Organometallics **1989,** *8,* 2615–2618 2615

100-20-9; *m*-$NO_2PhCOCl$, 121-90-4; *p*-$ClPhCOCl$, 122-01-0; $(ClMe_2Si)_2$, 4342-61-4; $(Cl_2MeSi)_2$, 4518-98-3; $PhMe_2SiCl$, 768-33-2; *p*-$ClOCPhSiMe_2Cl$, 17902-45-3; *m*-$NO_2PhSiMe_2Cl$, 116088-85-8; *p*-$CH_3PhSiMe_2Cl$, 17881-63-9; *p*-$ClPhSiMe_2Cl$, 825-92-3; $PhSiMeCl_2$, 149-74-6; *p*-$ClPhSiMeCl_2$, 825-93-4; $(PhCN)_2PdCl_2$, 14220-64-5; P(*c*-Hx)$_3$, 2622-14-2; $P(Bu)_3$, 998-40-3; P(*o*-MeOPh)$_3$, 4731-65-1; P(*p*-MePh)$_3$, 1038-95-5; PPh_3, 603-35-0; P(*p*-ClPh)$_3$, 1159-54-2; Et_3N, 121-44-8; $Pd(PPh_3)_4$, 14221-01-3; $Pd(PPhMe_2)_2Cl_2$, 15616-85-0; Pd, 7440-05-3; trimellitic acid anhydride chloride, 1204-28-0; *N*-methyltrimellitimide acid chloride, 3969-16-2; 4-(chlorodimethylsilyl)phthalic anhydride, 116088-82-5; 4-(dichloromethylsilyl)-*N*-methylphthalimide, 115609-78-4; 4-(dichloromethylsilyl)phthalic anhydride, 104209-26-9; pyridine, 110-86-1.

Dimethylzirconocene-Catalyzed Polymerization of Alkylsilanes

William H. Campbell and Terrence K. Hilty*

Dow Corning Corporation, Midland, Michigan 48640

Lori Yurga

The Dow Chemical Company, Midland, Michigan 48640

Received March 8, 1989

The polymerization of *n*-butylsilane was carried out using bis(η^5-cyclopentadienyl)dimethylzirconium(IV) as the catalyst. Rapid conversion of the silane to low molecular weight catenated Si–Si oligomers took place. The characterization revealed that a large percentage of the Si_5 through Si_7 oligomers were cyclic, whereas previous reports cited only linear products from similar reactions. Oligomers with degrees of polymerization (Dp) of 2 through 8 were also observed showing clear demonstration of a step growth mechanism. The difference in products is believed to be due to the ability of zirconium to react reversibly with both primary and secondary alkylsilanes. The lability of the zirconium–silicon bond allows for a dynamic equilibrium in which intermediate products are liberated from the metal center. These intermediates undergo further reaction including cyclization. Some possible mechanistic implications are discussed in light of previous literature postulates.

Introduction

Polysilanes have received a large amount of attention in the literature due to their potential uses as positive and negative photoresist materials, as photopolymerization catalysts, and as precursors to and reinforcing agents in ceramic materials.[1-3] The only viable route to high molecular weight polysilanes to date has been through the Wurtz coupling reaction, which has several commercial drawbacks: (1) poor control over molecular weight and large polydispersity, (2) potential hazards associated with the use of molten alkali metals, and (3) large amounts of salt waste generated.

Recently, the possibility of using transition metals to catalyze Si–Si catenation has been addressed by using group VII and group VIII transition-metal complexes,[4] but the best results for preparing longer Si–Si chains catalytically has been with group IV complexes. Harrod and co-workers have been the primary investigators of the group IV catalysts using bis(η^5-cyclopentadienyl)dimethyltitanium(IV) (Cp_2TiMe_2) and bis(η^5-cyclopentadienyl)dimethylzirconium(IV) (Cp_2ZrMe_2) in the dehydrogenative coupling of primary organosilanes.[5a-f] Their method employs alkyl or aryl silanes as monomers in the catenation reaction (eq 1).

$$n\mathrm{RSiH_3} \xrightarrow{\mathrm{Cp_2TiMe_2}} \mathrm{H{-}(R{-}SiH)_{\mathit{n}}{-}H} + (n-1)\mathrm{H_2} \qquad (1)$$

Harrod and co-workers focused primarily on the use of phenylsilane ($PhSiH_3$) as the substrate and Cp_2TiMe_2 as the catalyst in these reactions. Although they report results from Cp_2ZrMe_2 catalysis and other aryl- and alkylsilanes as substrates, most of the conclusions are drawn from the $PhSiH_3$ work and extrapolated to include the other silane substrates and the zirconium catalyst.

Harrod's polysilane products were characterized by a number of spectral and chromatographic techniques and were claimed to be linear with Dp values between 10 and 20, but all analyses were carried out on bulk product mixtures. There is no evidence that individual components have been characterized. Harrod further claims that no low Dp species (Dp = 2–6) were detectable.

Our results using $PhSiH_3$ are in reasonable agreement with those reported by Harrod et al., but, in our hands, alkylsilanes give a very different chemistry with Cp_2ZrMe_2. Herein, we focus on the chemistry of *n*-butylsilane ($BuSiH_3$) as the substrate for the Cp_2ZrMe_2-catalyzed dehydrogenative coupling reaction. We chose this substrate for its small size, giving more facile analysis by gas chromatographic techniques. This zirconium-catalyzed process gives both linear and cyclic products with Dp values

---

(1) (a) Zeigler, J. M.; Harrah, L. A.; Johnson, A. W. *Polym. Prepr.* **1987**, *28*(1), 424. (b) Harrah, L. A.; Zeigler, J. M., *Macromolecules* **1987**, *20*, 2039.

(2) (a) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (b) Gilman, H.; Atwell, W. H.; Schwebke, G. L. *J. Organomet. Chem.* **1964**, *2*, 369. (c) Baney, R. H.; Gaul, J. H.; Hilty, T. K. (*Organometallics* **1983**, *2*, 859. (d) Gobbi, G. C.; Fleming, W. W.; Sooriyakumaran, R.; Miller, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 5624. (e) Yajima, S.; Shishodo, T.; Kayano, H. *Nature (London)* **1976**, *264*, 237. (f) Wolff, A. R.; West, R.; Peterson, D. G. Eighteenth Organosilicon Symposium, April, 1984. (g) Yajima, S. *Am. Ceram. Soc. Bull.* **1983**, *62*, 893.

(3) (a) Zeldin, M., Allcock, H. R., Wynne, K., Eds. *Inorganic and Organometallic Polymers*; ACS Symposium Monograph 360; American Chemical Society: Washington, DC, 1988. (b) Ed. Laine, R. M. *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*; NATO AST Series E, 1988; No. 141.

(4) (a) Pannell, K. H.; Vincenti, S. P.; Scott, R. C., III *Organometallics* **1987**, *6*, 1593. (b) Corey, J. Y.; Chang, L. S.; Corey, E. R. *Organometallics* **1987**, *6*, 1595. (c) Brown-Wensley, K. A. *Organometallics* **1987**, *6*, 1590.

(5) (a) Aitken, C.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* **1985**, *279*, C11–C13. (b) Aitken, C. T.; Harrod, J. F.: Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059. (c) Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381. (d) Harrod, J. F. *Polym. Prepr.* **1987**, *28*(1) 403. (e) Aitken, C.; Harrod, J. F.; Samuel, E. *Can, J. Chem.* **1986**, *64*, 1677. (f) Aitken, C.; Harrod, J. F.; Gill; U. S. *Can. J. Chem.* **1987**, *65*, 1804.

0276-7333/89/2308-2615$01.50/0

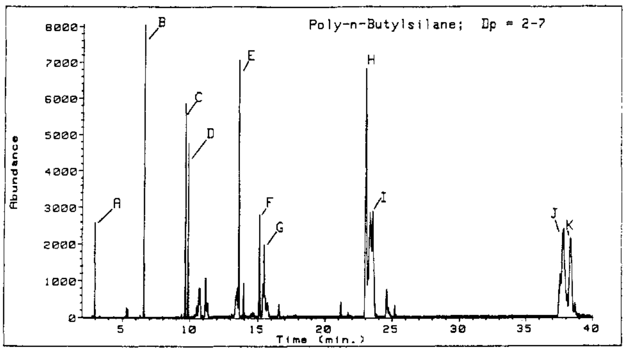

Figure 1. Gas chromatogram of $(RSiH)_xH_y$ (R = *n*-butyl) polysilane product mixture.

ranging between 2 and 8. We will discuss our characterization of the components of the product mixture and propose some alternative suggestions for the previously proposed mechanism of dehydrogenative coupling to account for the low Dp and cyclic products.

Results and Discussion

The Zr-catalyzed polymerization of polysilanes gives a series of products with differing Dp, and in this process the possibility of cyclization exists. Characterization on whole reaction product mixtures using techniques such as NMR, IR, or direct inlet mass spectroscopy will give structural information and may demonstrate the existence of linear products. However, these techniques are not sufficient to rule out the existence of cyclic products.

Our investigation focused on the polymerization of *n*-butylsilane (n-$C_4H_9SiH_3$) using Cp_2ZrMe_2 as the polymerization catalyst. Each sample was analyzed by ^1H NMR, ^{29}Si NMR, IR, and GPC after isolation of the polymer mixture,[6] and our data were in good agreement with similar products reported in the literature. On closer examination of our data some interesting clues were noted that further confirmed that the system was not as simple as originally believed. We expanded the Si–H stretching region in the IR spectrum for several polymer product mixtures and found the major band was, in most cases, near 2100 cm^{-1}, but each sample showed a pronounced lower frequency shoulder centered near 2080 cm^{-1}. The relative intensities of these two bands also seemed to vary from sample to sample.

The polymer mixtures were then analyzed by GC/FT-IR and GC-MS. Using toluene as an internal standard, we demonstrated total sample elution from a capillary GC column. In this way, the oligomeric components could be individually analyzed. A typical GC trace from the polymer product mixture is shown in Figure 1, and the peak identities and GC integrations are found in Table I. Note that the di- and trisilane products show only one peak in the GC trace, whereas the tetrasilane $[(H_2BuSi)_2(HBuSi)_2]$ shows two peaks corresponding to the disasteriomers resulting from the two chiral centers in the molecule. The corresponding analogy to the penta-, hexa-, and heptasilane oligomers increases the complexity due to the stereoisomerism as well as the presence of both cyclic and linear products.

Table I. GC/FT-IR Data for *n*-Butyl Pendant Polysilanes

peak	Si–H stretch, cm^{-1}	SiH_2 vibration, cm^{-1}	degree of polymerizatn		%
A	2116	934	2	linear	1.6
B	2116	931	3	linear	4.9
C	2111	930	4	linear	6.1
D	2114	931	4	linear	4.0
E	2110	929	5	linear	9.9
F	2113/2084	934	5	linear/cyclic	4.4
G	2086	absent	5	cyclic	5.5
H	2110	930	6	linear	19.9
I	2077	absent	6	cyclic	16.9
J	2103/2085	929 (vw)[a]	7	linear/cyclic	10.8
K	2076	absent	7	cyclic	10.7

[a] vw indicates that these bands are very weak in relation to what is typically observed.

Table II. Mass Spectra Data for *n*-Butyl Pendant Polysilanes $H_2BuSi(SiHBu)_nSiBuH_2$ (n = 0–2)

m/e (% abundance)	mass loss	fragment lost[a]	ion[a]
RH_2SiSiH_2R	$R_2Si_2H_4$	MW = 174	peak A
174 (4.6)			M^+
117 (4.4)	57	R	$(RH_2SiSiH_2)^+$
88 (5.5)	86	RSiH	$(RSiH_3)^+$
87 (20)	87	$RSiH_2$	$(RSiH_2)^+$
86 (35.7)	88	$RSiH_3$	$(RSiH)^+$
$(RSiH_2)_2(RSiH)$	$R_3Si_3H_5$	MS = 260	peak B
203 (1.3)	57	R	$(R_2Si_3H_5)^+$
172 (61.7)[b]	88	$RSiH_3$	$(R_2Si_2H_2)^+$
116 (54.7)	114	$RSiH_3$ + (R–H)[c]	$(RSi_2H_3)^+$
$(RSiH_2)_2(RSiH)_2$	$R_4Si_4H_6$	MW = 346	peak C[d]
289 (0.8)	57	R	$(R_3Si_4H_6)^+$
258 (46.5)	88	$RSiH_3$	$(R_3Si_3H_3)^+$
202 (100)	144	$RSiH_3$ + (R–H)	$(R_2Si_3H_4)^+$
146 (47.5)	200	$RSiH_3$ + 2(R–H)	$(RSi_3H_5)^+$

[a] R = C_4H_9. [b] Peaks at *m/e* = 174 and 173 were present, but their percent abundances corresponded to the theoretical isotopic values, indicating that the $M^+ - 86$ and $M^+ - 87$ ions are not occurring to an appreciable extent in the spectra of the Si_3, Si_4, or Si_5 linear products. [c] (R–H) indicates the loss of a neutral fragment of C_4H_8. [d] The mass spectra for peaks C and D were identical.

The mass spectral data (major peaks for the high mass region) of the polysilane oligomers produced from n-$C_4H_9SiH_3$ with Dp = 2–4 are shown in Table II. These products are all linear and are correlated to the GC trace by the letter designation in Figure 1. The characteristics of the linear polysilane spectra are weak or absent molecular ions, a weak or absent peak due to the loss of an alkyl group, and a more intense ion due to the loss of a neutral $RSiH_3$. Subsequent losses result from rearrangements involving the loss of alkenyl fragments arising from a hydride transfer presumably from a β-carbon to the silicon atom. This pattern is consistent for Dp = 2–7 for linear products. Table III gives the mass spectral data for the prominent products from Dp = 5–7, and again the letter designations refer to the corresponding peaks in the GC trace of Figure 1. These data include both linear and cyclic products.

The cyclic products have greater intensity high mass peaks, since the ring must be opened prior to Si fragmentation. A reasonable molecular ion is present for the Si_5 cyclic. We also note that fragments due to the loss of alkyl radicals are not present in the high mass region of the spectra, but even with the lower Dp materials these

---

[6] The proton NMR data showed two overlapping resonances between δ 3.5 and 4.1 ppm which we attribute to SiH_2 and SiH protons, respectively. The alkyl hydrogens appeared as an envelope between δ 0.8 and 1.9 ppm. From the NMR integration data we calculated an average Dp of 9 for typical reaction mixture, but this assumes only linear products. The IR data for all of the samples gave Si–H stretching regions centered near 2100 cm^{-1}.[7] The gel permeation chromatogram of these samples showed a monomodal distribution of low molecular weight polymer (<1000) exhibiting several shoulder maxima.

[7] Hofler, F.; Bauer, G.; Hengge, E. *Spectrochim. Acta* **1976**, *32A*, 1435.

Table III. Mass Spectral Data for *n*-Butyl Pendant Polysilanes $H_2BuSi(SiHBu)_nSiBuH_2$ (n = 3–5)

m/e (% abundance)	mass loss	fragment lost[a]	ion[a]
$(RSiH_2)_2(RSiH)_3$	$R_5Si_5H_7$	MW = 432 (linear)	peak E
344 (39.6)	88	$RSiH_3$	$(R_4Si_4H_4)^+$
288 (50.1)	144	$RSiH_3$ + (R–H)[b]	$(R_3Si_4H_5)^+$
232 (72.8)	200	$RSiH_3$ + 2(R–H)	$(R_2Si_4H_6)^+$
$(RSiH)_5$	$R_5Si_5H_5$	MW = 430 (cyclic)	peak G
430 (13.8)			M^+
342 (30.2)	88	$RSiH_3$	$(R_4Si_4H_2)^+$
286 (61.1)	144	$RSiH_3$ + (R–H)	$(R_3Si_4H_3)^+$
230 (100)	200	$RSiH_3$ + 2(R–H)	$(R_2Si_4H_4)^+$
$(RSiH_2)_2(RSiH)_4$	$(R_6Si_6H_8)$	MW = 518 (linear)	peak H
432 (4.2)	86	RSiH	$(R_5Si_5H_7)^+$
430 (9.8)	87	$RSiH_2$	$(R_5Si_5H_6)^+$
344 (18.7)	174	$R_2Si_2H_4$	$(R_4Si_4H_4)^+$
342 (30.5)	176	$R_2Si_2H_6$	$(R_4Si_4H_2)^+$
288 (28.6)	230	$R_3Si_2H_3$	$(R_3Si_4H_5)^+$
286 (45.5)	232	$R_3Si_2H_5$	$(R_3Si_4H_3)^+$
$(RSiH)_6$	$R_6Si_6H_6$	MW = 516 (cyclic)	peak I
428 (43.8)	88	$RSiH_3$	$(R_5Si_5H_3)^+$
372 (43.2)	144	$RSiH_3$ + (R–H)	$(R_4Si_5H_4)^+$
316 (69.0)	200	$RSiH_3$ + 2(R–H)	$(R_3Si_5H_5)^+$
$(RSiH)_7$	$R_7Si_7H_7$	MS = 602 (cyclic)	peak J
516 (13)	86	RSiH	$(R_6Si_6H_6)^+$
515 (34.5)	87	$RSiH_2$	$(R_6Si_6H_5)^+$
514 (46.4)	88	$RSiH_3$	$(R_6Si_6H_4)^+$
459 (15.4)	143	R_2SiH	$(R_5Si_6H_6)^+$
458 (8.3)	144	$RSiH_3$ + (R–H)	$(R_5Si_6H_5)^+$
428 (8.3)	174	$R_2Si_2H_4$	$(R_5Si_5H_3)^+$
403 (30.9)	199	$RSiH_2$ + 2(R–H)	$(R_4Si_6H_7)^+$
402 (22.6)	200	$RSiH_3$ + 2(R–H)	$(R_4Si_6H_6)^+$

[a] R = C_4H_9. [b] (R–H) indicates the loss of a neutral fragment of C_4H_8.

peaks were very small. The high mass peaks are due to loss of an $RSiH_3$ neutral, followed by subsequent losses of neutral alkenes. Although the mass difference between the cyclic and the linear products is only 2, the fragmentation pattern of the spectra is significantly characteristic to allow easy differentiation. The spectra for the cyclics are consistent even through the Si_7 products.

Subsequent analysis by GC/FT-IR corroborated the mass spectral data. Table I gives the IR data of relevance for the corresponding peaks of the GC trace in Figure 1. The absorption bands of interest are the intense Si–H stretch near 2100 cm^{-1} and the SiH_2 bending vibration near 930 cm^{-1}. Note the correlation between the Si–H stretch and the presence or absence of the SiH_2 vibration.

The partial IR spectra for two Si_6 products are shown in Figure 2, for example. Peak H shows a clear band at 930 cm^{-1} and an Si–H stretch at 2110 cm^{-1}. In contrast, peak I shows no band in the region around 930 cm^{-1} but does have a band at 2077 cm^{-1}. The lack of the 930 cm^{-1} band for peak I shows that no SiH_2 is present in this product. A similar correlation is also drawn throughout *all* of the data between the position of the Si–H stretch and the presence or absence of the 930 cm^{-1} band. A further point to consider is that the position of the Si–H stretch shifts to lower frequency with increasing Dp for the linear polysilanes. The position of the Si–H band assigned to the cyclic products is well outside of the range for the Si–H band noted for the linear products within the Dp range under consideration. We have found that cyclic products are readily produced and predominate in the Cp_2ZrMe_2-catalyzed catenation of primary alkylsilanes but are not exclusive at Dp greater than 5.

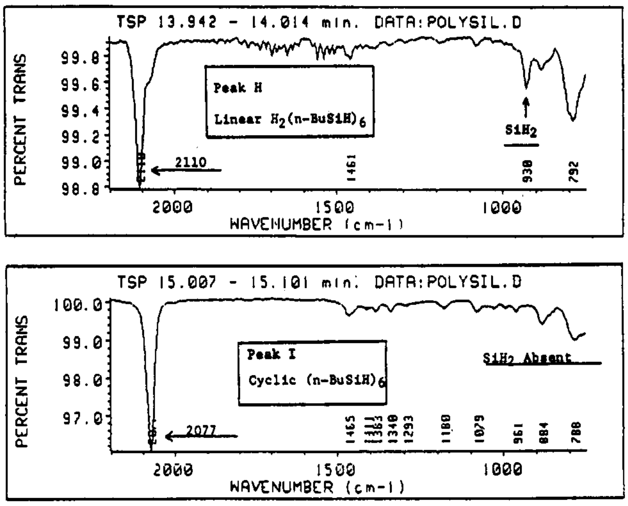

Figure 2. GC/FT-IR spectra of the *n*-butyl pendant hexasilanes: comparison of the cyclic and linear products.

Our reaction mixtures contained each possible Dp from monomer to heptamer. If the reactions are sampled early in the reaction, a large amount of the di- through the tetrasilane products are present and with time are consumed and replaced by the larger oligomers.

Conclusion

Our work describes the in depth GC/IR/MS analysis of the product distribution for the reaction of the small alkylsilane, n-$BuSiH_3$, in the dehydrogenative coupling reaction using Cp_2ZrMe_2 as the catalyst with the finding of unequivocal demonstration of a step-growth mechanism.

Mechanistically, the speculation reported by Harrod is appropriate with the added cyclization step of eq 2 being added to explain the formation of cyclics, which significantly serves as a chain termination step in the polymerization scheme. The brackets are only intended to symbolize the active zirconium intermediate. Formation of significant amount of cyclic oligomers now raises the issues of the thermodynamics of linear versus cyclics, as the substituents are varied from alkyl- or arylsilanes and the role of the various metal centers in this polymerization process.

$$[Zr\text{–}(SiRH)_n\text{–}SiH_2] \rightarrow [ZrH] + (SiRH)_{n+1} \qquad (2)$$

Experimental Section

General Comments. All experiments were carried out by using conventional Schlenk techniques or a drybox for air- and moisture-sensitive materials. Solvents were dried with CaH_2 prior to use, and polymerization solvents and reactants were freeze–thaw outgassed prior to use in catalytic reactions. All solvents were purchased from Fisher Scientific Co. Alkyltrichlorosilanes used in the preparation of alkylsilanes were obtained in house, and $LiAlH_4$, Cp_2ZrCl_2, and MeLi were purchased from Aldrich Chemical Co. The preparation of Cp_2ZrMe_2 was carried out according to the literature procedure of Atwood[8] and was purified by sublimation at reduced pressure at 90 °C and stored in a drybox.

GPC data were collected by using a Waters GPC system consisting of a set of ultrastyragel columns of 100, 500, 10^4, and 10^6 Å that were standardized by using polystyrene and an ultraviolet (254 nm) detector. The carrier solvent was tetrahydrofuran. Data reduction was carried out with Perkin-Elmer/Nelson Analytical GPC chromatography software on an IBM AT computer system.

All NMR data were collected on either a Varian XL-200 NMR spectrometer or a Varian EMT-390 NMR spectrometer using deuterated benzene as the solvent and tetramethylsilane as the internal standard. The standard IR data were collected on a Beckman 4240 infrared spectrometer. The mass spectra and GC data were collected on a Hewlett-Packard 5790 GC/MS system using a split column injector leading to two columns: one a 12.5-m capillary column for flame ionization detection and the other a 25-m capillary column for mass detection. Standard injection volumes of 0.02 μL were used.

The GC/FT-IR analyses were carried out as follows. For each analysis, 1.0 μL of the neat sample was injected into a Hewlett-Packard 5890A gas chromatograph coupled to a Hewlett-Packard 5965A IRD, an FT-IR spectrometer dedicated for gas chromatography. The chromatographic conditions for the separations were as follows: a 15 m × 0.32 mm i.d. 1.0 μm film DB-5 column (J&W) Scientific) with a flow rate of 3 mL/min Helium, operated at a 30/1 split ratio, temperature programmed from 150 to 285 °C at 10 °C/min. To facilitate resolutions and/or elution of high boiling components, one sample was also analyzed by using a temperature program to 70–260 °C at 10 °C/min. The injection temperature was 250 °C, and the temperature of the interface and light pipe was 300 °C for all analyses. The HP 5965A IRD utilized a 120 mm × 1 mm i.d. light pipe and a narrow band MCT detector. FT-IR spectral data were recorded at 8 cm^{-1} resolution. A Gram-Schmidt reconstruction produced a total response chromatogram for each run, and collected spectra were ratioed against background spectra to produce transmittance spectra from 4000 to 750 cm^{-1} for each component.

Preparation of $C_4H_9SiH_3$. Although this material is known in the literature, we believe that the following represents an improved synthesis. A 1000-mL three-neck round-bottom flask was equipped with a reflux condenser and a pressure equalizing dropping funnel. The flask was charged with 300 mL of dry diglyme, and 22.8 g (0.60 mol) of $LiAlH_4$, and this mixture was stirred under an Ar atmosphere while 152.3 g (0.79 mol) of n-$C_4H_9SiCl_3$ was added over a period of 2 h. When the addition was complete, stirring was continued for 1 h. Fractional distillation directly from the reaction mixture gave the desired product n-$C_4H_9SiH_3$, 62.6 g (89.9% yield). Spectral analysis agreed with literature values.[9]

Polymerization of n-$C_4H_9SiH_3$. The following is a representative procedure used for the Cp_2ZrMe_2-catalyzed polymerization of n-$C_4H_9SiH_3$. In a 50-mL Schlenk tube was added 4.59 g (0.052 mol) of n-$C_4H_9SiH_3$ and 5.0 mL of dry toluene. This solution was freeze–thaw degassed under reduced pressure and allowed to warm to room temperature under an Ar atmosphere. The above mixture was then stirred while 0.2 g (8.0×10^{-4} mol, 1.5 mol %) of Cp_2ZrMe_2 was added as a solution in 0.5 mL of dry toluene. The reaction immediately turned light yellow, and after 5 min mild gas evolution had begun and the color had intensified. After 1 h the gas evolution was strong, and the solution had turned to a dark orange color. After 3 h the gas evolution began to slow. After 24 h the reaction ceased. The mixture was analyzed by GC, and then all volatile components were removed at reduced pressure, and the nonvolatile materials were taken up in 10 mL of hexane and exposed to air by bubbling air through the stirred solution for 5 min. The yellow hexane mixture was then passed through a Florosil column (10 cm × 2 cm) to remove the Zr species giving 2.52 g (56%) of a clear, water white oil.

---

[8] Hunter, W. E.; Hencir, D. C.; Vann Bynum, R.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.

[9] Spectral data including ^1H NMR and IR were consistent with literature values. Doyle, M. P.; DeBruym, D. J.; Donnelly, S. J.; Kooistra, D. A.; Oclubela, A. A.; West, C. T.; Zonnebelt, S. M. *J. Org. Chem.* **1974**, *39*(18), 2740.

Transition-Metal Derivatives of the Cyclopentadienyl Phosphine Ligands. 3. New Pathways to Polymetallic Complexes

Xiao Dong He, André Maisonnat, Françoise Dahan, and René Poilblanc*

Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241 liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 route de Narbonne, 31077 Toulouse Cedex, France

Received December 7, 1988; Revised Manuscript Received May 24, 1989

A series of new derivatives of heterodifunctional ligands have been synthesized starting from lithium (diphenylphosphino)- or ((diphenylphosphino)ethyl)cyclopentadienide and from ((diphenylphosphino)-cyclopentadienyl)- or ((dimethylphosphino)cyclopentadienyl)thallium. These are monometallic (**1**, **2**, and **4**) and heterobimetallic molybdenum(0), tungsten(0), rhodium(I), and iridium(I) complexes (**3**) together with dissymmetric (**5**) and symmetric (**6**) homobimetallic rhodium(I) and iridium(I) complexes. They have been fully characterized by their spectroscopic data (including phosphorus–rhodium and phosphorus–tungsten coupling constant measurements) and by electron-impact mass spectroscopy. Interestingly, the synthesis of the bimetallic compounds involves a novel pathway beginning with steps of coordination of the phosphorus extremity of the bifunctional ligands. Of special interest are the compounds $L_2Rh(\eta^5\text{-}C_5H_4)Ph_2PRhCl(PPh_3)L$ (**5**), which associate one 18-electron and one 16-electron site, and the compounds $[M(\eta^5\text{-}C_5H_4)PR_2(CO)]_2$ (M = Rh, Ir; R = Ph, Me) (**6**), which associate two 18-electron sites. Complex **6a** (M = Rh; R = Ph) crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the unit cell of dimensions a = 9.475 (1) Å, b = 9.527 (1) Å, c = 9.145 (1) Å, α = 99.80 (1)°, β = 109.86 (1)°, γ = 90.36 (1)°, and V = 763.2 (3) Å^3. Least-squares refinement leads to a value of 0.032 for the conventional R index for 2938 reflections having $I > 3\sigma(I)$. The dinuclear molecule consists of two "Rh(CO)" moieties bridged by two (diphenylphosphino)cyclopentadienyl ligands that are in a mutual head-to-tail arrangement, and the large Rh–Rh separation, 4.3029 (6) Å, precludes any metal–metal interaction.

Introduction

The preparation of polymetallic complexes is a major tool in the main fields of application of coordination chemistry, namely, catalysis, materials, or biomimetic studies.

It enlightens the growing interest on accurate ligands, leading to prefer, in a specific attempt to control synthetic processes, heterodifunctional ligands rather than symme-

0276-7333/89/2308-2618$01.50/0