Mono- and Dinuclear Rhodium and Iridium Complexes with Chiral Phospholanes as Ligands

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Dedicated to Professor Christoph Elschenbroich on the occasion of his 65th birthday

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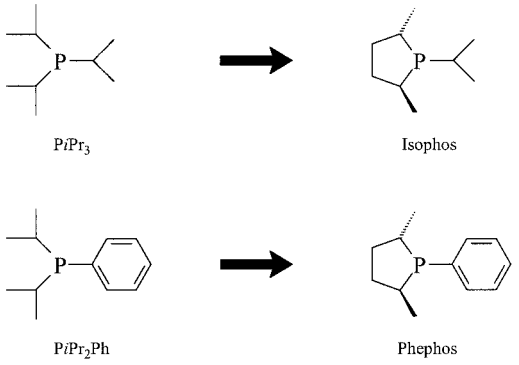
The dinuclear complexes $[RhCl(L)_2]_2$ (**1**, **2**) with L = 1-isopropyl-(2*S*,5*S*)-2,5-dimethylphospholane (Isophos) and (2*S*,5*S*)-2,5-dimethyl-1-phenylphospholane (Phephos), respectively, prepared from $[RhCl(C_8H_{14})_2]_2$ and four equivalents of L, react with Lewis bases such as L, CO, ethene and diphenylacetylene by cleavage of the chloride bridges. Mononuclear compounds of the general composition $[RhCl(L)_3]$ (**3**, **4**) and *trans*-$[RhCl(L')(L)_2]$ (**5**–**9**; L′ = CO, C_2H_4, C_2Ph_2) were obtained, of which **4** (L = Phephos) and **8** (L′ = C_2H_4; L = Phephos) are in equilibrium with the precursors. Oxidative addition of H_2 to **1** (L = Isophos) and $[RhCl(PiPr_2Ph)_2]_2$ (**10**) affords the mononuclear dihydrido complexes $[RhH_2Cl(L)_2]$ (**13**) and $[RhH_2Cl(PiPr_2Ph)_2]$ (**14**), respectively, via the unsymmetrical compounds $[RhH_2(L)_2(\mu\text{-}Cl)_2Rh(L)_2]$ (**11**) and $[RhH_2(PiPr_2Ph)_2(\mu\text{-}Cl)_2Rh(PiPr_2Ph)_2]$ (**12**) as intermediates. These intermediates can be isolated by treatment of **13** and **14** with one half equivalent of **1** or **10**, respectively. The hydrogenation of the η^3-allyl and η^3-benzyl complexes $[(\eta^3\text{-}2\text{-}RC_3H_4)Rh(L)_2]$ (**16**–**18**) and $[(\eta^3\text{-}CH_2Ph)Rh(L)_2]$ (**19**, **20**), which were prepared from **1** or **2** and the corresponding Grignard reagent, leads to the dinuclear $Rh^{III}Rh^{I}$ products $[RhH_2(L)_2(\mu\text{-}H)_2Rh(L)_2]$ (**21**, **22**), which are structurally related to the dichloro(dihydrido) derivatives **11** and **12**. Compound **21** (L = Isophos) reacts with CO to give *trans*-$[RhH(CO)(L)_2]$ (**23**). While treatment of **1** with phenylacetylene yields the vinylidene complex *trans*-$[RhCl(=C=CHPh)(Isophos)_2]$ (**26**), via η^2-alkyne and alkynyl(hydrido) intermediates, the reaction of **2** with PhC≡CH affords the labile enyne compound *trans*-$[RhCl\{\eta^2\text{-}(E)\text{-}PhC{\equiv}CCH{=}CHPh\}(Phephos)_2]$ (**27**). Reaction of **27** with CO gives **6** and the free enyne. The carbene complexes *trans*-$[RhCl(=CPh_2)(L)_2]$ (**30**, **31**), obtained from *trans*-$[RhCl(=CPh_2)(SbiPr_3)_2]$ (**29**) and L, react with ethene not by olefin metathesis but by formation of the isomeric olefins $Ph_2C{=}CHCH_3$ (**32**) and $CH_2{=}CHCHPh_2$ (**33**) in different ratios. With iridium as the metal center, carbonyl, dihydrido, and dihydrido(carbonyl) compounds with $[IrCl(Isophos)_2]$ as the building block have been prepared.

Introduction

In the context of our investigations on low-valent organorhodium compounds containing bulky tertiary phosphanes as supporting ligands,[1] we recently observed that even an apparently minor change in the size of the phosphane upon going from $PiPr_3$ to $PiPr_2Ph$ causes a difference in the reactivity of the corresponding complexes.[2] A striking example is the behavior of the acetato derivatives $[Rh(\kappa^2\text{-}O_2CCH_3)(PiPr_3)_2]$ and $[Rh(\kappa^2\text{-}O_2CCH_3)(PiPr_2Ph)_2]$, of which the first reacts with two equivalents of phenylacetylene to give a vinylrhodium(III) compound containing a Rh(CH=CHPh) unit,[3] while under the same conditions the second affords a product with $Rh(CPh{=}CH_2)$ as a molecular fragment.[2]

Taking these results into consideration, we started a systematic study of the reactivity of rhodium (and some iridium) complexes with 1-isopropyl-(2*S*,5*S*)-2,5-dimethylphospholane (abbreviated as Isophos) and (2*S*,5*S*)-2,5-dimethyl-1-phenylphospholane (abbreviated as Phephos) as ligands. As depicted in Scheme 1, these phospholanes are similar in size to $PiPr_3$ and $PiPr_2Ph$, but in contrast to these tertiary phosphanes are chiral, which for catalytic purposes



Scheme 1

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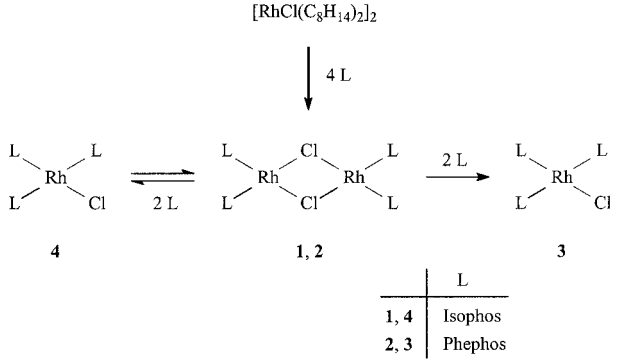
could be an important factor. In this paper we report the preparation of the starting materials $[RhCl(Isophos)_2]_2$ (**1**) and $[RhCl(Prephos)_2]_2$ (**2**), the reactivity of these compounds toward H_2, CO, ethene, internal and terminal alkynes, and the conversion of **1** and **2** to η^3-allyl- and η^3-benzylrhodium(I) complexes, and discuss very briefly some exploratory experiments regarding the synthesis and reactivity of iridium compounds with Isophos as ligand.

Results and Discussion

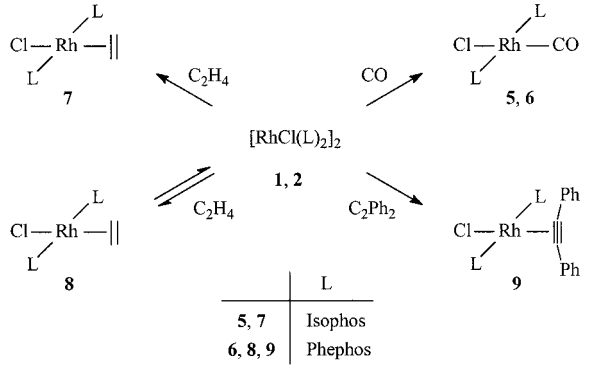
The method previously used by us for the preparation of $[RhCl(P\mathit{i}Pr_3)_2]_2$ [4] could also be applied to the synthesis of **1** and **2** (Scheme 2). Treatment of a suspension of the bis(cyclooctene) derivative $[RhCl(C_8H_{14})_2]_2$ with four equivalents of Isophos[5] or Phephos[6] in acetone or benzene gives the required products in 92% (**1**) and 75% (**2**) isolated yields. Both **1** and **2** are red or orange-red solids, which, like $[RhCl(P\mathit{i}Pr_3)_2]_2$, are thermally not very stable, but in contrast to their $P\mathit{i}Pr_3$ counterpart are less air-sensitive. The ^{31}P NMR spectra of **1** and **2** display a sharp doublet with a large $^1J_{Rh,P}$ coupling constant of 196.2 Hz (**1**) and 198.0 Hz (**2**) that is characteristic for a $Rh(PR_3)_2$ moiety with the P-donors in a *cis* arrangement.[4,7] The ^1H NMR spectra of **1** and **2** show two signals for the protons of the different methyl groups of the phospholane units but are otherwise quite complicated due to the overlap of the resonances for the CH_2 and CH protons of the five-membered ring. Similar observations have also been made for the other Isophos and Phephos complexes described in this paper and thus the corresponding ^1H NMR spectroscopic data will not be discussed.



Scheme 2

Treating a suspension of $[RhCl(C_8H_{14})_2]_2$ with eight instead of four equivalents of Isophos or Phephos leads to the formation of the mononuclear compounds **3** and **4**, respectively (see Scheme 2). However, while **3** could be isolated as an analytically pure product, the analogue **4** is in equilibrium with **1** and free Isophos. The equilibrium lies completely on the side of **4** only in the presence of excess Isophos and thus all attempts to obtain **4** without Isophos as a by-product failed. The ^{31}P NMR spectrum of **3** at room temperature displays, apart from a sharp doublet of triplets for the ^{31}P nuclei *trans* to chloride, a broad signal that becomes a doublet of doublets at 330 K owing to an increase in the rate of the exchange process for the phospholanes. The $^1J_{Rh,P}$ and $^2J_{P,P}$ coupling constants for **3** are very similar to those of the Wilkinson complex $[RhCl(PPh_3)_3]$.[8]

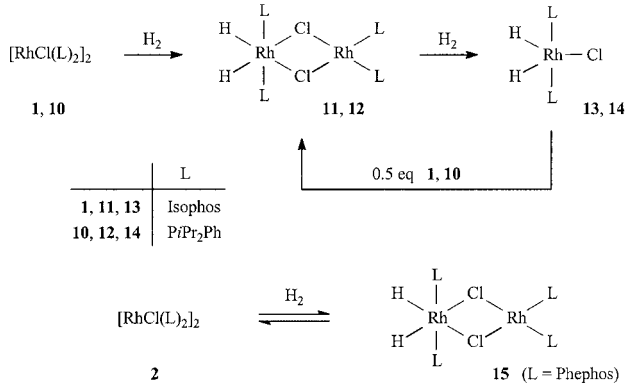
The reactions of compounds **1** and **2** with CO, ethene and diphenylacetylene, that all lead to cleavage of the chloro bridges, are summarized in Scheme 3. The carbonyl complexes **5** and **6** are formed almost instantaneously and were isolated as yellow, moderately air-sensitive solids in ca. 90% yields. Compound **5** is also accessible from **7** and CO and compound **6** similarly from **3** and carbon monoxide by ligand exchange. In contrast to the behavior of **1** and **2** toward an excess of Isophos or Phephos, the reaction of **2** (with Phephos as ligand) with ethene approaches an equilibrium, while the corresponding reaction of **1** (with Isophos as ligand) affords the mononuclear complex **7** nearly quantitatively. Treatment of **2** with diphenylacetylene does not lead to an equilibrium but gives compound **9** as a yellow solid in 72% yield. The ^{31}P NMR spectra of **5**−**9** all display one sharp doublet, indicating that in each case the two phospholane ligands are *trans*-disposed. The wavenumbers for the ν(CO) stretching mode in the IR spectra of **5** and **6** (1947 and 1961 cm^{-1}) are nearly identical to those of their phosphane counterparts *trans*-$[RhCl(CO)(P\mathit{i}Pr_3)_2]$ (1943 cm^{-1})[9] and *trans*-$[RhCl(CO)(P\mathit{i}Pr_2Ph)_2]$ (1960 cm^{-1})[10] which suggests that the coordinative capabilities of $P\mathit{i}Pr_3$ and $P\mathit{i}Pr_2Ph$ on one hand and those of the phospholanes on the other are similar. With regard to the lability of **8** we note that the bis(triphenylphosphane) complex *trans*-$[RhCl(C_2H_4)(PPh_3)_2]$ also loses the ethene ligand in the absence of an excess of C_2H_4 and rearranges to $[RhCl(PPh_3)_2]_2$.[11]



Scheme 3

The course of the oxidative addition of H_2 to the metal centers of **1**, **2** and the related compound $[RhCl(P\mathit{i}Pr_2Ph)_2]_2$ (**10**)[2] is also dependent on the type of phosphorus donor. Passing a slow stream of dry dihydrogen through a solution of **1** or **10** in toluene or pentane at low temperatures leads, after warming to 20 °C, to the formation of the dihydrido complexes **13** and **14** in 76−87% isolated yields. In contrast, the reaction of **2** with H_2 generates an equilibrium which, even after stirring the solution for 12 h under a dihydrogen

atmosphere, could not be completely shifted to the side of product **15** (Scheme 4). In the absence of H_2, **15** is reconverted into **2**. The fact that **15** is not an analogue of **13** and **14** is confirmed by the ^{31}P NMR spectrum, which displays two resonances (both doublets) at $\delta = 69.9$ and 52.2 ppm, respectively. Since the signal at lower field shows a large $^1J_{Rh,P}$ coupling constant of 195.8 Hz, it is assigned to the *cis*-oriented phospholanes at the lower coordinated rhodium center. The chemical shift and the coupling constant (118.4 Hz) for the signal at higher field are very similar to those of **14** ($\delta = 53.7$ ppm; $^1J_{Rh,P} = 119.1$ Hz) with P*i*Pr$_2$Ph as ligand. The ^{31}P NMR spectra of **13** and **14** (which are both yellow solids that can be stored under argon for weeks) show only one resonance, confirming that the two P-donors are in the *trans* positions. In the ^1H NMR spectra of **13** and **14** there is also only one set of signals (doublet of triplets) at $\delta = -22.00$ and -21.24 ppm for the hydride ligands, which is in agreement with the proposed structure shown in Scheme 4. An X-ray crystal structure analysis of [RhH$_2$Cl(P*i*Pr$_3$)$_2$] has been carried out, and this proved that the coordination geometry is trigonal bipyramidal with the phosphanes in the apical positions.[12]



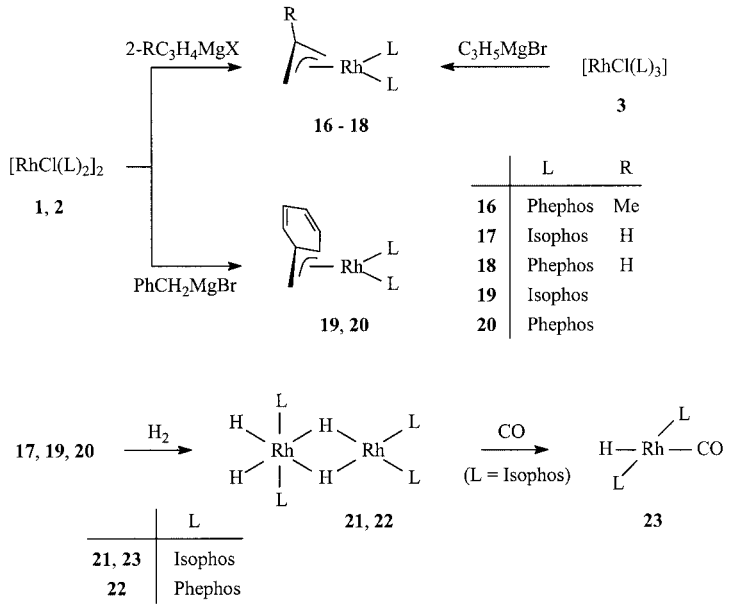
Scheme 4

The plausible assumption that compounds **13** and **14** are formed via **11** and **12** as intermediates was confirmed by the reactions of **13** and **14** with one half equivalent of **1** or **10**, respectively. The conversion is relatively slow (3 h at 20 °C in C_6D_6) and was monitored by NMR spectroscopy. The ^1H and ^{31}P NMR spectra of **11** and **12** are similar to those of **15** and also to those of [RhH$_2$(PPh$_3$)$_2$(μ-Cl)$_2$Rh(PPh$_3$)$_2$], which is the first compound of this structural type reported in the literature.[8] It should be mentioned that dimer **1**, with Isophos as ligand, reacts in C_6D_6 at 60 °C with a tenfold excess of cyclooctane to give **11** and cyclooctene. However, this dehydrogenation is a stoichiometric reaction and all attempts to convert C_8H_{16} into C_8H_{14} catalytically using **1** as the catalyst failed.

In analogy to the preparation of [Rh(η^3-C$_3$H$_5$)(PR$_3$)$_2$] (PR$_3$ = P*i*Pr$_3$,[7,13] P*i*Pr$_2$Ph[2]), the starting materials **1** and **2**, both generated in situ from [RhCl(C$_8$H$_{14}$)$_2$]$_2$ and the corresponding phospholane, react with a solution of the Grignard reagent 2-RC$_3$H$_4$MgBr in diethyl ether to give the η^3-allyl complexes **16**−**18** in 72−82% isolated yield (Scheme 5). The Phephos derivative **18** is equally accessible from **3** and C$_3$H$_5$MgBr in the molar ratio of 1:4. Similarly to the related P*i*Pr$_3$ and P*i*Pr$_2$Ph compounds, **16**−**18** are orange-yellow solids that are not only air sensitive but also thermally quite labile. In contrast to the ^{31}P NMR spectra of [Rh(η^3-C$_3$H$_5$)(PR$_3$)$_2$] (PR$_3$ = P*i*Pr$_3$, P*i*Pr$_2$Ph) and [Rh(η^3-2-MeC$_3$H$_4$)(P*i*Pr$_3$)$_2$],[2,13] which display a sharp doublet, the ^{31}P NMR spectra of **16**−**18** exhibit the AB part of an ABX system, which reflects the non-equivalence of the chiral phospholane ligands. Owing to this non-equivalence, the ^1H NMR spectra of **16**−**18** show two signals for the *anti*- and two for the *syn*-protons of the terminal allylic CH$_2$ units, with a significant difference in the chemical shifts. Since the spectrum of **16** remains unchanged in the temperature range between 278 and 330 K, there is no doubt that in solution the Rh(η^3-2-MeC$_3$H$_4$) moiety is rigid on the NMR timescale and does not undergo an η^3-η^1-η^3 rearrangement.[14]

Under similar conditions as used for the preparation of **16**−**18**, the in situ generated dimers **1** and **2** also react with the benzyl Grignard reagent PhCH$_2$MgBr to give the η^3-benzylrhodium(I) compounds **19** and **20** in about 80% yield. The red air-sensitive solids are thermally even less stable than their Rh(η^3-C$_3$H$_5$) counterparts **17** and **18** and under argon slowly decompose at room temperature. In benzene, **19** and **20** are stable for ca. 1 h, while in CHCl$_3$ and CH$_2$Cl$_2$ they decompose almost instantaneously. The ^1H NMR spectrum of **19** shows, apart from a triplet for the CH$_2$ protons of the benzylic group, five distinct resonances for the six-membered ring protons H^3 − H^7, which, as for **16**−**18**, indicates that the bonding between the C$_6$H$_5$CH$_2$ ligand and the metal is rigid on the NMR timescale. As expected, the ^{31}P NMR spectra of **19** and **20** display two doublets of doublets of which those at lower fields ($\delta = 76.0$ ppm for **19** and $\delta = 65.2$ ppm for **20**), owing to their larger $^1J_{Rh,P}$ coupling constant of ca. 260 Hz, are assigned to the ^{31}P nuclei *trans* to the ring and those at higher fields ($\delta = 64.9$ ppm for **19** and $\delta = 58.1$ ppm for **20**), with a $^1J_{Rh,P}$ coupling constant of ca. 180 Hz, to the ^{31}P nuclei *trans* to the benzylic CH$_2$ unit.

The η^3-allyl and η^3-benzyl complexes **17**, **19** and **20** react smoothly with H_2 at a pressure of 1 bar to give the Rh$_2$H$_4$ derivatives **21** and **22**, respectively (see Scheme 5). Compounds of the general composition [Rh$_2$H$_4$(L)$_4$] with L = P*i*Pr$_3$,[15] P(OR)$_3$,[16] P(NMe$_2$)$_3$,[17] and L$_2$ = *i*Pr$_2$P(CH$_2$)$_n$-P*i*Pr$_2$ (n = 2, 3)[18] are well-known, but in most cases are rather labile and can be handled only under a hydrogen atmosphere. The X-ray crystal structure analysis of the stable complex [Rh$_2$H$_4$\{P(NMe$_2$)$_3$\}$_4$] revealed that the two rhodium centers, which are bridged by two hydride ligands, have a different coordination geometry, one being octahedral and the other square planar.[17] According to the spectroscopic data, we assume that the phospholane complexes **21** and **22** are structurally related to their P(NMe$_2$)$_3$ counterpart. The ^1H NMR spectrum of **21** (which is a dark green, extremely air-sensitive solid) displays two resonances at $\delta = -10.20$ and -17.50 ppm in the high-field region, of which the first is split into a triplet of quintets due to ^{103}Rh-

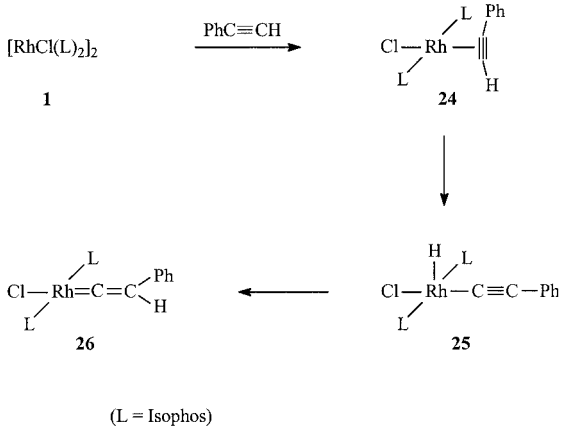


Scheme 5

^{1}H and ^{31}P-^{1}H couplings. Therefore, this signal is assigned to the bridging hydrides. The second resonance is a doublet of triplets and belongs to the terminal hydrides at the Rh^{III} center. The ^{1}H NMR spectrum of **22** also shows two hydride signals (with similar chemical shifts as for **21**), but these signals are rather broad, possibly due to a slow intramolecular rearrangement process as found for $[Rh_2H_4\{P(O\textit{i}Pr)_3\}_4]$.[19] In agreement with the proposed structure, the ^{31}P NMR spectra of **21** and **22** display two doublets at δ = 77.8 and 72.1 ppm (**21**) and δ = 73.8 and 65.4 ppm (**22**) with similar intensities, confirming that the four phospholane units are pairwise equivalent. Owing to the significant difference in the coupling constants, the signals at lower field are assigned to the *trans*-disposed P-donors at the Rh^{III} centers and the signals at higher field to the *cis*-disposed P-donors at the Rh^{I} centers of the molecules.

The Isophos complex **21** reacts quite rapidly with CO by cleavage of the hydride bridges and elimination of H_2 to afford the mononuclear carbonyl(hydrido)rhodium(I) compound **23** in nearly quantitative yield (see Scheme 5). Typical spectroscopic features of **23** (which is a yellow air-sensitive solid for which a correct elemental analysis has been obtained) are the sharp doublet at δ = 64.7 ppm in the ^{31}P NMR spectrum, confirming the equivalence of the phospholane ligands, the doublet of triplets at δ = −10.36 ppm for the hydride in the ^{1}H NMR spectrum, and the ν(CO) and ν(RhH) stretching modes at 1965 and 2065 cm^{-1} in the IR spectrum. Whereas the triisopropylphosphane derivative $[Rh_2H_4(P\textit{i}Pr_3)_4]$ reacts smoothly with CO to give $[Rh(CO)_3(P\textit{i}Pr_3)]_2$,[15b] a similar conversion of **23** to $[Rh(CO)_3(Isophos)]_2$ was not observed, even if the carbonyl(hydrido) compound is stored for 12 h under a CO atmosphere.

The reactivity of the Isophos complex **1** toward phenylacetylene is quite similar to that of the phosphane analogue $[RhCl(P\textit{i}Pr_3)_2]_2$.[20] Treatment of a solution of **1** in benzene with two equivalents of PhC≡CH at room temperature leads to a quick change of color from brick-red to yellow. If the reaction is carried out in C_6D_6 and monitored by ^{1}H NMR spectroscopy, after a few minutes a doublet is observed at δ = 4.11 ppm, which we assign to the alkyne proton of the η^2-alkyne intermediate **24** (Scheme 6). The ^{31}P NMR spectrum of **24** exhibits the AB part of an ABX spin system indicating that the rotation of the alkyne around the metal-alkyne axis is slow on the NMR timescale.



Scheme 6

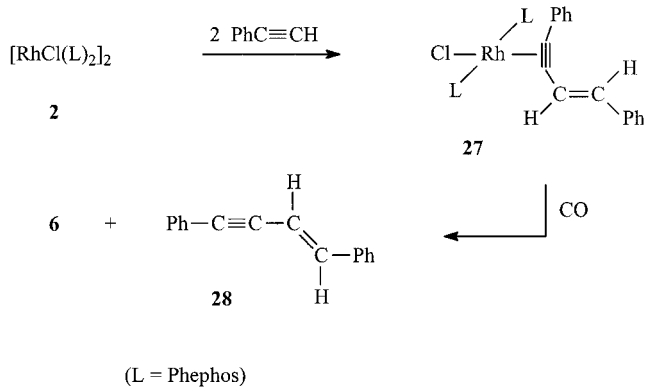
Only 10 min after the signals of **24** have appeared, a subsequent rearrangement takes place which generates the alkynyl(hydrido)rhodium(III) species **25**. Noteworthy spectroscopic data of this intermediate are the hydride signal in the ^{1}H NMR spectrum at δ = −19.38 ppm, which is split by the ^{103}Rh and ^{31}P nuclei into a doublet of triplets, and the doublet at δ = 50.1 ppm in the ^{31}P NMR spectrum. The $^1J_{Rh,P}$ coupling constant of 99.2 Hz is consistent with a *trans* disposition of the two phospholanes, and thus a

square-pyramidal structure for the five-coordinate compound can be proposed.

The final conversion of **25** to the stable isomer **26** proceeds upon warming the solution to 80 °C and affords, after chromatographic workup, the vinylidene complex in 84% isolated yield. In contrast to yellow **24** (which we failed to isolate), **26** is a violet, moderately air-stable solid, which is soluble in all common organic solvents apart from pentane and hexane. The ^{13}C NMR spectrum of **26** shows two resonances (both doublets of triplets) in the low-field region at δ = 296.3 and 112.3 ppm, which are characteristic for a Rh=C=CHR unit.[20,21] With regard to the course of the conversion of **25** to **26**, we note that owing to recent ab inito MO calculations both a mononuclear as well as a bimolecular mechanism seems possible.[22] In contrast to the related ruthenium system,[23] the alkynyl(hydrido)rhodium(III) species lies in a relative energy minimum, which is in agreement with the results presented in Scheme 6.

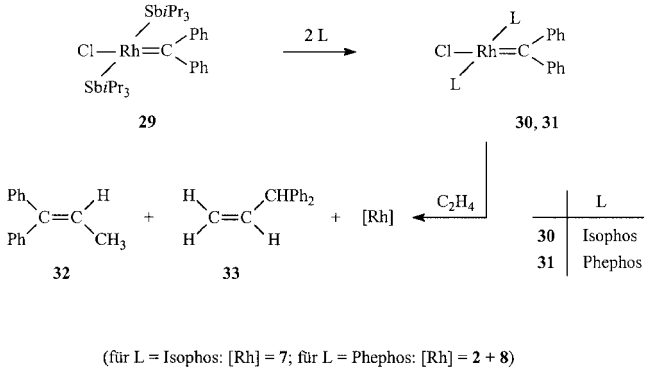
Compared with its Isophos counterpart **1**, the Phephos complex **2** behaves differently toward PhC≡CH. Instead of a vinylidene compound, the square-planar enynerhodium(I) complex **27** is generated which, however, is quite labile and could not be isolated in an analytically pure state. The ^1H NMR spectrum of **27** displays two signals for the olefinic protons at δ = 6.88 and 7.36 ppm, which, as indicated by the large $^3J_{H,H}$ coupling constant of 15.4 Hz, are *trans*-disposed at the C=C double bond. Other spectroscopic data are similar to those of *trans*-[RhCl{η^2-(*E*)-PhC≡CCH=CHPh}($P i Pr_3$)$_2$], which is obtained from the alkynyl(vinylidene) derivative *trans*-[Rh(C≡CPh)(=C=CHPh)($P i Pr_3$)$_2$] and protic acids.[3,24]

Upon passing a slow stream of CO through a solution containing **27**, a gradual change of color from yellow to pale yellow occurs and the formation of the carbonyl complex **6** and free (*E*)-PhC≡CCH=CHPh (**28**) can be detected (Scheme 7). It should be mentioned that the reaction of [RhCl(PMe_3)$_2$]$_2$ with excess phenylacetylene leads to PhC≡CC(Ph)=CH_2, which means that in this case the head-to-tail instead of the head-to-head dimerization is preferred.[25]



Scheme 7

Square-planar rhodium carbenes of the general composition *trans*-[RhCl(=CPh_2)(L)$_2$] could be obtained with both Isophos and Phephos as ligands L. The reaction of the starting material **29** with two equivalents of the corresponding phospholane proceeds under mild conditions and affords the required products **30** and **31** in 79−93% isolated yield (Scheme 8). The carbene complexes are green air-sensitive solids that decompose slowly in benzene and acetone but rapidly in $CHCl_3$ solution. Since the ^{31}P NMR spectra of **30** and **31** show a single resonance (doublet), there is no doubt that the two phospholane ligands are coordinated in the *trans* positions.

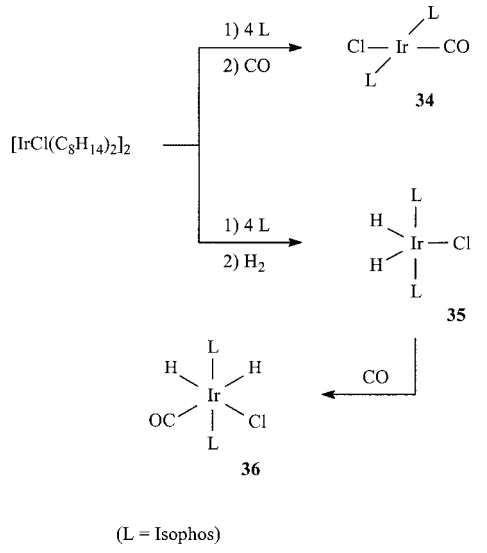


Scheme 8

Similarly to **29** and the phosphane analogues *trans*-[RhCl(=CPh_2)(PR_3)$_2$] (PR_3 = $P i Pr_3$, $P i Pr_2 Ph$, $P i PrPh_2$, PPh_3),[26] the related phospholane derivatives **30** and **31** are catalytically inactive in olefin metathesis. However, they do react with ethene relatively fast (10 min in C_6D_6 at room temperature) to give, apart from the ethene complexes **7** and **8** (and the dimer **2** in the case of Phephos as ligand), a mixture of two olefins **32** and **33** (see Scheme 8). With **30** as the precursor, the ratio of **32**:**33** is 94:6, while with **31** as precursor the ratio is 86:14. In our previous work we have already postulated that the major isomer **32** is probably generated via a rhodiacyclobutane, which, following a β-H shift, affords a RhH(η^3-CH_2CHCPh_2) intermediate. This reacts, in the presence of ethene, by reductive elimination to give the trisubstituted olefin.[3] The route to the minor isomer is not clear as yet, but possibly also proceeds via a rhodiacyclobutane as an intermediate.[27] For comparison it should be mentioned that by using *trans*-[RhCl(=CPh_2)($P i Pr_3$)$_2$] as the precursor, the ratio of **32**:**33** is 90:10 and with *trans*-[RhCl(=CPh_2)($P i Pr_2 Ph$)$_2$] it is 81:19.[27]

Some preliminary results regarding the preparation of iridium complexes with Isophos as ligand are summarized in Scheme 9. In contrast to [RhCl(C_8H_{14})$_2$]$_2$, the iridium counterpart reacts with four equivalents of Isophos to give a product which, even after storing for 12 h in vacuo, contains some cyclooctene. A similar situation results if [IrCl(C_8H_{14})$_2$]$_2$ is treated with $P i Pr_3$ in a 1:4 molar ratio.[28] Attempts to crystallize the crude product, obtained from [IrCl(C_8H_{14})$_2$]$_2$ and Isophos, from acetone led partly to the carbonyl derivative **34**. This complex is more conveniently prepared if a slow stream of CO is passed through the solution generated from [IrCl(C_8H_{14})$_2$]$_2$ and Isophos. The IR spectrum of the yellow solid displays a ν(CO) stretch at

1937 cm^{-1} which is nearly identical to the value (1935 cm^{-1}) reported for *trans*-[IrCl(CO)(P*i*Pr$_3$)$_2$].[29]



Scheme 9

If instead of CO a stream of H_2 is passed through the solution obtained from [IrCl(C_8H_{14})$_2$]$_2$ and Isophos, the dihydridoiridium(III) compound **35** is generated. Similarly to the rhodium analogue **13**, it is a yellow air-sensitive solid which is readily soluble in all common organic solvents. Since there is only one resonance (triplet) for the hydrides at $\delta = -26.98$ ppm in the ^{1}H NMR spectrum and only one singlet (triplet in off-resonance) for the ^{31}P nuclei at $\delta = 51.2$ ppm in the ^{31}P NMR spectrum, we assume that the coordination geometry around the iridium center corresponds to a trigonal bipyramid with the P-donors in the apical positions. This geometry has been confirmed crystallographically for [IrH$_2$Cl(*t*Bu$_2$PCH$_2$CMe$_3$)$_2$].[30] As expected, the five-coordinate dihydrido complex **35** adds one molecule of CO to give the octahedral compound **36**, which, in contrast to the precursor, is only slightly air sensitive. The ^{1}H NMR spectrum of **36** displays two signals in the high-field region at $\delta = -8.57$ ppm and $\delta = -19.97$ ppm, which is consistent with the assumption that one of the hydrido ligands is *trans* to CO and the other *trans* to chloride. The triisopropylphosphane counterpart [IrH$_2$Cl(CO)(P*i*Pr$_3$)$_2$] is also known and shows the hydride resonances in the ^{1}H NMR spectrum at $\delta = -8.64$ ppm and $\delta = -20.20$ ppm, respectively.[31]

In conclusion, the work described in this paper illustrates that a series of rhodium and iridium complexes with the phospholanes Isophos and Phephos is accessible following similar preparative routes to those used for the synthesis of the P*i*Pr$_3$ and P*i*Pr$_2$Ph analogues. Owing to the similar size of the phosphanes and the phospholanes (see Scheme 1) and owing to the related donor/acceptor capabilities, it is also not surprising that both the chemical properties and the spectroscopic data of the M(P*i*Pr$_3$)$_2$ and the M(Isophos)$_2$ as well as those of the Rh(P*i*Pr$_2$Ph)$_2$ and the Rh(Phephos)$_2$ complexes are similar. Some preliminary results from catalytic studies reveal that in the hydrogenation of styrene (toluene, 60 °C, ratio catalyst to substrate = 1:100) the Isophos derivative **1** is significantly less active (TOF = 46.6 h^{-1}) than the Wilkinson complex [RhCl(PPh$_3$)$_3$] (TOF = 1250 h^{-1}). Moreover, the optical yield in the hydrogenation of PhCH=C(CO$_2$R)NHC(O)Me (R = H, Me) with **1** as the catalyst under similar conditions is rather low (14% *ee*) and could only be improved slightly in the presence of excess Isophos. Therefore, the aim for the future is to modify the coordination sphere around rhodium (and possibly iridium) in such a way that the phospholanes also become attractive ligands for catalysis, not necessarily only for hydrogenation reactions.

Experimental Section

All operations were carried out under argon using standard Schlenk techniques. The starting materials [RhCl(C_8H_{14})$_2$]$_2$,[32] [RhCl(P*i*Pr$_2$Ph)$_2$]$_2$ (**10**),[2] *trans*-[RhCl(=CPh$_2$)(Sb*i*Pr$_3$)$_2$] (**29**),[26] and [IrCl(C_8H_{14})$_2$]$_2$ [33] were prepared as described in the literature. NMR spectra were recorded at room temperature (if not otherwise stated) on Bruker AC 200 and AMX 400 instruments and IR spectra on a Perkin−Elmer 1420 infrared spectrophotometer. Abbreviations used: s = singlet; d = doublet; t = triplet; q = quadruplet; quin = quintet; m = multiplet; vt = virtual triplet; br = broadened signal, $N = {}^3J_{P,H} + {}^5J_{P,H}$ or ${}^1J_{P,C} + {}^3J_{P,C}$. Melting points were measured by differential thermal analysis (DTA).

Preparation of [RhCl(Isophos)$_2$]$_2$ (1): A suspension of [RhCl(C_8H_{14})$_2$]$_2$ (176 mg, 0.25 mmol) in acetone (2 mL) was treated with Isophos (166 mg, 1.05 mmol) and stirred for 10 min at room temperature. A brick-red solid precipitated which was filtered, washed three times with 1 mL portions of pentane (0 °C) and dried; yield 209 mg (92%); m.p. 54 °C (dec.). ^{1}H NMR (200 MHz, C_6D_6): δ = 2.20 [m, 8 H, CH(ring)], 2.01 [m, 4 H, CH(*i*Pr)], 1.85 [m, 12 H, CH$_3$(*i*Pr)], 1.81 [dvt, $N = 23.3$, $J_{H,H} = 6.9$ Hz, 8 H, CH$_2$(ring)], 1.70 [dvt, $J_{P,H} = 20.8$, $J_{H,H} = 7.3$ Hz, 12 H, CH$_3$(*i*Pr)], 1.40 [m, 8 H, CH$_2$(ring)], 1.38 [dvt, $N = 19.9$, $J_{H,H} = 7.1$ Hz, 12 H, CH$_3$(ring)], 1.17 [dvt, $N = 19.0$, $J_{H,H} = 7.3$ Hz, 12 H, CH$_3$(ring)] ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 37.1 [dt, $J_{Rh,C} = 11.1$, $J_{P,C} = 3.7$ Hz, CH$_2$(ring)], 36.2, 35.0 [both s, CH(ring)], 34.8 [t, $J_{Rh,C} = 12.0$ Hz, CH$_2$(ring)], 28.7 [vt, $N = 18.6$ Hz, CH(*i*Pr)], 22.9 [d, $J_{Rh,C} = 29.6$ Hz, CH$_3$(ring)], 22.4, 17.3 [both s, CH$_3$(*i*Pr)], 14.9 [s, CH$_3$(ring)] ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 75.8 (d, $J_{Rh,P} = 196.2$ Hz) ppm. $C_{36}H_{76}Cl_2P_4Rh_2$ (909.6): calcd. C 47.54, H 8.42; found C 47.43, H 8.18.

Preparation of [RhCl(Phephos)$_2$]$_2$ (2): A suspension of [RhCl(C_8H_{14})$_2$]$_2$ (116 mg, 0.16 mmol) in benzene (2 mL) was treated with Phephos (127 mg, 0.66 mmol) and stirred for 10 min at room temperature. A clear orange-red solution was generated which, after stirring for 2 h, was dried in vacuo. The remaining orange-red solid was washed three times with 1 mL portions of pentane (−78 °C) and dried; yield 125 mg (75%); m.p. 60 °C (dec.). ^{1}H NMR (200 MHz, C_6D_6): δ = 7.74−6.84 (m, 20 H, C_6H_5), 1.62−0.75 [m, 24 H, CH(ring) and CH$_2$(ring)], 1.19, 0.67 [both m, 12 H each, CH$_3$(ring)] ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 71.1 (d, $J_{Rh,P} = 198.0$ Hz) ppm. $C_{48}H_{68}Cl_2P_4Rh_2$ (1045.7): calcd. C 55.13, H 6.55; found C 54.59, H 7.22.

Preparation of [RhCl(Phephos)$_3$] (3): This compound was prepared as described for **2**, with [RhCl(C_8H_{14})$_2$]$_2$ (120 mg, 0.17 mmol) and

Prephos (257 mg, 1.34 mmol) in acetone (2 mL) as starting materials. Orange solid; yield 204 mg (84%); m.p. 59 °C (dec.). ^{1}H NMR (200 MHz, C_6D_6, 295 K): δ = 7.86−6.90 (m, 15 H, C_6H_5), 3.20−0.02 (m, 36 H, ring protons) ppm. ^{13}C NMR (50.3 MHz, C_6D_6, 295 K): δ = 137.9 (br. d, $J_{P,C}$ = 26.8 Hz, *ipso*-C of PC_6H_5), 136.8 (vt, *N* = 26.9 Hz, *ipso*-C of PC_6H_5), 134.0 (vt, *N* = 9.2 Hz, *ortho*-C of PC_6H_5), 133.5 (d, $J_{P,C}$ = 8.3 Hz, *ortho*-C of PC_6H_5), 130.4, 128.7 (both s, *para*-C of PC_6H_5), 126.9 (vt, *N* = 9.2 Hz, *meta*-C of PC_6H_5), 126.8 (d, $J_{P,C}$ = 8.3 Hz, *meta*-C of PC_6H_5), 38.0 (br. dvt, *N* = 23.1 Hz, CH), 34.6, 34.4, 34.3, 34.2 (all br. s, CH_2), 33.7 (br. s, CH), 31.9 (d, $J_{P,C}$ = 25.9 Hz, CH), 23.7 [d, $J_{P,C}$ = 12.0 Hz, CH_3(ring)], 23.3 [vt, *N* = 12.0 Hz, CH_3(ring)], 16.6, 15.9 [both s, CH_3(ring)] ppm. ^{31}P NMR (81.0 MHz, C_6D_6, 295 K): δ = 69.1 (dt, $J_{Rh,P}$ = 145.2, $J_{P,P}$ = 39.6 Hz, Phephos *trans* to Cl), 49.4 (br. s, Phephos *cis* to Cl) ppm. ^{31}P NMR (81.0 MHz, C_6D_6, 330 K): δ = 69.4 (dt, $J_{Rh,P}$ = 185.1, $J_{P,P}$ = 39.2 Hz, Phephos *trans* to Cl), 49.9 (dd, $J_{Rh,P}$ = 137.9, $J_{P,P}$ = 39.2 Hz, Phephos *cis* to Cl) ppm. $C_{36}H_{51}ClP_3Rh$ (715.1): calcd. C 60.47, H 7.19; found C 60.34, H 7.08.

Generation of [RhCl(Isophos)$_3$] (4): A solution of $[RhCl(C_8H_{14})_2]_2$ (70 mg, 0.10 mmol) in [D_8]toluene (0.5 mL) was treated with Isophos (127 mg, 0.80 mmol) and stirred for 10 min at room temperature. The ^{31}P NMR spectrum revealed that a mixture of **1** and **4** in the ratio of 1:9 was formed. Attempts to separate **4** from the by-product failed. Data for **4**: ^{31}P NMR (81.0 MHz, [D_8]toluene): δ = 84.2 (dt, $J_{Rh,P}$ = 190.7, $J_{P,P}$ = 41.2 Hz, Isophos *trans* to Cl), 59.0 (br. s, Isophos *cis* to Cl].

Preparation of *trans*-[RhCl(CO)(Isophos)$_2$] (5): A slow stream of CO was passed through a solution of either **1** (120 mg, 0.13 mmol) or **7** (24 mg, 0.05 mmol) in benzene (5 mL) for 30 s at room temperature. A change of color from brick-red to pale yellow occurred. The solvent was evaporated in vacuo and, after recrystallization of the residue from pentane at −78 °C, a pale yellow solid was isolated; yield 111 mg (88%) from **1** or 22 mg (92%) from **7**; m.p. 174 °C (dec.). IR (benzene): ν(CO) = 1947 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 2.10−1.60 [m, 10 H, CH(ring), CH(*i*Pr), CH_2(ring)], 1.55 [dvt, *N* = 24.3, $J_{H,H}$ = 7.1 Hz, 6 H, CH_3(*i*Pr)], 1.40 [m, 4 H, CH_2(ring)], 1.31 [dvt, *N* = 23.0, $J_{H,H}$ = 7.1 Hz, 6 H, CH_3(*i*Pr)], 1.19 [dvt, *N* = 21.2, $J_{H,H}$ = 7.0 Hz, 6 H, CH_3(ring)], 1.18 [dvt, *N* = 21.6, $J_{H,H}$ = 7.1 Hz, 6 H, CH_3(ring)] ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 189.3 (dt, $J_{Rh,C}$ = 73.7, $J_{P,C}$ = 15.3 Hz, RhCO), 36.5 [vt, *N* = 28.1 Hz, CH(ring)], 36.0, 35.8 [both s, CH_2(ring)], 34.8 [vt, *N* = 24.1 Hz, CH(ring)], 25.0 [vt, *N* = 20.0 Hz, CH(ring)], 21.3 [s, CH_3(ring)], 20.5 [vt, *N* = 9.0 Hz, CH_3(ring)], 18.9, 15.4 [both s, CH_3(ring)] ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 53.1 (d, $J_{Rh,P}$ = 118.2 Hz) ppm. $C_{19}H_{38}ClOP_2Rh$ (482.82): calcd. C 47.27, H 7.93; found C 47.30, H 8.02.

Preparation of *trans*-[RhCl(CO)(Phephos)$_2$] (6): A slow stream of CO was passed through a solution of either **2** (120 mg, 0.12 mmol) or **3** (50 mg, 0.07 mmol) in benzene (5 mL) for 30 s at room temperature. The solution was then worked-up as described for **5**. Pale yellow solid; yield 111 mg (88%) from **2** or 36 mg (94%) from **3**; m.p. 131 °C (dec.). IR (benzene): ν(CO) = 1961 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.96 (m, 4 H, *ortho*-H of C_6H_5), 7.10 (m, 6 H, *meta*-, *para*-H of C_6H_5), 3.39−0.75 [m, 12 H, CH(ring), CH_2(ring)], 1.72, 0.86 [both m, 6 H each, CH_3(ring)] ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 186.5 (dt, $J_{Rh,C}$ = 74.0, $J_{P,C}$ = 16.2 Hz, RhCO), 134.1 (vt, *N* = 12.0 Hz, *ortho*-C of C_6H_5), 132.5 (vt, *N* = 32.4 Hz, *ipso*-C of C_6H_5), 129.7 (s, *para*-C of C_6H_5), 127.6 (vt, *N* = 9.2 Hz, *meta*-C of C_6H_5), 35.1 [d, $J_{P,C}$ = 25.0 Hz, CH(ring)], 34.3 [d, $J_{P,C}$ = 13.9 Hz, CH(ring)], 33.6 [vt, *N* = 13.0 Hz, CH_2(ring)], 21.3 [vt, *N* = 12.0 Hz, CH_3(ring)], 14.9 [s, CH_3(ring)] ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 48.6 (d, $J_{Rh,P}$ = 123.9 Hz) ppm. $C_{25}H_{34}ClOP_2Rh$ (550.85): calcd. C 54.51, H 6.22; found C 54.37, H 6.27.

Preparation of *trans*-[RhCl(C_2H_4)(Isophos)$_2$] (7): A slow stream of ethene was passed through a solution of **1** (120 mg, 0.13 mmol) in benzene (5 mL) for 2 min at room temperature. A change of color from brick-red to pale yellow occurred. The solution was worked up as described for **5**. Pale yellow solid; yield 110 mg (88%); m.p. 72 °C. IR (hexane): ν(C=C) = 1510 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 2.52, 2.28 (both m, 2 H each, C_2H_4), 2.12−1.80 [m, 10 H, CH(ring), CH(*i*Pr), CH_2(ring)], 1.78 [dd, $J_{P,H}$ = 16.0, $J_{H,H}$ = 8.7 Hz, 6 H, CH_3(*i*Pr)], 1.63 [dd, $J_{P,H}$ = 14.6, $J_{H,H}$ = 7.3 Hz, 6 H, CH_3(*i*Pr)], 1.33 [m, 4 H, CH_2(ring)], 1.26 [dd, $J_{P,H}$ = 14.7, $J_{H,H}$ = 7.3 Hz, 6 H, CH_3(ring)], 1.02 [dd, $J_{P,H}$ = 13.9, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3(ring)] ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 46.7 (d, $J_{Rh,P}$ = 121.4 Hz) ppm. $C_{20}H_{42}ClP_2Rh$ (482.87): calcd. C 49.75, H 8.77; found C 49.30, H 8.72.

Generation of *trans*-[RhCl(C_2H_4)(Phephos)$_2$] (8): A slow stream of ethene was passed through a solution of **2** (50 mg, 0.05 mmol) in C_6D_6 (0.5 mL) for 5 min at room temperature. The ^{31}P NMR spectrum revealed that **2** and **8** were present in equal amounts. If the ethene atmosphere was replaced by argon, the starting material was regenerated. Attempts to separate the two compounds failed. Data for **8**: ^{31}P NMR (81.0 MHz, C_6D_6): δ = 48.8 (d, $J_{Rh,P}$ = 125.5 Hz) ppm.

Preparation of *trans*-[RhCl(PhC≡CPh)(Phephos)$_2$] (9): A solution of $[RhCl(C_8H_{14})_2]_2$ (85 mg, 0.12 mmol) in benzene (10 mL) was treated dropwise with a solution of Phephos (102 mg, 0.53 mmol) in benzene (2 mL) at room temperature. After stirring the solution for 30 min, a solution of diphenylacetylene (21 mg, 0.12 mmol) in benzene (2 mL) was added. The reaction mixture was stirred for 4 h and then the solvent was evaporated in vacuo. The residue was dissolved in acetone (1 mL), the solution was layered with pentane (5 mL) and stored for 12 h at −78 °C. Orange-yellow crystals precipitated which were filtered, washed twice with 2 mL portions of pentane (0 °C) and dried; yield 109 mg (72%); m.p. 81 °C (dec.). ^{1}H NMR (200 MHz, C_6D_6): δ = 8.25, 7.86 (both m, 4 H each, C_6H_5), 7.65 (m, 2 H, C_6H_5), 7.24 (m, 10 H, C_6H_5), 2.78−1.05 [m, 6 H, CH(ring), CH_2(ring)], 2.22 [br. vt, *N* = 24.0 Hz, 6 H, CH_3(ring)], 0.68 [br. vt, *N* = 19.3 Hz, 6 H, CH_3(ring)] ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 135.0 (vt, *N* = 10.8 Hz, *ortho*-C of PC_6H_5), 132.7 (vt, *N* = 28.0 Hz, *ipso*-C of PC_6H_5), 132.0, 129.2, 128.7, 128.3 (all s, C_6H_5), 127.4 (vt, *N* = 8.2 Hz, *meta*-C of PC_6H_5), 88.2 (dt, $J_{Rh,C}$ = 15.7, $J_{P,C}$ = 2.8 Hz, Ph*C*≡*C*Ph), 37.1 [vt, *N* = 24.4 Hz, CH(ring)], 35.8, 35.5 [both s, CH_2(ring)], 31.9 [vt, *N* = 23.0 Hz, CH(ring)], 21.0 [vt, *N* = 11.6 Hz, CH_3(ring)], 15.7 [s, CH_3(ring)] ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 41.9 (d, $J_{Rh,P}$ = 121.3 Hz) ppm. $C_{38}H_{44}ClP_2Rh$ (701.1): calcd. C 65.10, H 6.33; found C 64.85, H 6.09.

Generation of [RhH_2(Isophos)$_2$(μ-Cl)$_2$Rh(Isophos)$_2$] (11): A solution of **1** (45 mg, 0.05 mmol) and **13** (45 mg, 0.10 mmol) in C_6D_6 (0.5 mL) was stirred for 3 h at room temperature. The ^{1}H and ^{31}P NMR spectra revealed that compound **11** was generated. Attempts to isolate **11** failed. Characteristic data for **11**: ^{1}H NMR (200 MHz, C_6D_6): δ = −21.50 (dt, $J_{Rh,H}$ = 24.7, $J_{P,H}$ = 14.5 Hz) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 74.5 [d, $J_{Rh,P}$ = 193.3 Hz, *cis*-Rh(Isophos)$_2$], 64.0 [d, $J_{Rh,P}$ = 114.4 Hz, *trans*-Rh(Isophos)$_2$] ppm.

Generation of [RhH_2(P*i*Pr_2Ph)$_2$(μ-Cl)$_2$Rh(P*i*Pr_2Ph)$_2$] (12): A solution of **10** (21 mg, 0.02 mmol) and **14** (21 mg, 0.04 mmol) in C_6D_6 (0.5 mL) was stirred for 3 h at room temperature. The ^{1}H and ^{31}P NMR spectra revealed that compound **12** had formed. Attempts

to isolate **12** failed. Characteristic data for **12**: ^{1}H NMR (200 MHz, C_6D_6): δ = −21.46 (dt, $J_{Rh,H}$ = 22.8, $J_{P,H}$ = 16.0 Hz) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 55.7 [d, $J_{Rh,P}$ = 196.2 Hz, *cis*-Rh(P*i*Pr$_2$Ph)$_2$], 48.5 [d, $J_{Rh,P}$ = 117.1 Hz, *trans*-Rh(P*i*Pr$_2$Ph)$_2$] ppm.

Preparation of [RhClH$_2$(Isophos)$_2$] (13): A solution of **1** (120 mg, 0.13 mmol) in toluene (5 mL) was stirred for 5 min at −78 °C under a H_2 atmosphere. Upon warming the solution slowly to room temperature, a change of color from brick-red to yellow occurred. After stirring for 15 min, the solvent was evaporated in vacuo and the residue was extracted with pentane (10 mL). The extract was dried in vacuo to give a yellow solid; yield 90 mg (76%); m.p. 64 °C (dec.). IR (KBr): ν(RhH) = 2155 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 2.04−1.84 [m, 10 H, CH(ring), CH(*i*Pr), CH$_2$(ring)], 1.83 [dd, $J_{P,H}$ = 16.3, $J_{H,H}$ = 6.9 Hz, 6 H, CH$_3$(*i*Pr)], 1.46 [dd, $J_{P,H}$ = 13.6, $J_{H,H}$ = 7.0 Hz, 6 H, CH$_3$(*i*Pr)], 1.32 [m, 4 H, CH$_2$(ring)], 1.30 [dd, $J_{P,H}$ = 13.9, $J_{H,H}$ = 6.9 Hz, 6 H, CH$_3$(ring)], 1.10 [dd, $J_{P,H}$ = 13.6, $J_{H,H}$ = 6.8 Hz, 6 H, CH$_3$(ring)], −22.00 (dt, $J_{Rh,H}$ = 26.0, $J_{P,H}$ = 14.6 Hz, 2 H, RhH) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 64.0 (d, $J_{Rh,P}$ = 113.1 Hz) ppm. $C_{18}H_{40}ClP_2Rh$ (456.8): calcd. C 47.33, H 8.83; found C 47.30, H 8.82.

Preparation of [RhClH$_2$(P*i*Pr$_2$Ph)$_2$] (14): A suspension of **10** (100 mg, 0.095 mmol) in pentane (2 mL) was stirred for 5 min at −50 °C under a H_2 atmosphere. The suspension was slowly warmed to room temperature, which led to a smooth change of color from dark violet to yellow. After stirring for 1 h at 20 °C, the yellow solution was concentrated in vacuo to ca. 1 mL and stored for 3 h at 0 °C. A yellow solid precipitated, which was separated from the mother liquor and dried; yield 88 mg (87%); m.p. 67 °C (dec.). IR (KBr): ν(RhH) = 2164 cm^{-1}. ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 7.85 (m, 4 H, *ortho*-H of C_6H_5), 7.12 (m, 6 H, *meta*- and *para*-H of C_6H_5), 2.63 (m, 4 H, PC*H*CH$_3$), 1.29 (dvt, *N* = 15.0, $J_{H,H}$ = 7.1 Hz, 12 H, PCHC*H*$_3$), 1.01 (dvt, *N* = 14.3, $J_{H,H}$ = 7.0 Hz, 12 H, PCHC*H*$_3$), −21.24 (dt, $J_{Rh,H}$ = 24.8, $J_{P,H}$ = 14.4 Hz, 2 H, RhH$_2$) ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 134.8 (vt, *N* = 11.6 Hz, *ortho*-C of C_6H_5), 129.9 (s, *para*-C of C_6H_5), 127.9 (vt, *N* = 9.1 Hz, *meta*-C of C_6H_5), 127.7 (d, $J_{P,C}$ = 18.5 Hz, *ipso*-C of C_6H_5), 24.3 (vt, *N* = 24.6 Hz, P*C*HCH$_3$), 19.4, 18.9 (both s, PCH*C*H$_3$) ppm. ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ = 53.7 (d, $J_{Rh,P}$ = 119.1 Hz) ppm. $C_{24}H_{40}ClP_2Rh$ (528.9): calcd. C 54.50, H 7.62; found C 54.24, H 7.49.

Generation of [RhH$_2$(Phephos)$_2$(μ−Cl)$_2$Rh(Phephos)$_2$] (15): A slow stream of H_2 was passed for 20 s through a solution of **2** (50 mg, 0.05 mmol) in C_6D_6 (0.5 mL) at room temperature. The ^{1}H and ^{31}P NMR spectra revealed that an equilibrium between **2** and **15** was established which, even after repeated addition of H_2, could not be completed shifted to the side of the dinuclear complex. If the hydrogen atmosphere was replaced by argon, compound **15** was reconverted into **2**. Characteristic data for **15**: ^{1}H NMR (200 MHz, C_6D_6): δ = −20.77 (dt, $J_{Rh,H}$ = 24.7, $J_{P,H}$ = 14.5 Hz) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 69.9 [d, $J_{Rh,P}$ = 195.8 Hz, *cis*-Rh(Phephos)$_2$], 52.2 [d, $J_{Rh,P}$ = 118.4 Hz, *trans*-Rh(Phephos)$_2$] ppm.

Preparation of [Rh(η^3-2-MeC$_3$H$_4$)(Phephos)$_2$] (16): A suspension of [RhCl(C$_8$H$_{14}$)$_2$]$_2$ (82 mg, 0.11 mmol) in diethyl ether (2 mL) was treated at 0 °C with Phephos (88 mg, 0.46 mmol) and stirred for 30 min at 0 °C. A clear orange-red solution was formed to which a 0.8 M solution of 2-MeC$_3$H$_4$MgCl in THF (0.58 mL, 0.46 mmol) was added dropwise. A change of color from orange-red to yellow occurred. After stirring the reaction mixture for 30 min at room temperature, the solvent was removed in vacuo and the residue was extracted with pentane (20 mL). The extract was dried in vacuo, the remaining orange-yellow air-sensitive solid was washed three times with 1 mL portions of acetone (0 °C) and dried; yield 98 mg (82%); m.p. 55 °C (dec.). ^{1}H NMR (200 MHz, 278 K, C_6D_6): δ = 7.52 (m, 6 H, *meta*-, *para*-H of C_6H_5), 7.20 (m, 4 H, *ortho*-H of C_6H_5), 2.92−0.72 [m, 12 H, CH(ring), CH$_2$(ring)], 2.84 (d, $J_{P,H}$ = 3.3 Hz, 1 H, allyl-H$_{syn}$), 2.64 (d, $J_{P,H}$ = 2.9 Hz, 1 H, allyl-H$_{syn}$), 2.18 (d, $J_{P,H}$ = 6.2 Hz, 1 H, allyl-H$_{anti}$), 1.78 (d, $J_{P,H}$ = 5.8 Hz, 1 H, allyl-H$_{anti}$), 1.66 (d, $J_{Rh,H}$ = 2.2 Hz, 3 H, allyl-CH$_3$), 1.31 [dd, $J_{P,H}$ = 15.4, $J_{H,H}$ = 7.3 Hz, 3 H, CH$_3$(ring)], 1.22 [dd, $J_{P,H}$ = 15.4, $J_{H,H}$ = 6.9 Hz, 3 H, CH$_3$(ring)], 0.49 [dd, $J_{P,H}$ = 13.2, $J_{H,H}$ = 6.9 Hz, 3 H, CH$_3$(ring)], 0.35 [dd, $J_{P,H}$ = 13.5, $J_{H,H}$ = 6.9 Hz, 3 H, CH$_3$(ring)] ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 139.9 (d, $J_{P,C}$ = 21.3 Hz, *ipso*-C of C_6H_5), 139.4 (d, $J_{P,C}$ = 22.2 Hz, *ipso*-C of C_6H_5), 134.1 (d, $J_{P,C}$ = 2.8 Hz, *ortho*-C of C_6H_5), 133.8 (d, $J_{P,C}$ = 1.9 Hz, *ortho*-C of C_6H_5), 128.8, 128.7 (both s, *para*-C of C_6H_5), 127.5, 127.4 (both d, $J_{P,C}$ = 3.7 Hz, *meta*-C of C_6H_5), 117.0 [d, $J_{Rh,C}$ = 6.5 Hz, CH$_2$*C*(CH$_3$)CH$_2$], 51.6, 51.2 [both ddd, $J_{P,C}$ = 12.0 and 7.4, $J_{Rh,C}$ = 1.9 Hz, *C*H$_2$C(CH$_3$)CH$_2$], 40.9 [ddd, $J_{P,C}$ = 41.6 and 19.5, $J_{Rh,C}$ = 3.7 Hz, CH(ring)], 35.4 [s, CH$_2$(ring)], 33.2 [t, $J_{P,C}$ = 19.0 Hz, CH(ring)], 26.4 [s, CH$_3$(ring)], 23.5 [d, $J_{P,C}$ = 16.1 Hz, CH$_2$C(*C*H$_3$)CH$_2$], 14.7 [s, CH$_3$(ring)] ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ$_A$ = 62.1, δ$_B$= 62.9 (AB part of ABX spectrum; A, B = P, X = Rh; $J_{A,B}$ = 27.8, $J_{A,X}$ = 195.0, $J_{B,X}$ = 195.7 Hz) ppm. $C_{28}H_{41}P_2Rh$ (542.5): calcd. C 61.99, H 7.62; found C 62.06; H 7.58.

Preparation of [Rh(η^3-C$_3$H$_5$)(Isophos)$_2$] (17): This compound was prepared as described for **16**, with [RhCl(C$_8$H$_{14}$)$_2$]$_2$ (169 mg, 0.24 mmol), Isophos (168 mg, 1.06 mmol) and a 0.56 M solution of C$_3$H$_5$MgBr in diethyl ether (0.42 mL, 0.48 mmol) as starting materials. Orange-yellow air-sensitive solid; yield 159 mg (72%); m.p. 71 °C (dec.). ^{1}H NMR (200 MHz, C_6D_6): δ = 4.76 (m, 1 H, CH$_2$C*H*CH$_2$), 3.55, 3.42 (both m, 1 H each, allyl-H$_{syn}$), 2.31−1.62 [m, 12 H, CH(ring), CH(*i*Pr), CH$_2$(ring), allyl-H$_{anti}$], 1.35 [m, 4 H, CH$_2$(ring)], 1.24 [dd, $J_{H,H}$ = 7.6, $J_{P,H}$ = 3.3 Hz, 6 H, CH$_3$(*i*Pr)], 1.20 [dd, $J_{P,H}$ = 11.0, $J_{H,H}$ = 7.1 Hz, 6 H, CH$_3$(*i*Pr)], 1.15 [dd, $J_{P,H}$ = 11.0, $J_{H,H}$ = 7.1 Hz, 6 H, CH$_3$(ring)], 1.07 [dd, $J_{H,H}$ = 7.1, $J_{P,H}$ = 5.1 Hz, 6 H, CH$_3$(ring)] ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ$_A$ = 65.7, δ$_B$= 67.7 (AB part of ABX spectrum; A, B = P, X = Rh; $J_{A,B}$ = 24.7, $J_{A,X}$ = 206.4, $J_{B,X}$ = 206.0 Hz) ppm. $C_{21}H_{43}P_2Rh$ (460.4): calcd. C 54.78, H 9.41; found C 55.23, H 9.78.

Preparation of [Rh(η^3-C$_3$H$_5$)(Phephos)$_2$] (18): a) This procedure was analogous to that described for **16**, with [RhCl(C$_8$H$_{14}$)$_2$]$_2$ (67 mg, 0.09 mmol), Phephos (72 mg, 0.37 mmol) and a 0.74 M solution of C$_3$H$_5$MgBr in diethyl ether (0.5 mL, 0.37 mmol) as starting materials. Orange-yellow air-sensitive solid; yield 70 mg (74%). b) A suspension of **3** (100 mg, 0.14 mmol) in benzene (5 mL) was treated with a 0.70 M solution of C$_3$H$_5$MgBr in diethyl ether (0.8 mL, 0.56 mmol) at room temperature. A quick change of color from orange to yellow occurred. After stirring the reaction mixture for 30 min, the solvent was evaporated in vacuo, the residue was extracted with pentane (5 mL) and the extract was dried in vacuo. The residue was recrystallized from acetone (1 mL) at −78 °C to give an orange-yellow air-sensitive solid; yield 55 mg (75%), m.p. 49 °C (dec.). ^{1}H NMR (200 MHz, 278 K, C_6D_6): δ = 7.61−7.48 (m, 6 H, *meta*-, *para*-H of C_6H_5), 7.06 (m, 4 H, *ortho*-H of C_6H_5), 5.11 (m, 1 H, CH$_2$C*H*CH$_2$), 3.50, 3.29 (both m, 1 H, allyl-H$_{syn}$), 2.66−1.11 [m, 14 H, CH(ring), CH$_2$(ring), allyl-H$_{anti}$], 1.34, 1.31 [both dd, $J_{P,H}$ = 15.0, $J_{H,H}$ = 7.5 Hz, 3 H each, CH$_3$(ring)], 0.69, 0.47 [both dd, $J_{P,H}$ = 13.4, $J_{H,H}$ = 6.9 Hz, 3 H each, CH$_3$(ring)] ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 139.5, 139.3 (both d, $J_{P,C}$ = 19.5 Hz, *ipso*-C of C_6H_5), 133.7 (d, $J_{P,C}$ = 4.6 Hz, *ortho*-C of C_6H_5), 133.5 (d, $J_{P,C}$ = 3.7 Hz, *ortho*-C of C_6H_5), 128.3, 128.2

(both s, *para*-C of C_6H_5), 127.1, 127.0 (both d, $J_{P,C}$ = 2.8 Hz, *meta*-C of C_6H_5), 105.9 (d, $J_{P,C}$ = 5.9 Hz, CH_2CHCH_2), 52.4 (ddd, $J_{P,C}$ = 25.0 and 7.4, $J_{Rh,C}$ = 1.9 Hz, CH_2CHCH_2), 51.2 (ddd, $J_{P,C}$ = 25.0 and 7.4, $J_{Rh,C}$ = 2.8 Hz, CH_2CHCH_2), 40.9 [ddd, $J_{P,C}$ = 41.6, $J_{P,C}$ = 19.5, $J_{Rh,C}$ = 3.7 Hz, CH(ring)], 35.4 [d, $J_{P,C}$ = 11.9 Hz, CH_2(ring)], 35.2 [s, CH_2(ring)], 34.3 [d, $J_{P,C}$ = 21.1 Hz, CH(ring)], 33.3 [d, $J_{P,C}$ = 20.5 Hz, CH(ring)], 23.0 [d, $J_{P,C}$ = 15.7 Hz, CH_3(ring)], 22.6 [d, $J_{P,C}$ = 17.6 Hz, CH_3(ring)], 14.6, 14.5 [both s, CH_3(*i*Pr)] ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ_A = 58.5, δ_B = 61.0 (AB part of ABX spectrum; A, B = P, X = Rh; $J_{A,B}$ = 27.9, $J_{A,X}$ = 116.2, $J_{B,X}$ = 116.9 Hz) ppm. $C_{27}H_{39}P_2Rh$ (528.5): calcd. C 61.37, H 7.44; found C 61.41, H 7.38.

Preparation of [Rh(η^3-$CH_2C_6H_5$)(Isophos)$_2$] (19): A suspension of **1** (90 mg, 0.10 mmol) in diethyl ether (10 mL) was treated dropwise at 0 °C with a 0.86 M solution of $C_6H_5CH_2MgBr$ in diethyl ether (0.23 mL, 0.20 mmol). A gradual change of color from brick-red to deep red occurred. After stirring the reaction mixture for 30 min, it was warmed to room temperature, and then the solvent was evaporated in vacuo. The residue was extracted with pentane (20 mL) and the extract was dried in vacuo. The remaining deep red, air-sensitive solid was washed three times with 1 mL portions of acetone (0 °C) and dried; yield 83 mg (82%). ^{1}H NMR (200 MHz, [D$_8$]toluene): δ = 7.17 (t, $J_{H,H}$ = 8.2 Hz, 1 H, H^3), 7.07 (t, $J_{H,H}$ = 6.9 Hz, 1 H, H^4), 6.72 (t, $J_{H,H}$ = 6.9 Hz, 1 H, H^2), 6.16 (d, $J_{H,H}$ = 6.2 Hz, 1 H, H^1), 5.79 (d, $J_{H,H}$ = 6.2, 1 H, H^5), 2.11 (t, $J_{P,H}$ = 2.4 Hz, 2 H, CH_2), 2.30−0.23 (m, 38 H, Isophos protons) ppm; the phenyl protons are numbered clockwise beginning at the position next to the carbon atom carrying the CH_2 group. ^{31}P NMR (81.0 MHz, [D$_8$]toluene): δ = 76.0 (dd, $J_{Rh,P}$ = 260.8, $J_{P,P}$ = 24.0 Hz), 64.9 (dd, $J_{Rh,P}$ = 177.7, $J_{P,P}$ = 24.4 Hz) ppm. $C_{25}H_{45}P_2Rh$ (510.5): calcd. Rh 20.16; found Rh 20.08.

Preparation of [Rh(η^3-$CH_2C_6H_5$)(Phephos)$_2$] (20): This compound was prepared as described for **16**, with $[RhCl(C_8H_{14})_2]_2$ (120 mg, 0.17 mmol), Phephos (135 mg, 0.70 mmol) and a 0.86 M solution of $C_6H_5CH_2MgBr$ in diethyl ether (0.39 mL, 0.34 mmol) as starting materials. Deep red, air-sensitive solid; yield 156 mg (80%). ^{1}H NMR (200 MHz, C_6D_6): δ = 7.73−6.90 (m, 10 H, C_6H_5), 6.60 (t, $J_{H,H}$ = 7.3 Hz, 1 H, H^2), 6.11 (d, $J_{H,H}$ = 7.3 Hz, 1 H, H^1), 6.04 (d, $J_{H,H}$ = 7.7 Hz, 1 H, H^5), 2.74−0.23 [m, 12 H, CH(ring), CH_2(ring)], 0.78 [dd, $J_{P,H}$ = 14.3, $J_{H,H}$ = 7.3 Hz, 6 H, CH_3(ring)], 0.66 [dd, $J_{P,H}$ = 15.7, $J_{H,H}$ = 7.3 Hz, 3 H, CH_3(ring)], 0.46 (dd, $J_{P,H}$ = 13.2, $J_{H,H}$ = 7.0 Hz, 3 H, CH_3(ring)] ppm; the phenyl protons are numbered clockwise beginning at the position next to the carbon atom carrying the CH_2 group; signal for benzylic CH_2 protons partially covered by signals of H^1 and H^2, signals of H^3 and H^4 probably covered by that of the C_6H_5 protons. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 139.1 (d, $J_{P,C}$ = 23.1 Hz, *ipso*-C of C_6H_5), 137.8 (d, $J_{P,C}$ = 19.4 Hz, *ipso*-C of C_6H_5), 133.1 (d, $J_{P,C}$ = 4.6 Hz, *ortho*-C of C_6H_5), 132.9 (d, $J_{P,C}$ = 2.8 Hz, *ortho*-C of C_6H_5), 132.1 (s, C^{2,4}), 129.3, 128.8 (both s, *para*-C of C_6H_5), 126.9, 126.7 (both d, $J_{P,C}$ = 2.8 Hz, *meta*-C of C_6H_5), 120.5 (s, CCH_2), 115.8 (s, C^3), 105.8 (d, $J_{P,C}$ = 7.4 Hz, C^{1,3}), 39.0 [br. d, $J_{P,C}$ = 25.0 Hz, CH(ring)], 37.8 [d, $J_{P,C}$ = 25.6 Hz, CH(ring)], 36.1 [d, $J_{P,C}$ = 17.6 Hz, CH(ring)], 34.5, 32.5 [both m, CH_2(ring)], 31.6 [d, $J_{P,C}$ = 19.4 Hz, CH(ring)], 23.6 [d, $J_{P,C}$ = 14.8 Hz, CH_3(ring)], 22.5 [d, $J_{P,C}$ = 16.7 Hz, CH_3(ring)], 14.6, 13.1 [both d, $J_{P,C}$ = 2.8 Hz, CH_3(ring)] ppm; signal of benzylic CH_2 carbon atom not located exactly. ^{31}P NMR (81.0 MHz, C_6H_6): δ = 65.2 (dd, $J_{Rh,P}$ = 256.8, $J_{P,P}$ = 28.0 Hz), 58.10 (dd, $J_{Rh,P}$ = 180.6, $J_{P,P}$ = 30.5 Hz) ppm. $C_{31}H_{41}P_2Rh$ (578.5): calcd. Rh 17.79; found Rh 18.21.

Preparation of [Rh_2H_4(Isophos)$_4$] (21): A solution of **17** (150 mg, 0.33 mmol) in pentane (10 mL) was stirred at −78 °C for 5 min under a H_2 atmosphere. The solution was then slowly warmed to room temperature, which led to a change of color from yellow dark green. After stirring for 15 min, the solvent was evaporated in vacuo, the remaining dark green, extremely air-sensitive solid was washed three times with 2 mL portions of acetone (−78 °C) and dried; yield 128 mg (92%). IR (hexane): ν(RhH) = 2001 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 2.76−0.18 (m, 76 H, Isophos protons), −10.20 (tquint, $J_{P,H}$ = 27.6, $J_{Rh,H}$ = 8.2 Hz, 2 H, RhH_2Rh), −17.50 (dt, $J_{P,H}$ = 16.7, $J_{Rh,H}$ = 1.5 Hz, 2 H, RhH_2) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 77.8 [d, $J_{Rh,P}$ = 109.0 Hz, *trans*-Rh(Isophos)$_2$], 72.1 [d, $J_{Rh,P}$ = 161.3 Hz, *cis*-Rh(Isophos)$_2$] ppm. Alternatively, instead of **17** compound **19** could be used as starting material; the yield of **21** (determined by NMR spectroscopy) was quantitative.

Generation of [Rh_2H_4(Prephos)$_4$] (22): A slow stream of H_2 was passed through a solution of **20** (50 mg, 0.09 mmol) in C_6D_6 (0.5 mL) at room temperature. A change of color from deep red to black occurred. Removal of the solvent in vacuo led to quick decomposition. Therefore, the product was characterized by ^{1}H and ^{31}P NMR spectroscopy in the presence of hydrogen. Data for **22**: ^{1}H NMR (200 MHz, C_6D_6): δ = −11.2 (br. m), −18.1 (br. m) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 73.8 [d, $J_{Rh,P}$ = 111.9 Hz, *trans*-Rh(Prephos)$_2$], 65.4 [d, $J_{Rh,P}$ = 157.7 Hz, *cis*-Rh(Prephos)$_2$].

Preparation of *trans*-[RhH(CO)(Isophos)$_2$] (23): A slow stream of CO was passed through a solution of **21** (130 mg, 0.15 mmol) in hexane (10 mL) for 30 s at room temperature. A quick change of color from dark green to yellow occurred. The solvent was evaporated in vacuo, the residue was dissolved in pentane (3 mL) and the solution was stored for 12 h at −78 °C. Yellow air-sensitive crystals precipitated which were separated from the mother liquor and dried; yield 126 mg (94%); m.p. 64 °C. IR (hexane): ν(RhH) = 2065, ν(CO) 1965 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 2.15 [m, 2 H, CH(*i*Pr)], 2.00−1.43 [m, 12 H, CH(ring), CH_2(ring)], 1.24 [dvt, *N* = 23.6, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3(*i*Pr)], 1.10 [dvt, *N* = 23.7, $J_{H,H}$ = 7.9 Hz, 6 H, CH_3(*i*Pr)], 1.09 [dvt, *N* = 21.7, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3(ring)], 0.88 [dvt, *N* = 21.7, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3(ring)], −10.36 (dt, $J_{P,H}$ = 6.9, $J_{Rh,H}$ = 4.9 Hz, 1 H, RhH) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 35.8 (d, $J_{Rh,P}$ = 136.6 Hz) ppm. $C_{19}H_{39}OP_2Rh$ (448.4): calcd. C 50.90, H 8.77; found C 51.04, H 8.79.

Generation of *trans*-[RhCl(PhC≡CH)(Isophos)$_2$] (24) and [RhHCl-(C≡CPh)(Isophos)$_2$] (25): A solution of **1** (15 mg, 0.02 mmol) in C_6D_6 (0.5 mL) was treated dropwise with phenylacetylene (11 μL, 10 mg, 0.10 mmol) at room temperature. A quick change of color from brick-red to yellow occurred. The ^{1}H and ^{31}P NMR spectra indicated that compound **24** had formed. If the solution was stored for 10 min, new signals appeared in the NMR spectra which were assigned to intermediate **25** and the final product **26**. Attempts to isolate **24** or to separate **25** from **26** failed. Characteristic data for **24**: ^{1}H NMR (200 MHz, C_6D_6): δ = 4.11 (d, $J_{Rh,H}$ = 2.9 Hz, ≡CH), 1.88 (m, 6 H, CH_3), 1.59 (m, 6 H, CH_3), 1.30 (m, 6 H, CH_3), 0.90 (m, 3 H, CH_3), 0.60 (m, 3 H, CH_3) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ_A = 44.8, δ_B = 44.0 (AB part of ABX spectrum; A, B = P, X = Rh; $J_{A,B}$ = 36.0, $J_{A,X}$ = 116.2, $J_{B,X}$ = 117.0 Hz) ppm. Characteristic data for **25**: ^{1}H NMR (200 MHz, C_6D_6): δ = −19.38 (dt, $J_{Rh,H}$ = 21.8, $J_{P,H}$ = 11.6 Hz) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 50.1 (d, $J_{Rh,P}$ = 99.2 Hz) ppm.

Preparation of [RhCl(=C=CHPh)(Isophos)$_2$]$_2$ (26): A solution of **1** (80 mg, 0.09 mmol) in benzene (5 mL) was treated dropwise with a solution of phenylacetylene (24 μL, 22 mg, 0.22 mmol in benzene (2 mL) at room temperature. A quick change of color from brick-

red to yellow occurred. After the solution was stirred for 3 h at 90 °C, a subsequent change of color from yellow to violet took place. The solution was cooled to room temperature, the solvent was evaporated in vacuo, the residue was dissolved in benzene (2 mL) and the solution was chromatographed on Al_2O_3 (neutral, activity grade III, length of column 5 cm). With benzene (20 mL) a colorless fraction was eluted which was discarded. With a mixture of benzene/acetone (10:1), a violet fraction was eluted which was dried in vacuo. The remaining violet solid was washed three times with 2 mL portions of pentane (0 °C) and dried; yield 47 mg (84%); m.p. 118 °C (dec.). ^{1}H NMR (200 MHz, C_6D_6): δ = 7.32−6.83 (m, 5 H, C_6H_5), 3.20−0.84 [m, 14 H, CH(ring), CH(*i*Pr), CH_2(ring)], 1.87 (dt, $J_{P,H}$ = 3.3, $J_{Rh,H}$ = 1.2 Hz, 1 H, =C*H*Ph), 1.61 (m, 6 H, CH_3), 1.34 (m, 12 H, CH_3), 1.17 (m, 6 H, CH_3) ppm. ^{13}C NMR (50.30 MHz, C_6D_6): δ = 296.3 (dt, $J_{Rh,C}$ = 58.5, $J_{P,C}$ = 17.2 Hz, Rh=*C*=C), 128.9, 128.4, 125.4, 125.1 (all s, C_6H_5), 112.3 (dt, $J_{Rh,C}$ = 15.3, $J_{P,C}$ = 7.0 Hz, Rh=C=*C*), 35.6 (s, CH_2), 34.8 [vt, *N* = 23.0 Hz, CH(ring)], 34.4, 34.3 (both vt, *N* = 23.2 Hz, P*C*HCH$_3$), 24.7 [vt, *N* = 17.6 Hz, CH(ring)], 21.5, 21.4 [both s, CH_3(ring)], 19.9, 15.0 (both s, PCH*C*H$_3$) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 47.7 (d, $J_{Rh,P}$ = 134.8 Hz) ppm. $C_{26}H_{44}ClP_2Rh$ (556.9): calcd. C 56.07, H 7.96; found C 55.76, H 7.92.

Generation of *trans*-[RhCl(η^2-(*E*)-PhC≡CCH=CHPh)(Phephos)$_2$] (27): A solution of **2** (100 mg, 0.19 mmol) in C_6D_6 (0.5 mL) was treated dropwise with phenylacetylene (0.12 mL, 1.14 mmol) at room temperature. A gradual change of color from orange-red to deep red occurred. The reaction was monitored by NMR spectroscopy. After 1 h, the starting material had been consumed and the signals of a new compound were observed. Typical data for **27**: ^{1}H NMR (200 MHz, C_6D_6): δ = 7.36, 6.88 (both d, $J_{H,H}$ = 15.4 Hz, CH=CH *trans*-disposed) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 43.4 (d, $J_{Rh,P}$ = 136.2 Hz) ppm.

Reaction of Compound 27 with CO: A slow stream of CO was passed through a solution of **27**, generated as described above, for 20 s at room temperature. The ^{1}H NMR spectrum revealed that besides **6** the enyne (*E*)-PhC≡CCH=CHPh (**28**) was formed which was identified by comparison of the NMR spectroscopic data with those of an authentic sample.[3]

Preparation of *trans*-[RhCl(=CPh$_2$)(Isophos)$_2$] (30): A suspension of **29** (50 mg, 0.06 mmol) in pentane (10 mL) was treated at −78 °C with a solution of Isophos (20 mg, 0.12 mmol) in pentane (5 mL) and, after warming to room temperature, stirred for 1 h. The solvent was evaporated in vacuo, the residue was dissolved in hexane (2 mL) and the solution was chromatographed on Al_2O_3 (neutral, activity grade III, length of column 3.0 cm). With diethyl ether a green fraction was eluted, which was dried in vacuo. The remaining green solid was washed twice with 2 mL portions of hexane (0 °C) and dried; yield 30 mg (79%); m.p. 65 °C (dec.). ^{1}H NMR (200 MHz, C_6D_6): δ = 7.99 (m, 2 H, *ortho*-H of C_6H_5), 7.30 (m, 1 H, *para*-H of C_6H_5), 6.98 (m, 2 H, *meta*-H of C_6H_5), 2.37−0.69 [m, 12 H, CH(ring), CH(*i*Pr), CH_2(ring)], 1.90 [dvt, *N* = 16.9, $J_{H,H}$ = 7.2 Hz, 6 H, CH_3(ring)], 1.44 [dvt, *N* = 13.5, $J_{H,H}$ = 7.0 Hz, 6 H, CH_3(*i*Pr)], 1.09 [dvt, *N* = 14.2, $J_{H,H}$ = 7.2 Hz, 6 H, CH_3(*i*Pr)], 0.74 [dvt, *N* = 12.3, $J_{H,H}$ = 7.0 Hz, 6 H, CH_3(ring)] ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 29.5 (d, $J_{Rh,P}$ = 166.9 Hz) ppm. $C_{31}H_{48}ClP_2Rh$ (621.0): calcd. C 59.96, H 7.79, Rh 16.57; found C 60.87, H 7.43, Rh 16.48.

Preparation of *trans*-[RhCl(=CPh$_2$)(Phephos)$_2$] (31): A solution of **29** (112 mg, 0.14 mmol) in pentane (10 mL) was treated at −78 °C with a solution of Phephos (56 mg, 0.29 mmol) in pentane (2 mL) and, after warming to room temperature, stirred for 1 h. The solution was concentrated to ca. 1 mL in vacuo and stored for 2 h. A green microcrystalline solid precipitated, which was separated from the mother liquor, washed twice with 2 mL portions of pentane (0 °C) and dried; yield 90 mg (93%); m.p. 70 °C. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.38−6.64 (m, 20 H, C_6H_5), 3.31−1.10 [m, 12 H, CH(ring), CH_2(ring)], 2.09, 0.85 [both m, 6 H each, CH_3(ring)] ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = 162.2 (vt, *N* = 7.6 Hz, *ipso*-C of C_6H_5), 134.5 (s, *ortho*-C of C_6H_5), 133.2 (vt, *N* = 11.1 Hz, *ortho*-C of C_6H_5), 128.3, 127.5 (both s, *para*-C of C_6H_5), 126.8 (vt, *N* = 7.6 Hz, *meta*-C of C_6H_5), 126.7 (s, *meta*-C of C_6H_5), 34.9, 34.0 [both s, CH_2(ring)], 33.9, 32.0 [both vt, *N* = 22.8 Hz, CH(ring)], 22.5 [vt, *N* = 10.2 Hz, CH_3(ring)], 15.21 [s, CH_3(ring)] ppm; signal of carbene carbon atom could not be exactly located. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 37.3 (d, $J_{Rh,P}$ = 172.5 Hz) ppm. $C_{37}H_{44}ClP_2Rh$ (689.1): calcd. C 64.49, H 6.44, Rh 14.93; found C 64.56, H 6.43, Rh 15.12.

Preparation of *trans*-[IrCl(CO)(Isophos)$_2$] (34): A suspension of $[IrCl(C_8H_{14})_2]_2$ (140 mg, 0.16 mmol) in pentane (10 mL) was treated with Isophos (99 mg, 0.62 mmol) and stirred for 5 min at room temperature. A slow stream of CO was then passed through the solution for 10 min. A yellow solid precipitated which was filtered and recrystallized from a mixture of pentane/THF (10:1). Yellow air-stable crystals were isolated; yield 148 mg (81%); m.p. 232 °C (dec.). IR (CH_2Cl_2): ν(CO) = 1937 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 2.00−1.54 [m, 10 H, CH(ring), CH(*i*Pr), CH_2(ring)], 1.46 [dvt, *N* = 22.8, $J_{H,H}$ = 7.0 Hz, 6 H, CH_3(*i*Pr)], 1.38 [m, 4 H, CH_2(ring)], 1.29 [dvt, *N* = 23.2, $J_{H,H}$ = 7.0 Hz, 6 H, CH_3(*i*Pr)], 1.18 [dvt, *N* = 21.5, $J_{H,H}$ = 7.1 Hz, 6 H, CH_3(ring)], 1.11 [dvt, *N* = 21.4, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3(ring)] ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 7.3 (s) ppm. $C_{19}H_{38}ClIrOP_2$ (572.1): calcd. C 39.89, H 6.70; found C 39.47, H 6.70.

Preparation of [IrClH$_2$(Isophos)$_2$] (35): A suspension of $[IrCl(C_8H_{14})_2]_2$ (140 mg, 0.16 mmol) in hexane (10 mL) was treated with Isophos (99 mg, 0.62 mmol) and stirred for 5 min at room temperature. A slow stream of H_2 was then passed through the solution for 10 min. The solvent was evaporated in vacuo, the residue was dissolved in pentane (3 mL) and the solution was stored for 12 h at −78 °C. Pale yellow air-sensitive crystals precipitated which were filtered, washed twice with 0.5 mL portions of pentane (−20 °C) and dried; yield 133 mg (76%); m.p. 98 °C (dec.). IR (KBr): ν(IrH) = 2290 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 2.10−1.70 [m, 10 H, CH(ring), CH(*i*Pr), CH_2(ring)], 1.78 [dvt, *N* = 22.3, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3(*i*Pr)], 1.44 [dvt, *N* = 21.2, $J_{H,H}$ = 7.0 Hz, 6 H, CH_3(*i*Pr)], 1.34 [m, 4 H, CH_2(ring)], 1.28 [dvt, *N* = 20.7, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3(ring)], 1.08 [dvt, *N* = 21.1, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3(ring)], −26.98 [t, $J_{P,H}$ = 14.2 Hz, 2 H, IrH] ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 51.2 (br. s, t in off-resonance) ppm. $C_{18}H_{40}ClIrP_2$ (546.1): calcd. C 39.59, H 7.38; found C 39.43, H 7.38.

Preparation of [IrClH$_2$(CO)(Isophos)$_2$] (36): A slow stream of CO was passed through a solution of **35** (120 mg, 0.22 mmol) in pentane (5 mL) for 10 min at room temperature. A pale yellow solid precipitated which was filtered and then dissolved in methanol (10 mL). The solution was concentrated to ca. 2 mL in vacuo and stored for 6 h at −78 °C. Pale yellow, moderately air-sensitive crystals precipitated which were washed twice with 0.5 mL portions of methanol (−20 °C) and dried; yield 99 mg (78%); m.p. 185 °C (dec.). IR (KBr): ν(IrH) = 2210, 2005, ν(CO) 1975 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 2.10−1.60 [m, 10 H, CH(ring), CH(*i*Pr), CH_2(ring)], 1.54 [dvt, *N* = 22.7, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3(*i*Pr)], 1.48 [dvt, *N* = 21.2, $J_{H,H}$ = 7.0 Hz, 6 H, CH_3(*i*Pr)], 1.28 [m, 4 H,

CH_2(ring)], 1.24 [dvt, N = 21.2, $J_{H,H}$ = 7.0 Hz, 6 H, CH_3(ring)], 0.94 [dvt, N = 19.7, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3(ring)], −8.57 (dt, $J_{P,H}$ = 18.9, $J_{H,H}$ = 5.8 Hz, 1 H, IrH *trans* to CO), −19.97 (dt, $J_{P,H}$ = 11.6, $J_{H,H}$ = 5.8 Hz, 1 H, IrH *trans* to Cl) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 36.1 (s, t in off-resonance) ppm. $C_{19}H_{40}ClIrOP_2$ (574.1): calcd. C 39.75, H 7.02; found C 39.70, H 7.01.

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[1] Reviews: [1a] H. Werner, *Nachr. Chem. Tech. Lab.* **1992**, *40*, 435−444. [1b] H. Werner, *J. Organomet. Chem.* **1994**, *475*, 45−55. [1c] H. Werner, *Chem. Commun.* **1997**, 903−910.
[2] H. Werner, F. Kukla, P. Steinert, *Eur. J. Inorg. Chem.* **2002**, 1377−1389.
[3] M. Schäfer, J. Wolf, H. Werner, *J. Organomet. Chem.* **1995**, *485*, 85−100.
[4] H. Werner, J. Wolf, A. Höhn, *J. Organomet. Chem.* **1985**, *287*, 395−407.
[5] [5a] W. Oppolzer, M. Wills, C. Starkemann, G. Bernardinelli, *Tetrahedron Lett.* **1990**, 4117−4120. [5b] J. Bakos, A. Orosz, B. Heil, M. Laghmari, P. Lhoste, D. Sinou, *J. Chem. Soc., Chem. Commun.* **1991**, 1684−1685.
[6] M. J. Burk, *J. Am. Chem. Soc.* **1991**, *113*, 8518−8519.
[7] H. Werner, M. Schäfer, O. Nürnberg, J. Wolf, *Chem. Ber.* **1994**, *127*, 27−38.
[8] C. A. Tolman, P. Z. Meakin, D. L. Lindner, J. P. Jesson, *J. Am. Chem. Soc.* **1974**, *96*, 2762−2774.
[9] K. Wang, M. E. Goldman, T. J. Emge, A. S. Goldman, *J. Organomet. Chem.* **1996**, *518*, 55−68.
[10] F. Kukla, Dissertation, University of Würzburg, **1997**.
[11] [11a] J. A. Osborn, F. H. Jardine, J. F. Young, G. Wilkinson, *J. Chem. Soc., A* **1966**, 1711−1732. [11b] Y. Ohtani, A. Yamagishi, M. Fujimoto, *Chem. Lett.* **1977**, 1187−1190.
[12] R. L. Harlow, D. L. Thorn, R. T. Baker, N. L. Jones, *Inorg. Chem.* **1992**, *31*, 993−997.
[13] M. Schäfer, Dissertation, University of Würzburg, **1994**.
[14] K. Vrieze, H. C. Volger, P. W. N. M. van Leeuwen, *Inorg. Chim. Acta Rev.* **1977**, *16*, 211−239.
[15] [15a] D. L. Thorn, J. A. Ibers, *Adv. Chem. Ser.* **1982**, *196*, 117−131. [15b] J. Wolf, O. Nürnberg, M. Schäfer, H. Werner, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1157−1162.
[16] R. K. Brown, J. M. Williams, A. J. Sivak, E. L. Muetterties, *Inorg. Chem.* **1980**, *19*, 370−374.
[17] E. B. Meier, R. R. Burch, E. L. Muetterties, V. W. Day, *J. Am. Chem. Soc.* **1982**, *104*, 2661−2663.
[18] M. D. Fryzuk, W. E. Piers, S. J. Rettig, F. W. B. Einstein, T. Jones, T. A. Albright, *J. Am. Chem. Soc.* **1989**, *111*, 5709−5721.
[19] [19a] A. J. Sivak, E. L. Muetterties, *J. Am. Chem. Soc.* **1979**, *101*, 4878−4887. [19b] R. R. Burch, E. L. Muetterties, V. W. Day, *Organometallics* **1982**, *1*, 188−197.
[20] H. Werner, F. J. Garcia-Alonso, H. Otto, J. Wolf, *Z. Naturforsch., Teil B* **1988**, *43*, 722−726.
[21] H. Werner, U. Brekau, *Z. Naturforsch., Teil B* **1989**, *44*, 1438−1446.
[22] Y. Wakatsuki, N. Koga, H. Werner, K. Morokuma, *J. Am. Chem. Soc.* **1997**, *119*, 360−366.
[23] Y. Wakatsuki, N. Koga, H. Yamazaki, K. Morokuma, *J. Am. Chem. Soc.* **1994**, *116*, 8105−8111.
[24] M. Schäfer, J. Wolf, H. Werner, *J. Chem. Soc., Chem. Commun.* **1991**, 1341−1343.
[25] W. T. Boese, A. S. Goldman, *Organometallics* **1991**, *10*, 782−786.
[26] H. Werner, P. Schwab, E. Bleuel, N. Mahr, P. Steinert, J. Wolf, *Chem. Eur. J.* **1997**, *3*, 1375−1384.
[27] E. Bleuel, Dissertation, University of Würzburg, **2000**.
[28] M. Schulz, Dissertation, University of Würzburg, **1993**.
[29] W. Strohmeier, W. Rheder-Stirnweiss, *Z. Naturforsch., Teil B* **1969**, *24*, 939−940.
[30] L. Dahlenburg, A. Yardimcioglu, *J. Organomet. Chem.* **1985**, *291*, 371−386.
[31] H. Werner, A. Höhn, M. Dziallas, *Angew. Chem.* **1986**, *98*, 1112−1114; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 1090−1092.
[32] A. van der Ent, A. L. Onderdelinden, *Inorg. Synth.* **1990**, *28*, 90−92.
[33] [33a] A. van der Ent, A. L. Onderdelinden, *Inorg. Synth.* **1973**, *14*, 94−95. [33b] J. L. Herde, J. C. Lambert, C. V. Senoff, *Inorg. Synth.* **1974**, *15*, 18−20.

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