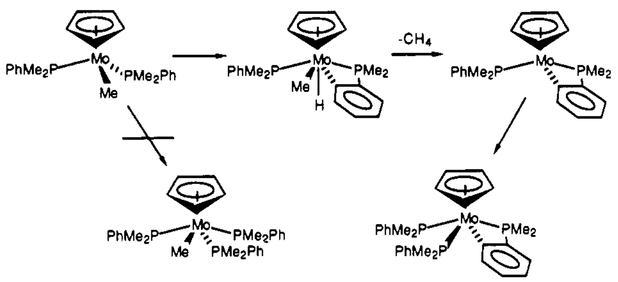
Scheme II



by reduction or vice versa, of the 16-electron CpMoMe($PMe_2Ph)_2$ complex. This molecule could undergo oxidative addition of one of the ortho C–H bonds, followed by reductive elimination of methane, to produce another 16-electron intermediate, CpMo(o-$C_6H_4PMe_2$)(PMe_2Ph) (Scheme II). This molecule is less sterically congested than CpMoMe($PMe_2Ph)_2$ and can thus accept a third phosphine molecule in the coordination sphere to form the observed product.

Conclusions

The different stability and reactivity of 17-electron compounds of the $CpMoX_2L_2$ class (X = electronegative π-donor ligand (halide) or less electronegative π-neutral ligand (methyl)) has been given a simple molecular orbital interpretation based on the π-acidic properties of the phosphine ligands and the synergic stabilization due to the contemporary presence of π acids and π bases. The structural distortions observed for the ortho-metalated phosphine molecule CpMo(o-$C_6H_4PMe_2$)($PMe_2Ph)_2$ are in agreement with the π-acidic nature of the phosphine in this molecule.

Further synthetic and mechanistic studies of the alkylation reaction of 17-electron $CpMoX_2L_2$ (X = halogen, L = phosphine) compounds are in progress.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and calculated hydrogen atom coordinates for CpMo(o-$C_6H_4PMe_2$)($PMe_2Ph)_2$ (5 pages); listings of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Relative Consecutive–Competitive Rate Constants in the Synthesis of Organoalkoxysilanes Using Molten Sodium

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Relative specific rate constants for replacing successive alkoxy groups with phenyl groups on $R_xSi(OR')_{4-x}$ (R = Me, Ph; R′ = Me, Et; x = 0–2) to make industrially important phenylalkoxysilanes were determined by addition of chlorobenzene to a dispersion of molten sodium in the alkoxysilanes. For $(MeO)_4Si$, the relative values of $k_4/k_3/k_2/k_1$ are 1/23/72/65. For $MeSi(OMe)_3$, the values $k_4/k_3/k_2$ are 1/5.9/9.8. For $Me_2Si(OEt)_2$, the values of k_4/k_3 are 1/3.6. Syntheses are much easier to carry out if a mixture of chlorobenzene containing 1 equiv of a chlorosilane is added to the molten sodium. The chlorosilane did not change the relative rate constants, and quantitative yields of phenylalkoxysilanes were obtained not only with PhCl but also with PhBr and PhI. The same procedure formed organo-functional alkoxysilanes in excellent yields when $CH{=}CH_2CH_2Cl$, $F_3CCH_2CH_2Br$, p-$Me_2NC_6H_4Br$, p-$(Me_3Si)_2NC_6H_4Cl$, 2-chlorothiophene, $PhCH_2Cl$, or $EtOCH_2Cl$ mixed with 1 eqiv of a chlorosilane was added to molten sodium dispersed in alkoxysilanes.

Introduction

We recently used a procedure patented 45 years ago[1] to prepare phenylalkoxysilanes and then used improvements in that procedure patented by Tiganik 40 and 30 years ago.[2a–c] The procedure proved to be superb, but no references could be found to its use in the last 30 years.

Addition of an organic halide to molten sodium dispersed in an alkoxysilane leads to vigorously exothermic reactions that quantitatively produce organoalkoxysilanes. Use of an organic halide mixed with 1 equiv of a chlorosilane[2] forms the same quantitative yield of organoalkoxysilane in a mixture that is much easier to stir and filter.

Organic halides react with molten sodium extremely rapidly.

$$RX + 2Na \rightarrow RNa + NaX\downarrow$$

RNa reacts with the surrounding medium of alkoxysilanes.

$$\equiv SiOR' + RNa \rightarrow \equiv SiOR'R^-Na^+$$

A chlorosilane then reacts to re-form an alkoxysilane.

$$\equiv SiOR'R^-Na^+ + \equiv SiCl \rightarrow \equiv SiR + \equiv SiOR' + NaCl\downarrow$$

The number of equivalents of alkoxysilyl groups remains constant in this system.

A slurry of finely divided NaX and NaCl is formed that remains easily stirrable and from which the solids are easily filtered. The distribution of organoalkoxysilanes that are

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[1] Bondy, C.; Reiser, K. Brit. Patent 573, 906, Dec 12, 1945.

[2] (a) Tiganik, L. U.S. Patent 2,521,267, Sept 5, 1950. (b) Tiganik, L. Brit. Patent 668,532, March 18, 1952. (c) Tiganik, L. Can. Patent 598,441, May 24, 1960.

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Table I

$(MeO)_4Si + nPhCl + 2nNa \rightarrow Ph_xSi(OMe)_{4-x} + nNaCl + nNaOMe$

	mole percentage			
n	$(MeO)_4Si$	$PhSi(OMe)_3$	$Ph_2Si(OMe)_2$	Ph_3SiOMe
0.156	88.5	8	2.5	0
0.5	61.0	29	11	0
0.871	43.0	31.7	21	4.6
1.0	34.5	35	26	6
1.19	26.8	36	28	9
2.00	4.0	16	50	30
2.37	1.0	6	46.3	46.3

formed is determined by the molar ratio, n, of RX added to the alkoxysilane and by the relative rates of reaction of each alkoxysilane, $R_xSi(OR')_{4-x}$, as the values of x change from 0 to 3. No references could be found for such relative rates for any polyfunctional silane reacting with any organometallic reagent.

The relative rate constants for PhCl reacting with $Si(OMe)_4$, $PhSi(OMe)_3$, $MeSi(OMe)_3$, and $Me_2Si(OEt)_2$ were determined.

Discussion

Consecutive–competitive reactions take place when PhCl is dripped into a stirred dispersion of molten sodium in an alkoxysilane. For example, with tetramethoxysilane these reactions can be written

$$(MeO)_4Si + PhCl + 2Na \xrightarrow{k_1} PhSi(OMe)_3 + NaOMe + NaCl \quad (1)$$

$$PhSi(OMe)_3 + PhCl + 2Na \xrightarrow{k_2} Ph_2Si(OMe)_2 + NaOMe + NaCl \quad (2)$$

$$Ph_2Si(OMe)_2 + PhCl + 2Na \xrightarrow{k_3} Ph_3SiOMe + NaOMe + NaCl \quad (3)$$

$$Ph_3SiOMe + PhCl + 2Na \xrightarrow{k_4} Ph_4Si + NaOMe + NaCl \quad (4)$$

The rates of formation of the phenylsilanes at any time are then

$$d/dt\,[PhSi(OMe)_3] = k_1[(MeO)_4Si][PhCl][Na] - k_2[PhSi(OMe)_3][PhCl][Na]$$

$$d/dt\,[Ph_2Si(OMe)_2] = k_2[PhSi(OMe)_3][PhCl] \times [Na] - k_3[Ph_2Si(OMe)_2][PhCl][Na]$$

$$d/dt\,[Ph_3SiOMe] = k_3[Ph_2Si(OMe)_2][PhCl][Na] - k_4[Ph_3SiOMe][PhCl][Na]$$

When the change in concentration of a product is zero

$$k_2/k_1 = [(MeO)_4Si]/[PhSi(OMe)_3] \quad (5)$$

$$k_3/k_2 = [PhSi(OMe)_3]/[Ph_2Si(OMe)_2] \quad (6)$$

$$k_4/k_3 = [Ph_2Si(OMe)_2]/[Ph_3SiOMe] \quad (7)$$

Table II

$PhSi(OMe)_3 + nPhCl + 2nNa \rightarrow Ph_{x+1}Si(OMe)_{3-x} + nNaCl + nNaOMe$

	mole percentage			
n	$PhSi(OMe)_3$	$Ph_2Si(OMe)_2$	Ph_3SiOMe	Ph_4Si
0.16	87.9	7.7	4.3	0.0
0.5	58.0	35.0	7.1	0.0
0.96	24.0	55.0	21.0	0.0
1.47	4.0	46.0	51.0	1.0
1.78	1.0	21.5	78.5	2.0
1.92	0.5	12.5	83.0	4.4
2.1	0.0	2.9	85.0	11.6

Table III

$MeSi(OMe)_3 + nPhCl + 2nNa \xrightarrow{PhMe} MePh_xSi(OMe)_{3-x} + nNaCl + nNaOMe$

	mole percentage			
n	$MeSi(OMe)_3$	$MePhSi(OMe)_2$	$MePh_2SiOMe$	$MePh_3Si$
0.2	81.0	16.0	2.5	0
0.687	41.0	45.0	14.0	0
0.75	42.7	40.5	16.0	.9
0.857	35.0	44.7	19.0	1.0
0.937[a]	30.0	47.8	21.0	1.3
1.0	30.8	41.2	25.7	2.0
1.1[b]	25.8	42.2	27.7	4.3
1.15[b]	24.4	41.0	30.2	4.5
1.43	8.0	44.0	42.0	4.0
1.97	2.3	15.2	65.4	17.0
2.19	1.0	8.0	60.0	31.0

[a] PhBr was used instead of PhCl. [b] No toluene.

Table IV

$Me_2Si(OEt)_2 + nPhCl + 2nNa \rightarrow Me_2Ph_xSi(OEt)_{2-x} + nNaCl + nNaOMe$

	mole percentage		
n	$Me_2Si(OEt)_2$	$Me_2PhSiOEt$	Me_2Ph_2Si
0.45	57.0	40.4	2.3
0.656	39.0	55.0	6.0
0.860	28.0	58.0	14.0
1.060	16.0	61.0	23.0
1.187	8.8	63.5	27.6
1.440	3.0	49.6	47.3

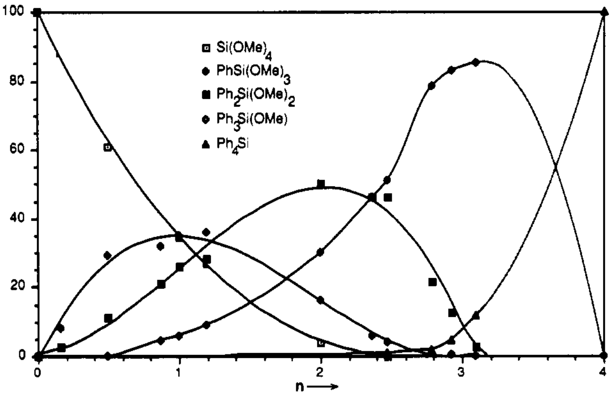

Figure 1. Distribution of alkoxysilanes versus equivalents of chlorobenzene for $Si(OMe)_4 + nPhCl + 2nNa \rightarrow Ph_xSi(OMe)_{4-x} + nNaCl + nNaOMe$.

This treatment of four consecutive competitive reactions was described by Fuoss.[3] The mole fractional distribution of alkoxysilanes was determined as a function of the equivalents of chlorobenzene added to moles of $Si(OMe)_4$, $PhSi(OMe)_3$, $MeSi(OMe)_3$, and $Me_2Si(OEt)_2$. Data for different alkoxysilanes are found in the following tables: $Si(OMe)_4$, Table I; $PhSi(OMe)_3$, Table II; $MeSi(OMe)_3$, Table III; $Me_2Si(OEt)_2$, Table IV.

Plots of the distribution of alkoxysilanes versus equivalents of chlorobenzene were made from values in these tables. Figure 1 illustrates such a plot from Tables I and

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[3] Fuoss, R. M. *J. Am. Chem. Soc.* **1943**, *66*, 2406.

Table V. Miscellaneous Syntheses

reagents		n	products	% yield	mass spectra
$Si(OMe)_4$	$F_3C(CH_2)_2Br$	1.73	$F_3C(CH)_2Si(OMe)_3$[a,b]	50	141 ($M^+ - F_2C_3H_3$, 72), 121 ($M^+ - F_3C_3H_4$, 100)
			$(F_3C(CH_2)_2)_2Si(OMe)_2$[a,b]	30	155 ($M^+ - F_3C_3H_4 - CH_4O$, 28), 125 ($M^+ - F_3C_3H_4 - 2\ MeO$, 47)
			$(F_3C(CH_2)_2)_3SiOMe$[c]	20	253 ($M^+ - F_3C_3H_4$, 6)
	p-$(Me_3Si)_2NC_6H_4Cl$	0.14	p-$(Me_3Si)_2NC_6H_4Si(OMe)_3$	82	357 (M^+, 29), 342 ($M^+ - Me$, 100)
	Me_3CCl	1.0	$Me_3CSi(OMe)_3$	65[d]	178 (M^+, 2), 121 ($M^+ - C_4H_9$, 100)
$MeSi(OMe)_3$	$F_3C(CH_2)_2Br$	0.21	$F_3C(CH_2)_2MeSi(OMe)_2$[b]	75	125 ($M^+ - F_2C_3H_3$, 47), 105 ($M^+ - F_3C_3H_4$, 100)
			$(F_3C(CH_2)_2)_2MeSiOMe$	8	171 ($M^+ - F_3C_3H_4$, 3)
	p-$Me_2NC_6H_4Br$	0.22	p-$Me_2NC_6H_4MeSi(OMe)_2$	92[e]	225 (M^+, 71), 210 ($M^+ - Me$, 100)
	$CH_2{=}CHCH_2Cl$	0.21	$CH_2{=}CHCH_2MeSi(OMe)_2$	74[f]	131 ($M^+ - CH_3$, 3), 105 ($M^+ - CH_2CH{=}CH_2$, 100)
			$(CH_2{=}CHCH_2)_2MeSiOMe$	24[f]	156 (M^+, 1), 115 ($M^+ - CH_2CH{=}CH_2$, 100)
	2-chlorothiophene	0.13	$C_4H_4SMeSi(OMe)_2$	60	188 (M^+, 38), 173 ($M^+ - Me$, 100)
			$(C_4H_4S)_2MeSiOMe$	16	292 (M^+, 19), 277 ($M^+ - Me$, 100)
	$PhCH_2Cl$	0.16	$PhCH_2MeSi(OMe)_2$	91	196 (M^+, 11), 105 ($M^+ - C_6H_5CH_2$, 100), 91 ($M^+ - MeSi(OMe)_2$, 20)
			$(PhCH_2)_2MeSiOMe$	4	256 (M^+, 10), 165 ($M^+ - C_6H_5CH_2$, 100)
	Me2CHBr	0.23	$Me_2CHMeSi(OMe)_2$	40[d]	148 (M^+, 1), 105 ($M^+ - Me_2C$, 100)
$Si(OEt)_4$	p-$(Me_3Si)_2NC_6H_4Cl$	0.23	p-$(Me_3Si)_2NC_6H_4Si(OEt)_3$	63	399 (M^+, 65), 384 ($M^+ - Me$, 100)
	PhCl	1.70	$PhSi(OEt)_3$[b]	52[e]	240 (M^+, 20), 195 ($M^+ - OEt$, 49), 163 ($M^+ - C_6H_5$, 11)
			$Ph_2Si(OEt)_2$[b]	17[e]	272 (M^+, 6), 227 ($M^+ - OEt$, 16), 195 ($M^+ - C_6H_5$, 58)
			Ph_3SiOEt[b]	17[e]	304 (M^+, 36), 259 ($M^+ - OEt$, 17), 227 ($M^+ - C_6H_5$, 71)
	PhI	0.44	$PhSi(OEt)_3$[b]	60	
			$Ph_2Si(OEt)_2$[b]	28	
			Ph_3SiOEt[b]	5	
	$EtOCH_2Cl$	0.30	$EtOCH_2Si(OEt)_3$	51[f]	193 ($M^+ - Et$, 50), 163 ($M^+ - CH_2OEt$, 66)
			$(EtOCH_2)_2Si(OEt)_2$	7	207 ($M^+ - Et$, 12), 177 ($M^+ - CH_2OEt$, 49)
			$(EtOCH_2)_3SiOEt$	4.5	191 ($M^+ - CH_2OEt$)
			$(EtOCH_2)_4Si$	37[f]	235 ($M^+ - Et$, 3), 205 ($M^+ - CH_2OEt$, 76)
$F_3C(CH_2)_2Si(OMe)_3$	$F_3C(CH_2)_2Br$	0.70	$(F_3C(CH_2)_2)_2Si(OMe)_2$	68	
			$(F_3C(CH_2)_2)_3SiOMe$	28	
		0.50	$(F_3C(CH_2)_2Si(OMe)_2$	>80	
	PhCl	0.38	$F_3C(CH_2)_2PhSi(OMe)_2$	72	167 ($M^+ - F_3C_3H_4$, 100)
$Me_2Si(O$-n-$C_6H_{13})_2$		0.38	$PhMe_2SiO$-n-C_6H_{13}	100	221 ($M^+ - CH_3$, 73), 135 ($M^+ - OC_6H_{13}$, 45)

[a] Described by: McBee, E.; Roberts, C.; Judd, G.; Chao, T. *J. Am. Chem. Soc.* **1955**, *77*, 1292. [b] Available from Petrarch Systems, Bristol, PA 19007. [c] Described by: Kupnova, N.; Chugunov, V.; Klebanskii, A. *Zh. Obschch. Khim.* **1965**, *35*, 2022. [d] Gases were liberated, presumably isobutylene and propylene. [e] Made from p-$Me_2NC_6H_4Li$ in 31% yield by: Rosenberg, S. D.; Rochow, E. G. *J. Am. Chem. Soc.* **1953**, *77*, 2907. [f] Isolated yields after distillation.

II. The relative specific rate constants for $Si(OMe)_4$ were taken as the ratios of the mole fractions of the alkoxysilanes shown in eqs 5–7. In this example, $k_4/k_3 = 0.043$, $k_3/k_2 = 0.32$, and $k_2/k_1 = 1.1$. When a value of 1 is assigned to k_4, the relative rate constants $k_4/k_3/k_2/k_1$ are 1/23/72/65. The second phenyl substituent is attached slightly faster than the first, but the third and especially the fourth are much less rapidly attached. For $MeSi(OMe)_3$, $k_4/k_3 = 0.17$ and $k_3/k_2 = 0.6$. These values give $k_4/k_3/k_2 = 1/5.9/9.8$. For $Me_2Si(OEt)_2$, k_4/k_3 is 0.28 and $k_4/k_3 = 1/3.6$.

The procedure employed to determine these relative competitive rate constants was used to synthesize organoalkoxysilanes from PhBr, PhI, $PhCH_2Cl$, $CH_2{=}CHCH_2Cl$, $F_3CCH_2CH_2Br$, $EtOCH_2Cl$, 2-chlorothiophene, p-$Me_2NC_6H_4Br$, and p-$(Me_3Si)_2NC_6H_4Cl$, all with remarkable success. See Table V.

Experimental Section

Consecutive-Competitive Relative Rate Constants. Carefully measured amounts of chlorobenzene were dripped into a stirred dispersion of sodium in a known amount of refluxing tetramethoxysilane (bp 122 °C). After an increment of chlorobenzene was added, the liquid mixture was analyzed with an F and M Model 810 chromatograph interfaced with a Perkin-Elmer Sigma 10 integrator–minicomputer. The column used was $^3/_{16}$ in. × 10 ft stainless steel packed with 16.6% OV210 on Chromosorb P. Known mixtures of authentic samples were injected to determine the response factors to convert area percent into mole percent from the computer. The GLC curves were remarkably free of any detectable byproducts.

Sodium (202.5 g, 8.81 mol) was dispersed in refluxing tetraethoxysilane (305.8 g, 1.47 mol) and heptane (485 mL) at 102 °C. A mixture of chlorobenzene (495.7 g, 4.41 mol) and tetrachlorosilane (187.7 g, 1.105 mol) was added in 77 min. The mixture was then cooled to 50 °C, filtered free of NaCl, and analyzed by GC to contain $Si(OEt)_4$ (0.27 mol), $PhSi(OEt)_3$ (0.56 mol), $Ph_2Si(OEt)_2$ (1.15 mol), Ph_3SiOEt (0.39 mol), and Ph_4Si (0.03 mol). The mole fractions are as follows: $Si(OEt)_4$, 0.11; $PhSi(OEt)_3$, 0.23; $Ph_2Si(OEt)_2$, 0.48; Ph_3SiOEt, 0.16; Ph_4Si, 0.01. These values fall very close to the curves in Figure 1 if n is taken as 4.41/(1.47 + 1.105) = 1.71. Thus, it appears that the use of an inert solvent (heptane) and the mixture of $PhCl/SiCl_4$ had little or no effect upon relative competitive rate constants. Because the tetrachlorosilane was converted to tetraethoxysilane, the number of moles of alkoxysilane used to calculate n in this example was the sum of the number of moles of $(EtO)_4Si + SiCl_4$.

Typical Syntheses. The structures of compounds for which authentic samples were not available were confirmed by NMR. All ^1H NMR were recorded on a Varian EM-390 spectrometer in $CDCl_3$ solvent with $CHCl_3$ as internal standard. All chemical shifts were reported relative to $CHCl_3$ at 7.24 ppm. GC/MS data were obtained from a Hewlett-Packard 5790 GC with 20 mm × 0.2 mm i.d. cross-linked methylsilicone capillary collum and a 5970 mass-selective detector. GC data were obtained from a Hewlett-Packard 5710 GC equipped with a 20 ft × $^1/_8$ in. 10% SE30 on Chromosorb W HP 90/100-mesh column and a thermal conductivity detector. A Hewlett-Packard 3380 recording integrator was used for quantification. All alkoxysilanes were distilled from sodium prior to use to remove residual silanol, chloride, and alcohol.

Sodium (15.2 g, 0.66 mol) was dispersed in refluxing tetramethoxysilane (16.82 g, 0.11 mol) and toluene (125 mL) at 103 °C. A mixture of 3,3,3-trifluoropropyl bromide (58.5 g, 0.33 mol) and tetrachlorosilane (14.2 g, 0.083 mol) was added dropwise in 24 min. The mixture was filtered at 50 °C through a coarse glass sintered disk. The solids were washed twice with toluene. All the liquids were combined and analyzed by GLC/MS. The products were 50% $F_3CCH_2CH_2Si(OMe)_3$, 30% $(F_3CCH_2CH_2)_2Si(OMe)_2$, and 20% $(F_3CCH_2CH_2)_3SiOMe$ with a detectable trace of $(F_3CCH_2CH_2)_4Si$. n in this example was calculated as 0.33 mol/(0.11 + 0.083) mol = 1.7.

Sodium (69 g, 3 mol) was dispersed in refluxing (3,3,3-trifluoropropyl)trimethoxysilane (130.3 g, 0.6 mol) and isooctane

(2750 mL). A mixture of 3,3,3-trifluoropropyl bromide (264.7 g, 1.5 mol) and (3,3,3-trifluoropropyl)trichlorosilane (115.9 g, 0.5 mol) was added dropwise in 99 min, which kept the mixture gently refluxing with no external heat. The products were worked up as above, and GC analysis indicated the presence of $F_3CCH_2CH_2Si(OMe)_3$ (4%), $(F_3CCH_2CH_2)_2Si(OMe)_2$ (68%), and $(F_3CCH_2CH_2)_3SiOMe$ (28%). $n = 1.5\ \mathrm{mol}/(0.6 + 0.5)\ \mathrm{mol} = 1.36$.

Sodium (1.88 g, 0.082 mol) was dispersed in refluxing (3,3,3-trifluoropropyl)trimethoxysilane (16.54 g, 0.076 mol) and isooctane (25 mL). A mixture of 3,3,3-trifluoropropyl bromide (7.26 g, 0.041 mol) and trimethylchlorosilane (4.42 g, 0.041 mol) was added. GC analysis indicated the products were trimethylmethoxysilane (25%), $F_3CCH_2CH_2Si(OMe)_3$ (45.3%), $(F_3CCH_2CH_2)_2Si(OMe)_2$ (21%), and $(F_3CCH_2CH_2CH_2)_3SiOMe$ (5.5%). No $F_3CCH_2CH_2SiMe_3$ was detected. $n = 0.041\ \mathrm{mol}/0.076\ \mathrm{mol} = 0.7$. Me_3SiOMe did not enter into competitive reactions.

Sodium (152.8 g, 6.65 mol) was dispersed in refluxing (104 °C) methyltrimethoxysilane (2040 g, 15 mol). A mixture of allyl chloride (281.14 g, 3.67 mol, 10% excess) and methyltrichlorosilane (166 g, 1.11 mol) was added in 115 min, which was the maximum rate at which the condenser could condense the boil up. The products from several such runs were combined and distilled to recover allyl chloride and methyltrimethoxysilane followed by $CH_2{=}CHCH_2MeSi(OMe)_2$ (bp 128 °C; 366 g, 2.5 mol) and $(CH_2{=}CHCH_2)_2MeSiOMe$ (bp 153 °C; 66 g, 0.42 mol), leaving a small undistilled residue containing mostly what appeared to be $(CH_2{=}CHCH_2)_3MeSi$ and small amounts of several high-boiling unidentified compounds believed to be siloxanes. $n = 3.30\ \mathrm{mol}/(0.5 + 1.1)\ \mathrm{mol} = 0.21$.

Sodium (2.82 g, 0.12 mol) was dispersed in dimethyldi-*n*-hexoxysilane (34.3 g, 0.13 mol) at 104 °C, and a mixture of chlorobenzene (6.9 g, 0.06 mol) and dimethyldichlorosilane (4 g, 0.03 mol) was added. The temperature rose to 170 °C in 1 min. The mixture was cooled with an ice bath and kept at about 130 °C until the addition was completed in 7 min. Analysis by GC/MS indicated 100% yield of Me_2Ph SiO-*n*-Hex. $n = 0.06\ \mathrm{mol}/(0.13 + 0.03) = 0.38$.

Some of the products were needed at Dow Corning for miscellaneous applications, and these were scaled up and distilled to isolate alkoxysilanes that were more than 98% pure by GC analyses. Such examples include the allyl-, (trifluoropropyl)-, (ethoxymethyl)-, and phenylethoxysilanes. In each of these, yields by analytical distillation were in very good agreement with GC analysis.

Only 1 equiv of any chlorosilane should be mixed with the organic halide, and the organic groups on the chlorosilane should be the same as those on the alkoxysilane. If an excess of chlorosilane is used, the products contain chlorosilane impurities that are exceedingly difficult to separate. If the organic groups on the chlorosilane are not the same as those on the alkoxysilane, the products will be a mixture of organoalkoxysilanes with the different organo groups.

A convenient exception to this is the use of Me_3SiCl, which can be used in any case because it forms Me_3SiOR', which is volatile, easily separated from the other products, and slow to react with RNa to form Me_3SiR.

Data of Compounds Isolated Pure by Distillation. $EtOCH_2Si(OEt)_3$: bp 72 °C (10 mm); ^1H NMR δ 3.87 (6 H, q), 3.46 (2 H, q, 3.2 (2 H, s), 1.29 (12 H, t). $(EtOCH_2)_4Si$: bp 112 °C (10 mm); ^1H NMR δ 3.41 (8 H, s), 1.23 (12 H, t). $CH_2{=}CHCH_2MeSi(OMe)_2$: bp 128 °C (1 atm); ^1H NMR δ 5.75 (1 H, m), 3.5 (2 H, s), 1.64 (2 H, d), 0.13 (3 H, s). $(CH_2{=}CHCH_2)_2MeSiOMe$: bp 153 °C (1 atm); ^1H NMR δ 5.83 (2 H, d), 4.9 (4 H, m), 3.5 (3 H, s), 1.73 (4 H, d), 0.22 (3 H, s). $CH_2{=}CHCH_2Me_2SiOMe$: ^1H NMR δ 5.7 (1 H, m), 4.86 (2 H, m) 3.44 (3 H, s), 1.66 (2 H, d), 0.18 (6 H, s). $(F_3CCH_2CH_2)_3SiOMe$: bp 133 °C (71 mm); ^1H NMR δ 3.55 (3 H, s), 2.1 (6 H, m), 0.9 (4 H, m). $(F_3CCH_2CH_2)_2Si(OMe)$: bp 103 °C (76 mm); ^1H NMR δ 3.57 (6 H, s), 2.1 (4 H, m), 0.9 (4 H, m). $F_3CCH_2CH_2PhSi(OMe)_2$: bp 107 °C (12 mm); ^1H NMR δ 7.4 (5 H, m), 3.5 (6 H, s), 2.0 (2 H, m), 1.0 (2 H, m).

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Investigation of Substituent Effects in Substituted (η^5-Cyclopentadienyl)dicarbonylrhodium Compounds Using ^{103}Rh NMR and IR Data

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The effect of substituents on a series of ring-substituted (η^5-cyclopentadienyl)dicarbonylrhodium complexes was investigated by means of changes in C–O stretching frequencies as well as ^{103}Rh NMR chemical shifts. The effect of electron-donating and -withdrawing substituents on the ^{103}Rh NMR shift and CO stretching frequencies was found to be qualitatively consistent with the traditional model of dπ electron back-donation. The effect of the substituents was found to be neither a purely resonance or inductive phenomenon.

Introduction

^{103}Rh NMR spectroscopy has been used to gain information about the metal center in a variety of complexes.[1–6] The ^{103}Rh nucleus has a natural abundance of 100% and a nuclear spin of $^1/_2$. The combination of the resulting narrow resonance bands and very large chemical shift

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