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THE REACTION BETWEEN TRANSITION METAL CARBENE COMPLEXES AND ORGANOMETALLIC HYDRIDES. A SIMPLE ROUTE TO α-ALKOXY AND α-DIALKYLAMINO BENZYL COMPOUNDS OF SILICON, GERMANIUM AND TIN

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SUMMARY

Carbene compounds of the Group VI metals, $(CO)_5MC(X)C_6H_4Y$ in which $M=Cr$, Mo, W; $X=OMe$, NC_nH_{2n} ($n=2, 4$) and $Y=p$-OMe, p-Me, H, p-Cl, react with triorganoelement hydrides of the Group IV elements, R_3EH, in which $R=$alkyl, Ph and $E=$Si, Ge, Sn, in the presence of a coordinating base (pyridine, acetonitrile) in hexane solution to give compounds of the type $R_3ECHXC_6H_4Y$ whose characterisation is reported.

Competition experiments are used to show that the susceptibility of R_3EH to insertion of the fragment [PhCOMe] varies in the order $Et_3SiH > Ph_3SiH < Ph_3GeH < Ph_3SnH$, Pr_3SnH. The formation of Ph_3SiOMe in the reaction of Ph_3SiH with the complexes $(CO)_5CrC(OMe)C_6H_4Y$ is discussed.

INTRODUCTION

Halomethyl metal compounds, particularly of mercury, react with hydrides of silicon and germanium to give compounds in which a carbene fragment, usually [CXY] (X,Y = halogen)[1] but also [CXR] ($R=H$[2], alkyl[3], aryl[4]) is inserted in the Si–H or Ge–H bonds. This procedure has been developed by Seyferth and his associates so that it is now a synthetic method of considerable generality. The mechanism of the reaction involves an electrophilic singlet carbene in a three centre transition state[5].

Limitations are imposed upon this method by the type of precursor which can be synthesised. Thus, while $PhHgCX_2Y$ (X,Y = Cl, Br) compounds are readily prepared[6] from the reaction of PhHgX, haloform and potassium tert-butoxide in tert-butanol in tetrahydrofuran at −25°, the synthesis and manipulation of $PhHgCCl_2Ph$[4] involves $PhCCl_2Li$ and presents considerable problems. It has not so far proved possible to extend the scope of mercurial reagents so that they can act as precursors for heterocarbenes of the types $[CZ_2]$ ($Z=OR, NR_2$ etc.,) and [CRZ]. Also, the reaction between halomethyl mercury compounds and organotin hydrides results in reduction of the halomethyl group rather than insertion into the Sn–H bond[7]. Alkoxycarbenes have been derived from organosilicon compounds such as $(MeO)_3SiCH(OMe)_2$[8] and $Ph_3SiCH(OMe)_2Ph$[9] by thermolysis. The carbenes obtained in this way, [MeOCQ] ($Q=H,Ph$) react with R_3MH ($M=Si,Ge$) to give $R_3MCH(OMe)Q$.

The electronic effects of α-metalloalkyl groups upon the properties of systems in which they are present, especially those systems in which such groups are bonded to transition metals are of interest in relation to the concept of vertical stabilisation[10]. The synthesis of such groups when they include a further heteroatom substituent on the α-carbon atom, as for example in the benzyl derivatives $R_3ECHZPh$, is difficult[9]. These considerations have led to an investigation of the use of transition metal carbene complexes as possible sources of carbenes for insertion into Group IV element–hydrogen bonds.

RESULTS AND DISCUSSION

The carbene complexes used in this work were prepared by standard methods[11]. The reactions leading to the inserted products $R_3ECH(X)C_6H_4Y$ [$R=$ alkyl, aryl; $E=Si, Ge, Sn$; $X=OMe$, NC_nH_{2n} ($n=2, 4$); $Y=p$-OMe, p-Me, H, p-Cl] were carried out using a simple procedure which is described in detail in the Experimental section. The length of the reaction, as measured by the time required for the complete disappearance of $(CO)_5MC(X)C_6H_4Y$, was found to vary over a wide range and to be influenced by each of the substituents R, E, X and Y in the final product as well as by the metal, M ($M=Cr$, Mo, W), of the precursor carbene complex. The yield of pure product isolated from these reactions varied from quite good for $X=OMe$ (50–85%) to less satisfactory for $X=NC_4H_8$ (less than 50%).

Although a very slow reaction between R_3EH and the carbene complex $(CO)_5MC(X)C_6H_4Y$ will occur in the absence of base, to give $R_3ECH(X)C_6H_4Y$ in low overall yield, the addition of a coordinating base, L, accelerates the insertion reaction and greatly increases the yield. The coordinating base is recovered from the reaction in the form of the coordination complexes, $L_nM(CO)_{6-n}$ ($n=1$–3), the exact ratio of which depends upon a number of factors including the length of the reaction, however there is substantial evidence from kinetic studies to show that $LM(CO)_5$ and $L_2M(CO)_4$ may be produced by different paths[23].

A number of simple competition reactions have been carried out which involve $(CO)_5CrC(OMe)Ph$ as the subject of competition. These reactions showed the Et_3SiH is approximately four times more reactive than Ph_3SiH with respect to the formation of $R_3SiCH(OMe)Ph$ ($R=Et,Ph$). When Ph_3SiH and Ph_3GeH are placed in competition with one another, the only insertion product is $Ph_3GeCH(OMe)Ph$. Competition between Ph_3GeH and Ph_3SnH resulted in exclusive insertion into the Sn–H bond with the formation of $Ph_3SnCH(OMe)Ph$. The pattern of increasing susceptibility to insertion of the carbene species [PhCOMe], namely, $Et_3SiH < Ph_3SiH < Ph_3GeH < Ph_3SnH$, Pr_3SnH, is difficult to reconcile with any one particular interpretation in mechanistic terms, but it might be taken as evidence for the participation of an electrophilic carbene species.

In this regard, the observation that, qualitatively at least, the pyrrolidin-1-yl carbene complex, $(CO)_5CrC(NC_4H_8)Ph$ reacts much more slowly than the methoxy carbene complex $(CO)_5CrC(OMe)Ph$ with each of Et_3SiH, Ph_3SiH, Et_3GeH, Ph_3GeH, Bu_3SnH and Ph_3SnH fits well with evidence from ^{13}C NMR spectra of both carbene compounds[12] which shows that the *s*-character or carbenium ion character of the carbene carbon atom is much greater for the methoxy complex than for the pyrrolidinyl complex. Such an explanation might imply that the insertion reaction occurs without the carbene ligand coming free from the metal.

On the other hand, a mechanism involving complete displacement of the carbene ligand [CXY] from the complex $(CO)_5MCXY$ by the coordinating base, L, followed by nucleophilic attack by the free carbene upon the organometallic hydride would be consistent with the known susceptibility of the latter to nucleophilic reactions and the expected, but for this class of compound so far largely unproved, nucleophilic character of free carbenes such as [PhCOMe]. In this respect it is perhaps significant that, under similar conditions, reaction between $(CO)_5CrC(OMe)$-Ph and the nucleophilic hydride Ph_2PH in the presence of pyridine gave *cis*-$(Ph_2PH)_2Cr(CO)_4$; no trace of a product such as $Ph_2PCH(OMe)Ph$ could be found. This result is similar to that obtained when monophosphine, PH_3, is mixed with the carbene complex $(CO)_5CrC(OMe)Me$[13]. The reaction of $(CO)_5MC(OMe)Ph$ with Ph_3SiH and pyridine in hexane showed that the rate of the insertion reaction depends on the metal, M, and decreases in the order $M = Mo \gg Cr > W$.

The reaction between Ph_3SiH and each of the *para* substituted phenyl carbene complexes, $(CO)_5CrC(OMe)(C_6H_4Y)$ (Y = *p*-OMe, *p*-Me, H, *p*-Cl) gives Ph_3SiOMe as one of the products in addition to the expected insertion product, $Ph_3SiCH(OMe)C_6H_4Y$. The relative proportion of Ph_3SiOMe produced in the reaction depends upon the substituent Y and decreases in the order Y = *p*-OMe > *p*-Me > H > *p*-Cl, which is very similar to the order of the Hammett substituent constants, σ_p, for these groups. In the case where Y = *p*-Me, the presence of 4,4'-dimethylstilbene was also detected among the reaction products. While the formation of the insertion product, $Ph_3SiCH(OMe)C_6H_4Y$ can proceed via a three centre transition state, the formation of Ph_3SiOMe and a stilbene in the same reaction can most readily be explained in terms of an alternative (competing) 4-centre transition state (Fig. 1).

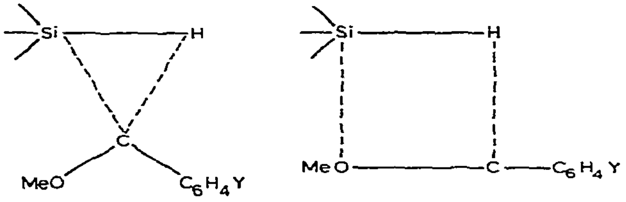

Fig. 1.

It is noteworthy that we did not find either α,α'-dimethoxystilbene or benzyl methyl ether among the products of the reaction between $(CO)_5CrC(OMe)Ph$ and Et_3SiH. The former product is formed in high yield from the thermal decomposition of the carbene complex[14] whilst the latter product might be expected to be formed, together with Et_6Si_2, if the carbene ligand were to be reduced by the silane. These observations indicate a remarkable specificity in the insertion reaction.

Further discussion of the mechanism of this insertion reaction must await the completion of kinetic studies which are being made at present.

The presence of an easily identifiable methine proton resonance in the ^1H

TABLE 1

CHEMICAL SHIFT (δ, ppm) OF THE METHINE PROTON IN THE COMPOUNDS p-YC_6H_4-$CH(X)ER_3$ (CCl_4 SOLUTION)

E	*R*	*X*	*Y*	δ
Si	Ph	OMe	H	4.58
Si	Ph	OMe	OMe	4.55
Si	Ph	OMe	Me	4.56
Si	Ph	OMe	Cl	4.58
Si	Et	OMe	H	3.96
Si	Et	NC_2H_4	H	1.98
Si	Et	NC_4H_8	H	2.94
Ge	Ph	OMe	H	4.83
Ge	Ph	NC_4H_8	H	3.92
Ge	Et	OMe	H	4.28
Sn	Ph	OMe	H	5.07
Sn	Pr	OMe	H	4.58
Sn	Bu	OMe	H	4.55
Sn	Bu	NC_4H_8	H	3.57

NMR spectrum of the product, R_3ECHXY, of these insertion reactions has been very useful in the detection and estimation of these compounds (Table 1). For strictly comparable compounds such as $Ph_3ECH(OMe)Ph$, the methine proton resonance moves to lower field as E changes from silicon through germanium to tin. Replacement of Ph_3E by R_3E (R = Et, Pr, Bu) results in a shift of the methine proton resonance to higher field in the case of each element E, in a manner which is consistent with the greater inductive effect of the alkyl groups. In the tin compounds the methine proton appears as a pair of doublets in the NMR, from which ^2J(Sn–C–H) is measured to be 35 ± 2 Hz for both ^{117}Sn and ^{119}Sn in each case. Attempts to measure $^2J(^{29}$Si–C–H) in $Et_3SiCH(OMe)Ph$ have been unsuccessful. The replacement of the methoxy substituent at the methine carbon by an amino substituent causes the methine proton resonance to shift to higher field which is consistent with a superior electron donor strength of the nitrogen atom.

The mass spectra of the compounds usually contain a molecular ion of low relative abundance. The methoxy compounds, $R_3ECH(OMe)C_6H_4Y$ (E = Si, Ge), will undergo fragmentation by loss of the *O*-methyl group followed by cleavage of the E–C bond to give $YC_6H_4CHO^+$ and R_3E^+. Fragmentation of the molecular ion by simple cleavage of the E–C bond becomes increasingly important in the order E = Si < Ge < Sn for both alkoxy and amino compounds. The IR spectra of the compounds are complex and an exact assignment is not important. However, the pattern of frequencies in the 2900–2800 cm^{-1} region is distinctive and we tentatively assign the medium intensity band lying between 2820–2800 cm^{-1} to the methine C–H stretching vibration.

EXPERIMENTAL

General features of the instrumentation and techniques used in this investigation are similar to those given in earlier papers[15]. Triethylsilane was reagent grade

(Pierce). Pyridine was AnalaR grade (BDH) and was dried over KOH and freshly distilled before use. Triphenylsilane was prepared from trichlorosilane[16]; triethylgermane, triphenylgermane[17], and the triorganotin hydrides, R_3SnH (R = Pr, Bu, Ph)[18], were prepared by lithium aluminium hydride reduction of the corresponding halide.

The carbene complexes $(CO)_5CrC(OMe)C_6H_4Y$ (Y = p-MeO, p-Me, H, p-Cl) were prepared by standard methods[19]. The complex $(CO)_5CrC(NC_2H_4)Ph$ was prepared by the addition of ethyleneimine to $(CO)_5CrC(OMe)Ph$ and was obtained as pale yellow prisms (85%) m.p. 89–90°. (Found: C, 52.1; H, 3.2; Cr, 15.9; N, 4.1. $C_{14}H_9CrNO_5$ calcd.: C, 52.0; H, 2.8; Cr, 16.1; N, 4.3%.) ν_{max} (hexane): 2060 m, 1979 w, 1945 s, 1939 s cm^{-1}. NMR: see ref. 20. λ_{max} (log ε): 243 (4.58), 390 (3.86) nm. Mass spectrum (m/e, I) 333, 16 (M^+); 305, 9; 277, 5; 249, 11; 211, 26; 183, 100; 131, 3.

The complex $(CO)_5CrC(NC_4H_8)Ph$ was prepared by the addition of pyrrolidine to $(CO)_5CrC(OMe)Ph$ and was obtained as yellow needles (74%) m.p. 101–102°. (Found: C, 54.9; H, 3.6; Cr, 14.5; N, 3.8. $C_{16}H_{13}CrNO_5$ calcd.: C, 54.7; H, 3.7; Cr, 14.8; N, 4.0%.) ν_{max} (hexane): 2058 m, 1976 w, 1941 s, 1935 s cm^{-1}. NMR: see ref. 20. λ_{max} (log ε): 245 (4.38), 365 (3.80). Mass spectrum (m/e, I) 361, 1 (M^+); 333, 7; 335, 5; 277, 3; 249, 10; 211, 100; 159, 12.

The insertion reactions were usually carried out in a single necked round bottom flask (50 ml) which was fitted with a simple reflux condenser (with mercury bubbler) and a magnetic stirring bar. All the operations prior to and following the reaction were performed under a nitrogen atmosphere, but the reactions were carried out under an atmosphere of argon. At the end of the reaction, the condenser was replaced as quickly as possible by a 1 cm serum cap. Separation of the liquid phase from any solid products of the reaction was effected by means of a syringe via the serum cap. Fresh solvent for washing the solid was added and removed in a similar manner. Unless stated to the contrary, the Group IV element hydride was added to a stirred solution of the metal carbene complex and then pyridine was added as quickly as possible thereafter. Yields are based on the amount of metal carbene complex consumed and refer to pure, isolated materials.

(α-*Methoxybenzyl*)*triethylsilane*

Triethylsilane (0.50 g, 4.33 mmol) and pyridine (0.4 ml, 4.96 mmol) were added to a solution of $(CO)_5CrC(OMe)Ph$ (1.04 g, 3.34 mmol) in hexane (20 ml). The mixture was stirred at reflux for 1 h during which time a solid was deposited from the solution. At the end of the reaction period the solution, originally deep red in colour, had become yellow and a yellow solid was present. The solid was isolated, washed with hexane (4 × 2 ml), dissolved in acetone (5 ml), the solution filtered and the solid then reprecipitated by the addition of water. After drying for several hours under vacuum the orange-yellow crystalline solid was shown to be bis(pyridine)tetracarbonylchromium, $Py_2Cr(CO)_4$, by elemental analysis and IR spectroscopy (0.40 g, 38%). All liquid fractions were combined (ca. 30 ml), reduced to ca. 10 ml by distillation under reduced pressure and then stored at −20°. In this way, yellow needles of pyridinepentacarbonylchromium, $PyCr(CO)_5$, were isolated and identified by elemental analysis and IR spectroscopy (0.38 g, 42%). The solvent was removed from the mother liquor leaving a yellow oil which was purified by repeated distillation under reduced pressure to give (α-methoxybenzyl)triethylsilane as a colourless liquid (0.64 g, 82%)

b.p. 76–78°/1 mmHg. (Found: C, 71.4, H, 10.3. $C_{14}H_{24}OSi$ calcd.: C, 71.2; H, 10.2%.) δ (CCl_4): 0.75 (15H, m, Et_3Si), 3.20 (3H, s, OCH_3), 3.96 (1H, s, CH), 7.1 (5H, m, C_6H_5) ppm. ν_{max}(liq. film): 3095 w, 3080 m, 3060 m, 3025 m, 2950 s, 2935 s, 2910 s, 2875 s, 2815 s, 1600 m, 1582 w, 1496 s, 1462 s, 1452 s, 1435 m, 1416 s, 1380 m, 1337 w, 1280 w, 1240 s, 1207 m, 1155 m (sh), 1146 s, 1086 vs, 1071 vs, 1030 vs, 1018 s(sh), 1010 vs, 976 m, 935 s, 909 w, 842 m, 776 vs, 736 vs, 717 vs, 702 vs, 683 s, 658 m cm^{-1}. Mass spectrum (*m/e*, *I*): 236, 1; 121, 17; 115, 69; 87, 100.

The following compounds were prepared in a similar manner:

(α-Aziridin-1-ylbenzyl)triethylsilane

From Et_3SiH (3.68 mmol), $(CO)_5CrC(NC_2H_4)Ph$ (2.56 mmol) and pyridine (7.1 mmol); reflux for 10 h. Obtained (46%) as a clear liquid b.p. 80–82°/0.1 mmHg. (Found: C, 76.2; H, 10.0; N, 5.4. $C_{15}H_{25}NSi$ calcd.: C, 72.9; H, 10.1; N, 5.6%.) δ(CCl_4): 0.7 (15H, m, Et_3Si), 1.6 (4H, m, NCH_2), 1.98 (1H, s, CH), 7.0 (5H, m, C_6H_5) ppm. ν_{max} (liq. film): 3095 w, 3075 m, 3055 m, 3020 m, 2975 s, 2950 s, 2935 s(sh), 2910 s, 2875 s, 2785 m, 2770 m, 1600 m, 1582 w, 1496 s, 1468 s, 1452 s, 1418 m, 1379 m, 1332 m, 1301 m, 1279 m, 1252 m, 1241 m, 1200 m, 1167 m, 1135 m, 1092 w, 1075 m, 1050 w, 1031 m, 1018 s, 1007 s, 975 m, 950 w, 910 m, 873 m, 843 s, 830 w, 795 s, 758 m, 739 s(sh), 731 s, 714 s, 700 s, 680 w, 654 w cm^{-1}. Mass spectrum (*m/e*, *I*): 247, 14; 246, 60; 218, 41; 191, 20; 190, 81; 132, 12; 131, 3; 115, 18; 87, 100.

(α-Pyrrolidin-1-ylbenzyl)triethylsilane

From Et_3SiH (3.58 mmol), $(CO)_5CrC(NC_4H_8)Ph$ (3.05 mmol) and pyridine (3.9 mmol); reflux for 20 h. Obtained (53%) as a clear liquid b.p. 87–89°/0.1 mmHg. (Found: C, 73.8; H, 10.1; N, 4.8. $C_{17}H_{29}NSi$ calcd.: C, 74.2; H, 10.5; N, 5.1%.) δ(CCl_4): 0.75 (15H, m, Et_3Si), 1.7 (4H, m, β-CH_2), 2.50 (4H, m, N-CH_2), 2.94 (1H, s, CH), 7.25 (5H, m, C_6H_5) ppm. ν_{max} (liq. film): 3080 m, 3060 m, 3020 m, 2950 s, 2930 s, 2905 s, 2870 s, 2775 s, 1580 w, 1493 m, 1478 m, 1460 s, 1450 s, 1416 m, 1337 m, 1357 m, 1267 m, 1239 m, 1194 m, 1124 s, 1068 m, 1028 m, 1010 s, 970 m, 914 m, 880 m, 836 m, 776 m, 730 s, 714 s, 703 s, 673 m cm^{-1}. Mass spectrum (*m/e*, *I*): 275, 1; 246, 2; 160, 100; 131, 2; 121, 3; 115, 1; 107, 2; 87, 4.

(α-Methoxybenzyl)triethylgermane

From Et_3GeH (1 mmol), $(CO)_5CrC(OMe)Ph$ (1 mmol) and pyridine (6 mmol); reflux for 10 min. Obtained (66%) as a clear liquid, b.p. 63–67°/0.15 mmHg. (Found: C, 60.8; H, 8.8. $C_{14}H_{24}GeO$ calcd.: C, 59.8; H, 8.5%.) δ(CCl_4): 0.95 (15H, m, Et_3Ge), 3.27 (3H, s, OCH_3), 4.27 (1H, s, CH) 7.17 (5H, m, C_6H_5) ppm. ν_{max} (liq. film): 3085 w(sh), 3070 m, 3050 m, 3015 m, 2940 s, 2912 s, 2900 s, 2865 s, 2825 m, 2808 m, 1598 m, 1493 m, 1460 m(sh), 1450 m, 1425 m, 1378 w, 1300 w, 1205 m, 1134 m, 1084 s, 1071 s, 1015 m, 970 m, 937 m, 907 w, 830 w, 769 s, 704 s, 700 s(sh), 660 m cm^{-1}. Mass spectrum (*m/e*, *I*): 282, 16 (M^+); 267, 54; 252, 4; 224, 1; 209, 1; 195, 1; 181, 1; 161, 71; 133, 93; 132, 26; 121, 100; 120, 2; 106, 3; 105, 33; 104, 9; 103, 32.

(α-Methoxybenzyl)tripropyltin

Pyridine (3.1 mmol) and $(CO)_5CrC(OMe)Ph$ (1.90 mmol) were placed in a Schlenk tube and hexane (5 ml) added. A solution of Pr_3SnH (2.0 mmol) in hexane (1 ml) was added dropwise to the mixture at room temperature. After 5 min the red colour had been discharged leaving a yellow solution, which was elaborated in the usual manner to give a colourless liquid (82%) b.p. 142–144°/5 mmHg. (Found: C, 55.1; H, 8.0. $C_{17}H_{30}OSn$ calcd.: C, 55.3; H, 8.1%.) δ(CCl_4): 1.15 [21H, m, $(C_3H_7)_3$-Sn], 3.29 (3H, s, OCH_3), 4.58 (1H, dd, CH), 7.15 (5H, m, C_6H_5) ppm. ν_{max} (liq. film): 3095 w, 3075 m, 3060 m, 3020 m, 2950 s, 2930 s, 2895 s, 2865 s, 2850 s, 2815 m, 1601 m, 1580 w, 1492 s, 1464 s, 1451 s, 1415 w, 1375 m, 1332 m, 1297 w, 1276 m, 1202 m, 1185 w, 1152 w, 1095 m, 1072 s, 1065 vs, 1028 m, 1021 w, 991 m, 933 m, 903 w, 821 w, 795 m, 760 s, 701 vs, 665 m cm^{-1}. Mass spectrum (*m/e*, *I*): 249, 8; 206, 7; 163, 49; 121, 100; 120, 35.

(α-Methoxybenzyl)triphenylsilane

From Ph_3SiH (2.5 mmol), $(CO)_5CrC(OMe)Ph$ (2.4 mmol) and pyridine (12.4 mmol); reflux for 1 h. Obtained (61%) as colourless crystals, m.p. 147–148° (lit.^{9}, m.p. 148.5–149.5°). δ (CCl_4): 3.28 (3H, s, OCH_3), 4.58 (1H, s, CH), 7.1 (20H, m, C_6H_5) ppm. ν_{max} (CS_2, $CHCl_3$): 3130 w, 3065 s, 3045 s, 3020 s, 2990 m, 2970 m, 2925 s(sh), 2915 s, 2890 w, 2870 w, 2845 w, 2810 s, 1598 m, 1485 w, 1460 m(sh), 1450 m, 1430 m, 1331 w, 1300 w, 1278 w, 1260 w, 1205 m(sh), 1185 m, 1155 m, 1146 m, 1110 vs, 1082 vs, 1070 vs, 1030 s, 999 m, 937 m, 908 w, 772 vs, 738 vs, 697 vs, 671 w cm^{-1}. Mass spectrum (*m/e*, *I*): 380, 0.3; 365, 26; 259, 100; 182, 19; 121, 4; 120, 1; 105, 16.

Methoxytriphenylsilane (30%) was also isolated from the reaction and characterised by comparison with an authentic sample^{21}.

[α-Methoxy(p-methoxy)benzyl]triphenylsilane

Obtained from a similar reaction in 41% yield, as colourless crystals, m.p. 124–127°. (Found: C, 79.0; H, 6.1. $C_{27}H_{26}O_2Si$ calcd.: C, 79.1; H, 6.3%.) δ(CCl_4): 3.25 (3H, s, OCH_3), 3.67 (3H, s, *p*-$CH_3OC_6H_4$), 4.55 (1H, s, CH), 6.64 (4H, q, C_6H_4), 7.38 (15H, m, C_6H_5) ppm. ν_{max} (CS_2, $CHCl_3$): 3130 w, 3080 m, 3060 s, 3040 s, 3020 s, 3000 w, 2990 m, 2970 m, 2940 m, 2920 m, 2890 w, 2820 s, 1608 m, 1590 m, 1500 m, 1485 m, 1462 m, 1445 m, 1428 m, 1328 w, 1301 w, 1243 s, 1185 m, 1170 m, 1146 w, 1116 s, 1108 vs, 1086 s, 1072 s, 1047 m, 1039 m, 1029 m, 998 m, 938 w, 916 w, 830 m(sh), 821 m, 774 m, 736 s, 712 s, 699 s, 674 m cm^{-1}. Mass spectrum (*m/e*, *I*): 410, 0.3; 395, 14; 259, 100; 182, 12; 151, 8; 150, 2; 136, 2; 105, 22. Methoxytriphenylsilane (58%) was also isolated from the reaction.

(α-Methoxy-p-chlorobenzyl)triphenylsilane

Obtained in a 49% yield, as a colourless crystalline solid (ex methanol) m.p. 120–122°. (Found: C, 75.1; H, 5.4; Cl, 8.1. $C_{26}H_{23}ClOSi$ calcd.: C, 75.3; H, 5.6; Cl, 8.6%.) δ(CCl_4): 3.26 (3H, s, OCH_3) 4.58 (1H, s, CH), 6.88 (4H, q, C_6H_4), 7.35 (15H, m, C_6H_5) ppm. ν_{max} (CS_2, $CHCl_3$): 3130 w, 3060 s, 3040 s, 3020 s, 3010 s, 2995 m, 2970 m, 2915 s, 2890 w, 2810 s, 1592 m, 1481 m, 1458 m(sh), 1428 m, 1325 w, 1300 w, 1258 w, 1185 m, 1144 m, 1110 vs, 1090 vs, 1077 vs, 1030 m, 999 m, 930 w, 827 m, 817 m, 801 s, 733 vs, 699 s, 675 m cm^{-1}. Mass spectrum (*m/e*, *I*): 414, 0.4; 399, 11; 259, 100; 182, 8; 155, 17; 154, 3; 140, 2; 120, 5; 105, 25. Methoxytriphenylsilane (12%) was also isolated from the reaction.

(α-Methoxybenzyl)triphenylgermane

From Ph_3GeH (1.10 mmol), $(CO)_5CrC(OMe)Ph$ (1.1 mmol) and pyridine

(6.2 mmol); reflux for 0.25 h. Obtained (92 %) as colourless crystals, m.p. 142–143° (lit. 144–145°). δ(CCl_4): 3.29 (3H, s, OCH_3), 4.83 (1H, s, CH), 7.05 (20H, m, C_6H_5) ppm. ν_{max} (CS_2, $CHCl_3$): 3130 w, 3065 s, 3045 s, 3020 s, 2990 m, 2970 m, 2925 s, 2915 s, 2890 w, 2870 w, 2830 m, 2810 s, 1599 m, 1490 m(sh), 1482 m, 1449 m, 1428 m, 1332 w, 1278 w, 1205 m, 1185 m, 1152 w, 1091 s, 1081 s, 1069 s, 1027 s, 999 m, 938 m, 908 w, 767 s, 732 s, 697 s cm^{-1}. Mass spectrum (*m/e*, *I*): 305, 100; 228, 15; 151, 28; 121, 18; 120, 1; 106, 3.

(α-Methoxybenzyl)triphenylstannane

From Ph_3SnH (1.23 mmol) $(CO)_5CrC(OMe)Ph$ (1.21 mmol) and pyridine (12.4 mmol) in hexane/benzene (1/5); 0.25 h at room temperature. Obtained (53 %) as colourless crystals m.p. 99–102°. (Found: C, 65.9; H, 5.0. $C_{26}H_{24}OSn$ calcd.: C, 66.2; H, 5.1 %.) δ(CCl_4): 3.32 (3H, s, OCH_3), 5.07 (1H, dd, CH), 7.25 (20H, m, C_6H_5) ppm. ν_{max} (CS_2,$CHCl_3$): 3135 w, 3060 s, 3045 s, 3020 s, 2990 s, 2930 s, 2920 s, 2890 w, 2875 w, 2845 m, 2810 s, 1601 m, 1538 m, 1495 s, 1484 s, 1452 s, 1430 s, 1332 m, 1299 m, 1202 m, 1189 m, 1089 s, 1074 s, 1065 vs, 1022 s, 1000 s, 930 m, 900 w, 760 s, 727 s, 698 s, 655 m cm^{-1}. Mass spectrum (*m/e*, *I*): 351, 100; 274, 2; 197, 39; 121, 46; 120, 20; 106, 2. Hexaphenylditin (44 %) was also isolated from the reaction and identified by comparison with an authentic sample[22].

(α-Pyrrolidin-1-ylbenzyl)triphenylgermane

From Ph_3GeH (1.1 mmol) $(CO)_5CrC(NC_4H_8)Ph$ (1.0 mmol) and pyridine; reflux 7 h. Obtained (60 %) as a pale buff solid, m.p. 48–52°. (Found: C, 76.9; H, 5.8; N, 4.1. $C_{29}H_{29}NGe$ calcd.: C, 75.2; H, 6.3; N, 3.0 %.) δ(CCl_4): 1.50 (4H, m, β-CH_2), 2.46 (4H, m, α-CH_2), 3.92 (1H, s, CH), 2.80 (15H, m, C_6H_5) ppm. ν_{max} (CS_2, $CHCl_3$): 3130 w, 3080 m, 3040 s, 3020 s, 3000 w, 2960 s, 2950 s, 2930 s, 2910 s, 2870 s, 2740 m, 1600 m, 1490 m, 1481 m, 1462 m, 1450 m, 1430 m, 1360 w, 1315 m, 1292 m, 1270 m, 1205 m, 1190 m, 1125 m, 1090 s, 1070 m, 1028 s, 999 m, 910 m, 880 m, 760 m, 732 s, 701 s, 675 m cm^{-1}. Mass spectrum (*m/e*, *I*): 305, 56; 228, 22, 160, 100; 151, 39.

(α-Methoxybenzyl)tributyltin

From Bu_3SnH (1 mmol), $(CO)_5CrC(OMe)Ph$ (1 mmol) and pyridine (10 mmol); room temperature 10 min. Obtained (60 %) as a clear liquid, b.p. 90–100°/0.15 mmHg. (Found: C, 58.7; H, 8.9. $C_{20}H_{36}OSn$ calcd.: C, 58.5; H, 8.8 %.) δ(CCl_4): 0.85 (9H, m, CH_3), 1.65 (18H, m, CH_2), 3.29 (3H, s, CCH_3), 4.55 (1H, dd, CH), 7.12 (5H, m, C_6H_5) ppm. ν_{max} (liq. film): 3080 w, 3065 m, 3045 m, 3010 m, 2945 s, 2915 s, 2863 s, 2845 s, 2803 m, 2720 w, 1600 m, 1520 m, 1464 m, 1450 m, 1375 m, 1202 m, 1093 m, 1072 s, 1065 s, 1036 m, 960 m, 935 m, 875 m, 865 m, 760 s, 701 s, 665 s cm^{-1}. Mass spectrum (*m/e*, *I*): 412, 0.8 (M^+); 311, 2; 291, 100; 235, 68; 179, 56; 121, 30; 120, 16; 105, 4.

(α-Pyrrolidin-1-ylbenzyl)tributyltin

From Bu_3SnH (1 mmol), pyridine (6 mmol) and $(CO)_5CrC(NC_4H_8)Ph$ (1 mmol); reflux 1.5 h. Obtained (61 %) as a pale yellow liquid, b.p. 168–170°/6.5 mmHg. (Found: C, 59.9; H, 9.1; N, 3.4. $C_{23}H_{41}NSn$ calcd.: C, 61.2; H, 9.3; N, 3.1 %.) δ(CCl_4): 1.15 [27 H, m, $(C_4H_9)_3Sn$], 1.85 (4H, m, β-CH_2), 2.50 (4H, m, α-CH_2), 3.58 (1H, dd, CH), 7.35 (5H, m, C_6H_5) ppm. ν_{max} (liq. film): 3090 w, 3050 m, 3015 m, 2955 s, 2920 s, 2900 s, 2865 s, 2855 s, 2780 m, 1600 m, 1489 m, 1460 m, 1430 m, 1375 m, 1359 m, 1339 m, 1290 m, 1245 m, 1179 m, 1145 m, 1126 m, 1069 m, 1030 m, 1000 m, 960 m, 908 m, 872 m, 862 m, 700 s, 686 m, 660 m cm^{-1}. Mass spectrum (*m/e*, *I*): 291, 14; 235, 17; 179, 16; 175, 60; 161, 7; 160, 10; 106, 10; 105, 100.

Competition reactions

The two competing hydrides (ca. 1.5 mmol of each) and pyridine (12.4 mmol) were added to $(CO)_5CrC(OMe)Ph$ (ca. 1.3 mmol) in hexane (20 ml). Elaboration of the mixture produced after the lapse of a specified period at a particular temperature and subsequent rapid cooling, followed the usual pattern: the amount of each hydride remaining and of the insertion product(s) formed was estimated by NMR.

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