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PHENYLS AND ALKYLS OF THE GROUP IIIA METALS

F. A. HART, A. G. MASSEY AND MOHAN SINGH SARAN*
Department of Chemistry, Queen Mary College, Mile End, London E.1. (Great Britain)

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SUMMARY

Reaction of scandium, yttrium, lanthanum or praseodymium chlorides with phenyl- or methyllithium gives air-sensitive solid products. Simple reactions, infrared spectra and analyses indicate that the phenyls are $Sc(C_6H_5)_3$, $Y(C_6H_5)_3$, $LiLa(C_6H_5)_4$ and $LiPr(C_6H_5)_4$; the constitution of the methyls is uncertain. $Sc(C{\equiv}C{-}C_6H_5)_3$ is also described.

INTRODUCTION

A consideration of the distribution of known aryl and alkyl compounds among the elements of the Periodic Table led us to conclude that the Group IIIA metals Sc, Y, La–Lu and Ac–Lw might possibly form isolable phenyls and alkyls. Any such compounds would be of some interest because their rather fundamental character might provide new insight into the principles of bonding and reactivity in organometallic chemistry. In addition, there might be synthetic and catalytic applications.

We now wish to report the isolation of a number of Group IIIA organometallics (a preliminary communication of part of this work has already appeared[1]).

We first discuss previous reports of oganometallic compounds of Groups IA, IIA and IIIA. It is well known[2] that the alkali metals readily form reactive alkyls and aryls, MR, which except for those of lithium are ionic in nature. Organometallic compounds of all the metals Be, Mg, Ca, Sr, Ba are also known but vary in accessibility from $BeMe_2$ and $BePh_2$, easily obtained as unsolvated solids, to the Ca, Sr and Ba aryls and alkyls known chiefly in the form MRX (X = halogen) in solution. The report[3] of the isolation of MMe_2 (M = Ca, Sr, Ba) is apparently in error[4]; nor could it be repeated in these laboratories[5].

Boron and aluminium form easily isolable, though reactive, phenyls and alkyls. However, scandium phenyls and alkyls were unknown. In this respect, scandium contrasted suggestively with its neighbouring elements, titanium and calcium. It might be considered that tripositive scandium of ionic radius 0.68 Å is unlikely to be sufficiently strongly polarising to induce an appreciable covalent contribution to the bonding as can Al^{3+} or Ti^{4+} while its ionisation potentials are yet too high for ionic

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* Present address: Department of Chemistry, University of Georgia, Athens, Georgia, U.S.A.

organometallic compounds of the alkali metal type to be feasible. Our present experimental data refute this view. It is rather difficult to predict whether phenyls or alkyls of yttrium and the lanthanides should theoretically exist. However, our experiments now indicate that they do.

A report[6] of the isolation of $ScEt_3(Et_2O)$ and $YEt_3(Et_2O)$ appeared in 1938; we believe this to be false. It has not been confirmed in 31 years, it could not be repeated[7,8] and the reported properties of these etherates (liquids stable at boiling points 172° and 225°) are as remarkable as the twice theoretical yields in which they were obtained.

The reaction of lanthanum chloride with phenyl- and methyllithium has been investigated previously[9]. The phenyl did not react in ether solution but in benzene gave a brown reactive solution containing a little lanthanum. In ether solution, the methyl gave a pyrophoric involatile solid qualitatively containing halogen, lanthanum and lithium which gave colours with Michler's ketone and with *p*-iodo-*N*,*N*-dimethylaniline. These observations were considered[9] indirect evidence for the formation of organometallic compounds of lanthanum.

RESULTS AND DISCUSSION

The aryl compounds

When a suspension of scandium chloride was treated with phenyllithium in ether and THF at 0°, a reaction took place and the scandium chloride dissolved. After isolation procedures, a good yield of a yellowish-brown powder was obtained, which was purified by precipitation from benzene by hexane. This product has the following properties. It takes fire upon exposure to air. It gives an intense green-blue colour upon treatment with Michler's ketone. Treatment with mercuric chloride (3 mol) gives 74% C_6H_5HgCl. Treatment with carbon dioxide gives benzoic acid (62% theoretical). Treatment with benzophenone gives triphenylcarbinol (75%). The compound contains no lithium or chlorine and its scandium content, 16.02% corresponds with the formula $Sc(C_6H_5)_3$ which requires 16.27%. We have been quite unable to obtain meaningful carbon analyses on this or any other of the compounds presently reported. This is probably due to the ready formation of carbide by these metals rather than to the more obvious difficulties of microanalysis of pyrophoric material. In many cases the carbon analytical figures (typically about 2/3 theory) were demonstrably low, being insufficient to account for the experimentally observed yield of organic derivative in reaction with mercuric chloride or other reagents. Metal analysis, however, revealed no complicating factors and was entirely reproducible.

Triphenylscandium prepared as above, is ultimately insoluble in benzene and ether, but slightly soluble in tetrahydrofuran. It is stable to 140° *in vacuo*. Reaction with traces of air or water vapour is instant. The material could not be induced to sublime. The IR spectrum is rather similar to that of triphenyl aluminium dimer (Al_2Ph_6) but except to conclude that triphenylscandium is probably not monomeric because of its involatility, insolubility and relatively complex IR spectrum, we draw no conclusions about its structure. The solubilities of this compound and the phenyls described below are inadequate for determination of molecular weight.

In the light of the preceding experiments, it is not surprising that scandium also forms a phenylacetylide. The $-C{\equiv}C{-}C_6H_5$ group, when combined with this electropositive metal, could form an anion with dispersed charge, thus contributing to stability in a way denied to the phenyl. Thus (phenylethynyl) lithium in a THF/hexane mixture reacts with scandium chloride to give, after isolation, a quantitative yield of a dark brown solid whose analysis (Sc, 12.76%; Li and Cl absent) indicates the formulation $Sc(C{\equiv}C{-}C_6H_5)_3$ (Sc, 12.93%). The pyrophoric material is stable to 250° *in vacuo* and gives phenylpropiolic acid upon carbonation.

Reaction of phenyllithium with yttrium chloride proceeded under conditions similar to those employed for scandium, and a brown solid product was isolated in good yield by a similar procedure. The product contained no lithium or chlorine; the yttrium content (27.69%) was appropriate for $Y(C_6H_5)_3$ (27.76%). The product, which is pyrophoric in air and has solubility properties similar to $Sc(C_6H_5)_3$, gave 71% of the theoretical yield of C_6H_5HgCl upon treatment with mercuric chloride. The IR spectrum, discussed below, was appropriate for a metal phenyl.

Reaction of phenyllithium with lanthanum or praseodymium chlorides yields products which are not simple phenyls. Reaction of phenyllithium, whether in three or four molar proportions, with lanthanum chloride gave a dark brown solid in good yield. Conditions of preparation were similar to those for the scandium and yttrium compounds; purification was from THF/hexane mixtures. This product is suggested by analysis (La, 30.29%; Li, 1.21%; Cl, 0) to be $LiLa(C_6H_5)_4$ (La, 30.57%, Li, 1.52%). It inflames in air and has solubility properties similar to the scandium and yttrium compounds. Phenylmercuric chloride (65%) was obtained on reaction with mercuric chloride. This phenyl is unlikely to be a mixture of lanthanum and lithium phenyls as the purification procedure would have removed the soluble lithium phenyl; moreover, different preparations gave consistent analyses. A formally analogous compound $LiAl(C_6H_5)_4$ is known[10].

Using praseodymium chloride, an entirely similar product is obtained whose analysis and properties suggest the formulation $LiPr(C_6H_5)_4$. It is very possible that heavier lanthanides will form phenyls $M(C_6H_5)_3$ as there is no known substantial difference between the chemistry of yttrium and that of the heavier trivalent lanthanides; we have not yet investigated this question.

All the phenyl compounds described above are soluble in benzene when first obtained from THF solution, but after complete drying *in vacuo* they are insoluble in benzene. It is clearly possible that the original product is a tetrahydrofuran complex of low molecular weight which polymerises upon removal of tetrahydrofuran.

Reactions of scandium, yttrium and lanthanum halides with lithium alkyls

We regard the following experiments as good evidence that alkyls of these metals exist but we have as yet been unable to purify our involatile pyrophoric products from contamination with lithium halides, whose solubility properties in inert solvents resemble those of the products. In a typical experiment, yttrium chloride (which is almost insoluble in a THF/ether mixture) dissolved upon addition of methyllithium. After concentration, repeated precipitation from THF/ether and drying, the resulting yellow solid gave an analysis as follows: Y, 39.1%; Li, 0.84%; Cl, 5.24%. Treatment with mercuric chloride gave a 67% yield of CH_3HgCl (taking the mol. wt. of the methyl as 134). Scandium and lanthanum chlorides when they were similarly treated with methyllithium gave products with substantially similar properties. The methyls are stable indefinitely at room temperature and give a strong colour with Michler's ketone.

Infrared spectra

The spectra of the phenyl compounds, obtained as mulls in nujol or fluorolube, show absorption characteristic of the phenyl group. However, the spectra are more complex than would be expected for a C_6H_5 group weakly bonded to a heavy atom. In particular there are broad, medium intensity peaks in the region of 900 cm^{-1} and the C–H in-plane and out-of-plane bending regions are richer than might be expected if only one type of MC_6H_5 grouping were present. In the case of the lanthanum and praseodymium compounds a certain additional complexity might have arisen from the presence of Li–C linkages, but none is observed. It is noteworthy that the absorption in the CH stretching region occurs at 3035–2835 cm^{-1} suggesting some weakening of these bonds. $Sc(C{\equiv}C{-}C_6H_5)_3$ shows, at 2050 cm^{-1}, the expected acetylenic absorption.

Not much can be learned from the spectra of the methyl compounds, as they appear (both from the IR spectra and from the analytical values) to contain THF of solvation whose bands cannot be distinguished with any certainty from those of the methyl group.

The observed spectra are as follows (cm^{-1}).

*Triphenylscandium**: 3035 m, 2970 m, 2885 m, 1592 m, 1486 w, 1418 w, 1285 w, 1236 w, 1217 m, 1179 w, 1144 w, 1102 w, 1042 (sh), 1036 s, 1005 m, 979 m, 907 w, 877 m, 855 w, 821 (sh), 750 w, 727 (sh), 712 (sh), 697 s, 667 w, 623 w.

Triphenylyttrium: 3035 m, 2940 m, 2855 m, 1594 m, 1480 m, 1420 w, 1283 w, 1245 m, 1203 w, 1171 m, 1155 w, 1107 m, 1078 (sh), 1060 (sh), 1040 s, 1006 w, 981 m, 942 m, 915 w, 886 m, 818 m, 762 m, 738 m, 698 s, 675 w, 620 m.

Lithium tetraphenyl praseodymate (the La spectrum is closely similar): 3020 w, 2955 m, 2880 m, 2835 (sh), 2700 w, 1580 w, 1390 w, 1340 w, 1280 w, 1239 m, 1169 m, 1153 (sh), 1103 (sh), 1075 (sh), 1037 s, 961 m, 913 m, 888 m, 821 w, 739 s, 719 (sh), 698 s, 617 w.

Tris(phenylethynyl)scandium: 3060 m, 2970 (sh), 2885 (sh), 2175 w, 2115 w, 2050 m, 1950 w, 1880 w, 1805 w, 1595 m, 1485 m, 1440 w, 1198 w, 1177 w, 1155 w, 1070 m, 1038 (sh), 1026 s, 968 (sh), 912 m, 888 w, 861 w, 841 w, 756 s, 692 s, 620 (sh), 540 (sh), 516 m.

CONCLUSIONS

These experiments provide unequivocal evidence that thermally stable phenyls and methyls of scandium, yttrium and lanthanides can be obtained in the solid state. The evidence indicates that the scandium and yttrium phenyls may safely be formulated $M(C_6H_5)_3$. The constitution of the lanthanum and praseodymium phenyls is fairly strongly indicated to be $LiM(C_6H_5)_4$. The constitution of the methyls is uncertain, but may be $M(CH_3)_3 \cdot (C_4H_8O)_n$.

It is worth notice that the organometallic compounds of scandium although intensely reactive chemically, are in general more stable thermally than those of

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* This spectrum is amended in some details from that quoted in our preliminary publication[1].

either of the neighbouring elements calcium[5] and titanium. Furthermore, no decrease in stability is observed in the series Sc, Y, La. Detailed theoretical discussion must await further work.

EXPERIMENTAL

Solvents

Benzene, diethyl ether, tetrahydrofuran and hexane were boiled over calcium hydride under reflux, distilled therefrom and redistilled from blue sodium benzophenone as required for use.

Glove box

This was manufactured by Lintott Engineering Ltd., Horsham, Sussex and was found to be very suitable for handling intensely reactive materials.

Nitrogen circulation

Nitrogen (white spot) was continuously recirculated through the glove box and a purification train consisting of (a) molecular sieve (B.D.H. Type 3A), (b) phosphorus pentoxide and (c) B.T.S. catalyst (reduced CuO), Badische Anilin und Soda-Fabrik A.G. The catalyst was maintained at 150°. Preparation and manipulation of all organometallics was carried out in a nitrogen atmosphere in the glove box except where appropriate.

Analysis

Scandium, yttrium, lanthanum and praseodymium were determined gravimetrically by alkaline precipitation followed by washing and ignition to the oxide. Lithium was determined by flame photometry of the residual solution.

Anhydrous metal chlorides

Scandium oxide (Johnson, Matthey and Co. Ltd) was converted into hydrated scandium chloride by dissolution in hydrochloric acid and subsequent evaporation. The powdered hydrated chloride was treated under reflux with boiling thionyl chloride for 48 h, removed and ground to a powder, and again treated with boiling thionyl chloride for 7 h. The resulting material when dried *in vacuo* gave satisfactory analytical figures for Sc and Cl. Anhydrous yttrium, lanthanum and praseodymium chlorides were similarly obtained. It is important that commercial $SOCl_2$ be purified before use by distillation first from quinoline and then from boiled linseed oil.

Phenyllithium

It is desirable but not essential that phenyllithium be prepared from diphenylmercury and lithium in ether followed by removal of ether and crystallisation from benzene. Otherwise lithium halides tend to contaminate the Group IIIA phenyls.

Triphenylscandium

A suspension of scandium trichloride (1.61 g, 10.6 mmoles) in THF (50 ml) was treated at 0° with phenyllithium in ether (94 ml, 31.9 mmoles). After being stirred at 0° for 2 h the $ScCl_3$ had dissolved. The reaction mixture was allowed to warm to room temperature and after 2 h further stirring a white precipitate had formed. The solvent was removed under reduced pressure, which was further maintained for two h at 60–70°. The residue was extracted with benzene (50 ml) giving a yellow solution and leaving a white solid (LiCl). The benzene was removed after filtration and the residue again dissolved in benzene (50 ml), which was filtered, evaporated to about 5 ml and treated with n-hexane (50 ml). The yellowish-brown precipitate was collected, well washed with hexane and dried at 50°/0.1 mm overnight (yield 2.0 g, 68%). (Found: Sc, 16.02; Li and Cl absent. $C_{18}H_{15}Sc$ calcd.: Sc, 16.27%.) This final product is insoluble in hexane, benzene and ether but slightly soluble in THF.

Reactions of triphenylscandium

(*a*). $Sc(C_6H_5)_3$ (0.235 g) in THF (25 ml) was treated with $HgCl_2$ (0.70 g, 3 mol). The solution became warm but was boiled under reflux for 64 h; it soon became light yellow. The solvent was removed under reduced pressure, and the residue extracted with hot water, dried and sublimed giving 0.595 g (74%) C_6H_5HgCl m.p. 250° (lit. 251.5°). If only 1.5 mol $HgCl_2$ were used, no mercury diphenyl was isolated.

(*b*). $Sc(C_6H_5)_3$ (1.18 g) in THF (30 ml) was treated with CO_2 gas at −78° for 90 min. The reaction mixture was allowed to attain room temperature, CO_2 still passing. After acid hydrolysis, extraction with ether and subsequent purification gave 0.90 g (62%) benzoic acid m.p. 120° (lit. m.p. 121°).

(*c*). $Sc(C_6H_5)_3$ (0.46 g) in THF (25 ml) was treated with benzophenone (0.91 g, 3 mol) and the solution boiled under reflux overnight. The solvent having been removed under reduced pressure, the residue was hydrolysed with dilute aqueous HCl, extracted with ether, the ether removed under reduced pressure and the residue heated at 50°/0.1 mm to remove benzophenone. The $(C_6H_5)_3COH$ crystallised from CCl_4 (0.985 g, 75%), m.p. 162° (lit. m.p. 162.5°).

Triphenylscandium is stable to 140° *in vacuo* and on heating to 200° it darkens and gives only a weak reaction with Michlers ketone. It is however stable at 215° under nitrogen for 15 min as shown by a strong Michler's ketone reaction.

Triphenylyttrium

A suspension of yttrium trichloride (0.84 g, 4.3 mmoles) in THF (75 ml) at 0° was treated with phenyllithium in ether (8.75 ml, 2 *N*). The YCl_3 dissolved in 5 min stirring to give a clear orange-brown solution. After 6 h the reaction mixture was allowed to warm to room temperature and was stirred overnight. The solvent was removed under reduced pressure and the residue extracted with benzene (30 ml). After filtration from LiCl (0.54 g) the solution was concentrated to about 10 ml and treated with n-hexane (50 ml). The resulting brown solid was washed thrice with n-hexane (20 ml portions) and dried at 50°/0.1 mm. Yield: 0.97 g (70%). (Found: Y, 27.69; Li and Cl absent. $C_{18}H_{15}Y$ calcd.: Y, 27.76%.) The material is pyrophoric and its solubilities are similar to those of $Sc(C_6H_5)_3$. When a portion (0.130 g) was treated with $HgCl_2$ under the same conditions as for the scandium compound, 0.271 g C_6H_5HgCl (71%) was obtained. The material appears unchanged and gives a Michler's ketone test after heating to 210° *in vacuo* or in N_2.

Reaction of phenyllithium with lanthanum chloride

Lanthanum chloride (2.51 g) in THF (70 ml) was treated at 0° with phenyllithium in ether (34.5 ml, 1.18 *M*, 4 mols). After being stirred at 0° during 8 h, the mixture was allowed to reach room temperature and was stirred overnight. Very little $LaCl_3$ remained undissolved. The THF was removed under reduced pressure, benzene (40 ml) was added and the dark brown solution was filtered from LiCl and the benzene removed under reduced pressure. The residue was dissolved in THF (15 ml) and n-hexane (60 ml) added to precipitate a dark brown solid which was collected and thrice again similarly precipitated from THF/hexane. Yield: 2.60 g after drying overnight at 50° *in vacuo*, after which treatment the product was insoluble in benzene. (Found: La, 30.29; Li, 1.21; Cl absent. $C_{24}H_{20}LaLi$ calcd.: La, 30.57; Li, 1.52%.) The product takes fire in air. It is unchanged *in vacuo* at 200° but in N_2 pales and gives only a feeble Michler's ketone test.

Reaction of lithium tetraphenyllanthanate with mercuric chloride

When the product of the preceding experiment [0.637 g; 1 mol $LiLa(C_6H_5)_4$] was boiled overnight in THF (20 ml) with $HgCl_2$ (1.403 g; 3.67 mol), 1.15 g (2.6 mol) $HgCl(C_6H_5)$ was isolated.

Reaction of phenyllithium with praseodymium chloride

Praseodymium chloride (2.2 g) was treated with phenyllithium under the same conditions as for lanthanum chloride. Similar working up procedures gave a similar yield of pyrophoric dark brown solid having similar solubilities to the lanthanum compound. (Found: Pr, 31.10; Li, 1.24; Cl absent. $C_{24}H_{20}LiPr$ calcd.: Li, 1.52; Pr, 30.87%. The compound is unchanged at 200° *in vacuo* or in N_2.

Reaction of lithium tetraphenylpraseodymate with mercuric chloride

When the product of the preceding experiment [0.217 g; 1 mol $LiPr(C_6H_5)_4$] was boiled overnight in THF (20 ml) with $HgCl_2$ (0.518 g; 4.00 mol), 0.401 g (2.7 mol) $HgCl(C_6H_5)$ was isolated.

Preparation of tris(phenylethynyl)scandium

Phenylethyne (6.55 g; 64.2 mmoles) in THF (60 ml) was treated at −78° with n-butyllithium in n-hexane (42 ml; 1.56 *M*). After 1 h at room temperature, scandium chloride (3.24 g; 21.4 mmoles) was added. There was an exothermic reaction and after 3 h the solvent was removed under reduced pressure. The residue was extracted with benzene (40 ml). After filtration, removal of benzene and drying at 50° overnight, there remained a dark brown product (7.40 g; 99%) which inflamed in air. It is stable to 250° *in vacuo* and gives a positive test with Michler's ketone .(Found: Sc, 12.76%; Li and Cl absent. $C_{24}H_{15}Sc$ calcd.: Sc, 12.93%.) Carbonation of the product (0.54 g) in THF (25 ml) at −78° for 1.5 h followed by warming to room temperature with CO_2 still passing gave phenylpropiolic acid (38%) identified by m.p. and IR spectrum.

Reaction of methyllithium with Group IIIA chlorides

Scandium chloride (1.106 g), suspended in THF at 0° was treated with methyllithium in ether (7.48 ml, 2.93 *M*, 3 mol). The $ScCl_3$ dissolved upon stirring which was continued for 6 h. The solution was next stirred at room temperature for 4 h and the solvent reduced to about 5 ml volume. The deposited LiCl was removed. Ether (20 ml) then precipitated an orange-yellow solid which was collected and thrice again precipitated from THF/ether; however, it still contained LiCl. It is insoluble in benzene (at all stages) and hexane. It is pyrophoric in air and darkens at about 140° *in vacuo*. (Found: Cl, 25.8; Li, 2.05; Sc, 25.14%.)

A precisely similar experiment with yttrium chloride gave a similar product. (Found: Cl, 5.2; Li, 0.84; Y, 39.1%.)

A similar experiment with lanthanum chloride gave a brown insoluble solid product which precipitated from the reaction mixture and was collected, washed with THF and dried. (Found: Cl, 4.59; La, 55.29; Li, 0.45%.) The substance is pyrophoric in air.

All three products yield CH_3HgCl with $HgCl_2$. Thus the yttrium product (0.132 g) was boiled in THF (25 ml) with $HgCl_2$ (0.802 g). Removal of solvent and extraction with benzene gave CH_3HgCl (0.45 g) m.p. 170° (lit. m.p. 170°). Expressed as a percentage weight of CH_3 in the yttrium methyl, this is 20.4%. The IR spectrum indicates the additional presence of tetrahydrofuran.

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