H n.m.r., complex multiplets centred at δ 6.7 (7 H), 4.8 (7 H), and 1.8 (6 H) {the spectrum was the same as that of [$Mo(C_{10}H_7Me)_2$] made from Mo atoms and $C_{10}H_7Me$ [10]}.

(b) *Toluene.* $MoCl_5$ (1.1 g, 4.03 mmol) was dissolved in thf (130 cm^3) and toluene (30 cm^3), and the orange-brown solution was reduced with K atoms at −110 °C until the colour had changed through green to blue to a cloudy brown. Evaporation of K was stopped and the solution was rotated in the flask at −80 °C for a few minutes before the solvent was pumped away as the flask warmed to room temperature. The grey-black residue was extracted with thf (2 × 100 cm^3); the solution was filtered and evaporated and the product recrystallized from pentane to give green [$Mo(C_6H_5Me)_2$] (114 mg, 0.41 mmol, 10%); ^1H n.m.r. δ 4.60 (10 H) and 1.85 (6 H).[13]

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References

1 R. Hammer, H. F. Klein, P. Friedrich, and G. Huttner, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 485.

2 J. E. Ellis, C. P. Parnell, and G. P. Hagen, *J. Am. Chem. Soc.*, 1978, **100**, 3605.

3 G. K. Barker, A. M. Galas, M. Green, J. A. K. Howard, F. G. A. Stone, T. W. Turney, A. J. Welch, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1977, 256.

4 K. A. Jensen, B. Nygaard, G. Elisson, and P. H. Nielsen, *Acta Chem. Scand.*, 1965, **19**, 768.

5 P. N. Hawker, E. P. Kündig, and P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 1978, 730.

6 M. Chang, P. L. Timms, and R. B. King, *J. Organomet. Chem.*, 1980, **199**, C3.

7 G. Henrici-Olivé and S. Olivé, *J. Am. Chem. Soc.*, 1970, **92**, 4831.

8 F. S. Dainton, D. M. Wiles, and A. N. Wright, *Trans. Faraday Soc.*, 1960, 4283.

9 M. T. Anthony, M. L. H. Green, and D. Young, *J. Chem. Soc., Dalton Trans.*, 1975, 1412.

10 Ch. Elschenbroich and R. Mockel, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 870; E. P. Kündig and P. L. Timms, *J. Chem. Soc., Chem. Commun.*, 1977, 912; E. P. Kündig and P. L. Timms, *J. Chem. Soc., Dalton Trans.*, 1980, 991.

11 'Cryochemistry,' eds. M. Moskovits and G. A. Ozin, Wiley, New York, 1976, p. 129.

12 G. Henrici-Olivé and S. Olivé, *Z. Phys. Chem.*, 1967, **56**, 223.

13 M. L. H. Green and W. E. Silverthorn, *J. Chem. Soc., Dalton Trans.*, 1973, 301.

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