Organometallic Rhodium Complexes Containing Peralkylated Arsino(phosphino)methanes as Ligands

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The peralkylated arsino(phosphino)methanes $R_2AsCH_2PR_2$ (R = *i*Pr, Cy) reacted with [{(η^4-C_8H_{12})RhCl}$_2$] by cleavage of the chloro bridges to give the mononuclear compounds [RhCl(η^4-C_8H_{12})(κ-*P*-$R_2PCH_2AsR_2$)] (**1**, **2**). In contrast, treatment of the dimeric cyclooctadiene complex with the *t*Bu-substituted derivative $tBu_2AsCH_2PiPr_2$ afforded dinuclear [{Rh(η^4-C_8H_{12})}{Rh(κ^2-*As*,*P*-$tBu_2AsCH_2PiPr_2$)}(μ-Cl)$_2$] (**3**), the first example of a d^8 transition-metal compound containing a CH_2-bridged As/P donor system as a chelating ligand. The X-ray crystal structure of **3** has been determined. Cationic complexes [Rh(η^4-C_8H_{12})(κ^2-*As*,*P*-$R_2AsCH_2PR'_2$)]PF_6 (**4a**, **5a**, **6a**) were obtained from [{(η^4-C_8H_{12})RhCl}$_2$], $R_2AsCH_2PR'_2$, and MPF_6 (M = K, Ag). The corresponding BPh_4 salts (**4b**, **5b**, **6b**) were prepared from the PF_6 salts upon metathesis with $NaBPh_4$. The chelate compounds **4**−**6** reacted with CH_2N_2 by insertion of CH_2 into the Rh−As bond to yield the complexes [Rh(η^4-C_8H_{12})(κ^2-*C*,*P*-$CH_2As(R)_2CH_2PR'_2$)]PF_6 (**7**−**9**), which contain a five-membered metallacycle adopting an envelope conformation in the crystal. The reaction of the BPh_4 salts **4b** and **5b** with H_2 gave the half-sandwich-type complexes [(η^6-$C_6H_5BPh_3$)Rh(κ^2-*As*,*P*-$R_2AsCH_2PR'_2$)] (**10**, **11**), in which the tetraphenylborate is coordinated like a substituted arene to the metal center. Treatment of the PF_6 salt **6a** with H_2 in the presence of CF_3CO_2H led to the formation of the unusual dinuclear hydrido-bridged complex [{RhH(κ^2-*As*,*P*-$Cy_2AsCH_2PCy_2$)}$_2$(μ-H)(μ-O_2CCF_3)$_2$]PF_6 (**12**).

Introduction

There have been but few comparative studies concerning the reactivity of homologous tertiary phosphine, arsine, and stibine transition-metal complexes to date.[1] Recent work in our laboratory has shown that the replacement of P*i*Pr$_3$ by its higher homologues Sb*i*Pr$_3$ and As*i*Pr$_3$ or by the functionalized arsine *i*Pr$_2$As(CH$_2$)$_2$-OMe as a ligand leads to remarkable differences in the reactivity of low-valent metal complexes of the iron and cobalt triad.[2−4] Moreover, in almost all cases which have been studied to date, the M−E*i*Pr$_3$ (E = Sb, As) bond is more labile than its M−P*i*Pr$_3$ counterpart, and this can be put to advantage for synthetic purposes.[2,4b,5] Although some of these differences are probably steric in nature, they mainly reflect the unequal σ-donor and π-acceptor capabilities of trialkylphosphine and -arsine or -stibine ligands.

To combine the favorable parts of the ligand behavior of bulky trialkylphosphines on one side and of related trialkylstibines or -arsines on the other, we set out to prepare mixed (possibly hemilabile) P/E donor systems (E = Sb, As). Very recently, we reported the synthesis of the first representatives of ligands of the type $R_2PCH_2SbR'_2$ with bulky alkyl or cycloalkyl groups R and R′ and the application of the unsymmetrical ligands in preparing organometallic rhodium complexes.[6] Here we describe some similarities as well as some remarkable differences in the behavior of the corresponding arsine derivatives $R_2AsCH_2PR'_2$ in the coordination sphere of rhodium as the metal center.

Results and Discussion

1. Reaction of [{(η^4-C_8H_{12})RhCl}$_2$] with $R_2AsCH_2PR'_2$. According to the reactivity of bulky phosphino(stibino)methanes,[6] the reactions of [{(η^4-C_8H_{12})RhCl}$_2$] with 2 equiv of the symmetrically sub-

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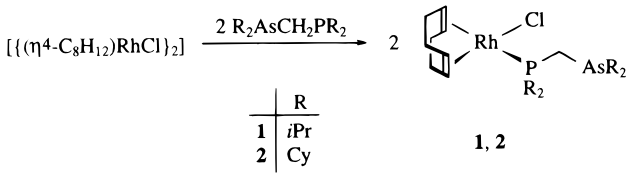
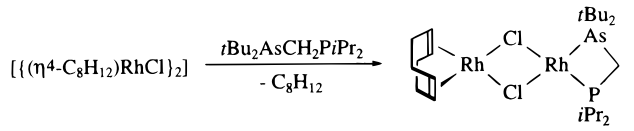
Scheme 1



	R
1	*i*Pr
2	Cy

1, 2

Scheme 2



3

stituted ligands $R_2AsCH_2PR_2$ (R = *i*Pr, Cy)[7] in CH_2Cl_2/ether or pentane at room temperature involve a facile cleavage of the chloro bridges by the P-donor site of the substrate but no replacement of the cyclooctadiene or chloro ligands. The resulting neutral compounds **1** and **2** (Scheme 1) form yellow, moderately air-stable solids that decompose between 50 and 60 °C.

Although the ^{31}P NMR spectra of **1** and **2** display a sharp doublet at δ 32.6 (for **1**) and 25.2 (for **2**) with a $^{103}Rh-^{31}P$ coupling constant of ca. 144 Hz, which corresponds to the data found for the structurally related complexes [RhCl(η^4-C_8H_{12})(PR_3)][8] and also for the stibine derivatives [RhCl(η^4-C_8H_{12})(κ-*P*-R_2PCH_2-SbR′$_2$)],[6] the ^1H NMR spectra of **1** and **2** differ from those of the latter. Instead of two sets of signals for the chemically nonequivalent protons of the −CH=CH− double bonds of the cyclooctadiene unit, the ^1H NMR spectra of **1** and **2** display only one broadened signal at δ 4.6−4.7, which we attribute to an intermolecular exchange process at room temperature. At lower temperatures, this dynamic behavior is slowed and two broadened signals appear at the supposed chemical shift (δ 5.60 and 3.50). A similar situation is found in complexes of the type [MCl(diene)L] (M = Rh, Ir; L = $AsPh_3$, $SbPh_3$; diene = η^4-C_8H_{12}, η^4-norbornadiene).[9] Owing to the monodentate coordination mode of the arsino(phosphino)methanes, the signal of the bridging As*C*H_2P carbon atom in the ^{13}C NMR spectrum of **1** exhibits a slight upfield shift of about 1.7 ppm compared to that of *i*Pr_2AsCH_2P*i*Pr_2 (δ 11.6), while at the same time the ^1J(PC) coupling constant decreases from 31.4 to 12.2 Hz.

In contrast to the reaction of [{(η^4-C_8H_{12})RhCl}$_2$] with *i*Pr_2PCH_2As*i*Pr_2 and $Cy_2PCH_2AsCy_2$ leading to the formation of **1** and **2**, treatment of the same organometallic precursor with 2 equiv of *t*Bu_2AsCH_2P*i*Pr_2[7] gives a mixture of products, which could not be separated by chromatographic techniques. However, dropwise treatment of a suspension of [{(η^4-C_8H_{12})RhCl}$_2$] with exactly 1 equiv of the ligand in hexane at room temperature affords a different result. Removal of the solvent and recrystallization of the crude product from acetone yields an orange-red microcrystalline solid that is thermally quite stable and readily soluble in CH_2Cl_2 or nonpolar solvents such as benzene and ether. In comparison to those of **1** and **2**, the signal of the ^{31}P nuclei in the ^{31}P NMR spectrum of **3** appears unexpectedly at higher field, and the $^{103}Rh-^{31}P$ coupling constant increases from ca. 144 Hz to 172.0 Hz. A similar value results for the dinuclear complex [{(κ^2-*P*,*P*-*t*Bu_2-PCH_2P*t*Bu_2)Rh}$_2$(μ-Cl)$_2$], which is formed upon treatment of [{(C_8H_{14})$_2$RhCl}$_2$] with 2 equiv of *t*Bu_2-PCH_2P*t*Bu_2.[10] The ^1H and ^{13}C NMR spectra of **3** (which in contrast to those of **1** and **2** show no temperature dependence) confirm that one C_8H_{12} ligand is still present. Since the chemical shift of the proton and the carbon signals for the bridging $AsCH_2P$ unit are in agreement with a chelating coordination mode of the arsino(phosphino)methane ligand, we conclude that from [{(η^4-C_8H_{12})RhCl}$_2$] and *t*Bu_2AsCH_2P*i*Pr_2 a dinuclear complex is formed by substitution of one of the diolefin ligands in the starting material (Scheme 2).

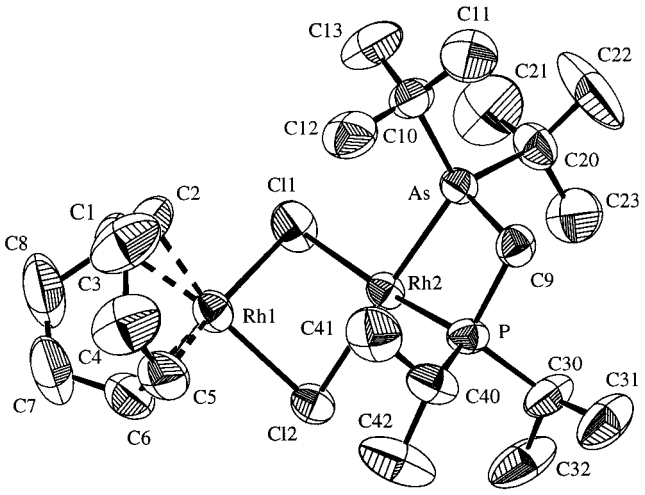


Figure 1. Molecular structure (ORTEP plot) of compound **3**.

To obtain information about the detailed structural aspects of **3** (which is the first structurally characterized transition-metal complex containing an arsino(phosphino)methane as a chelating ligand), an X-ray crystal structure investigation was carried out. The ORTEP diagram (Figure 1) reveals that both metal centers are coordinated in a square-planar fashion. The angle between the two planes [Cl1, Rh1, Cl2] and [Cl1, Rh2, Cl2] is 116.9(7)° and is thus slightly smaller (ca. 6°) than in the related compound [{Rh(η^4-C_8H_{12})}{Rh-[$P(OC_6H_5)_3$]$_2$}(μ-Cl)$_2$].[11] We note that the central Rh(μ-Cl)$_2$Rh unit of the starting material [{(η^4-C_8H_{12})RhCl}$_2$] is strictly planar.[12] In contrast to the mononuclear cationic complex [Rh(η^4-C_8H_{12})(κ^2-*P*,*Sb*-*i*Pr_2PCH_2-Sb*t*Bu_2)]$^+$, where the RhPCSb fragment is planar,[6] the

(7) The arsino(phosphino)methanes have been prepared in the same way as the corresponding phosphino(stibino)methanes.[6]

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Table 1. Selected Bond Distances and Angles with Esd's for Compound 3

Bond Distances (Å)			
Rh2−As	2.306(2)	Rh1−C1	2.116(8)
Rh2−P	2.187(2)	Rh1−C2	2.098(8)
Rh2−Cl1	2.441(2)	Rh1−C5	2.101(8)
Rh2−Cl2	2.401(3)	Rh1−C6	2.105(9)
Rh1−Cl1	2.389(3)	As−C9	1.958(8)
Rh1−Cl2	2.391(2)	P−C9	1.851(9)
Bond Angles (deg)			
Cl1−Rh1−Cl2	85.47(8)	Cl2−Rh2−P	101.37(9)
Cl1−Rh2−Cl2	84.12(9)	Rh2−As−C9	93.0(3)
Rh1−Cl1−Rh2	77.62(7)	As−Rh2−P	74.90(8)
Rh1−Cl2−Rh2	78.35(6)	Rh2−P−C9	100.0(3)
Cl1−Rh2−As	99.55(8)	P−C9−As	91.7(4)

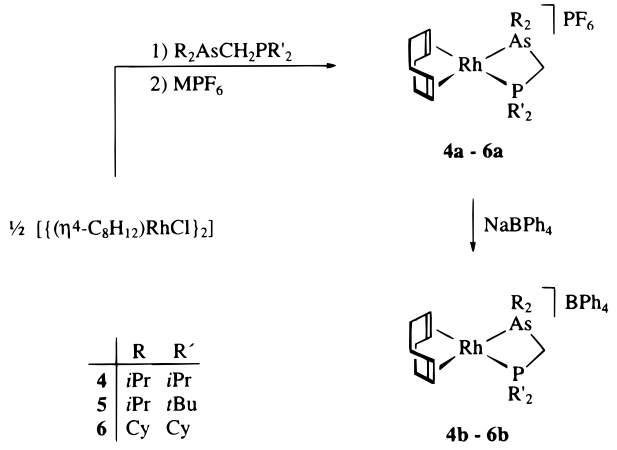
RhAsCP four-membered ring of **3** is somewhat bent, the dihedral angle being 6.6(7)°. The As−Rh−P bite angle (74.90(8)°) is relatively small and comparable to the bite angle of $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}P,Sb\text{-}i\text{Pr}_2\text{PCH}_2\text{Sb}t\text{Bu}_2)]^+$ and to that of neutral rhodium(I) compounds with $t\text{Bu}_2\text{PCH}_2\text{P}t\text{Bu}_2$ as chelating ligand.[10] The Rh−As distance of **3** is 2.306(2) Å (see Table 1) and therefore significantly shorter than the Rh−As bond length in *trans*-$[RhCl(\eta^2\text{-}CH_2{=}C{=}CH_2)(As i\text{Pr}_3)_2]$ (average value 2.43 Å).[13] The Rh−P distance of 2.187(2) Å is comparable to that of chloro-bridged rhodium(I) complexes with mono- or bidentate phosphine ligands;[10,11] however, it is shorter than the Rh−P bond length in $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}P,Sb\text{-}i\text{Pr}_2\text{PCH}_2\text{Sb}t\text{Bu}_2)]^+$ (2.317(1) Å).[6] The distances between the two rhodium centers and the bridging chlorides as well as those between Rh1 and the sp^2 carbon atoms of the diolefin fall into the expected range and thus deserve no further comment.

One notable structural feature is the Rh1−Rh2 distance of 3.028(1) Å. It is not only shorter than in the bent complex $[\{(\kappa^2\text{-}P,P\text{-}t\text{Bu}_2\text{PCH}_2\text{P}t\text{Bu}_2)\text{Rh}\}_2(\mu\text{-Cl})_2]$ (ca. 3.27 Å)[10] but also shorter than in the unsymmetrical complex $[\{Rh(\eta^4\text{-}C_8H_{12})\}\{Rh[P(OC_6H_5)_3]_2\}(\mu\text{-Cl})_2]$ (3.138(2) Å)[11] mentioned above. Although the oxidation number of Rh in **3** is undoubtedly +1, we think that in agreement with the structural data found for other dinuclear rhodium(I) compounds[14] a weak interaction between the two metal centers of **3** can be taken into consideration.

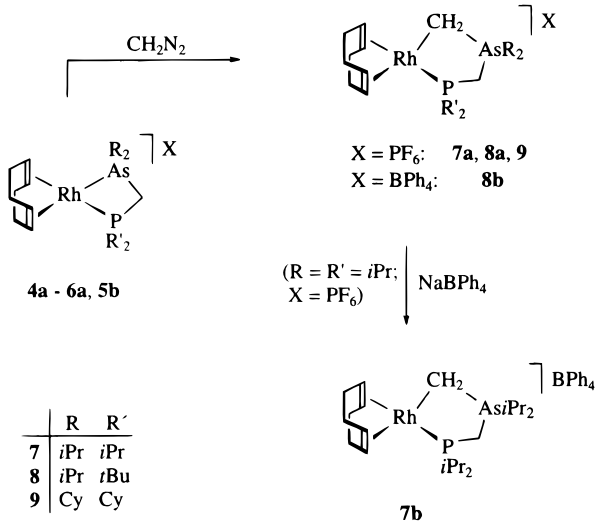
2. Cationic (Cyclooctadiene)rhodium(I) Complexes Containing Arsino(phosphino)methanes as Ligands. The reactions of $[\{(\eta^4\text{-}C_8H_{12})\text{RhCl}\}_2]$ with $R_2\text{AsCH}_2\text{PR}_2$ (R = *i*Pr, Cy) or $t\text{Bu}_2\text{AsCH}_2\text{P}i\text{Pr}_2$ in the presence of KPF_6 or $AgPF_6$ afford the cationic complexes **4a**−**6a** in 60−75% yield. The corresponding BPh_4 salts **4b**−**6b** are obtained on treatment of the PF_6 salts with an excess of $NaBPh_4$ in methanol (Scheme 3). The easy formation of **4**−**6** is noteworthy insofar as related chelate complexes of the general composition $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}P,P\text{-}R_2\text{PCH}_2\text{PR}_2)]X$ have not yet been isolated. For R = Ph, such a species is presumably generated as an intermediate on treatment of $[\{(\eta^4\text{-}C_8H_{12})\text{RhCl}\}_2]$ with dppm, but it reacts quite rapidly with a second molecule of $Ph_2\text{PCH}_2\text{PPh}_2$ to give $[Rh(dppm)_2]Cl$ as the final product.[15] Compounds **4a**−**6a** are orange-red and **4b**−**6b** orange-yellow solids that are air-stable and readily soluble in polar solvents. The most significant difference between the spectroscopic data of **4**−**6** and those of **1** and **2** is the downfield shift of the signals of the $AsCH_2P$ unit in the ^1H and ^{13}C NMR and the high-field shift of the PR_2 nuclei in the ^{31}P NMR spectra. These features are in close analogy to those of the corresponding stibine complexes $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}P,Sb\text{-}R_2\text{PCH}_2\text{SbR}'_2)]X$.[6] Moreover, the ^1H and ^{13}C NMR spectra of **4**−**6** display two sets of signals for the protons and the carbon atoms of the −CH=CH− double bonds of the cyclooctadiene ligand, as is anticipated if two different donor atoms in *trans* disposition to the double bond are coordinated to the rhodium center.

The reactions of the compounds **4a**−**6a** and **5b** with diazomethane in CH_2Cl_2 at low temperature proceed with elimination of N_2 and insertion of the remaining CH_2 unit into the supposedly labile Rh−As bond. The resulting As−ylide complexes **7a**, **8a**,**b**, and **9,** which are isolated in 80−95% yield, form yellow, moderately air-stable solids that decompose with the exception of **7a** at 100−130 °C. The corresponding BPh_4 salt **7b** is prepared from the PF_6 salt **7a** via anion exchange with

Scheme 3



Scheme 4



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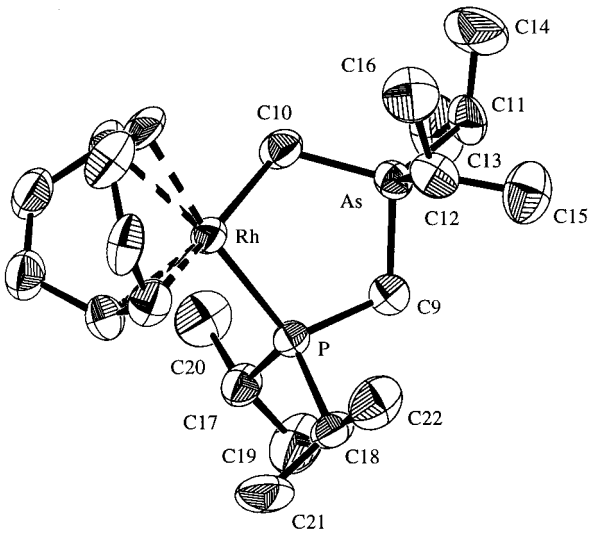


Figure 2. Molecular structure (ORTEP plot) of compound **7b**.

Table 2. Selected Bond Distances and Angles with Esd's for Compound 7b

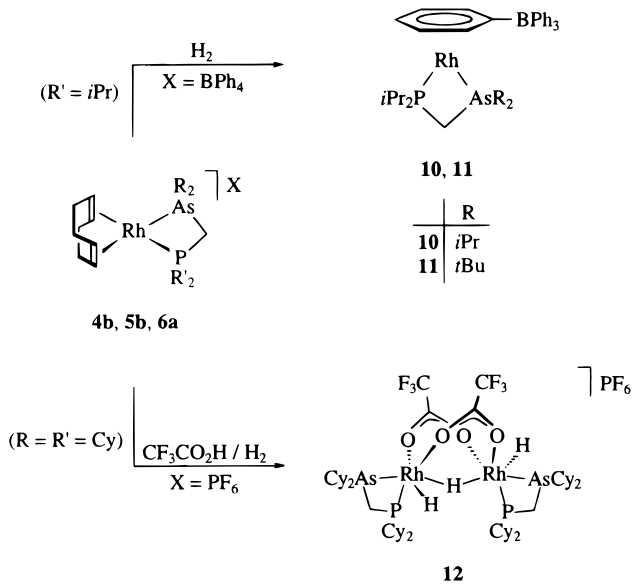
	Bond Distances (Å)		
Rh−C10	2.111(7)	As−C9	1.915(7)
Rh−P	2.312(2)	P−C9	1.846(7)
As−C10	1.880(7)		
	Bond Angles (deg)		
Rh−C10−As	109.9(3)	As−C9−P	108.0(3)
P−Rh−C10	87.7(2)	C10−As−C9	102.5(3)
C9−P−Rh	110.4(2)		

$NaBPh_4$ (Scheme 4). In analogy to the spectroscopic data of the Sb-ylide complexes $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}C,P\text{-}CH_2Sb(R'_2)CH_2PR_2)]X$,[6] the ^{13}C NMR spectra of **7**−**9** display a resonance for the carbon atom linked to rhodium at $\delta \sim 8.0$, which is split into a doublet of doublets owing to Rh−C and P−C coupling. In the ^1H NMR spectra of **7**−**9**, the signals of the corresponding methylene protons appear at $\delta \sim 1.0$ and thus at somewhat higher field than for neutral rhodium(I) compounds with CH_2PiPr_3 as ligand.[16] According to the different stereoelectronic features resulting from the ring expansion of a four-membered chelate ring in **4**−**6** to a five-membered ring in **7**−**9**, the ^{31}P NMR spectra of the latter exhibit a doublet which is shifted downfield by ca. 54 ppm compared to that of **4**−**6**. Moreover, the $^{103}Rh-^{31}P$ coupling constant increases from ca. 144 Hz to ca. 161 Hz for the chelate complexes **7**−**9**.

The result of the X-ray crystal structure analysis of **7b** is shown in Figure 2. The most notable feature is that the five-membered chelate ring adopts an envelope conformation that leads to a dihedral angle of 47.50(3)° between the two planes [C10, Rh, P, C9] and [C10, As, C9]. The P−Rh−C10 bite angle [87.7(2)°] (see Table 2) is virtually the same as the As1−Cr−C6 bite angle of the structurally related chromium complex $[Cr(CO)_4\{\kappa^2\text{-}C,As\text{-}CH_2As(Ph)_2CH_2AsPh_2\}]$ (88.1(1)°), which has been prepared by Weber et al. from $[Cr(CO)_5\{\kappa\text{-}C\text{-}CH_2S(O)Me_2\}]$ and $Ph_2AsCH_2AsPh_2$.[17] In comparison to the angle Cr−C6−As2 of this chromium compound (113.6(2)°), the corresponding angle Rh−C10−As of **7b** is somewhat smaller (109.9(3)°), while the intraligand angle As−C9−P (108.0(3)°) is slightly larger by 2.3° than in $[Cr(CO)_4\{\kappa^2\text{-}C,As\text{-}CH_2As(Ph)_2CH_2AsPh_2\}]$.[17] The Rh−P bond length of **7b** (2.312(2) Å) is almost identical with that of other cationic square-planar (cyclooctadiene)rhodium(I) complexes with bidentate phosphines as ligands;[18] it is, however, significantly shorter than in the cationic (ylide)rhodium(III) complex $[\{(\eta^5\text{-}C_5Me_5)RhI\{\kappa^2\text{-}C,P\text{-}CH_2P(Me)_2CH_2CH_2PMe_2\}\}]^+$ (2.259(2) Å).[19] In contrast, the Rh−C10 distance (2.111(7) Å) is comparable to that of the respective half-sandwich complex (2.121(5) Å)[19] and to that of the related cation $[\{(\eta^5\text{-}C_5H_5)Rh(\kappa\text{-}C\text{-}CH_2PiPr_3)(CH_3)(CO)\}]^+$ (2.126(7) Å).[16]

In analogy to the reactivity of complexes of the type $[Rh(\eta^4\text{-}C_8H_{12})(PR_3)_2]X$,[20] the cyclooctadiene ligand of the cationic derivatives $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}As,P\text{-}R_2AsCH_2PR'_2)]X$ can easily be replaced on treatment with H_2 in CH_2Cl_2 at room temperature. The reaction of the resulting, probably solvated hydridorhodium(III) intermediate depends on the type of the corresponding anion X^- and on the reaction conditions in particular. While treatment of the BPh_4 salts **4b** and **5b** with H_2 leads to the formation of the neutral half-sandwich type compounds **10** and **11** in excellent yield, for $X^- = PF_6^-$ complete decomposition occurs in the absence of any substrate. However, the reaction of **6a** with H_2 in the presence of a slight excess of CF_3CO_2H gives the unusual dinuclear hydrido-bridged rhodium(III) complex **12** that can be isolated as a light yellow, almost air-stable solid in about 75% yield (Scheme 5).

Scheme 5



The most significant difference between the spectroscopic data of **10** (light red solid) and **11** (orange-yellow solid) and those of **4b** and **5b** is the high-field shift of

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the resonance of the protons and the carbon atoms of one phenyl group of the BPh_4 anion. This feature is also typical for related compounds of the general composition $[(\eta^6\text{-}C_6H_5BPh_3)RhL_2]$ with $L_2 = \{P(OR)_3\}_2$,[21] $R_2PCH_2\text{-}SbR'_2$,[6] or $R_2PCH_2CH_2PR_2$[22] and clearly indicates that one ring is coordinated to rhodium. Moreover, the change from a 16-electron metal center in **4b** and **5b** to an 18-electron metal center in **10** and **11** results in a downfield shift of the signal of the PR'_2 nuclei in the ^{31}P NMR spectra by ca. 17 ppm, whereas the $^{103}Rh-^{31}P$ coupling constant increases from 125 to 129 to ca. 170−173 Hz. Similar values are found for the corresponding complexes containing a phosphino(stibino)-methane as ligand[6] and also for the cyclopentadienyl compound $[(\eta^5\text{-}C_5H_5)Rh(\kappa^2\text{-}P,P\text{-}Ph_2PCH_2PPh_2)]$.[23]

Despite a closed (18-electron) valence shell for each rhodium due to the three-center−two-electron bond between the two metal centers and the bridging hydrido ligand, the $^{103}Rh-^{31}P$ coupling constant in the ^{31}P NMR spectrum of **12** (111.2 Hz) is quite small compared with that of the starting material **6a**. This indicates that the oxidation state of the rhodium has changed from +1 to +3. In the ^1H NMR spectrum of **12**, the signal assigned to the bridging hydrido ligand appears at δ −17.52 and is split into a triplet of triplets due to coupling with two equivalent ^{103}Rh and two equivalent ^{31}P nuclei. The large $^{103}Rh-^1H$ coupling constant of 25.0 Hz seems to be typical for a bridging RhHRh moiety.[24] The chemical shift of the signal assigned to the PCH_2As carbon atom in the ^{13}C NMR spectrum of **12**, which is almost identical with that of the starting material **6a**, leaves no doubt that the coordination mode of the arsino-(phosphino)methane is unchanged. We note that with bulky phosphino(stibino)methanes $iPr_2PCH_2SbR'_2$ as ligands similar dinuclear rhodium complexes of composition $[\{RhH(\kappa^2\text{-}P,Sb\text{-}iPr_2PCH_2SbR'_2)\}_2(\mu\text{-}H)(\mu\text{-}O_2CCF_3)_2]\text{-}PF_6$ have recently been obtained, one of which (with R′ = *t*Bu) has been characterized by X-ray crystal structure analysis.[25]

Conclusions

The work presented in this paper has shown that phosphino(arsino)methanes $R_2AsCH_2PR'_2$ with bulky alkyl or cycloalkyl groups R and R′, which are accessible from $Ph_3SnCH_2PR'_2$ via $LiCH_2PR'_2$ as intermediates,[7] behave as monodentate (P-bonded) as well as bidentate ligands toward rhodium. One of the most remarkable features is that the unsymmetrical arsino(phosphino)-methane $tBu_2AsCH_2PiPr_2$ reacts with $[\{(\eta^4\text{-}C_8H_{12})\text{-}RhCl\}_2]$ by substitution of only one diolefin unit. The dinuclear complex **3** thus formed is one of the rare examples in which the coordination sphere around the central Rh_2Cl_2 core is completed by two different chelating ligands.

With regard to the chemistry of the readily available mononuclear complexes $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}As,P\text{-}R_2AsCH_2\text{-}PR'_2)]X$ (**4**−**6**), it is in particular worth mentioning that they react with diazomethane by insertion of CH_2 into the Rh−As bond. This observation strongly supports the assumption that in a $M(\kappa^2\text{-}As,P\text{-}R_2As\text{-}X\text{-}PR'_2)$ chelate the M-As linkage is more labile than the M−P counterpart. Finally we note that on treatment of the cations $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}As,P\text{-}R_2AsCH_2PR'_2)]^+$ with hydrogen the cyclooctadiene is easily replaced and, if BPh_4 is the corresponding anion, the neutral half-sandwich type compounds **10** and **11** are generated. The more spectacular result, however, is the formation of the triply bridged dinuclear complex **12** in which one hydrido and two trifluoracetato ligands connect the two metal centers.

Experimental Section

General Considerations. All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by known procedures and distilled before use. The starting materials $R_2AsCH_2PiPr_2$ (R = *i*Pr, *t*Bu),[7] $Cy_2AsCH_2PCy_2$,[7] and $[\{(\eta^4\text{-}C_8H_{12})RhCl\}_2]$[26] were prepared as described in the literature.

Physical Measurements. NMR spectra were recorded at room temperature or at the temperature mentioned in the appropriate procedure on Bruker AC 200 and Bruker AMX 400 instruments. Chemical shifts are expressed in ppm downfield from $SiMe_4$ (^1H and ^{13}C) and (85%) H_3PO_4 (^{31}P). Abbreviations used: s, singlet; d, doublet; q, quartet; sept, septet; m, multiplet; br, broadened signal. Coupling constants *J* are given in hertz. Melting points were measured by DTA. For the assignment of H_A and H_B see procedure for the preparation of compound **4a** (Figure 3).

Preparation of $[RhCl(\eta^4\text{-}C_8H_{12})(\kappa\text{-}P\text{-}iPr_2PCH_2AsiPr_2)]$ (1). A solution of $[\{(\eta^4\text{-}C_8H_{12})RhCl\}_2]$ (113 mg, 0.23 mmol) in CH_2Cl_2 (4 mL) was treated with a solution of $iPr_2AsCH_2PiPr_2$ (135 mg, 0.46 mmol) in ether (3 mL) and stirred for 1 h at room temperature. The solvent was removed, the oily residue was suspended in ether (4 mL), and the suspension was stirred for 10 min. After removal of the solvent, the procedure was repeated twice and the remaining solid was washed with ether (4 mL). The solid was dissolved in acetone (5 mL), and the solution was stored at −60 °C for 12 h. Yellow crystals were obtained which were separated from the mother liquor and dried: yield 53 mg (21%); mp 51 °C dec. ^1H NMR (400 MHz, C_6D_6): δ 4.64 (br s, 4H, =CH of C_8H_{12}), 2.50 (m, 2H, $PCHCH_3$), 2.22 (br m, 4H, CH_2 of C_8H_{12}), 2.00 [sept, *J*(HH) = 7.2 Hz, 2H, $AsCHCH_3$], 1.75 (br m, 4H, CH_2 of C_8H_{12}), 1.58 [d, *J*(PH) = 7.6 Hz, 2H, $AsCH_2P$], 1.33, 1.27 [both dd, *J*(PH) = 14.2, *J*(HH) = 7.2 Hz, 12H, $PCHCH_3$], 1.12, 1.10 [both d, *J*(HH) = 7.2 Hz, 12H, $AsCHCH_3$]. ^{13}C NMR (100.6 MHz, C_6D_6): δ 86.0 (br s, =CH of C_8H_{12}), 31.2 (br s, CH_2 of C_8H_{12}), 25.3 [d, *J*(PC) = 21.2 Hz, $PCHCH_3$], 25.0 [d, *J*(PC) = 3.5 Hz, $AsCHCH_3$], 21.5 (s, $AsCHCH_3$), 20.1 (br s, $PCHCH_3$), 19.5 (s, $AsCHCH_3$), 9.9 [d, *J*(PC) = 12.2 Hz, $AsCH_2P$]. ^{31}P NMR (162.0 MHz, C_6D_6): δ 32.6 [d, *J*(RhP) = 144.8 Hz]. Anal. Calcd for $C_{21}H_{42}AsClPRh$ (538.8): C, 46.81; H, 7.85. Found: C, 46.99; H, 7.75.

Preparation of $[RhCl(\eta^4\text{-}C_8H_{12})(\kappa\text{-}P\text{-}Cy_2PCH_2AsCy_2)]$ (2). A suspension of $[\{(\eta^4\text{-}C_8H_{12})RhCl\}_2]$ (145 mg, 0.30 mmol) in pentane (5 mL) was treated with a solution of $Cy_2AsCH_2\text{-}PCy_2$ (268 mg, 0.60 mmol) in hexane (3 mL) and stirred for 10

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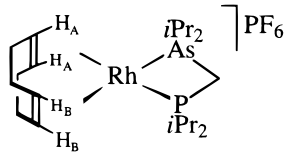

Figure 3.

min at room temperature. The solvent was removed, and the oily residue was washed with acetone (2 mL) and dried: yellow solid, yield 345 mg (83%); mp 62 °C dec. ^{1}H NMR (200 MHz, C_6D_6): δ 4.71 (br s, 4H, =CH), 2.48−1.24 (br m, 54H, $AsCH_2P$ and CH_2 of C_8H_{12} and C_6H_{11}). ^{31}P NMR (81.0 MHz, C_6D_6): δ 25.2 [d, J(RhP) = 143.9 Hz]. Anal. Calcd for $C_{33}H_{58}AsClPRh$ (699.1): C, 56.70; H, 8.36. Found: C, 57.18; H, 8.54.

Preparation of [{Rh(η^4-C_8H_{12})}{Rh(κ^2-*As,P*-*t*Bu$_2$AsCH$_2$P*i*Pr$_2$)}(μ-Cl)$_2$] (3). A suspension of [{(η^4-C_8H_{12})RhCl}$_2$] (424 mg, 0.86 mmol) in hexane (15 mL) was treated at room temperature dropwise (over 45 min) with a solution of *t*Bu$_2$AsCH$_2$P*i*Pr$_2$ (275 mg, 0.86 mmol) in hexane (20 mL). After the addition had been completed, the reaction mixture was stirred for 1 h at 25 °C. It was then filtered, and the filtrate was brought to dryness in vacuo. The oily residue was dissolved in warm acetone (8 mL), and the solution was stored at −60 °C. Small orange-red crystals precipitated, which were separated from the mother liquor, washed with 2 mL of acetone (−40 °C), and dried: yield 448 mg (74%); mp 146 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.20 (br s, 4H, =CH of C_8H_{12}), 2.84 [dd, J(RhH) = 1.6, J(PH) = 8.8 Hz, 2H, $AsCH_2P$], 2.43 (br m, 4H, CH_2 of C_8H_{12}), 2.06 (br m, 2H, PC*H*CH$_3$), 1.72 (br m, 4H, CH_2 of C_8H_{12}), 1.45 (br s, 18H, AsCCH$_3$), 1.38 [dd, J(PH) = 16.0, J(HH) = 7.2 Hz, 6H, PCHC*H*$_3$], 1.27 [dd, J(PH) = 14.4, J(HH) = 7.2 Hz, 6H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 76.9 [d, J(RhC) = 13.9 Hz, =CH of C_8H_{12}], 39.2 [d, J(PC) = 2.5 Hz, As*C*CH$_3$], 34.4 [d, J(PC) = 16.4 Hz, $AsCH_2P$], 31.3 (s, CH_2 of C_8H_{12}), 30.0 (s, AsC*C*H$_3$), 27.8 [d, J(PC) = 17.6 Hz, P*C*HCH$_3$], 20.1 [d, J(PC) = 2.4 Hz, PCH*C*H$_3$], 19.3 (br s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 10.6 [d, J(RhP) = 172.0 Hz]. Anal. Calcd for $C_{23}H_{46}AsCl_2PRh_2$ (705.2): C, 39.17; H, 6.57. Found: C, 39.14; H, 6.48.

Preparation of [Rh(η^4-C_8H_{12})(κ^2-*As,P*-*i*Pr$_2$AsCH$_2$P*i*Pr$_2$)]PF$_6$ (4a). A solution of [{(η^4-C_8H_{12})RhCl}$_2$] (360 mg, 0.73 mmol) in CH_2Cl_2 (20 mL) was treated with a solution of *i*Pr$_2$AsCH$_2$P*i*Pr$_2$ (465 mg, 1.58 mmol) in CH_2Cl_2 (15 mL) and stirred for 10 min at room temperature. A change of color from yellow to orange-red occurred. A solution of KPF_6 (270 mg, 1.47 mmol) in methanol (15 mL) was then added dropwise, and the reaction mixture was stirred for 2 h. An almost colorless solid (KCl) precipitated, and a red solution was formed. The solution was filtered, and the filtrate was brought to dryness in vacuo. The oily residue was dissolved in 4 mL of methanol (50 °C), and the solution was stored for 24 h at −60 °C. Red needlelike crystals were obtained, which were washed twice with 3 mL portions of pentane and dried: yield 724 mg (76%); mp 126 °C dec. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 5.51 (br s, 2H, H_A), 5.10 (br s, 2H, H_B), 3.12 [d, J(PH) = 10.0 Hz, 2H, $AsCH_2P$], 2.52 [sept, J(HH) = 6.0 Hz, 2H, AsC*H*CH$_3$], 2.19 (br m, 10H, CH_2 of C_8H_{12} and PC*H*CH$_3$), 1.36 (br m, 24H, AsCHC*H*$_3$ and PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 98.8 [dd, J(RhC) = 8.5, J(PC) = 7.3 Hz, =CH_A], 89.4 [d, J(RhC) = 9.3 Hz, =CH_B], 30.8, 30.0 (both br s, CH_2 of C_8H_{12}), 28.6 (br s, As*C*HCH$_3$), 26.4 [d, J(PC) = 16.7 Hz, P*C*HCH$_3$], 25.6 [d, J(PC) = 17.6 Hz, $AsCH_2P$], 20.4, 20.1 (both br s, AsCH*C*H$_3$), 19.0 [d, J(PC) = 3.7 Hz, PCH*C*H$_3$], 17.8 (br s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ −1.3 [d, J(RhP) = 126.6 Hz, *i*Pr$_2$P], −144.0 [sept, J(FP) = 712.8 Hz, PF_6^-]. Anal. Calcd for $C_{21}H_{42}AsF_6P_2Rh$ (648.3): C, 38.91; H, 6.53; As, 11.56. Found: C, 39.10; H, 6.30; As, 11.11.

Preparation of [Rh(η^4-C_8H_{12})(κ^2-*As,P*-*i*Pr$_2$AsCH$_2$P*i*Pr$_2$)]BPh$_4$ (4b). A solution of **4a** (149 mg, 0.23 mmol) in methanol (10 mL) was treated with a solution of $NaBPh_4$ (212 mg, 0.62 mmol) in methanol (8 mL) and stirred for 20 min at room temperature. An orange-yellow precipitate was formed, which was separated from the mother liquor, washed with 6 mL of methanol and then twice with 5 mL portions of pentane, and dried: yield 182 mg (71%); mp 138 °C dec. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.40−6.88 (m, 20H, C_6H_5), 5.51 (br s, 2H, H_A), 5.10 (br s, 2H, H_B), 3.03 [dd, J(RhH) = 0.9, J(PH) = 9.5 Hz, 2H, $AsCH_2P$], 2.50 [sept, J(HH) = 7.0 Hz, 2H, AsC*H*CH$_3$], 2.29 (br s, 8H, CH_2 of C_8H_{12}), 2.11 (m, 2H, PC*H*CH$_3$), 1.29 (m, 24H, AsCHC*H*$_3$ and PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 164.3 [q, J(BC) = 48.0 Hz, *ipso*-C of C_6H_5], 136.2 (s, *meta*-C of C_6H_5), 125.8 (br s, *ortho*-C of C_6H_5), 121.9 (s, *para*-C of C_6H_5), 98.4 (m, =CH_A), 89.6 (m, =CH_B), 30.9, 30.1 (both s, CH_2 of C_8H_{12}), 28.8 (s, As*C*HCH$_3$), 26.6 [d, J(PC) = 17.6 Hz, P*C*HCH$_3$], 25.7 [d, J(PC) = 18.4 Hz, $AsCH_2P$], 20.6, 20.3 (both s, AsCH*C*H$_3$), 19.2 [d, J(PC) = 2.8 Hz, PCH*C*H$_3$], 19.0 (br s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ −1.1 [d, J(RhP) = 128.8 Hz]. Anal. Calcd for $C_{45}H_{62}AsBPRh$ (822.6): C, 65.71; H, 7.60. Found: C, 65.66; H, 7.48.

Preparation of [Rh(η^4-C_8H_{12})(κ^2-*As,P*-*t*Bu$_2$AsCH$_2$P*i*Pr$_2$)]PF$_6$ (5a). This was prepared as described for **4a**, from [{(η^4-C_8H_{12})RhCl}$_2$] (403 mg, 0.82 mmol), *t*Bu$_2$AsCH$_2$P*i*Pr$_2$ (524 mg, 1.64 mmol), and KPF_6 (302 mg, 1.64 mmol): red crystals; yield 551 mg (50%); mp 88 °C dec. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 5.56 (br s, 2H, H_A), 5.04 (br s, 2H, H_B), 3.16 [dd, J(RhH) = 1.1, J(PH) = 9.6 Hz, 2H, $AsCH_2P$], 2.34 (br m, 10H, CH_2 of C_8H_{12} and PC*H*CH$_3$), 1.44 (s, 18H, AsCCH$_3$), 1.37 [dd, J(PH) = 11.5, J(HH) = 7.3 Hz, 6H, PCHC*H*$_3$], 1.27 [dd, J(PH) = 15.0, J(HH) = 6.9 Hz, 6H, PCHC*H*$_3$]. ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 98.7 [dd, J(RhC) = 9.1, J(PC) = 7.4 Hz, =CH_A], 88.2 [d, J(RhC) = 10.1 Hz, =CH_B], 42.2 (br s, As*C*CH$_3$), 30.9 [d, J(RhC) = 2.5 Hz, CH_2 of C_8H_{12}], 30.1 (s, AsC*C*H$_3$), 30.0 (br s, CH_2 of C_8H_{12}), 26.6 [d, J(PC) = 14.8 Hz, P*C*HCH$_3$], 26.3 [d, J(PC) = 16.6 Hz, $AsCH_2P$], 19.4, 18.6 (both br s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ −5.5 [d, J(RhP) = 126.4 Hz, *i*Pr$_2$P], −144.0 [sept, J(FP) = 710.5 Hz, PF_6^-]. Anal. Calcd for $C_{23}H_{46}AsF_6P_2Rh$ (676.4): C, 40.84; H, 6.86. Found: C, 40.58; H, 6.64.

Preparation of [Rh(η^4-C_8H_{12})(κ^2-*As,P*-*t*Bu$_2$AsCH$_2$P*i*Pr$_2$)]BPh$_4$ (5b). This was prepared as described for **4b**, from **5a** (171 mg, 0.25 mmol) and $NaBPh_4$ (186 mg, 0.54 mmol) as starting materials: orange-yellow solid; yield 186 mg (87%); mp 150 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.42−6.86 (m, 20H, C_6H_5), 5.58 (br s, 2H, H_A), 4.91 (br s, 2H, H_B), 2.96 [dd, J(RhH) = 0.8, J(PH) = 9.4 Hz, 2H, $AsCH_2P$], 2.66 (m, 4H, CH_2 of C_8H_{12}), 2.17 (br m, 6H, CH_2 of C_8H_{12} and PC*H*CH$_3$), 1.36 (s, 18H, AsCCH$_3$), 1.25 [dd, J(PH) = 15.6, J(HH) = 7.2 Hz, 6H, PCHC*H*$_3$], 1.16 [dd, J(PH) = 15.2, J(HH) = 7.2 Hz, 6H, PCHC*H*$_3$]. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 164.3 [q, J(BC) = 48.3 Hz, *ipso*-C of C_6H_5], 136.3 (s, *meta*-C of C_6H_5), 125.4 (br s, *ortho*-C of C_6H_5), 121.5 (s, *para*-C of C_6H_5), 98.5 [dd, J(RhC) = 9.3, J(PC) = 6.2 Hz, =CH_A], 87.9 [d, J(RhC) = 9.4 Hz, =CH_B], 42.0 (s, As*C*CH$_3$), 30.7 (s, CH_2 of C_8H_{12}), 30.1 (s, AsC*C*H$_3$), 29.8 (s, CH_2 of C_8H_{12}), 26.5 [d, J(PC) = 16.1 Hz, P*C*HCH$_3$], 25.9 [d, J(PC) = 16.1 Hz, $AsCH_2P$], 19.3, 18.7 (both s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ −5.4 [d, J(RhP) = 125.0 Hz]. Anal. Calcd for $C_{47}H_{62}AsBPRh$ (850.7): C, 66.36; H, 7.82. Found: C, 66.54; H, 7.66.

Preparation of [Rh(η^4-C_8H_{12})(κ^2-*As,P*-Cy$_2$AsCH$_2$PCy$_2$)]PF$_6$ (6a). A solution of [{(η^4-C_8H_{12})RhCl}$_2$] (230 mg, 0.47 mmol) was treated with a solution of Cy$_2$AsCH$_2$PCy$_2$ (430 mg, 0.95 mmol) in CH_2Cl_2 (5 mL) and stirred for 10 min at room temperature. A solution of $AgPF_6$ (238 mg, 0.94 mmol) in CH_2Cl_2 (4 mL) was then added dropwise, and the reaction mixture was stirred for 1 h under exclusion of light. An almost colorless solid (AgCl) precipitated. The solution was filtered and worked up as described for **3a**: orange-red crystals; yield 558 mg (74%); mp 178 °C dec. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 5.46 (br s, 2H, H_A), 5.05 (br s, 2H, H_B), 3.14 [br d, J(PH) = 9.3 Hz, 2H, $AsCH_2P$], 2.36−1.70 (br m, 30H, CH_2 of C_8H_{12} and AsC*H*C*H*$_2$ and PC*H*C*H*$_2$), 1.58−1.29 (br m, 24H, CH_2 of C_6H_{11}).

^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 98.4 [dd, J(RhC) = 9.1, J(PC) = 6.6 Hz, =CH_A], 89.0 [d, J(RhC) = 9.0 Hz, =CH_B], 38.6 (s, As*C*HCH$_2$), 35.9 [d, J(PC) = 16.2 Hz, P*C*HCH$_2$], 30.8−26.0 (m, CH_2 of C_8H_{12} and C_6H_{11}), 25.0 [d, J(PC) = 18.7 Hz, AsCH$_2$P]. ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ −12.0 [d, J(RhP) = 125.0 Hz, Cy_2P], −144.0 [sept, J(FP) = 711.4 Hz, PF_6^-]. Anal. Calcd for $C_{33}H_{58}AsF_6P_2Rh$ (808.6): C, 49.06; H, 7.23; Rh, 12.73. Found: C, 49.56; H, 7.74; Rh, 12.89.

Preparation of [Rh(η^4-C_8H_{12})(κ^2-*As,P*-$Cy_2AsCH_2PCy_2$)]-BPh_4 (6b). This was prepared as described for **4b**, from **6a** (251 mg, 0.31 mmol) and $NaBPh_4$ (212 mg, 0.62 mmol) as starting materials: yellow solid; yield 284 mg (93%); mp 164 °C dec. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.40−6.90 (m, 20H, C_6H_5), 5.39 (br s, 2H, H_A), 4.99 (br s, 2H, H_B), 2.98 [br d, J(PH) = 9.4 Hz, 2H, AsCH$_2$P], 2.27−1.79 (br m, 30H, CH_2 of C_8H_{12} and AsC*H*C*H*$_2$ and PC*H*C*H*$_2$), 1.39−1.26 (br m, 24H, CH_2 of C_6H_{11}). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 164.2 [q, J(BC) = 49.3 Hz, *ipso*-C of C_6H_5], 136.2 (s, *meta*-C of C_6H_5), 125.3 (br s, *ortho*-C of C_6H_5), 121.4 (s, *para*-C of C_6H_5), 98.1 [dd, J(RhC) = 9.1, J(PC) = 6.5 Hz, =CH_A], 88.7 [d, J(RhC) = 8.8 Hz, =CH_B], 38.4 (s, As*C*HCH$_2$), 35.7 [d, J(PC) = 16.0 Hz, P*C*HCH$_2$], 30.6−27.2 (m, CH_2 of C_8H_{12} and C_6H_{11}), 26.7 [d, J(PC) = 12.7 Hz, PCH*C*H$_2$], 26.3 [d, J(PC) = 9.7 Hz, PCH*C*H$_2$], 25.7, 25.6 (both s, CH_2 of C_6H_{11}), 25.0 [d, J(PC) = 18.5 Hz, AsCH$_2$P]. ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ −11.9 [d, J(RhP) = 125.0 Hz]. Anal. Calcd for $C_{57}H_{78}AsBPRh$ (982.9): C, 69.66; H, 8.00. Found: C, 69.76; H, 7.94.

Preparation of [Rh(η^4-C_8H_{12}){κ^2-*C,P*-$CH_2As(iPr)_2$-CH_2PiPr_2}]PF_6 (7a). A solution of **4a** (132 mg, 0.20 mmol) in THF (6 mL) was treated at −50 °C with a solution of CH_2N_2 (ca. 0.25 M, 2.50 mL, ca. 0.63 mmol) in ether. Under slightly reduced pressure, the solution was slowly warmed to room temperature and stirred for 45 min. The resulting brown solution was brought to dryness in vacuo. The oily residue was washed several times with pentane and dried: yellow solid; yield 109 mg (81%); mp 60 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.95 (br s, 2H, H_A), 4.35 (br s, 2H, H_B), 2.72 [sept, J(HH) = 7.2 Hz, 2H, AsC*H*CH$_3$], 2.36 [dd, J(RhH) = 0.8, J(PH) = 8.0 Hz, 2H, AsCH$_2$P], 2.15 (br m, 10H, CH_2 of C_8H_{12} and PC*H*CH$_3$), 1.42, 1.37 [both d, J(HH) = 7.2 Hz, 12H, AsCHC*H*$_3$], 1.24 (m, 12H, PCHC*H*$_3$), 0.98 [dd, J(RhH) = J(PH) = 1.6 Hz, 2H, RhCH$_2$]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 96.8 [dd, J(RhC) = 10.6, J(PC) = 8.1 Hz, =CH_A], 81.7 [d, J(RhC) = 8.4 Hz, =CH_B], 31.7 [d, J(RhC) = 1.9 Hz, CH_2 of C_8H_{12}], 28.4 [d, J(PC) = 4.2 Hz, As*C*HCH$_3$], 26.7 [d, J(PC) = 18.5 Hz, P*C*HCH$_3$], 19.1 (br s, AsCH*C*H$_3$), 18.2, 17.9 (both s, PCH*C*H$_3$), 13.8 [br dd, J(RhC) = 2.3, J(PC) = 8.2 Hz, AsCH$_2$P], 8.1 [dd, J(RhC) = 30.0, J(PC) = 7.2 Hz, RhCH$_2$]. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 52.5 [d, J(RhP) = 159.7 Hz, iPr$_2$P], −144.3 [sept, J(FP) = 712.7 Hz, PF_6^-]. Anal. Calcd for $C_{22}H_{44}AsF_6P_2Rh$ (662.4): C, 39.89; H, 6.70; As, 11.31; Rh, 15.54. Found: C, 40.08; H, 6.53; As, 10.62; Rh, 15.00.

Preparation of [Rh(η^4-C_8H_{12}){κ^2-*C,P*-$CH_2As(iPr)_2$-CH_2PiPr_2}]BPh_4 (7b). A solution of **7a** (69 mg, 0.10 mmol) in methanol (6 mL) was treated with a solution of $NaBPh_4$ (72 mg, 0.21 mmol) in methanol (5 mL) and stirred for 10 min at room temperature. A gradual change of color from yellow to light yellow occurred, and a yellow solid precipitated. The mother liquor was removed, and the residue was washed twice with 5 mL portions of methanol and twice with 5 mL portions of pentane and dried: yield 72 mg (86%); mp 102 °C dec. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.31−6.87 (m, 20H, C_6H_5), 5.04 (br s, 2H, H_A), 4.37 (br s, 2H, H_B), 2.59 (m, 2H, As*C*HCH$_3$), 2.24 (br s, 8H, CH_2 of C_8H_{12}), 2.09 (br m, 2H, PC*H*CH$_3$), 1.98 [d, J(PH) = 6.6 Hz, 2H, AsCH$_2$P], 1.38, 1.35 [both d, J(HH) = 7.3 Hz, 12H, AsCHC*H*$_3$], 1.23 [dd, J(PH) = 16.1, J(HH) = 6.8 Hz, 6H, PCHC*H*$_3$], 1.20 [dd, J(PH) = 14.2, J(HH) = 6.6 Hz, 6H, PCHC*H*$_3$], 1.05 [dd, J(RhH) = J(PH) = 1.8 Hz, 2H, RhCH$_2$]. ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 164.1 [q, J(BC) = 49.9 Hz, *ipso*-C of C_6H_5], 136.1 (s, *meta*-C of C_6H_5), 125.7 (s, *ortho*-C of C_6H_5), 121.9 (s, *para*-C of C_6H_5), 98.5 [dd, J(RhC) = 10.6, J(PC) = 8.3 Hz, =CH_A], 82.7 [d, J(RhC) = 8.3 Hz, =CH_B], 31.8, 29.9 (both s, CH_2 of C_8H_{12}), 28.8 [d, J(PC) = 4.6 Hz, As*C*HCH$_3$], 27.0 [d, J(PC) = 17.6 Hz, P*C*HCH$_3$], 19.3, 19.2 (both s, AsCH*C*H$_3$), 18.3 [d, J(PC) = 1.8 Hz, PCH*C*H$_3$], 18.1 (s, PCH*C*H$_3$), 13.5 [dd, J(RhC) = J(PC) = 3.2 Hz, AsCH$_2$P], 8.9 [dd, J(RhC) = 30.1, J(PC) = 6.5 Hz, RhCH$_2$]. ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 53.6 [d, J(RhP) = 161.3 Hz]. Anal. Calcd for $C_{46}H_{64}AsBPRh$ (836.6): C, 66.04; H, 7.71. Found: C, 65.29; H, 7.49.

Preparation of [Rh(η^4-C_8H_{12}){κ^2-*C,P*-$CH_2As(tBu)_2$-CH_2PiPr_2}]PF_6 (8a). This was prepared as described for **7a**, from **5a** (114 mg, 0.17 mmol) and a solution of CH_2N_2 (ca. 0.25 M, 2.04 mL, ca. 0.51 mmol) in ether as starting materials: red-brown solid; yield 111 mg (95%); mp 128 °C dec. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.85 (br s, 2H, H_A), 4.48 (br s, 2H, H_B), 2.40 [dd, J(RhH) = 0.8, J(PH) = 7.4 Hz, 2H, AsCH$_2$P], 2.16 (br m, 10H, CH_2 of C_8H_{12} and PC*H*CH$_3$), 1.49 (s, 18H, AsCCH$_3$), 1.35 [dd, J(PH) = 15.2, J(HH) = 6.8 Hz, 6H, PCHC*H*$_3$], 1.21 [dd, J(PH) = 14.6, J(HH) = 7.6 Hz, 6H, PCHC*H*$_3$], 0.97 (br s, 2H, RhCH$_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 95.4 [dd, J(RhC) = 10.7, J(PC) = 8.6 Hz, =CH_A], 80.2 [d, J(RhC) = 8.3 Hz, =CH_B], 42.3 [d, J(PC) = 3.4 Hz, As*C*CH$_3$], 31.6 [br d, J(RhC) = 1.7 Hz, CH_2 of C_8H_{12}], 29.7 (br s, CH_2 of C_8H_{12}), 28.2 (s, AsC*C*H$_3$), 27.6 [d, J(PC) = 17.0 Hz, P*C*HCH$_3$], 19.5 [d, J(PC) = 2.4 Hz, PCH*C*H$_3$], 18.7 (br s, PCH*C*H$_3$), 15.0 [dd, J(RhC) = 2.0, J(PC) = 6.2 Hz, AsCH$_2$P], 7.7 [dd, J(RhC) = 30.1, J(PC) = 7.2 Hz, RhCH$_2$]. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 53.4 [d, J(RhP) = 161.2 Hz, iPr$_2$P], −144.2 [sept, J(FP) = 712.7 Hz, PF_6^-]. Anal. Calcd for $C_{24}H_{48}AsF_6P_2Rh$ (690.4): C, 41.75; H, 7.01. Found: C, 42.19; H, 6.81.

Preparation of [Rh(η^4-C_8H_{12}){κ^2-*C,P*-$CH_2As(tBu)_2$-CH_2PiPr_2}]BPh_4 (8b). A solution of **5b** (60 mg, 0.07 mmol) in CH_2Cl_2 (4 mL) was treated at −60 °C with a solution of CH_2N_2 (ca. 0.25 M, 0.84 mL, ca. 0.21 mmol) in ether, which led to a change of color from light red to yellow. The solution was slowly warmed to room temperature and stirred for 15 min. The reaction mixture was filtered, and the filtrate was concentrated to ca. 2 mL in vacuo. The concentrate was layered with pentane (8 mL) and stored at −25 °C for 48 h. Light yellow crystals precipitated, which were separated from the mother liquor, washed with pentane (5 mL), and dried: yield 57 mg (93%); mp 115 °C dec. ^{1}H NMR (400 MHz, $CDCl_2$): δ 7.40−6.88 (m, 20H, C_6H_5), 4.85 (br s, 2H, H_A), 4.45 (br s, 2H, H_B), 2.17 (m, 8H, CH_2 of C_8H_{12}), 1.98 (br m, 2H, PC*H*CH$_3$), 1.94 [dd, J(RhH) = 0.8, J(PH) = 7.2 Hz, 2H, AsCH$_2$P], 1.35 (s, 18H, AsCCH$_3$), 1.25 [dd, J(PH) = 14.8, J(HH) = 7.2 Hz, 6H, PCHC*H*$_3$], 1.16 [dd, J(PH) = 14.8, J(HH) = 7.2 Hz, 6H, PCHC*H*$_3$], 0.90 [dd, J(RhH) = J(PH) = 2.0 Hz, 2H, RhCH$_2$]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 164.3 [q, J(BC) = 49.3 Hz, *ipso*-C of C_6H_5], 136.3 (s, *meta*-C of C_6H_5), 125.4 [q, J(BC) = 3.0 Hz, *ortho*-C of C_6H_5], 121.5 (s, *para*-C of C_6H_5), 96.4 [dd, J(RhC) = 10.7, J(PC) = 7.9 Hz, =CH_A], 80.8 [br d, J(RhC) = 8.4 Hz, =CH_B], 42.4 [d, J(PC) = 3.4 Hz, As*C*CH$_3$], 30.7 [d, J(RhC) = 1.6 Hz, CH_2 of C_8H_{12}], 29.7 (s, CH_2 of C_8H_{12}), 28.3 (s, AsC*C*H$_3$), 27.7 [d, J(PC) = 17.5 Hz, P*C*HCH$_3$], 19.5 [d, J(PC) = 2.1 Hz, PCH*C*H$_3$], 18.9 (br s, PCH*C*H$_3$), 14.8 [d, J(PC) = 2.6 Hz, AsCH$_2$P], 7.5 [dd, J(RhC) = 30.1, J(PC) = 7.2 Hz, RhCH$_2$]. ^{31}P NMR (162.0 MHz, $CDCl_3$): δ 54.0 [d, J(RhP) = 161.2 Hz]. Anal. Calcd for $C_{48}H_{68}AsBPRh$ (864.7): C, 66.67; H, 7.93. Found: C, 66.09; H, 8.11.

Preparation of [Rh(η^4-C_8H_{12}){κ^2-*C,P*-$CH_2As(Cy)_2$-CH_2PCy_2}]PF_6 (9). A solution of **6a** (73 mg, 0.09 mmol) in THF (3 mL) was treated at −30 °C with a solution of CH_2N_2 (ca. 0.30 M, 0.90 mL, ca. 0.27 mmol) in ether. Under slightly reduced pressure, the solution was slowly warmed to room temperature and then stirred for 30 min. The resulting brown solution was brought to dryness in vacuo. The oily residue was extracted with CH_2Cl_2 (5 mL), and the solvent was removed. The remaining solid was washed twice with 15 mL portions of pentane/ether (4:1) and with pentane (10 mL) and dried: light yellow solid; yield 70 mg (94%); mp 112 °C dec.

Table 3. Crystallographic Data for 3 and 7b

formula	$C_{23}H_{46}AsCl_2PRh_2$ (**3**)	$C_{23}H_{64}AsBPRh$ (**7b**)
fw	705.71	836.58
cryst size, mm^3	0.2 × 0.2 × 0.07	0.18 × 0.15 × 0.12
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
cell dimens determn	24 rflns, 10° < θ < 15°	25 rflns, 10° < θ < 15°
a, Å	10.744(1)	15.580(3)
b, Å	20.174(2)	13.617(1)
c, Å	14.35(2)	20.386(4)
β, deg	111.20(5)	93.674(9)
V, A^3	2900(4)	4316(1)
Z	4	4
d_{calcd}, g cm^{-3}	1.617	1.287
diffractometer	CAD4 (Enraf-Nonius)	
radiation (λ, Å)	Mo Kα (0.710 73)	
filter factor (Zr filter)	15.4	15.4
temp, K	293(2)	293(2)
μ, mm^{-1}	2.503	1.217
scan method	ω/θ	ω/θ
2θ(max), deg	54	46
total no. of rflns	5465	7263
no. of unique rflns	5135 (R(int) = 0.0263)	5984 (R(int) = 0.0348)
no. of obsd rflns ($I > 2\sigma(I)$)	3126	3814
no. of rflns used for refinement	5132	5982
no. of params refined	280	525
final R indices ($I > 2\sigma(I)$)	R1 = 0.0457, wR2 = 0.0718[a]	R1 = 0.0529, wR2 = 0.0984[a]
R indices (all data)	R1 = 0.0968, wR2 = 0.0943[a]	R1 = 0.1058, wR2 = 0.1261[a]
rfln:param ratio	18.33	11.39
resid electron density, e $Å^{-3}$	0.448/−0.413	0.413/−0.338

[a] $w^{-1} = [\sigma^2F_o^2 + (0.0162P)^2 + 6.5172P]$ (**3**) and $w^{-1} = [\sigma^2F_o^2 + (0.0391P)^2 + 9.8224P]$ (**7b**), where $P = (F_o^2 + 2F_c^2)/3$.

^{1}H NMR (200 MHz, CD_2Cl_2): δ 4.89 (br s, 2H, H_A), 4.29 (br s, 2H, H_B), 2.58−1.17 (br m, 54H, $AsCH_2P$ and CH_2 of C_8H_{12} and C_6H_{11}), 0.91 (br s, 2H, $RhCH_2$). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 96.9 [dd, J(RhC) = 10.6, J(PC) = 8.1 Hz, $=CH_A$], 82.4 [d, J(RhC) = 10.3 Hz, $=CH_B$], 38.5 [d, J(PC) = 1.9 Hz, As*C*HCH$_2$], 36.5 [d, J(PC) = 17.6 Hz, P*C*HCH$_2$], 31.8 (br s, CH_2 of C_8H_{12}), 30.1−25.7 (m, CH_2 of C_8H_{12} and $AsCy_2$ and PCy_2), 12.7 (br s, $AsCH_2P$), 9.1 [dd, J(RhC) = 30.3, J(PC) = 7.2 Hz, $RhCH_2$]. ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 41.8 [d, J(RhP) = 160.0 Hz, Cy_2P], −143.9 [sept, J(FP) = 711.4 Hz, PF_6^-]. Anal. Calcd for $C_{34}H_{60}AsF_6P_2Rh$ (822.6): C, 49.64; H, 7.35; Rh, 12.51. Found: C, 49.94; H, 6.90; Rh, 12.51.

Preparation of [(η^6-$C_6H_5BPh_3$)Rh(κ^2-*As,P*-*i*Pr_2As-CH_2P*i*Pr_2)] (10). A slow stream of H_2 was passed through a solution of **4b** (182 mg, 0.22 mmol) in CH_2Cl_2 (10 mL) for 45 s. While the solution was stirred under H_2 for 1.5 h at room temperature, a light red solid precipitated. The solvent was removed in vacuo, and the residue was washed twice with 3 mL portions of pentane and dried: light red solid; yield 145 mg (92%); mp 68 °C dec. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.33−7.00 (br m, 15H, C_6H_5), 6.58 (br m, 1H, *para*-H of η^6-C_6H_5), 6.37 [br d, J(HH) = 5.8 Hz, 2H, *ortho*-H of η^6−C_6H_5], 5.90 (br m, 2H, *meta*-H of η^6−C_6H_5), 2.71 [dd, J(RhH) = 1.5, J(PH) = 9.5 Hz, 2H, $AsCH_2P$], 2.14 [sept, J(HH) = 6.9 Hz, 2H, As*C*H*C*H$_3$], 1.85 (br m, 2H, PC*H*CH$_3$), 1.05 (br m, 24H, PCHC*H*$_3$ and AsCHC*H*$_3$). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 135.9, 126.1, 123.0 (all s, C_6H_5), 100.6, 96.4, 92.0 (all s, η^6-C_6H_5), 28.1 [d, J(PC) = 18.5 Hz, $AsCH_2P$], 28.1 [d, J(PC) = 1.9 Hz, As*C*HCH$_3$], 27.5 [d, J(PC) = 20.4 Hz, P*C*HCH$_3$], 19.9, 19.3 (both s, AsCH*C*H$_3$), 18.7 [d, J(PC) = 2.8 Hz, PCH*C*H$_3$], 18.3 (s, PCH*C*H$_3$); the signals of the *ipso*-C of η^6-C_6H_5 and C_6H_5 were not exactly located. ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 16.8 [d, J(RhP) = 169.9 Hz]. Anal. Calcd for $C_{37}H_{50}AsBPRh$ (714.4): C, 62.21; H, 7.05. Found: C, 61.48; H, 7.03.

Preparation of [(η^6-$C_6H_5BPh_3$)Rh(κ^2-*As,P*-*t*Bu_2As-CH_2P*i*Pr_2)] (11). This was prepared as described for **10**, from **5b** (142 mg, 0.17 mmol) and H_2 as starting materials: orange-yellow solid; yield 110 mg (87%). ^{1}H NMR (200 MHz, CD_2Cl_2): δ 7.41−7.03 (br m, 15H, C_6H_5), 6.70 (br m, 1H, *para*-H of η^6-C_6H_5), 6.25 [br d, J(HH) = 6.2 Hz, 2H, *ortho*-H of η^6−C_6H_5], 5.84 (br m, 2H, *meta*-H of η^6−C_6H_5), 2.81 [dd, J(RhH) = 1.1, J(PH) = 9.3 Hz, 2H, $AsCH_2P$], 1.96 (br m, 2H, PC*H*CH$_3$), 1.14 (s, 18H, AsCC*H*$_3$), 1.10 (br m, 12H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 136.2, 126.1, 123.0 (all s, C_6H_5), 99.7, 98.3, 91.2 (all s, η^6-C_6H_5), 39.7 (s, As*C*CH$_3$), 29.4 [d, J(PC) = 18.5 Hz, P*C*HCH$_3$], 29.2 [d, J(PC) = 18.5 Hz, $AsCH_2P$], 29.1 (s, AsC*C*H$_3$), 19.3, 19.1 (both s, PCH*C*H$_3$); the signals of the *ipso*-C of η^6-C_6H_5 and C_6H_5 were not exactly located. ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 11.3 [d, J(RhP) = 172.9 Hz]. Anal. Calcd for $C_{39}H_{54}AsBPRh$ (742.5): C, 63.09; H, 7.33. Found: C, 62.89; H, 7.67.

Preparation of [{RhH(κ^2-*As,P*-$Cy_2AsCH_2PCy_2$)}$_2$(μ-H)(μ-O_2CCF_3)$_2$]PF_6 (12). A solution of **6a** (105 mg, 0.13 mmol) in CH_2Cl_2 (6 mL) was treated with CF_3CO_2H (30 μL, 0.39 mmol) and then stirred under H_2 (1.0 bar) for 10 min at room temperature. A change of color from orange-yellow to light yellow occurred. After the solvent was removed in vacuo, an oily residue was obtained which upon treatment with 10 mL of ether (twice) and 5 mL of pentane (twice) gave a light yellow, almost air stable solid: yield 70 mg (73%); mp 57 °C dec. IR (CH_2Cl_2): ν(RhH) 2100, $\nu(OCO_{asym})$ 1672, $\nu(OCO_{sym})$ 1447, ν(CF) 1200, 1149 cm^{-1}. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 3.03, 2.71−1.34 (all br m, 92H, C_6H_{11} and $AsCH_2P$), −17.52 [tt, J(RhH) = 25.0, J(PH) = 10.9 Hz, 1H, RhHRh], −17.92 [dd, J(RhH) = 15.0, J(PH) = 24.4 Hz, 2H, RhH]. ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 168.5 [q, J(FC) = 36.8 Hz, O_2CCF_3], 116.2 [q, J(FC) = 292.5 Hz, CF_3], 39.8, 38.5 (both s, As*C*HCH$_2$), 36.4 [d, J(PC) = 26.8 Hz, P*C*HCH$_2$], 35.4 [d, J(PC) = 21.5 Hz, P*C*HCH$_2$], 31.4−25.7 (br m, CH_2 of $AsCy_2$ and PCy_2), 25.1 [d, br, J(PC) = 23.1 Hz, $AsCH_2P$]. ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ −73.7 [d, J(PF) = 711.3 Hz, PF_6^-], −75.2 (s, CF_3). ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ 29.5 [d, J(RhP) = 111.2 Hz, Cy_2P], −144.0 [sept, J(FP) = 711.3 Hz, PF_6^-]. Anal. Calcd for $C_{54}H_{95}As_2F_{12}P_3Rh_2$ (1484.9): C, 43.68; H, 6.45. Found: C, 43.47; H, 6.24.

X-ray Structure Determination of Compounds 3 and 7b. Single crystals of **3** were grown from 2-propanol at 0 °C and single crystals of **7b** by diffusion of pentane into a saturated solution of **7b** in THF at room temperature. Crystal data collection parameters are summarized in Table 3. Intensity data were corrected by Lorentz and polarization effects, and a semiempirical absorption correction was applied in each

case (minimum transmission 75.30% (**3**), 93.88% (**7b**)). The structures were solved by direct methods (SHELXS-86).[27] Atomic coordinates and anisotropic displacement parameters of all non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-93).[28] The positions of all hydrogen atoms were calculated according to ideal geometry and refined by full-matrix least squares on F^2 using the riding method, except for H9a and H9b of **3**, which were found and refined without restrictions.

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Supporting Information Available: Tables of data collection parameters, bond lengths and angles, positional and thermal parameters, and least-squares planes for **3** and **7b** (14 pages). Ordering information is given on any current masthead page.

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