Journal of Organometallic Chemistry, 213 (1981) 493—502
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

VINYLMETALLICS AS LIGANDS

VII *. ACETYLACETONATOBIS(η^2-VINYLSILANE)RHODIUM(I) COMPLEXES

JOHN W. FITCH and WILLIAM T. OSTERLOH

Department of Chemistry, Southwest Texas State University, San Marcos, Texas 78666 (U.S.A.)

(Received October 9th, 1980)

Summary

Complexes of the type, [(acac)Rh$(ViSiR_3)_2$] and [(acac)Rh(Vi_2SiR_2)], are readily prepared by displacement of ethylene from [(acac)Rh$(C_2H_4)_2$]. The compounds, which are less reactive to air than similar carbon analogues, have been characterized by ^{1}H and ^{13}C NMR. The ^{13}C NMR results suggest that the vinylsilane ligands function as better π-acceptors than do similar carbon analogues, and that $d\pi$—$p\pi$ interactions between the silicon atom and the double bond are decreased upon coordination of the vinylsilane.

Introduction

Vinylsilanes readily form π-complexes with transition metals; however, the role played by the silicon atom in affecting the stability and reactivity of these complexes is not clear. For example, vinylmetallic-copper(I) complexes are surprisingly air stable and form more readily than similar all-carbon structural analogues [1]. The platinum(0) complexes, [$(Ph_3P)_2$PtViSiR$_3$], are also more stable than their carbon analogues, increase in stability as R is changed from methyl to ethoxy and, in contrast to platinum(II) complexes [2], do not react with water [3].

However, not all vinylsilane complexes are characterized by added stability (lack of reactivity) when compared to their carbon analogues. Palladium(II) reacts rapidly with vinylsilanes causing silicon—carbon bond fission and yielding various products depending on reaction conditions [4]. Platinum(II) forms the π-complex, K[PtCl$_3$ViSiMe$_3$], which undergoes slow hydrolysis in wet solvents

---

* For part VI see ref. 3.

forming K[$PtCl_3CH_2{=}CH_2$] and hexamethyldisiloxane [2].

In order to gain additional information on the changes in physical and chemical properties of vinylsilanes upon coordination we have prepared a series of complexes of the types, [(acac)Rh($ViSiR_3$)$_2$] and [(acac)Rh(Vi_2SiR_2)], and wish to report them at this time.

Results and discussion

Preparation of complexes

Vinylsilane-rhodium(I) complexes were prepared by the standard ligand exchange reaction shown below (eq. 1) [5].

$$[(acac)Rh(C_2H_4)_2] + 2\ ViSiR_3 \rightarrow [(acac)Rh(ViSiR_3)_2] + 2\ C_2H_4 \qquad (1)$$

The new rhodium(I) compounds (listed in Table 1) derived from low-boiling ligands were isolated in pure form by removing the excess ligand in vacuo (Procedure A). Complexes derived from high boiling ligands were isolated by low temperature crystallization (Procedure B) or chromatographically (Procedure C). The vinylsilane complexes were observed to be stable in air for days although they were routinely stored under argon at 0°C. This stability is in contrast to the behaviour of the 3,3-dimethyl-1-butene complex, 5, which shows evidence of decomposition within hours upon exposure to air. This contrasting behaviour between vinylsilane complexes and their carbon analogues has been noted to be even more extreme in platinum(0) complexes [3]. Cramer has noted that rhodium(I) complexes of ethylenes carrying electronegative substituents are more stable than those of comparable unsubstituted alkenes [6], and the observed stability of the vinylsilane complexes might have been anticipated since the -$SiMe_3$ group is a net weak electron-withdrawing group [7].

The stability of the rhodium(I)-vinylsilane complexes to water is also notable. The ^1H NMR spectrum of a sample of [(acac)Rh($CH_2{=}CHSiMe_3$)$_2$] in wet acetone-d_6 showed no change in signal intensities over a period of two weeks at room temperature. The complex can be refluxed in wet acetone for two hours without evidencing any change. In this regard the complexes resemble the earlier reported Pt^0 complexes [3] more than Pt^{II} complexes [2] which undergo hydrolysis in wet acetone.

^1H NMR spectra

The most striking characteristic in the ^1H NMR spectra of the new complexes is their sharpness at ambient temperature. Olefins in complexes of the type, [(acac)Rh(ol)$_2$] (ol = styrene, propene, vinylacetate), give rise to broad resonances unsuitable for complete analysis due to a large number of isomers [8]. Rotational line broadening has also been observed in [(acac)Rh($CH_2{=}CH_2$)$_2$] at ambient temperature [5]. These complications are apparently prevented in vinylsilane complexes by the bulkiness of the ligands.

Upon coordination to rhodium(I), the ABC pattern observed in free vinylsilanes is replaced by an ABX pattern as modified by $^{103}Rh{-}^1H$ coupling (chemical shifts and coupling constants are listed in Table 2 for those compounds analyzed). Complete spectral analyses for compounds 2, 3, 4 and 6 were not possible because of overlapping signals, but qualitative assignments are con-

TABLE 1

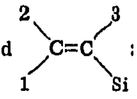
NEW RHODIUM(I) COMPLEXES

Compound	Number	Synthesis prodedure	Yields (%)	M.p.	Color	Anal. Found (calcd.) (%)	
						C	H
$[(acac)Rh(CH_2{=}CHSiMe_3)_2]$	1	A	100	66	yellow-orange	44.72 (44.76)	7.56 (7.76)
$(acac)Rh[CH_2{=}CHSiMe_2(OC_2H_5)]_2$	2	A	100	liq.	orange-red	43.75 (44.15)	7.33 (7.63)
$(acac)Rh[CH_2{=}CHSiMe(OC_2H_5)_2]_2$	3	C	85	liq.	orange-red	43.52 (43.67)	7.66 (7.52)
$(acac)Rh[CH_2{=}CHSi(OC_2H_5)_3]_2$	4	B	78	43	yellow	43.45 (43.30)	7.84 (7.44)
$[(acac)Rh(CH_2{=}CHCMe_3)_2]$	**5**	—	100	75	yellow	54.80 (55.14)	8.20 (8.44)
$[(acac)Rh(CH_2{=}CHCH_2SiMe_3)_2]$	6	A	100	37	orange-red	47.60 (47.43)	8.10 (8.19)
$[(acac)Rh(CH_2{=}CH)_2SiMe_2]$	7	A	100	95	yellow	42.00 (42.04)	6.01 (6.09)
$[(acac)Rh(CH_2{=}CH)_2Si(C_6H_5)_2]$	8	B	83	126	yellow	57.58 (57.54)	5.46 (5.29)
$[(acac)Rh(CH_2{=}CHSiMe_2)_2O]$	9	C	80	90	yellow	40.12 (40.20)	6.22 (6.49)

TABLE 2

100 MHz ^{1}H NMR ANALYSES OF OLEFINS AND RHODIUM(I)-OLEFIN COMPLEXES [a, b]

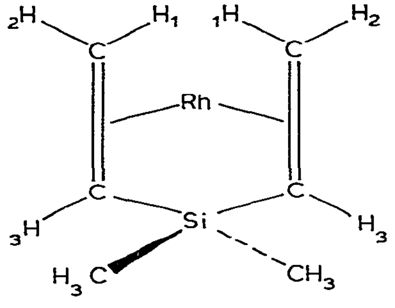
Compound	No.	δ (ppm)			J (Hz)					
		1	2	3	13	23	12	14	24	34
CH_2=$CHSiMe_3$ [c]		5.63	5.87	6.11	20.40	14.60	3.80			
[(acac)Rh(CH_2=$CHSiMe_3$)$_2$]	1	4.01	3.36	1.19	15.46	11.37	1.79	1.73	2.11	0.07
CH_2=$CHCMe_3$		4.90	4.80	5.81	17.45	10.71	1.43			
[(acac)Rh(CH_2=$CHCMe_3$)$_2$]	5	3.52	2.84	1.83	13.38	8.57	−0.03	1.41	1.84	1.00
(CH_2=CH)$_2$$SiMe_2$ [c]		5.76	6.18	6.44	20.20	14.60	3.70			
[(acac)Rh(CH_2=CH)$_2$$SiMe_2$]	7	2.78	3.72	3.39	15.42	11.80	1.13	1.81	1.68	0.86
(CH_2=CH)$_2$Si(C_6H_5)$_2$ [c]		5.66	5.93	6.11	20.40	14.70	3.60			
[(acac)Rh(CH_2=CH)$_2$Si(C_6H_5)$_2$]	8	2.77	3.53	3.29	15.85	11.76	0.60	1.84	1.66	0.67
(CH_2=$CHSiMe_2$)$_2$O		5.71	5.88	6.10	20.64	14.84	3.82			
[(acac)Rh(CH_2=$CHSiMe_2$)$_2$O]	9	3.04	4.53	3.51	15.69	12.10	1.63	1.61	2.02	0.92

[a] Protons numbered 

: Nucleus No. 4 is ^{103}Rh. [b] δ error 0.004–0.009 ppm; J error 0.08–0.10 Hz. [c] Ref. 26.

sistent with the results obtained from the completely analyzed spectra.

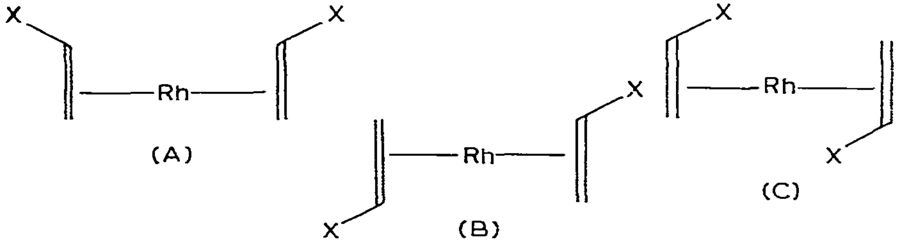
Structural assignments for the compounds studied followed from the analysis of the ^1H NMR spectrum of 7 since the orientation of the divinylsilane in 7 must be as shown.



(7)

Following Cramer's descriptions for "inner" and "outer" hydrogen [5], hydrogens 1 must be "inner" hydrogens because they are shifted to highest field (δ 2.78 ppm). They are attached to the same carbon as hydrogens 2 (δ 3.72 ppm) since $J_{1,2}$ = 1.1 Hz, which is typical of geminal protons. The other hydrogen, 3 (δ 3.39 ppm), is thus the "outer" hydrogen attached to the silicon-bearing carbon. This assignment is supported by $J_{1,3}$ and $J_{2,3}$ which are 15.4 and 11.8 Hz, respectively, for the *trans* and *cis* coupling constants. Thus "inner" hydrogens in this complex appear at higher field than "outer" hydrogens, in agreement with earlier work [5]. The spectra of 8 and 9 can be analyzed in the same way.

The spectral correlations are not so straightforward in 1 (or other complexes containing monovinyl ligands) since the vinylsilane could adopt several conformations, three of which are schematically shown. However, unsymmetrical permutations of A—C are ruled out by the very symmetrical spectra. The key to the structural assignment is the observation that in 1 both protons 2 and 3 (see Table 2 for proton numbering scheme) resonate at a higher field (3.36 and 1.19 ppm, respectively) than proton 1 (4.01 ppm). Thus, these protons are likely "inner" protons and compound 1 has been tentatively assigned either the structure A or B. Structure B is favored on steric grounds. Similar structures are proposed for the other monovinylsilane complexes and for 5, the all-carbon analogue of 1. However, as noted in Table 4, compounds 2 and 3 may contain a small amount of a second isomer. Finally, it will be noted that small $^{103}Rh—^1H$ couplings (0—2 Hz) are observed for all compounds studied, and these values



(A) (B) (C)

are typical of those reported earlier for other rhodium(I) complexes [5,9].

The large upfield shift of "inner" protons in rhodium(I) complexes has been attributed to long range shielding resulting from the anisotropic magnetic fields of the two coordinated olefins [5]. Certainly this effect appears to dominate any effect which might arise from electronic perturbations in the ligands due to silicon's presence since compound 5, the carbon analogue of 1, also has a very highly shielded proton attached to the carbon atom bearing the t-butyl group.

^{13}C *NMR spectra*

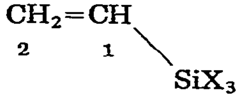
Table 3 contains ^{13}C NMR data for several of the new complexes along with similar data for the uncoordinated ligands. Several effects appear to be significant.

Upon coordination to rhodium(I) all vinylsilanes studied experienced large upfield shifts in their ^{13}C NMR spectra. The chelated complex, 7, showed an especially large coordination shift. These upfield coordination shifts ($\Delta\delta^{13}C$) are listed in Table 4 and are observed to be 10 to 15 ppm larger than the shifts observed in 5, 6 or the propene complex. The silicon atom seems to have considerable influence on the magnitude of the coordination shift when it is bound directly to the coordinating double bond, but apparently does not appreciably affect it when it is located in the allylic position. (see compound 6, Table 4)

Although the origin of $\Delta\delta^{13}C$ in coordinated alkenes is still the subject of some debate [13—18], the magnitude of the coordination shift has been shown to be related to the degree of metal-to-olefin backbonding [19—21]. The larger coordination shifts experienced by the vinylsilane ligands when compared to allylsilane or carbon analogues are therefore likely related to increased backbonding from rhodium to the vinylsilane. Thus the data indicate that the vinylsilanes studied are somewhat better π-acceptors than either allyltrimethylsilane or simple alkenes such as propene or 3,3-dimethyl-1-butene.

In addition to the bulk upfield shift effect observed for all vinylsilanes upon coordination, the individual C(1) and C(2) resonances (C(1) is the carbon atom attached to silicon) in 1 to 4 respond differently as ethoxy groups replace methyl groups in the ligands (Table 3). As the number of ethoxy groups in the ligand is increased, C(1) becomes progressively more shielded ($\delta^{13}C$ changes from 64.1 ppm in 1 to 54.6 ppm in 4), but $\Delta\delta^{13}C$ remains essentially constant at ca. 76 ppm. On the other hand $\delta^{13}C$ for C(2) remains essentially constant at about 69 ppm but $\Delta\delta^{13}C$ increases from 62.1 ppm in 1 to 66.7 ppm in 4. The value of $J(^{103}Rh—^{13}C)$ remains virtually unchanged for C(1) and C(2) (12.5 to 14.3 Hz) as ethoxy groups replace methyl groups.

These observations are likely related to changes in $d\pi—p\pi$ bonding when a vinylsilane is coordinated to a transition metal. The ^{13}C NMR spectra of the free ligands seem to be fairly well understood in terms of models involving $d\pi—p\pi$ bonding. The chemical shifts of C(1) and C(2) in vinyltrimethylsilane (140.2



$CH_2=CH—SiX_3$ (X = CH_3 or OC_2H_5)

and 131.1 ppm, respectively) are reversed in vinyltriethoxysilane (129.3 and 136.6 ppm, respectively) [10], and this reversal has been analyzed in terms of

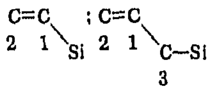
TABLE 3

^{13}C NMR SPECTRAL RESULTS FOR SEVERAL OLEFINS AND THEIR (acac)Rh^I COMPLEXES [a, b]

No.	Compound	C_1	C_2	C_3	Si—CH_3	acac			Comments
						CO	CH	CH_3	
.	CH_2=$CHSiMe_3$	140.2	131.1		−1.6				
1	[(acac)Rh(CH_2=$CHSiMe_3)_2$]	64.1	69.0		0.1	185.7	99.2	26.9	
		(14.3)	(12.7)				(2.3)		
	CH_2=$CHSiMe_2OEt$	138.3	132.6		−1.9				
2	[(acac)Rh(CH_2=$CHSiMe_2OEt)_2$]	62.3	69.4		−0.2	185.8	99.2	26.9	$OCCH_3$ (58.5); OCH_2C (19.0)
		(14.3)	(12.8)		−0.8		(2.1)		Contaminated with a small amount of another isomer
	CH_2=$CHSiMe(OEt)_2$	134.8	134.6		−4.4				
3	[(acac)Rh(CH_2=$CHSiMe(OEt)_2)_2$]	59.1	69.6		−3.1	185.9	99.1	26.8	$OCCH_3$ (d; 58.8, 58.1); OCH_2C (18.8) Note C(1) resonance overlaps OCH_2CH_3 resonance at 58.8
		(13.2)	(13.0)				(2.1)		Contaminated with small amount of another isomer
	CH_2=$CHSi(OEt)_3$	129.3	136.6						ref. 10
4	[(acac)Rh(CH_2=$CHSi(OEt)_3)_2$]	54.6	69.9			185.9	99.0	26.8	$OCCH_3$ (58.7); OCH_2C (18.6)
		(13.8)	(12.5)				(2.0)		
	CH_2=$CHCMe_3$	149.0	109.0						ref. 11
5	[(acac)Rh(CH_2=$CHCMe_3)_2$]	90.4	57.2			185.9	99.0	27.1	CMe_3 [34.5, $J(^{103}Rh—^{13}C = 1.0$ Hz)];
		(14.8)	(11.6)				(1.8)		$C(CH_3)$ (30.3)
	CH_2=$CHCH_2SiMe_3$	135.1	112.7	24.7					ref. 10
6	[(acac)Rh(CH_2=$CHCH_2SiMe_3)_2$]	75.9	59.8	25.5	−1.4	185.8	98.9	27.3	
		(14.1)	(13.1)				(1.8)		
	$(CH_2$=$CH)_2SiMe_2$	138.2	132.3		−3.3				
7	[(acac)Rh(CH_2=$CH)_2SiMe_2$]	50.6	66.7		1.8	186.4	99.3	27.0	The methyl groups are non-equivalent in the chelated silane
		(10.2)	(14.6)		2.4		(2.3)		
8	[(acac)Rh(CH_2=$CH)_2Si(C_6H_5)_2$]	48.4	68.4			186.6	99.4	26.9	
		(9.8)	(14.5)				(1.9)		
	CH_2=$CHCH_3$	136.8	118.6						ref. 12
	[(acac)Rh(CH_2=$CHCH_3)_2$]	75.5	65.0						ref. 12
		(15.5)	(13.7)						

---

[a] Chemical shifts are reported in ppm downfield from TMS (mean value reported for ^{103}Rh-coupled peaks); the values of $J(^{103}Rh—^{13}C)$ appear in parentheses (Hz); spectra observed in C_6D_6. [b] Carbons numbered

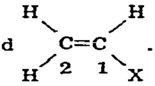


$\overset{2}{C}=\overset{1}{C}—Si$; $\overset{2}{C}=\overset{1}{C}—\overset{3}{C}—Si$

TABLE 4

UPFIELD COORDINATION SHIFTS OF VINYLIC CARBONS [a] IN COMPOUNDS OF FORMULA [(acac)RhL$_2$] (L = ALKENE)

Compound No.	L in [(acac)RhL$_2$]	$\Delta\delta$ ^{13}C (ppm)	
		C(1)	C(2)
1	$CH_2{=}CHSiMe_3$	76.1	62.1
2	$CH_2{=}CHSiMe_2(OEt)$	76.0	63.2
3	$CH_2{=}CHSiMe(OEt)_2$	75.7	65.0
4	$CH_2{=}CHSi(OEt)_3$	74.7	66.7
5	$CH_2{=}CHCMe_3$	58.6	51.8
6	$CH_2{=}CHCH_2SiMe_3$	59.2	52.9
7	$(CH_2{=}CH)_2SiMe_2$	87.6	65.6
—	$CH_2{=}CHCH_3$ [b]	61.3	53.6

[a] Carbons numbered . [b] Data taken from ref. 12.

the relative importance of canonical forms I and II below [22].

$$\underset{(I)}{CH_2{=}CH{-}SiX_3} \leftrightarrow \underset{(II)}{\overset{+}{C}H_2{-}CH{=}\overset{-}{Si}X_3}$$

Our results suggest that the vinyl group to silicon $d\pi$—$p\pi$ bonding decreases upon formation of the π-complex since the C(2) resonances are essentially identical from 1 to 4. Of particular interest is the behaviour of the -Si—CH_3 resonances in 1 to 3. In each case the methyl carbon becomes slightly less shielded upon complex formation, again in keeping with the suggestion of decreased $d\pi$—$p\pi$ bonding in the coordinated ligands. However, field anisotropy in the complexes could be responsible for these small changes in the methyl resonances.

Experimental

General

Pentane and hexane were first shaken with sulfuric acid several times to remove olefinic impurities. They were than washed with dilute sodium bicarbonate, dried by refluxing over calcium hydride, and distilled. Benzene was also dried and distilled from calcium hydride prior to use. Tetrahydrofuran was purified by distillation from sodium benzophenone ketyl under argon. Alcoa F-20 alumina was neutralized by stirring with 0.5 *M* nitric acid, washed with water, and dried at 120°C for 8 hours.

Melting points (uncorrected) were determined on a Thomas Hoover Uni-melt apparatus. Carbon and hydrogen analyses were performed locally on a Coleman Model 33 Analyzer or were obtained from Galbraith Laboratories, Knoxville, Tennessee. Gas chromatograms were obtained on a Gow-Mac Gas Chromatograph with a Series 550 thermal conductivity detector. A column (4′ × 1/4″) containing a stationary phase of carbowax was used.

Sixty MHz ^{1}H NMR spectra were determined with a Perkin Elmer Model R-12A Spectrometer while 100 MHz spectra were obtained on a Varian Model HA-100 Spectrometer. Samples were analyzed in benzene-d_6, chloroform-d or carbon tetrachloride; benzene (δ 7.24 ppm) or tetramethylsilane served as internal references and locking signals. The chemical shifts and coupling constants reported were obtained using the programs NMRIT and NMREN1 [23]. Carbon-13 NMR spectra were determined on a Varian FT 80-A Spectrometer operating at 20 MHz or on a Bruker HX-90 Spectrometer operating at 22.62 MHz. Benzene-d_6 was used as solvent, for deuterium lock, and as internal reference (center C_6D_6 resonance at δ 128.00 ppm). The ^{13}C spectra were obtained in proton-decoupled, off-resonance decoupled, and occasionally in coupled modes to aid in spectral assignments.

Starting materials

Commercially available silanes (PCR, Inc. Gainesville, Fla.; Research Organic/Inorganic Chem. Corp., Sun Valley, Calif.; Petrarch Systems, Levittown, Pa.) were distilled prior to use. The olefin, 3,3-dimethyl-1-butene was used as purchased from Aldrich Chemical Co. Dimethyldivinylsilane was prepared by the Grignard method [24], and the fraction boiling at 78—82° C was collected and used.

Di-μ-chlorotetrakis(ethylene)dirhodium(I) [25], and acetylacetonatobis-(ethylene)rhodium(I) [5] were both prepared according to the literature and showed acceptable analyses and IR and NMR spectra.

Preparation of rhodium(I) complexes

Illustrative examples of the basic procedure used are given. Procedures used in the synthesis of compounds not given here as examples are found in Table 1 as are yield and analytical data for all compounds prepared.

Procedure A: Preparation of acetylacetonatobis(vinyltrimethylsilane)rhodium-(I) (1). [(acac)Rh($CH_2{=}CH_2$)$_2$] (0.50 g, 1.9 mmol) was placed in a 50 ml Schlenk tube which was sealed with a serum cap, evacuated, and filled with argon. Vinyltrimethylsilane (3 ml) was syringed into the flask which had been cooled to —78° C. Brisk ethylene evolution occurred as the reaction mixture warmed to room temperature. The excess ligand was removed in vacuo to yield initially a viscous liquid which crystallized to give a free-flowing yellow-orange solid.

Procedure B: Preparation of acetylacetonato(diphenyldivinylsilane)rhodium-(I) (8). Compound 8 was prepared as described above using [(acac)Rh($CH_2{=}CH_2$)$_2$] (0.50 g, 1.9 mmol) as starting material. After evolution of ethylene was complete (about 5 min) absolute ethanol (20 ml) was added, and the solution was cooled to —78° C. The yellow product which precipitated was isolated by filtration, washed with cold absolute ethanol (5 ml) three times, and dried in vacuo. The analogous vinyltriethoxysilane complex was similarly prepared using pentane as the recrystallization solvent.

Procedure C: Preparation of acetylacetonatobis(vinylmethyldiethoxysilane)-rhodium(I) (3). Compound 3 was prepared as described above. After most of the excess ligand was removed in vacuo, the reaction mixture was dissolved in pentane (3 ml) and placed on a short alumina column. The column was eluted with pentane until the complex had moved three fourths of the way down the column at which time it was stripped from the column with ether/methanol (1/1 vol%). An orange, slightly viscous liquid was obtained upon removal of solvents in vacuo.

Preparation of acetylacetonatobis(3,3-dimethyl-1-butene)rhodium(I) (5). A solution of 3,3-dimethyl-1-butene (10 ml) in benzene (10 ml) was added to $[(\mathrm{acac})\mathrm{Rh}(\mathrm{CH_2{=}CH_2})_2]$ (0.50 g, 1.9 mmol) under an argon blanket. The mixture was heated for 1 hour at 75° C, after which solvent and excess ligand were removed in vacuo to yield the product as a yellow solid.

^{1}H NMR results for compounds with overlapping peaks

Spectra were recorded in benzene-d_6 and referenced to the proton impurity at δ 7.24 ppm. δ(ppm), Multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Chemical shifts were measured from the center of multiplets.

Compound 2: δ 0.28s, 0.55s($\mathrm{Si}\mathit{CH}_3$), 1.22t($\mathrm{\text{-}OCH_2}\mathit{CH}_3$), 1.1—1.5m($\mathrm{CH_2{=}}\mathit{CH}$-), 1.70s(acac-$\mathit{CH}_3$), 3.4—4.0m($\mathit{CH}_2\mathrm{{=}CH}$-), 3.83q($\text{-}\mathrm{O}\mathit{CH}_2\mathrm{CH_3}$), 5.12s(acac-$\mathit{H}$).
Compound 3: δ 0.40s($\mathrm{Si}\mathit{CH}_3$), 1.2t, 1.3t($\mathrm{\text{-}OCH_2}\mathit{CH}_3$), 1.1—1.5m($\mathrm{CH_2{=}}\mathit{CH}$-), 1.75s(acac-$\mathit{CH}_3$), 3.4—4.2m($\mathit{CH}_2\mathrm{{=}CH}$-), 3.7q, 3.8q($\text{-}\mathrm{O}\mathit{CH}_2\mathrm{CH_3}$), 5.22s(acac-$\mathit{H}$).
Compound 4: δ 1.25t($\mathrm{\text{-}OCH_2}\mathit{CH}_3$), 1.2—1.6m($\mathrm{CH_2{=}}\mathit{CH}$-), 1.85s(acac-$\mathit{CH}_3$), 3.3—4.1m($\mathit{CH}_2\mathrm{{=}CH}$-), 4.05q($\text{-}\mathrm{O}\mathit{CH}_2\mathrm{CH_3}$), 5.20s(acac-$\mathit{H}$).
Compound 6: δ 0.12s($\mathrm{Si}\mathit{CH}_3$), 1.1—1.7m($\mathrm{CH_2{=}CH}\mathit{CH}_2$-), 1.80s(acac-$\mathit{CH}_3$), 2.4—3.5m($\mathit{CH}_2\mathrm{{=}}\mathit{CH}\mathrm{CH_2}$-), 5.16s(acac-$\mathit{H}$).

Acknowledgements

The authors are pleased to acknowledge the support of this work by the Robert A. Welch Foundation (Grant No. AI-306) and the assistance of Dr. B.A. Shoulders of the University of Texas at Austin in obtaining some of the NMR results.

References

1 J.W. Fitch, D.P. Flores and J.E. George, J. Organometal. Chem., 29 (1971) 263.
2 E.M. Haschke and J.W. Fitch, J. Organometal. Chem., 57 (1973) C93.
3 J.W. Fitch, K.C. Chan and J.A. Froelich, J. Organometal. Chem., 160 (1978) 477.
4 W.P. Weber, R.A. Felix, A.K. Willard and K.E. Koenig, Tetrahedron Letters (1971) 4701; K. Yamamoto, K. Shinohara, T. Ohuchi and M. Kumada, Tetrahedron Letters (1974) 1153.
5 R. Cramer, J. Amer. Chem. Soc., 86 (1964) 217.
6 R. Cramer, J. Amer. Chem. Soc., 89 (1967) 4621.
7 H. Bock and H. Seidl, J. Amer. Chem. Soc., 90 (1968) 5694.
8 A.C. Jesse, H.P. Gyben, D.J. Stufkins and K. Vrieze, Inorg. Chim. Acta., 31 (1978) 203.
9 R. Cramer and G.S. Reddy, Inorg. Chem., 12 (1973) 346.
10 P.E. Rakita and L.S. Worsham, J. Organometal. Chem., 139 (1977) 135.
11 G. Mirjajama, K. Takahasi and K. Niskimoto, Org. Mag. Reson., 6, (1974) 413.
12 K.R. Aris, V. Aris and J.M. Brown, J. Organometal. Chem., 42 (1972) C67.
13 M.H. Chisholm, H.C. Clark, L.E. Manzer and J.B. Stothers, J. Amer. Chem. Soc., 94 (1972) 5087.
14 D.G. Cooper, R.P. Hughes and J. Powell, J. Amer. Chem. Soc., 94 (1972) 9244.
15 D.J. Thoennes and C.L. Wilkins, J. Magn. Reson., 13 (1974) 18.
16 J. Evans and J.R. Norton, Inorg. Chem., 13 (1974) 3042.
17 M.H. Chisholm, H.C. Clark, L.E. Manzer, J.B. Stothers and J.E.H. Ward, J. Amer. Chem. Soc., 97 (1975) 721.
18 D.G. Cooper and J. Powell, Inorg. Chem., 15 (1976) 1959.
19 R.G. Salomon and J.K. Kochi, J. Organometal. Chem., 64 (1974) 135.
20 C.A. Tolman, A.D. English and L.E. Manzer, Inorg. Chem., 14 (1975) 2353.
21 P.W. Clark, P. Hanisch and A.J. Jones, Inorg. Chem., 18 (1979) 2067.
22 R.K. Harris, J. Jones and S. Ng, J. Mag. Reson., 30 (1978) 521.
23 J.D. Swalen and C.A. Reilly, J. Chem. Phys., 37 (1962) 21.
24 S.D. Rosenberg, J.J. Walburn, T.D. Stankovich, A.E. Balint and H.E. Ramsden, J. Org. Chem., 22 (1957) 1200.
25 R. Cramer, Inorg. Chem., 1 (1962) 722.
26 T. Hobgood and J.H. Goldstein, Spectrochem. Acta, 19 (1963) 321.