Synthesis of Rh(acac)H($GeEt_3$)(PCy_3) and Rh(acac)H($SnPh_3$)(PCy_3) and Their Reactions with Alkynes

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The monoolefin complex Rh(acac)(cyclooctene)(PCy_3) (**1**) reacts with $HGeEt_3$ to give Rh(acac)H($GeEt_3$)(PCy_3) (**2**). On treatment of **2** with methyl propiolate and phenylacetylene the complexes Rh(acac){η^2-CH($GeEt_3$)=CHR}(PCy_3) (R = CO_2Me (**3**), Ph (**4**)) are obtained. The X-ray crystal structure analysis of **3** reveals that the coordination geometry around the rhodium center is almost square-planar with the olefin disposed perpendicular to the coordination plane of the rhodium atom. Complex **1** also reacts with $HSnPh_3$. The reaction leads to Rh(acac)H($SnPh_3$)(PCy_3) (**5**). In the presence of methyl propiolate, phenylacetylene, and (trimethylsilyl)acetylene complex **5** affords the alkenyl compounds Rh(acac){(*E*)-CH=CHR}($SnPh_3$)(PCy_3) (R = CO_2Me (**6**), Ph (**7**), $SiMe_3$ (**8**)). Similarly, the reactions of **5** with diethyl acetylenedicarboxylate and diphenylacetylene yield Rh(acac)(CR=CHR)($SnPh_3$)(PCy_3) (R = CO_2Et (**9**), Ph (**10**)). The addition of 1 equiv of 1-ethynyl-1-cyclohexanol to a pentane suspension of **5** leads to the hydroxyalkenyl derivative Rh(acac){(*E*)-CH=CHC(OH)$(CH_2)_4CH_2$}($SnPh_3$)(PCy_3) (**11**). The structure of **11** was determined by X-ray analysis. The coordination geometry around the metal center can be rationalized as a square pyramid with the stannyl ligand in the apical position. Although the hydroxyalkenyl ligand of **11** is stable and does not dehydrate to give the corresponding α,*β*-unsaturated alkenyl compound, complexes of this type can be prepared from enynes. Thus, the reaction of **5** with 2-methyl-1-buten-3-yne leads to the α,*β*-unsaturated alkenyl complex Rh(acac){(*E*)-CH=CHC(CH_3)=CH_2}($SnPh_3$)(PCy_3) (**12**), whereas in the presence of 1,1-diphenyl-2-propyn-1-ol complex **5** affords the allenyl derivative Rh(acac)(CH=C=CPh_2)($SnPh_3$)(PCy_3) (**13**).

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Introduction

The hydrosilylation mechanistic proposals employ conventional oxidative-addition, insertion, and reductive-elimination steps to explain the addition of silanes to olefins and alkynes.[1] In this respect, the study of the oxidative addition of silanes to transition-metal compounds and the reactions of the resulting hydrido derivatives with olefins and alkynes are of great interest and have received increasing attention in recent years.[2]

In general, the stereoselective formation of alkenylgermanes and alkenylstannanes by addition of germanes and stannanes to alkynes requires the presence of transition-metal catalysts.[3] Although from a mechanistic point of view these reactions are less clear cut than the hydrosilylation of alkynes, at first glance, there should not be a great difference between them, and one would expect mechanistic similarities. In this context, the synthesis of hydrido−germyl and hydrido−stannyl compounds by oxidative addition of germanes and stannanes to transition-metal complexes and the study of the reactivity of these derivatives toward alkynes are also significant and are of general interest.

In the search for transition-metal complexes which are catalytically active in the hydrogenation, hydrosi-

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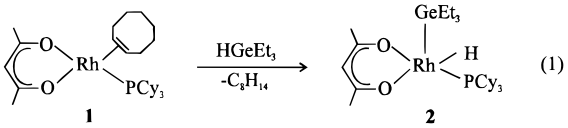
lylation, and hydrostannation of unsaturated organic substrates, we have previously reported the reactivity of the (acetylacetonato)iridium compound Ir(acac)(cyclooctene)(PCy_3), which is formed by ligand displacement from Ir(acac)(cyclooctene)$_2$ and tricyclohexylphosphine.[4] The complex Ir(acac)(cyclooctene)(PCy_3) reacts with dimethyl acetylenedicarboxylate to give Ir(acac)(η^2-$MeO_2CC{\equiv}CCO_2Me$)(PCy_3). The reaction of this compound with H_2SiPh_2 leads to Ir(acac){C[CH-(OCH$_3$)OSiPh$_2$]=CHCO$_2$CH$_3$}(PCy_3), which is a result of a transformation involving addition of one Si−H bond across the C=O bond and another across the alkyne triple bond.[4] The cyclooctene compound Ir(acac)(cyclooctene)(PCy_3) also reacts with silanes $HSiR_3$ to give Ir(acac)H(SiR_3)(PCy_3) and with $HSnPh_3$ to afford Ir(acac)H($SnPh_3$)(PCy_3). Moreover, the five-coordinate hydrido−silyl derivative Ir(acac)H($SiEt_3$)(PCy_3) adds one molecule of hydrogen to give the trihydride Ir(acac)H$_3$($SiEt_3$)(PCy_3) and is an active catalyst for the addition of $HSiEt_3$ to phenylacetylene.[5]

Recently, we have also observed that the reaction of Rh(acac)(cyclooctene)$_2$ with tricyclohexylphosphine, similar to that of the analogous iridium derivative, leads to Rh(acac)(cyclooctene)(PCy_3), which is a useful starting material for the preparation of new organometallic rhodium compounds, including π-alkynes, hydrido−alkynyl species, and cationic five-coordinate alkenyl derivatives.[6] As a continuation of our work in this field, we have now carried out the reactions of Rh(acac)(cyclooctene)(PCy_3) with $HGeEt_3$ and $HSnPh_3$, which afford Rh(acac)H($GeEt_3$)(PCy_3) and Rh(acac)H($SnPh_3$)(PCy_3), respectively. In this paper, we report the synthesis of these compounds and their reactivity toward alkynes.

Results and Discussion

1. Synthesis of Rh(acac)H($GeEt_3$)(PCy_3) and Its Reactions with Terminal Alkynes. The addition of 1 equiv of $HGeEt_3$ to a toluene solution of the monoolefin complex Rh(acac)(cyclooctene)(PCy_3) (**1**) affords, after 2 h at room temperature, a yellow solution from which the hydrido−germyl compound Rh(acac)H($GeEt_3$)(PCy_3) (**2**) can be isolated as a yellow solid in 43% yield, by addition of acetone (eq 1).



1 **2** (1)

The IR and ^{1}H and ^{31}P{^{1}H} NMR spectra of **2** strongly support the structure shown in eq 1, which is similar to that found for the hydrido−silyl derivative Ir(acac)H($SiEt_3$)(PCy_3) by X-ray diffraction analysis.[5] The IR spectrum in Nujol shows a ν(Rh−H) band at 2060 cm^{-1} and two strong ν(CO) absorptions at 1581 and 1522 cm^{-1}, corresponding to the acetylacetonato ligand coordinated in a η^2-oxygen bonding mode.[7] In the ^{1}H NMR spectrum in toluene-d_8 the hydrido signal appears as a double doublet with Rh−H and P−H coupling constants of 28 and 22 Hz, respectively. The ^{31}P{^{1}H} NMR spectrum shows a doublet at 59.2 ppm with a Rh−P coupling constant of 162 Hz. The presence of only one hydrido ligand in **2** was inferred from the ^{31}P{^{1}H} NMR spectrum recorded under off-resonance conditions, which contains a double doublet as a result of the Rh−P and P−H couplings.

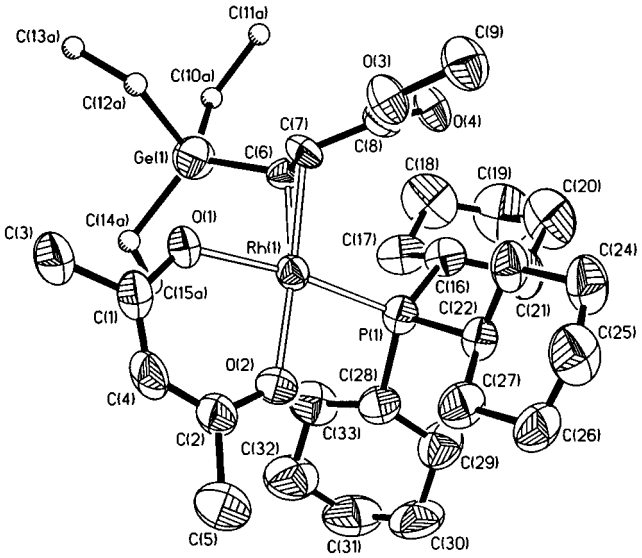
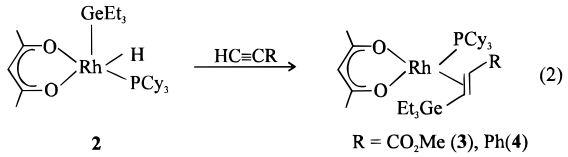


Figure 1. Molecular drawing for the complex Rh(acac){(*E*)-CH($GeEt_3$)=$CHCO_2Me$}(PCy_3)·0.25C_6H_6 (**3**).

Although rhodium hydrido−germyl species have been previously proposed as catalytic intermediates for the hydrogermylation of alkynes and olefins in the presence of rhodium compounds,[3a,b,i] as far as we know, complexes of this type have not been previously isolated. In agreement with their share in these reactions, we have also observed that complex **2** reacts with methyl propiolate and phenylacetylene to give the germane−olefin complexes Rh(acac){η^2-(*E*)-CH($GeEt_3$)=CHR}(PCy_3) (R = −CO_2Me (**3**), Ph(**4**)), which were isolated as orange solids in 43% (**3**) and 45% (**4**) yield (eq 2).



2 R = CO_2Me (**3**), Ph(**4**) (2)

Complexes **3** and **4** were characterized by elemental analysis and IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. Complex **3** was further characterized by an X-ray crystallographic study. The structure has two chemically equivalent but crystallographically independent molecules of complex **3** in the asymmetric unit. A drawing of one of them is shown in Figure 1. Selected bond distances and angles for both molecules are listed in Table 1.

The coordination geometry around the rhodium center is almost square planar, with the olefin disposed perpendicular to the coordination plane of the rhodium, as should be expected according to the Dewar−Chatt bonding scheme. The atoms O(1), O(2), P, and Rh are all in one plane, while the midpoint of the carbon−carbon double bond of the olefin (M) lies out of this plane, by 0.0020(9) Å (molecule **a**) and 0.0089(10) Å

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex Rh(acac){η^2-(*E*)-CH(GeEt$_3$)=CHCO$_2$Me}(PCy$_3$)·0.25C$_6$H$_6$ (3)

	a[a]	**b**[a]		**a**	**b**
Rh(1)−P(1)	2.247(2)	2.251(3)	C(2)−C(4)	1.363(13)	1.355(18)
Rh(1)−O(1)	2.067(5)	2.068(7)	C(2)−C(5)	1.517(14)	1.488(18)
Rh(1)−O(2)	2.030(6)	2.024(7)	Ge(1)−C(6)	1.921(11)	1.943(9)
Rh(1)−C(6)	2.117(8)	2.105(9)	C(6)−C(7)	1.406(14)	1.406(14)
Rh(1)−C(7)	2.108(8)	2.120(11)	C(7)−C(8)	1.472(14)	1.457(13)
O(1)−C(1)	1.262(11)	1.259(13)	O(3)−C(8)	1.341(12)	1.346(13)
C(1)−C(3)	1.492(13)	1.505(18)	O(3)−C(9)	1.431(14)	1.431(14)
C(1)−C(4)	1.361(15)	1.364(18)	O(4)−C(8)	1.184(10)	1.178(12)
O(2)−C(2)	1.270(11)	1.272(11)			
P(1)−Rh(1)−O(1)	172.5(2)	173.0(2)	Rh(1)−C(6)−Ge(1)	114.5(4)	112.8(5)
P(1)−Rh(1)−O(2)	84.6(2)	84.9(2)	Rh(1)−C(6)−C(7)	70.2(5)	71.1(6)
P(1)−Rh(1)−M(1)[b]	102.3(3)	101.8(3)	Rh(1)−C(7)−C(6)	70.9(5)	70.0(6)
O(1)−Rh(1)−O(2)	88.1(3)	88.2(3)	Rh(1)−C(7)−C(8)	117.5(6)	119.6(7)
O(1)−Rh(1)−M(1)[b]	85.1(3)	85.2(4)	Ge(1)−C(6)−C(7)	124.2(7)	125.8(7)
O(2)−Rh(1)−M(1)[b]	173.1(3)	172.2(2)	C(6)−C(7)−C(8)	121.0(8)	119.4(9)
C(6)−Rh(1)−C(7)	38.9(3)	38.9(4)	O(3)−C(8)−C(7)	109.2(8)	108.8(8)
			O(4)−C(8)−C(7)	127.8(9)	129(1)
			C(8)−O(3)−C(9)	116.5(7)	115.3(8)
			O(3)−C(8)−O(4)	123.0(9)	121.7(9)

[a] Related bond lengths and angles for the two molecules in the asymmetric unit (**a** and **b**). [b] M(1) is the midpoint of the olefinic C(6)−C(7) double bond.

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(molecule **b**), respectively. β-Diketonato bite angles O(1)−Rh−O(2) of 88.1(3)° (**a**) and 88.2(3)° (**b**) are similar to the values found in related chelated rhodium complexes,[8] whereas the P−Rh−M angles (102.3(3)° (**a**), 101.8(3)° (**b**)) strongly deviate from the ideal value of 90°, most probably as a result of the large steric hindrance experienced by the phosphine and olefin ligands, which are mutually *cis* disposed.

For the two molecules, the rhodium−olefin coordination exhibits statistically identical Rh−C distances (see Table 1), which agree well with those found in other rhodium−olefin complexes (mean values 2.102 Å).[9] Similarly, the olefinic bond distances C(6)−C(7) (1.41(1) Å (**a** and **b**)) are in the range reported for this type of complex (between 1.340 and 1.445 Å).[9]

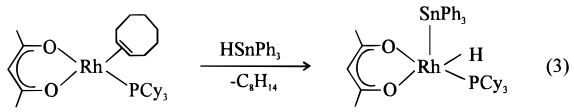
It should be also mentioned that the Rh−O(2) bond distances (O *trans* to olefin; 2.030(6) Å (**a**), 2.024(7) Å (**b**)) are significantly shorter than the Rh−O(1) bond lengths (O *trans* to PCy$_3$; 2.067(5) Å (**a**), 2.068(7) Å (**b**)), probably due to the different *trans* influences of the olefin and phosphine ligands.

In agreement with the η^2-oxygen bonding coordination mode of the acetylacetonato ligand in **3**, the IR spectrum in Nujol shows two strong ν(CO) absorptions at 1581 and 1518 cm^{-1}. In accord with the square-planar geometry, the ^{1}H NMR spectrum contains two singlets at 1.79 and 1.65 ppm, corresponding to the methyl protons of the β-diketonato ligand, while the olefinic protons display two double doublets at 4.44 and 3.25 ppm, with a H−H coupling constant of 13 Hz and Rh−H coupling constants of 1 and 5 Hz, respectively.

In the ^{13}C{^{1}H} NMR spectrum, the inequivalent carbonyl groups of the acetylacetonato ligand give rise to two singlets at 187.2 and 182.9 ppm, while the methyl groups appear as a singlet at 28.0 ppm and a doublet at 27.8 ppm with a P−C coupling constant of 3 Hz. The vinylic carbon atoms of the olefin display doublets at 55.9 and 50.6 ppm, with a Rh−C coupling constant of 16 Hz for both resonances. The ^{31}P{^{1}H} NMR spectrum shows a doublet at 43.4 ppm with a Rh−P coupling constant of 173 Hz.

The spectroscopic data for complex **4** suggest that this compound also has a square-planar geometry with the β-diketonato ligand coordinating in a η^2-oxygen bonding mode. Thus, the IR spectrum in Nujol contains the characteristic ν(CO) absorptions at 1574 and 1512 cm^{-1}. In the ^{1}H NMR spectrum, the methyl protons of the acetylacetonato ligand appear as two singlets at 1.85 and 1.63 ppm, while the vinyl protons of the olefin give rise to a doublet at 5.71 ppm, with a H−H coupling constant of 13 Hz, and a double doublet at 2.73 ppm, with the same H−H coupling constant and a Rh−H coupling constant of 5 Hz. The value of the H−H coupling constant strongly supports the *trans* disposition of the hydrogen atoms at the carbon−carbon double bond. In the ^{13}C{^{1}H} NMR spectrum the carbonyl groups of the β-diketonato ligand appear as two singlets at 186.4 and 183.2 ppm, while the carbon atoms of the methyl groups of this ligand display a singlet at 27.2 ppm and a doublet at 27.8 ppm with a P−C coupling constant of 6 Hz. The carbon atoms of the coordinated carbon−carbon double bond give rise to doublets at 77.9 and 41.7 ppm, with a Rh−C coupling constant of 16 Hz for both resonances. The ^{31}P{^{1}H} NMR spectrum shows a doublet at 43.2 ppm with a Rh−P coupling constant of 183 Hz.

2. Synthesis of Rh(acac)H(SnPh$_3$)(PCy$_3$) and Its Reactions with Terminal and Internal Alkynes. Similar to the reaction of **1** with HGeEt$_3$ to give **2** and cyclooctene, the treatment of a hexane solution of **1** with 1 equiv of HSnPh$_3$ leads, after 30 min at room temperature, to the five-coordinate hydrido−stannyl complex Rh(acac)H(SnPh$_3$)(PCy$_3$) (**5**), isolated as a yellow solid in 55% yield (eq 3).



1 **5** (3)

The IR and ^{1}H, ^{31}P{^{1}H}, and ^{119}Sn{^{1}H} NMR spectra of **5** strongly support the structure shown in eq 3. The IR spectrum in Nujol contains two strong ν(CO) absorp-

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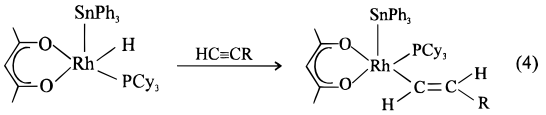
tions at 1563 and 1520 cm^{-1}, proving the η^2-oxygen coordination bonding mode of the acetylacetonato ligand. The ^1H NMR spectrum shows in the high-field region a double doublet at −18.20 ppm with Rh−H and P−H coupling constants of 25 and 18 Hz, respectively. The satellites due to the Sn isotopes are also observed near this resonance. The value of the Sn−H coupling constant, 18 Hz, is in agreement with a *cis* arrangement of the triphenylstannyl group and the hydrido ligand. The $^{31}P\{^1H\}$ NMR spectrum shows a doublet at 57.6 ppm, with a Rh−P coupling constant of 150 Hz. Similar to the ^1H NMR spectrum, satellites due to Sn isotopes are also observed along with the doublet. The value of the P−Sn coupling constant, 120 Hz, also agrees well with the mutually *cis* disposition of the $SnPh_3$ and PCy_3 groups. The presence of only one hydrido ligand in **5** was inferred from the $^{31}P\{^1H\}$ NMR spectrum under off-resonance conditions, which shows a double doublet as a result of the Rh−P and P−H couplings. The $^{119}Sn\{^1H\}$ NMR spectrum shows a double doublet with Rh−^{119}Sn and P−^{119}Sn coupling constants of 435 and 120 Hz, respectively.

Terminal alkynes such methyl propiolate, phenylacetylene, and (trimethylsilyl)acetylene undergo an insertion reaction into the Rh−H bond of **5** to afford the five-coordinate alkenyl derivatives Rh(acac){(*E*)-CH=CHR}($SnPh_3$)(PCy_3) (R = CO_2Me (**6**), Ph (**7**), SiMe (**8**); eq 4).



(4)

5

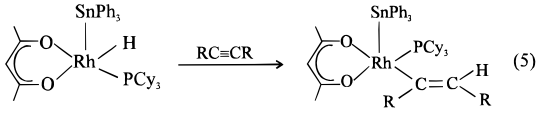
R = CO_2Me (**6**), Ph(**7**), $SiMe_3$(**8**)

Complexes **6** and **7** were isolated as orange (**6**) and red (**7**) solids in 71% (**6**) and 66% (**9**) yields, respectively, while complex **8** was isolated as a yellow oil in 73% yield. The presence in these compounds of an alkenyl group with a *E* stereochemistry is strongly supported by the resonances of the vinylic protons of the unsaturated η^1-carbon ligands in the ^1H NMR spectra. The value of the coupling constants between these protons is between 16 and 18 Hz, which is characteristic for this arrangement.[10] The $^{31}P\{^1H\}$ and $^{119}Sn\{^1H\}$ spectra of **6**−**8** are fully consistent with the structure proposed in eq 4. The $^{31}P\{^1H\}$ NMR spectra show a doublet at about 41 ppm, with a Rh−P coupling constant between 153 and 162 Hz, along with the satellites due to the Sn isotopes. The value of the Sn−P coupling constants is between 104 and 121 Hz. The $^{119}Sn\{^1H\}$ NMR spectra contain a double doublet between −108 and −130 ppm, with Rh−Sn coupling constants between 489 and 599 Hz.

The reactions of **2** with methyl propiolate and phenylacetylene to afford the germane−olefin complexes **3** and **4** most probably involve germanyl−alkenyl intermediates related to **6**−**8**, which evolve by reductive elimination into the corresponding germane olefins. Attempts to detect these intermediates have been unsuccessful, even at low temperatures. However, the reactions shown in eq 4 are strong evidence in favor of this proposal. The higher stability of the stannyl−alkenyl complexes **6**−**8** compared with the related germanyl−alkenyl derivatives is in agreement with the decrease in bond strength along the series C−Si > C−Ge > C−Sn.[11]

Thermochemical data for the series of transition-metal silyl, germyl, and stannyl complexes are quite limited. On the basis of appearance potential measurements for Fe(η^5-C_5H_5)(EMe_3)$(CO)_2$ (E = Si, Sn),[12] M(EMe_3)$(CO)_3$ (M = Cr, Mo, W; E = Ge, Sn),[13] and Re(EMe_3)$(CO)_5$ (E = Si, Ge, Sn),[14] bond strengths appear to follow the order M−Sn > M−Ge > M−Si. Thus, it is reasonable to assume that a similar sequence is operative in our case. Therefore, the reactivity patterns observed for **2** and **5** can be rationalized not only in terms of differences in C−ER_3 bond strengths but also as a result of the higher stability of the Rh−Sn bond compared with the Rh−Ge bond.

Complex **5** also reacts with internal alkynes. The reactions with diethyl acetylenedicarboxylate and diphenylacetylene afford the stannyl derivatives Rh(acac)-(CR=CHR)($SnPh_3$)(PCy_3) (R = CO_2Et (**9**), Ph (**10**)), which were isolated as orange solids in 75% (**9**) and 50% (**10**) yield (eq 5).



(5)

5

R = CO_2Et (**9**), Ph(**10**)

Characteristic spectroscopic features of the alkenyl ligands of these compounds are a singlet in the ^1H NMR spectra at 6.14 (**9**) and 6.94 (**10**) ppm for the =CHR proton and two resonances in the $^{13}C\{^1H\}$ NMR spectra at 174.1 (s, C_β) and 151.6 [dd, J(Rh−C) = 26 Hz, J(P−C) = 11 Hz, C_α] (**9**) and at 151.6 [dd, J(Rh−C) = 30 Hz, J(P−C) = 13 Hz, C_α] and 142.1 (s, C_β) (**10**) ppm, for the vinylic carbon atoms. As for **5**−**8**, the $^{31}P\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR spectra are in agreement with the mutually *cis* disposition of the phosphine and stannyl ligands. The $^{31}P\{^1H\}$ NMR spectra show doublets at 38.3 (**9**) and 39.0 (**10**) ppm, with Rh−P coupling constants of 148 and 156 Hz, respectively, along with the satellites due to the Sn isotopes. The $^{119}Sn\{^1H\}$ NMR spectra contain double doublets at −121.2 (**9**) and −157.7 (**10**) ppm, with Rh−Sn and P−Sn coupling constants of 526 (**9**) and 625 (**10**) Hz and 111 (**9**) and 138 (**10**) Hz, respectively.

3. Reactions of Rh(acac)H($SnPh_3$)(PCy_3) with Alkynols and 2-Methyl-1-buten-3-yne. The insertion reactions of alkynes into the metal−hydrido bonds are of considerable interest in connection with homogeneous catalysis,[15] and the alkynols have been found to be useful starting materials for the development of new catalytic processes.[16] However, the reactivity of the transition-metal hydrido complexes toward alkynols has

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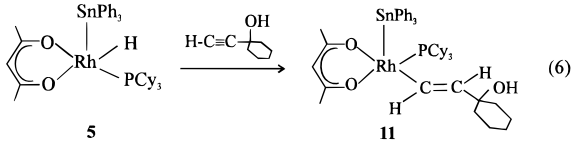
been scarcely studied. Previously, we have reported that the five-coordinate monohydrido complex OsHCl(CO)(P^iPr_3)$_2$ reacts with HC≡CC(OH)R^1R^2 to give the hydroxyalkenyl derivatives Os{(*E*)-CH=CHC(OH)R^1R^2}Cl(CO)(P^iPr_3)$_2$. In solution these compounds are unstable and decompose into the vinylcarbenes $OsCl_2$(=CHCH=CR^1R^2)(CO)(P^iPr_3)$_2$. When R^1 is hydrogen, small amounts of the complexes OsCl{CH=CHC(O)R^2}(CO)(P^iPr_3)$_2$ are also formed.[17] The related ruthenium complex RuHCl(CO)(P^iPr_3)$_2$ also reacts with alkynols to give *E* hydroxy−alkenyl compounds. In solution, the hydroxyalkenyl complexes derived from 2-propyn-1-ol, 1-phenyl-2-propyn-1-ol, and 1,1-diphenyl-2-propyn-1-ol are stable and do not undergo a subsequent transformation. On the other hand, the hydroxyalkenyl ligand of the complex Ru{(*E*)-CH=CHC(OH)$(CH_2)_4CH_2$}Cl(CO)(P^iPr_3)$_2$ dehydrates in toluene at 60 °C to afford the α,*β*-unsaturated alkenyl compound Ru{(*E*)-CH=CHC=CH$(CH_2)_3CH_2$}Cl(CO)(P^iPr_3)$_2$.[18]

As for the five-coordinate monohydrido RuHCl(CO)(P^iPr_3)$_2$, the hydrido−stannyl complex **5** reacts with 1-ethynyl-1-cyclohexanol by insertion of the carbon−carbon triple bond of the alkynol into the Rh−H bond, to afford the hydroxyalkenyl complex Rh(acac){(*E*)-CH=CHC(OH)$(CH_2)_4CH_2$}($SnPh_3$)(PCy_3) (**11**; eq 6). How-



5 **11** (6)

ever, the hydroxyalkenyl ligand of this complex is stable, and dehydration to give the corresponding α,*β*-unsaturated alkenyl derivative is not observed in toluene at 60 °C.

Complex **11** was isolated as a red solid in 76% yield and characterized by elemental analysis, IR and $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{119}Sn\{^1H\}$ NMR spectroscopy, and an X-ray crystallographic study. The molecular structure is shown in Figure 2. Selected bond distances and angles are listed in Table 2.

The most remarkable features of the structure are the square-pyramidal coordination of the metal with the stannyl group located at the apex and the *trans* disposition of the two substituents $C_6H_{10}OH$ and Rh(acac)($SnPh_3$)(PCy_3) at the C=C double bond. The four atoms O(1), O(2), P(1), and C(1), forming the base of the pyramid, are approximately in one plane, while the rhodium atom is located approximately 0.22 Å above this plane toward the apical position. Although we can without a doubt say that the alkenyl group has an *E* stereochemistry, it must be mentioned that this group was found to be disordered. Thus, the alkenyl ligand was modeled using two different moieties, refined with complementary occupancy factors (see Experimental Section). The presence in **11** of an alkenyl ligand with an *E* stereochemistry is also supported by the ^1H NMR spectrum, which shows a H−H coupling constant between the vinyl protons of 16 Hz.

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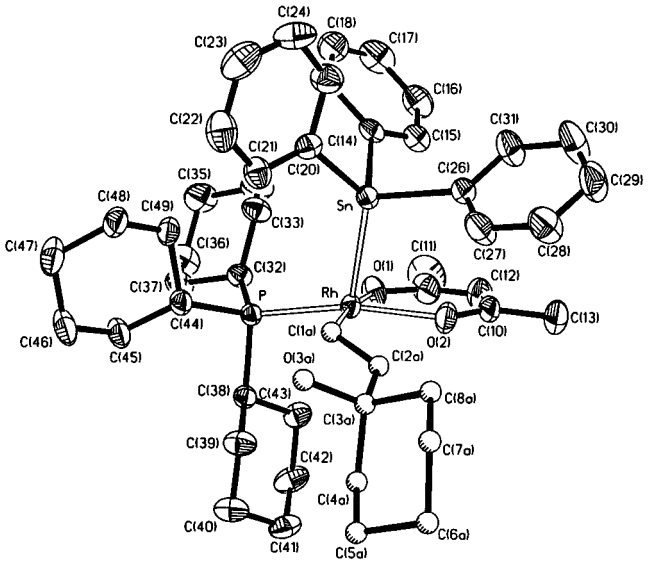

Figure 2. Molecular drawing for the complex Rh(acac){CH=CHC(OH)$(CH_2)_4CH_2$}(PCy_3)($SnPh_3$) (**11**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex Rh(acac){(*E*)-CH=CHC(OH)$(CH_2)_4CH_2$}($SnPh_3$)(PCy_3) (11)

Rh−Sn	2.5460(6)	O(2)−C(10)	1.282(6)
Rh−P	2.264(1)	C(10)−C(12)	1.385(9)
Rh−O(1)	2.113(3)	C(10)−C(13)	1.511(8)
Rh−O(2)	2.063(3)	C(1a)−C(2a)	1.359(10)
Rh−C(1a)	1.985(9)	C(2a)−C(3a)	1.532(12)
Rh−C(1b)	2.112(20)	O(3a)−C(3a)	1.408(8)
O(1)−C(9)	1.268(6)	C(1b)−C(2b)	1.381(16)
C(9)−C(11)	1.513(10)	C(2b)−C(3b)	1.550(16)
C(9)−C(12)	1.378(8)	O(3b)−C(3b)	1.403(11)
P−Rh−Sn	109.10(4)	Rh−O(1)−C(9)	125.6(3)
P−Rh−O(1)	88.2(1)	Rh−O(2)−C(10)	126.5(3)
P−Rh−O(2)	167.5(1)	Rh−C(1a)−C(2a)	118.6(5)
P−Rh−C(1a)	93.8(2)	Rh−C(1b)−C(2b)	118.8(9)
P−Rh−C(1b)	87.1(4)	C(1a)−C(2a)−C(3a)	122.8(6)
Sn−Rh−O(1)	104.69(9)	C(1b)−C(2b)−C(3b)	119(1)
Sn−Rh−O(2)	83.4(1)	C(2a)−C(3a)−O(3a)	112.5(6)
Sn−Rh−C(1a)	81.1(3)	C(2b)−C(3b)−O(3b)	109.2(9)
Sn−Rh−C(1b)	81.2(6)	C(2a)−C(3a)−C(4a)	108.5(7)
O(1)−Rh−C(1a)	172.9(3)	C(2b)−C(3b)−C(4b)	110.7(9)
O(1)−Rh−C(1b)	173.5(5)	C(2a)−C(3a)−C(8a)	108.3(6)
O(2)−Rh−C(1a)	88.5(3)	C(2b)−C(3b)−C(8b)	108.4(8)
O(2)−Rh−C(1b)	95.6(4)		
O(1)−Rh−O(2)	88.1(1)		

The *β*-diketonato ligand coordinates in a η^2-oxygen bonding mode. The bite angle O(1)−Rh−O(2) (88.1(1)°) is statistically identical with the O−Rh−O angles of **3** (88.1(3) and 88.2(3)°). The separation between the metallic center and the oxygen atom located *trans* to the phosphine ligand (Rh−O(2) = 2.063(3) Å) is also statistically identical with the Rh−O distances found in **3** for the Rh−O bond disposed *trans* to the phosphine (2.067(5) and 2.068(7) Å) and is approximately 0.05 Å shorter than the value of the other Rh−O bond length in **11** (Rh−O(1) = 2.113(3) Å). This possibly is due to the different *trans* influences of the phosphine and alkenyl ligands. In agreement with the η^2-oxygen coordination bonding mode of the acetylacetonato ligand in **11**, the IR spectrum in Nujol shows two strong ν(CO) bands at 1585 and 1520 cm^{-1}.

The P−Rh−Sn angle (109.10(4)°) strongly deviates from the ideal value of 90°. The relatively large value of this angle can be explained by the fact that the

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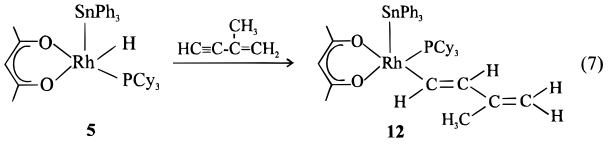
ligands, *cis* disposed, experience a large steric hindrance, as a result of the large cone angle of the tricyclohexylphosphine and triphenylstannyl groups. Despite this, the Rh−P bond length (2.264(1) Å) is not very different from the Rh−P distances in **3** (2.247(2) and 2.251(3) Å), and the Rh−Sn distance (2.5460(6) Å) is short. Although no other (trialkylstannyl)- and (triarylstannyl)rhodium derivatives have been structurally characterized, one can find examples of complexes of the types $Rh-SnCl_3$ and $Rh-Sn(NR_2)_2Cl$. The $Rh-SnX_3$ (X = Cl, NR_2) bond lengths reported are between 2.55 and 2.64 Å.[19] Thus, the Rh−Sn bond length of **11** is the shortest known Rh−Sn single-bond distance. For low-valent derivatives of the type $M-ER_3$ (E = Si, Ge, Sn), the M−E bond strengths and bond lengths appear to be significantly influenced by π-interactions between the transition metal and the group 14 atoms. The π-interaction increases in the sequence Si < Ge < Sn.[2c,3l,20]

The $^{31}P\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR spectra of **11** are fully consistent with the mutually *cis* disposition of the tricyclohexylphosphine and triphenylstannyl ligands. The $^{31}P\{^1H\}$ NMR spectrum shows a doublet at 41.3 ppm, with a Rh−P coupling constant of 154 Hz, along with the satellites due to the Sn isotopes. The value of the Sn−P coupling constant is 122 Hz. The $^{119}Sn\{^1H\}$ NMR spectrum contains a double doublet at −141.3 ppm, with a Rh−Sn coupling constant of 566 Hz.

Although the hydroxyalkenyl ligand of **11** does not dehydrate to give the corresponding α,β-unsaturated alkenyl compound, complexes of this type can be prepared by reaction with enynes. Thus, the treatment of a pentane suspension of **5** with 1 equiv of 2-methyl-1-buten-3-yne leads to the α,β-unsaturated alkenyl derivative Rh(acac){(*E*)-CH=CHC(CH$_3$)=CH$_2$}(SnPh$_3$)(PCy$_3$) (**12**; eq 7), which is a result of the selective

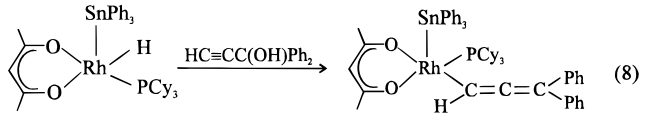


5 **12** (7)

addition of the Rh−H bond of **5** to the carbon−carbon triple bond of the enyne. A similar behavior has been previously found for the five-coordinate monohydrido complexes $MHCl(CO)(P^iPr_3)_2$ (M = Os, Ru).[21]

The α,β-unsaturated alkenyl complex **12** was isolated as a red solid in 81% yield. In agreement with the η^2-oxygen coordination bonding mode of the acetylacetonato ligand, the IR spectrum of this compound in Nujol contains two strong ν(CO) absorptions at 1580 and 1520 cm^{-1}, along with two ν(C=C) bands at 1560 and 1595 cm^{-1}, assigned to the α,β-unsaturated alkenyl ligand. In the ^1H NMR spectrum, this ligand exhibits resonances at 7.95 [d, J(H−H) = 17 Hz, =CHC], 7.32 [dd, J(H−H) = 17 Hz, J(Rh−H) = 9 Hz, RhCH=], 5.34 and 5.10 (s, $=CH_2$), and 2.24 (s, CH_3) ppm. The *trans* stereochemistry of the carbon−carbon double bond of the group RhCH=CHR is strongly supported by the H−H coupling constant of 17 Hz, which, as has been previously mentioned, is a typical value for this arrangement. In the ^{13}C NMR spectrum the RhCH= carbon atom appears at 136.7 ppm, as a double doublet with Rh−C and P−C coupling constants of 29 and 12 Hz, respectively, while the =*C*HC carbon atom displays a broad singlet at 138.0 ppm and the olefinic *C*(CH$_3$)= and $=CH_2$ carbon atoms give rise to singlets at 145.3 and 143.8 ppm. The *cis* disposition of the phosphine and stannyl groups is supported by the $^{31}P\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR spectra. The $^{31}P\{^1H\}$ NMR spectrum shows a doublet at 41.3 ppm, with a Rh−P coupling constant of 155 Hz, along with the satellites due to Sn isotopes, and the $^{119}Sn\{^1H\}$ NMR spectrum contains a double doublet at −135.4 ppm, with Rh−Sn and P−Sn coupling constants of 537 and 116 Hz, respectively.

Complex **5** also reacts with 1,1-diphenyl-2-propyn-1-ol. However, in contrast to the reaction with 1-ethynyl-1-cyclohexanol, we do not obtain a hydroxyalkenyl derivative but the allenyl complex Rh(acac)(CH=C=CPh$_2$)(SnPh$_3$)(PCy$_3$) (**13**), which is most probably a result of the spontaneous dehydration of a Rh{(*E*)-CHCHC(OH)Ph$_2$} intermediate (eq 8).



5 **13** (8)

Complex **13** was isolated as an orange solid in 70% yield. The presence of an allenyl ligand in this compound is supported by the C=C=C stretching frequency in the IR spectrum at 1990 cm^{-1}, and three resonances in the APT $^{13}C\{^1H\}$ NMR spectrum at 148.9 [d, J(Rh−C) = 2 Hz], 128.2 (overlapped with C_6D_6), and 80.7 (s) ppm for the C_β, C_α, and C_γ allenyl carbon atoms, respectively. The *cis* disposition of the tricyclohexylphosphine and triphenylstannyl ligands is proposed on the basis of the $^{31}P\{^1H\}$ and $^{119}Sn\{^1H\}$ spectra. The $^{31}P\{^1H\}$ NMR spectrum shows a doublet at 41.2 ppm, along with the satellites due to the Sn isotopes, whereas the $^{119}Sn\{^1H\}$ NMR spectrum contains a double doublet at −129.6 ppm. The values of the Rh−P, P−Sn, and Rh−Sn coupling constants are 153, 119, and 545 Hz, respectively.

There is a variety of η^1-allenyl transition-metal compounds known, but most have been prepared by oxidative addition of propargyl or allenyl halides to electron-rich metal centers.[22] Werner has observed that the osmium alkynyl−hydrido complexes OsHCl{C≡CC(OH)Ph$_2$}(NO)(PR$_3$)$_2$ react with acidic alumina to afford the allenylosmium(II) derivatives $OsCl_2(CH=C=CPh_2)(NO)(PR_3)_2$ (PR_3 = P^iPr_3, PPh^iPr_2).[23] Fisher has also reported that the allenylidene complex Cr(CO)$_5${C=C=C(C$_6$H$_4$NMe$_2$-*p*)$_2$} adds phosphine at the C_α carbon atom

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to give $Cr(CO)_5\{\eta^1\text{-}C(PR_3)=C=C(C_6H_4NMe_2\text{-}p)_2\}$ (PR_3 = PMe_3, $PHPh_2$, PH_2Me). At room temperature the complex $Cr(CO)_5\{\eta^1\text{-}C(PHPh_2)=C=C(C_6H_4NMe_2\text{-}p)_2\}$ rearranges to $Cr(CO)_5\{(PPh_2)[CH=C=C(C_6H_4NMe_2\text{-}P)_2\}$.[24] Recently, we have observed that the deprotonation of α,β-unsaturated alkoxycarbene and 2-azaallenyl complexes also yields allenyl derivatives.[25] In this context, it should be noted that the reaction shown in eq 8 is a new pathway to prepare allenyl complexes.

Concluding Remarks

This study has revealed that the monoolefin complex Rh(acac)(cyclooctene)(PCy_3) reacts with $HGeEt_3$ to give Rh(acac)H($GeEt_3$)(PCy_3) and with $HSnPh_3$ to afford Rh(acac)H($SnPh_3$)(PCy_3). In front of terminal alkynes, the reactivity patterns of these monohydrido compounds can be rationalized in terms of the differences in C−ER_3 (E = Ge, Sn) bond strengths (C−Ge > C−Sn) and as a result of the higher stability of the Rh−Sn bond compared with Rh−Ge bonds. Thus, while the hydrido−germyl complex reacts with methyl propiolate and phenylacetylene to give square-planar rhodium(I) complexes containing the corresponding germane−olefin ligands, the related reactions with the hydrido−stannyl compound lead to rhodium(III) alkenyl−stannyl derivatives, which are stable and do not evolve by reductive elimination of the stannaolefins.

The five-coordinate hydrido−stannyl complex Rh(acac)H($SnPh_3$)(PCy_3) is also a useful starting material to prepare hydroxyalkenyl, α,β-unsaturated alkenyl, and allenyl derivatives. The reaction of this complex with 1-ethynyl-1-cyclohexanol leads to the hydroxyalkenyl compound Rh(acac)$\{(E)\text{-}CH=CHC(OH)(CH_2)_4CH_2\}$($SnPh_3$)($PCy_3$), which has a square-pyramidal arrangement of ligands around the rhodium atom with the stannyl group in the apical position. The hydroxyalkenyl ligand is stable, and dehydration to give the corresponding α,β-unsaturated alkenyl group is not observed. However, α,β-unsaturated alkenyl complexes can be prepared by starting from enynes. Thus, we have observed that the Rh−H bond of Rh(acac)H($SnPh_3$)(PCy_3) is selectively added to the carbon−carbon triple bond of 2-methyl-1-buten-3-yne to afford Rh(acac)$\{(E)\text{-}CH=CHC(CH_3)=CH_2\}$($SnPh_3$)($PCy_3$). From 1,1-diphenyl-2-propyn-1-ol and Rh(acac)H($SnPh_3$)(PCy_3), in contrast to the reaction with 1-ethynyl-1-cyclohexanol, the allenyl derivative Rh(acac)$\{CH=C=CPh_2\}$($SnPh_3$)(PCy_3) is obtained. This reaction, which is a new pathway to prepare allenyl complexes, probably proceeds by spontaneous dehydration of a Rh$\{(E)\text{-}CH=CHC(OH)Ph_2\}$ intermediate.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere using Schlenk tube techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. The starting complex Rh(acac)(C_8H_{14})(PCy_3) (**1**) was prepared by a published method;[4] $HSn(Ph)_3$ (Aldrich Chemical Co.) and $HGe(Et)_3$ (ABCR) were used without further purification. Elemental analyses were performed with a Perkin-Elmer 240 XL microanalyzer. NMR spectra were recorded on Varian 200 XL or Varian Unity 300 instruments. Chemical shifts are expressed in parts per million, upfield from $Si(CH_3)_4$ ($^{13}C\{^1H\}$, ^1H) and 85% H_3PO_4 ($^{31}P\{^1H\}$). Infrared spectra were obtained from a Perkin-Elmer 783 instrument.

Preparation of Rh(acac)H($GeEt_3$)(PCy_3) (2). A solution of **1** (136 mg, 0.23 mmol) in 10 mL of toluene was treated with $HGeEt_3$ (77 mg, 0.22 mmol). After the mixture was stirred for 2 h at room temperature, the solution was filtered through Kieselguhr. The filtrate was concentrated to ca. 0.1 mL; addition of acetone caused the precipitation of a yellow solid. The solvent was decanted, and the solid was twice washed with acetone and dried in vacuo; yield 71 mg (43%). Anal. Calcd for $C_{29}H_{56}GeO_2PRh$: C, 54.15; H, 8.78. Found: C, 53.89; H, 9.10. IR (Nujol, cm^{-1}): ν(Rh−H) 2060; ν(acac) 1581, 1522. ^1H NMR (300 MHz, C_6D_6): 5.29 (s, 1 H, C*H* of acac); 2.10−1.00 (m, 48 H, C_6H_{11} and $GeEt_3$); 1.79 (s, 6 H, CH_3 of acac); −19.32 (dd, 1 H, J_{Rh-H} = 28 Hz, J_{P-H} = 22 Hz, Rh−*H*). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 59.2 (d, J_{Rh-P} = 162 Hz).

Preparation of Rh(acac)$\{\eta^2\text{-}(E)\text{-}CH(GeEt_3)=CHCO_2Me\}$($PCy_3$) (3). A solution of **2** (150 mg, 0.23 mmol) in 10 mL of pentane was treated with $CH_3O_2C{\equiv}CH$ (14 μL, 0.23 mmol). A spontaneous color change from yellow to orange-red occurred. After the mixture was stirred for 24 h at room temperature, the solvent was removed, the oily residue was dissolved in 2−3 mL of pentane, and the solution was stored at −78 °C. Orange crystals precipitated which were separated from the mother liquor, washed with pentane, and dried in vacuo; yield 72 mg (43%). Anal. Calcd for $C_{33}H_{60}GeO_4PRh$: C, 54.50; H, 8.32. Found: C, 54.75; H, 8.54. IR (Nujol, cm^{-1}): ν(C=O) 1709; ν(acac) 1581, 1518. ^1H NMR (300 MHz, C_6D_6): 5.27 (s, 1 H, C*H* of acac); 4.44 (dd, 1 H, J_{H-H} = 13 Hz, J_{P-H} = 1 Hz, =C*H*); 3.48 (s, 3 H, OCH_3); 3.25 (dd, 1 H, J_{H-H} = 13 Hz, J_{P-H} = 5 Hz, =C*H*); 2.10−1.00 (m, 48 H, C_6H_{11} and $GeEt_3$); 1.79 and 1.65 (both s, 6 H, CH_3 of acac). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6): δ 187.2 and 182.9 (both s, *C*O of acac); 176.8 (s, *C*$OOCH_3$); 99.3 (s, *C*H of acac); 55.9 (d, J_{Rh-C} = 16 Hz, *C*=*C*); 50.8 (s, O*C*H_3); 50.6 (d, J_{Rh-C} = 16 Hz, C=*C*); 34.5 (d, J_{P-C} = 22 Hz, P(Cy)$_3$); 30.8, 29.8 (s, P(Cy)$_3$); 28.1 (d, J_{P-C} = 10 Hz, P(Cy)$_3$); 28.0 (s, *C*H_3 of acac); 27.8 (d, J_{P-C} = 3 Hz, *C*H_3 of acac); 26.5 (s, P(Cy)$_3$); 9.7 and 6.3 (both s, $GeCH_2CH_3$). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 43.4 (d, J_{Rh-P} = 173 Hz).

Preparation of Rh(acac)$\{\eta^2\text{-}(E)\text{-}CH(GeEt_3)=CHPh\}$($PCy_3$) (4). The complex was prepared using the procedure described for **3** by starting with **2** (100 mg, 0.12 mmol) and PhC≡CH (13 μL, 0.12 mmol). Compound **4** was isolated as an orange solid; yield 40 mg (45%). Anal. Calcd for $C_{37}H_{62}GeO_2PRh$: C, 59.62; H, 8.38. Found: C, 59.75; H, 8.41. IR (Nujol, cm^{-1}): ν(acac) 1574, 1512. ^1H NMR (300 MHz, C_6D_6): 8.20−7.00 (m, 5 H, Ph); 5.71 (d, 1 H, J_{H-H} = 13 Hz, =C*H*); 5.21 (s, 1 H, C*H* of acac); 2.73 (dd, 1 H, J_{H-H} = 13 Hz, J_{Rh-H} = 5 Hz, =C*H*); 2.10−1.00 (m, 48 H, C_6H_{11} and $GeEt_3$); 1.85 and 1.63 (both s, 6 H, CH_3 of acac). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6): δ 186.4 and 183.2 (both s, *C*O of acac); 147.5, 126.6, and 125.4 (all Ph); 99.4 (s, *C*H of acac); 77.9 (d, J_{Rh-C} = 16 Hz, *C*=*C*); 41.7 (d, J_{Rh-C} = 16 Hz, *C*=*C*); 32.5 (d, J_{P-C} = 21 Hz, P(Cy)$_3$); 30.0 (s, P(Cy)$_3$); 28.4 (d, J_{P-C} = 10 Hz, P(Cy)$_3$); 27.8 (d, J_{P-C} = 6 Hz, *C*H_3 of acac); 27.2 (s, *C*H_3 of acac); 26.5 (s, P(Cy)$_3$); 9.9 and 6.9 (both s, $GeCH_2CH_3$). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 43.2 (d, J_{Rh-P} = 183 Hz).

Preparation of Rh(acac)H($SnPh_3$)(PCy_3) (5). A solution of **1** (130 mg, 0.22 mmol) in 10 mL of hexane was treated with $HSnPh_3$ (77 mg, 0.22 mmol). The resulting reaction mixture was stirred for 30 min at room temperature. A bright yellow precipitate was formed. The solvent was decanted, and the solid was washed with hexane and then dried in vacuo; yield 100 mg (55%). Anal. Calcd for $C_{41}H_{56}O_2PRhSn$: C, 59.08; H, 6.77. Found: C, 59.40; H, 7.02. IR (Nujol, cm^{-1}): ν(Rh−H) 1990; ν(acac) 1563, 1520. ^1H NMR (300 MHz, C_6D_6): δ 7.92−7.15 (m, 15 H, Ph); 5.22 (s, 1 H, C*H* of acac); 2.20−1.00 (m, 33 H, C_6H_{11}); 2.08 (s, 6 H, CH_3 of acac); −18.20 (dd, 1 H, J_{Rh-H} = 25 Hz, J_{P-H} = 18 Hz, with tin satellites J_{Sn-H} = 19 Hz, Rh−*H*). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 57.6 (dd, J_{Rh-P} =

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150 Hz, J_{Sn-P} = 120 Hz). $^{119}Sn\{^1H\}$ NMR (111.9 MHz, C_6D_6): δ −79.7 (dd, J_{Rh-Sn} = 435 Hz, J_{P-Sn} = 120 Hz).

Preparation of Rh(acac){(*E*)-CH═CHCO$_2$CH$_3$}(SnPh$_3$)(PCy$_3$) (6). A suspension of **5** (100 mg, 0.12 mmol) in 10 mL of pentane was treated with HC≡CCO$_2$CH$_3$ (7 μL, 0.12 mmol). A spontaneous color change from yellow to orange occurred, and the mixture was stirred for 30 min at room temperature. After an orange precipitate was formed, the solvent was decanted, and the solid was washed with pentane and dried in vacuo; yield 78 mg (71%). Anal. Calcd for $C_{45}H_{60}O_4PRhSn$: C, 58.92; H, 6.59. Found: C, 58.48; H, 6.85. IR (Nujol, cm^{-1}): ν(CO) 1701, 1525; ν(acac) 1580, 1515. ^1H NMR (300 MHz, C_6D_6, 20 °C): δ 9.57 (dd, 1 H, J_{H-H} = 16 Hz, J_{Rh-H} = 2 Hz, RhC*H*═); 7.80−7.15 (m, 15 H, Ph); 7.66 (d, 1 H, J_{H-H} = 16 Hz, ═C*H*CO$_2$CH$_3$), 5.21 (s, 1 H, C*H* of acac); 3.69 (s, 3 H, OC*H*$_3$); 2.19−1.20 (m, 33 H, C_6H_{11}); 1.71 (s, 6 H, C*H*$_3$ of acac). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6): δ 187.1 (br, *C*O of acac); 169.4 (dd, J_{Rh-C} = 28 Hz, J_{P-C} = 12 Hz, Rh*C*H═); 164.0 (s, *C*OOCH$_3$); 142.9, 137.9, 130.7 (all Ph); 100.8 (s, *C*H of acac); 50.5 (s, COO*C*H$_3$); 34.5 (d, J_{P-C} = 22 Hz, P(Cy)$_3$); 30.8, 29.8 (s, P(Cy)$_3$); 34.5 (d, J_{P-C} = 11 Hz, P(Cy)$_3$); 28.0 (s, *C*H$_3$ of acac); 26.5 (s, P(Cy)$_3$). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 40.0 (d, J_{Rh-P} = 153 Hz, with tin satellites J_{Sn-P} = 104 Hz). $^{119}Sn\{^1H\}$ NMR (111.86 MHz, C_6D_6): δ −108.0 (dd, J_{Rh-Sn} = 489 Hz, J_{P-Sn} = 104 Hz).

Preparation of Rh(acac){(*E*)-CH═CHPh)(SnPh$_3$)(PCy$_3$) (7). A suspension of **5** (105 mg, 0.13 mmol) in 10 mL of pentane was treated with PhC≡CH (15 μL, 0.13 mmol). A spontaneous color change from yellow to red occurred, and the mixture was stirred for 30 min at room temperature. After a red precipitate was formed, the solvent was decanted, and the solid was washed with pentane and dried in vacuo; yield 80 mg (66%). Anal. Calcd for $C_{49}H_{62}O_2PRhSn$: C, 62.91; H, 6.68. Found: C, 62.80; H, 6.10. IR (Nujol, cm^{-1}): ν(acac) 1570, 1502. ^1H NMR (300 MHz, C_6D_6): δ 8.13 (d, 1 H, J_{H-H} = 18 Hz, ═C*H*Ph), 7.97 (dd, 1 H, J_{H-H} = 18 Hz, J_{Rh-H} = 11 Hz, RhC*H*═), 7.95−7.15 (m, 20 H, Ph); 5.25 (s, 1 H, C*H* of acac); 2.20−1.00 (m, 33 H, C_6H_{11}); 1.86 (s, 6 H, C*H*$_3$ of acac). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6): δ 187.1 (br, *C*O of acac); 143.5, 137.9, 128.2, 127.8, 125.7, 125.6 (all Ph); 141.6 and 140.2 (both br, H*C*═*C*HPh); 99.8 (s, *C*H of acac); 34.3 (d, J_{P-C} = 22 Hz, P(Cy)$_3$); 30.8 and 29.8 (both s, P(Cy)$_3$); 28.1 (d, J_{P-C} = 10 Hz, P(Cy)$_3$); 27.8 (s, *C*H$_3$ of acac); 26.52 (s, P(Cy)$_3$). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 41.0 (d, J_{Rh-P} = 154 Hz, with tin satellites J_{Sn-P} = 114 Hz). $^{119}Sn\{^1H\}$ NMR (111.86 MHz, C_6D_6): δ −131.6 (dd, J_{Rh-Sn} = 546 Hz, J_{P-Sn} = 114 Hz).

Preparation of Rh(acac){(*E*)-CH═CHSiMe$_3$}(SnPh$_3$)(PCy$_3$) (8). A solution of **5** (105 mg, 0.13 mmol) in 10 mL of pentane was treated with HC≡CCSiMe$_3$ (21 μL, 0.13 mmol), and the mixture was stirred for 30 min at room temperature. The solvent was removed in vacuo, and the oily residue was dissolved in 5 mL of pentane. The solvent was again removed, and this procedure was repeated three times. A yellow air-sensitive oil was obtained; yield 85 mg (73%). ^1H NMR (300 MHz, C_6D_6): δ 8.04 (dd, 1 H, J_{H-H} = 18 Hz, J_{Rh-H} = 9 Hz, RhC*H*═); 7.89 (d, 6 H, J_{H-H} = 6 Hz, Ph); 7.52 (d, 1 H, J_{H-H} = 18 Hz, ═C*H*SiMe$_3$); 7.21 (m, 9 H, Ph); 5.20 (s, 1 H, C*H* of acac), 2.2−1.0 (m, 33 H, C_6H_{11}); 2.1 (s, 6 H, C*H*$_3$ of acac); 0.3 (s, 9 H, SiC*H*$_3$). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6): δ 187.0 (s, *C*O of acac); 157.3 (dd, J_{Rh-C} = 26 Hz, J_{P-C} = 11, Rh*C*H═); 145.1 (d, J_{Rh-C} = 3 Hz, ═*C*HSiCH$_3$); 143.4, 138.4, 138.1, 137.8 (s, Ph); 100.8 (s, *C*H of acac); 34.5 (d, J_{P-C} = 21 Hz, P(Cy)$_3$); 30.8 and 30.1 (both s, P(Cy)$_3$); 28.1 (d, J_{P-C} = 10 Hz, P(Cy)$_3$); 27.9 (s, *C*H$_3$ of acac); 26.5 (s, P(Cy)$_3$); 0.5 (s, SiCH$_3$). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 41.2 (d, J_{Rh-P} = 162 Hz, with tin satellites J_{Sn-P} = 121 Hz). $^{119}Sn\{^1H\}$ NMR (111.86 MHz, C_6D_6): δ −129.8 (dd, J_{Rh-Sn} = 599 Hz, J_{P-Sn} = 121 Hz).

Preparation of Rh(acac){C(CO$_2$Et)═CHCO$_2$Et}(SnPh$_3$)(PCy$_3$) (9). The complex was prepared using the procedure described for **6** by starting with **5** (100 mg, 0.12 mmol) and EtO$_2$CC≡CCO$_2$Et (21 μL, 0.12 mmol). Compound **9** was isolated as an orange solid; yield 90 mg (75%). Anal. Calcd for $C_{49}H_{66}O_6PRhSn$: C, 58.64; H, 6.63. Found: C, 58.33; H, 6.74. IR (Nujol, cm^{-1}): ν(acac) 1530, 1590. ^1H NMR (300 MHz, C_6D_6): δ 7.98 (d, 6 H, J_{H-H} = 6 Hz, Ph); 7.20−7.00 (m, 9 H, Ph); 6.14 (s, 1 H, ═C*H*CO$_2$Et); 5.10 (s, 1 H, C*H* of acac); 4.41 (m, 2H, OC*H*$_2$); 3.95 (m, 3H, CH$_2$C*H*$_3$); 2.40−0.80 (m, 33 H, C_6H_{11}); 1.80 (s, 6 H, C*H*$_3$ of acac). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6): δ 185.1 (br, *C*O of acac); 174.1 (s, ═*C*HCO$_2$Et); 151.6 (dd, J_{Rh-C} = 26 Hz, J_{P-C} = 11 Hz, Rh*C*═); 160.0 and 159.9 (both s, *C*O$_2$Et); 141.8, 136.2, 131.2 (Ph); 100.0 (s, *C*H of acac); 58.2 (s, O*C*H$_2$); 57.9 (s, CH$_2$*C*H$_3$); 32.7 (d, J_{P-C} = 21.6 Hz, P(Cy)$_3$); 30.9 and 30.7 (both s, P(Cy)$_3$); 28.0 (both d, J_{P-C} = 11 Hz, P(Cy)$_3$); 27.4 (s, *C*H$_3$ of acac); 26.5 (s, P(Cy)$_3$). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 38.3 (d, J_{Rh-P} = 148 Hz, with tin satellites J_{Sn-P} = 111 Hz). $^{119}Sn\{^1H\}$ NMR (111.86 MHz, C_6D_6): δ −121.2 (dd, J_{Rh-Sn} = 526 Hz, J_{P-Sn} = 111 Hz).

Preparation of Rh(acac)(CPh═CHPh)(SnPh$_3$)(PCy$_3$) (10). The complex was prepared using the procedure described for **6** by starting with **5** (115 mg, 0.19 mmol) and PhC≡CPh (35 mg, 0.19 mmol). Compound **10** was isolated as an orange solid; yield 98 mg (50%). Anal. Calcd for $C_{55}H_{66}O_2PRhSn$: C, 65.30; H, 6.58. Found: C, 65.83; H, 6.50. IR (Nujol, cm^{-1}): ν(acac) 1585, 1525. ^1H NMR (300 MHz, C_6D_6): δ 7.90−7.00 (m, 25 H, Ph); 6.94 (br, 1 H, ═C*H*Ph); 5.10 (s, 1 H, C*H* of acac); 2.29−0.75 (m, 33 H, C_6H_{11}); 1.80 (s, 6 H, C*H*$_3$ of acac). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6): δ 186.6 (br, *C*O of acac); 151.6 (dd, J_{Rh-C} = 30 Hz, J_{P-C} = 13 Hz, Rh*C*═); 147.1, 143.8 (both Ph); 142.1 (s br, ═*C*HPh); 139.8, 138.4, 130.0, 128.6, 128.5, 125.7, 124.8 (all Ph); 101.3 (s, *C*H of acac); 35.2 (d, J_{P-C} = 22 Hz, P(Cy)$_3$); 30.9 and 30.7 (both s, P(Cy)$_3$); 28.0 (both d, J_{P-C} = 11 Hz, P(Cy)$_3$); 27.4 (s, *C*H$_3$ of acac); 26.5 (s, P(Cy)$_3$). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 39.0 (d, J_{Rh-P} = 156 Hz, with tin satellites J_{Sn-P} = 138 Hz). $^{119}Sn\{^1H\}$ NMR (111.86 MHz, C_6D_6): δ −157.7 (dd, J_{Rh-Sn} = 625 Hz, J_{P-Sn} = 138 Hz).

Preparation of Rh(acac){(*E*)-CH═CHC(OH)(CH$_2$)$_4$CH$_2$}(SnPh$_3$)(PCy$_3$) (11). The complex was prepared using the procedure described for **6** by starting with **5** (110 mg, 0.13 mmol) and HC≡CC$_6$H$_{10}$OH (17 mg, 0.13 mmol). Compound **11** was isolated as a red solid; yield 95 mg (76%). Anal. Calcd for $C_{49}H_{68}O_3PRhSn$: C, 61.46; H, 7.16. Found: C, 61.80; H, 7.10. IR (Nujol, cm^{-1}): ν(acac) 1585, 1520. ^1H NMR (300 MHz, C_6D_6): δ 7.85 (d, 6 H, J_{H-H} = 6 Hz, Ph); 7.10 (m, 10 H, Ph and RhC*H*═); 6.9 (d, 1H, J_{H-H} = 16 Hz, ═C*H*C$_6$H$_{10}$OH); 5.15 (s, 1 H, C*H* of acac); 2.20−1.00 (m, 43 H, C_6H_{11} and C_6H_{10}); 1.86 (s, 6 H, C*H*$_3$ of acac). $^{13}C\{^1H\}$ NMR (APT) (75.45 MHz, C_6D_6): δ 186.8 (br, *C*O of acac); 149.2 (br, ═*C*HC$_6$H$_{10}$OH); 143.6; 138.1; 128.2; 127.9 (all Ph); 127.6 (s, RhH*C*═); 100.8 (s, *C*H of acac); 73.4 (s, OH*C*CH$_2$); 39.3 and 39.0 (both s, CH$_2$); 34.3 (d, J_{P-C} = 23 Hz, P(Cy)$_3$); 30.8 and 30.0 (both s, CH$_2$); 28.1 and 28.1 (both s, CH$_2$); 27.9 (d, J_{P-C} = 10 Hz, P(Cy)$_3$); 27.8 (s, *C*H$_3$ of acac); 26.5 and 22.7 (both s, CH$_2$). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 41.3 (d, J_{Rh-P} = 154 Hz, with tin satellites J_{Sn-P} = 122 Hz). $^{119}Sn\{^1H\}$ NMR (111.86 MHz, C_6D_6): δ −141.3 (dd, J_{Rh-Sn} = 566 Hz, J_{P-Sn} = 122 Hz).

Preparation of Rh(acac){(*E*)-CH═CHC(CH$_3$)═CH$_2$}(SnPh$_3$)(PCy$_3$) (12). The complex was prepared using the procedure described for **6** by starting with **5** (110 mg, 0.13 mmol) and HC≡CC(CH$_3$)═CH$_2$ (11 μL, 0.13 mmol). Compound **12** was isolated as a red solid; yield 96 mg (81%). Anal. Calcd for $C_{46}H_{62}O_2PRhSn$: C, 61.42; H, 6.95. Found: C, 60.96; H, 6.94. IR (Nujol, cm^{-1}): ν(C═C) 1560, 1595; ν(acac) 1580, 1520. ^1H NMR (300 MHz, C_6D_6): δ 7.95 (d, 1 H, J_{H-H} = 17 Hz, ═C*H*C(CH$_3$)═CH$_2$), 7.87 (d, 6 H, J_{H-H} = 7 Hz, Ph); 7.32 (dd, 1 H, J_{H-H} = 17 Hz, J_{Rh-H} = 9 Hz, RhC*H*═), 7.15 (m, 9 H, Ph); 5.34 (br s, 1 H, ═C*H*$_2$); 5.27 (s, 1 H, C*H* of acac); 5.10 (br s, 1 H, ═C*H*$_2$); 2.24 (s, 3 H, C*H*$_3$); 2.20−1.00 (m, 33 H, C_6H_{11}); 1.91 (s, 6 H, C*H*$_3$ of acac). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6): δ 187.3 (br, *C*O of acac); 145.3 (s, C═CH$_2$); 143.8 (s, C═CH$_2$); 143.6, 138.0, 127.8, 110.8 (all Ph); 138.0 (br, ═*C*HC(CH$_3$)═CH$_2$); 136.7 (dd, J_{Rh-C} = 29 Hz, J_{P-C} = 12 Hz, Rh*C*H═); 100.7 (s, *C*H of acac); 34.3 (d, J_{P-C} = 22 Hz, P(Cy)$_3$); 30.8, 29.9 (both s, P(Cy)$_3$); 28.1 (d, J_{P-C} = 11 Hz, P(Cy)$_3$); 27.9 (s, *C*H$_3$ of acac); 27.7 (s, *C*H$_3$); 26.5 (s, P(Cy)$_3$). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 41.3 (d, J_{Rh-P} = 155 Hz, with tin satellites J_{Sn-P} = 116 Hz).

Table 3. Crystal Data and Details of the Data Collection and Refinement for Rh(acac){(*E*)-CH(GeEt$_3$)=CHCO$_2$Me}(PCy$_3$)·0.25C$_6$H$_6$ (3) and Rh(acac){(*E*)-CH=CHC(OH)(CH$_2$)$_4$CH$_2$}(SnPh$_3$)(PCy$_3$) (11)

	3	11
	Crystal Data	
formula	$C_{33}H_{60}O_4PGeRh\cdot 0.25C_6H_6$	$C_{49}H_{68}O_2PRhSn$
mol wt	746.83	941.64
color, habit	orange, prismatic block	red, prismatic block
cryst size, mm	0.49 × 0.11 × 0.12	0.53 × 0.28 × 0.26
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	12.183(3)	11.382(2)
b, Å	18.120(4)	13.330(2)
c, Å	18.178(4)	15.598(3)
α, (deg)	73.979(9)	93.70(1)
β, (deg)	77.279(9)	100.89(1)
γ, (deg)	81.389(9)	101.96(1)
V, Å^3; *Z*	3745(2); 4	2260.2(7); 2
D(calcd), g cm^{-3}	1.324	1.384
temp, K	293	200
	Data Collection and Refinement	
diffractometer	Siemens-P4	Siemens-STOE AED-2
λ(Mo Kα) radiation, Å	0.710 73	0.710 73
technique	bisecting geom	
monochomator	graphite oriented	
μ, mm^{-1}	1.32	0.99
scan type	*θ*/2*θ*	*ω*/2*θ*
2*θ* range, deg	2 ≤ 2*θ* ≤ 50	3 ≤ 2*θ* ≤ 45
no. of data collected	14813	6268
no. of unique data	12814	5910
no. of params refined	740	489
R1[a]	0.0664	0.0307
wR2[b]	0.1731	0.0806

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

^{119}Sn{^{1}H} NMR (111.86 MHz, C_6D_6): *δ* −135.4 (dd, J_{Rh-Sn} = 537 Hz, J_{P-Sn} = 116 Hz).

Preparation of Rh(acac)(CH=C=CPh$_2$)(SnPh$_3$)(PCy$_3$) (13). The complex was prepared using the procedure described for **6** by starting with **5** (110 mg, 0.14 mmol) and HC≡CC(OH)Ph$_2$ (20 mg, 0.14 mmol). Compound **13** was isolated as an orange solid: yield 99 mg (70%). Anal. Calcd for $C_{56}H_{66}O_2PRhSn$: C, 65.70; H, 6.50. Found: C, 65.48; H, 6.32. IR (Nujol, cm^{-1}): *ν*(C=C=C) 1990; *ν*(acac) 1576, 1497. ^{1}H NMR (300 MHz, C_6D_6): *δ* 7.98−7.00 (m, 26 H, Ph and HC=C=CPh$_2$); 5.20 (s, 1 H, C*H* of acac); 2.29−0.75 (m, 33 H, C_6H_{11}); 1.84 (s, 6 H, C*H*$_3$ of acac). ^{13}C{^{1}H} NMR (75.45 MHz, C_6D_6): *δ* 187.0 (br, *C*O of acac); 148.9 (d, J_{Rh-C} = 2 Hz, C=*C*=C); 143.5, 143.2, 138.1, 127.9, 127.6, 126.8, 126.5, 126.3 (all Ph); 128.2 (overlaped with Ph signal, H*C*=C=CPh$_2$); 100.8 (s, *C*H of acac); 80.7 (s, =*C*Ph$_2$); 34.2 (d, J_{P-C} = 22 Hz, P(Cy)$_3$); 30.5 and 30.4 (both s, P(Cy)$_3$); 27.8 and 27.7 (both d, J_{P-C} = 10 Hz, P(Cy)$_3$); 27.8 (s, *C*H$_3$ of acac); 26.5 (s, P(Cy)$_3$). ^{31}P{^{1}H} NMR (121.45 MHz, C_6D_6): *δ* 41.2 (d, J_{Rh-P} = 153 Hz, with tin satellites J_{Sn-P} = 119 Hz). ^{119}Sn{^{1}H} NMR (111.86 MHz, C_6D_6): *δ* −129.6 (dd, J_{Rh-Sn} = 545 Hz, J_{P-Sn} = 119 Hz).

X-ray Structure Analysis of the Complexes Rh(acac)-{*η*^{2}-CH(GeEt$_3$)=CHCO$_2$Me}(PCy$_3$)·0.25C$_6$H$_6$ (3) and Rh(acac){(*E*)-CH=CHC(OH)(CH$_2$)$_4$CH$_2$}(PCy$_3$)(SnPh$_3$) (11). A summary of crystal data and refinement parameters is reported in Table 3. Data were collected on Siemens P4 (**3**) or Siemens-Stoe AED-2 (**11**) diffractometers, with graphite-monochromated Mo Kα radiation (*λ* = 0.710 73 Å) by the *ω*/2*θ* scan method. Three standard reflections were monitored at periodic intervals througout data collection; no significant variations were observed. All data were corrected for absorption using a semiempirical method.[26] All structures were solved by Patterson (Rh atoms) and conventional Fourier techniques and refined by full-matrix least squares on F^2 (SHELXL-93).[27] Atomic scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement program.

Data for 3. Crystals suitable for the X-ray diffraction study were obtained from a saturated solution of **3** in benzene at −20 °C. An orange prismatic block of approximate dimensions 0.49 × 0.11 × 0.12 mm was indexed to triclinic symmetry. A group of 43 reflections in the range 20 ≤ 2*θ* ≤ 30° were carefully centered and used to obtain by least-squares methods the unit cell dimensions. The asymmetric unit was formed by two crystallographically independent, but chemically analogous, molecules of **3**, and $^1/_2$ molecule of solvent (benzene related by a center of symmetry). The Ge(Et)$_3$ groups of the two molecules were observed to be disordered and refined with two different moieties with complementary occupancy factors and restrained geometry for each molecule. The hydrogen atoms were calculated (C−H = 0.96 Å) for all atoms not disordered and refined riding on carbon atoms with a commun isotropic thermal parameter. The refinement converged to R1 = 0.664 ($F^2 > 2\sigma(F^2)$) and wR2 = 0.1731 ($F^2 > 0$), with weighting parameters $x = 0.0938$ and $y = 0$.

Data for 11. Crystals suitable for the X-ray diffraction study were obtained from a toluene−acetone solution. A red prismatic block of approximate dimensions 0.53 × 0.28 × 0.26 mm was indexed to triclinic symmetry. A group of 64 reflections in the range 20 ≤ 2*θ* ≤ 45° were carefully centered and used to obtain by least-squares methods the unit cell dimensions. The CH=CHC(OH)(CH$_2$)$_4$CH$_2$ ligand was observed to be disordered and refined with two different moieties with complementary occupancy factors and restrained geometry. The hydrogen atoms were observed or calculated (C−H = 0.96 Å) for all atoms not disordered and refined riding on carbon atoms with a common isotropic thermal parameter. The refinement converged to R1 = 0.0307 ($F^2 > 2\sigma(F^2)$) and wR2 = 0.0806 ($F^2 > 0$), with weighting parameters $x = 0.0366$ and $y = 4.48$.

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Supporting Information Available: For **3** and **11**, tables of atomic coordinates, thermal parameters, experimental details of the X-ray study, bond distances and angles, and selected least-squares planes and interatomic distances (50 pages). Ordering information is given on any masthead page.

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