From Mononuclear $(C_5H_5CH_2C_5H_4)M$ to Unsymmetrical Dinuclear $M(C_5H_4CH_2C_5H_4)M$ and Heterodinuclear $M(C_5H_4CH_2C_5H_4)M'$ Transition-Metal Complexes[1]

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The reaction of $[CH_2(C_5H_4)_2]Na_2$ (**1**), generated in situ from $CH_2(C_5H_5)_2$ and $NaNH_2$ in THF at −70 °C, with $[RhH(C{\equiv}CR)Cl(py)(PiPr_3)_2]$ (**2**: R = Me; **3**: R = Ph) leads to a mixture of the mono- and dinuclear complexes $[(C_5H_5CH_2C_5H_4)Rh(=C=CHR)(PiPr_3)]$ (**4**, **7**) and $\{[CH_2(C_5H_4)_2][Rh(=C=CHR)(PiPr_3)]_2\}$ (**5**, **8**) which are separated by column chromatography. Traces of the square-planar compounds *trans*-$[RhCl(=C=CHR)(PiPr_3)_2]$ (**6**, **9**) are also obtained. Electrophilic addition of sulfur, tosyl azide, and CF_3CO_2H to the Rh=C bond of the vinylidene complexes **4**, **5**, **7**, and **8** affords thioketene-, ketenimine-, and vinyl–rhodium derivatives (**13**, **14**, **17**–**20**). Upon treatment of **5** or **8** with CuCl, the mixed-metal Rh–Cu and $(Rh–Cu)_2$ complexes **15** and **16** have been isolated. The mononuclear compounds $[(C_5H_5CH_2C_5H_4)MLL']$ [**23**, MLL′ = $Rh(PhC{\equiv}CPh)(PiPr_3)$; **25**, MLL′ = $Rh(\eta^2\text{-}CH_2{=}C{=}CHMe)(PiPr_3)$; **27**, MLL′ = $Ir(C_8H_{14})_2$; **30**, MLL′ = $Ir(C_8H_{14})(PiPr_3)$] are prepared from $(C_5H_5CH_2C_5H_4)Na$ (**10**) and the corresponding rhodium(I) and iridium(I) precursors; in these reactions small amounts of dinuclear $[CH_2(C_5H_4)_2]M_2$ complexes (M = Rh, Ir) are also obtained. The synthesis of the mixed-metal compounds $\{[CH_2(C_5H_4)_2][Rh(=C=CHMe)(PiPr_3)][Ir(C_8H_{14})(PiPr_3)]\}$ (**34**), $\{[CH_2(C_5H_4)_2][M(CO)_2][Ir(C_8H_{14})_2]\}$ (**37**, M = Co; **38**, M = Rh), and $\{[CH_2(C_5H_4)_2][Rh(PhC{\equiv}CPh)(PiPr_3)][Ir(C_6H_4CH{=}CPh)(PiPr_3)]\}$ (**42**) has been achieved from either the cyclopentadiene derivative (e.g. **30**) or the lithiated compoundes $[(LiC_5H_4CH_2C_5H_4)MLL']$ (**35**, **36**). Related unsymmetrical dirhodium complexes $\{[CH_2(C_5H_4)_2][RhLL'][Rh(PhC{\equiv}CPh)(PiPr_3)]\}$ [**33**, RhLL′ = $Rh(=C=CHPh)(PiPr_3)$; **39** RhLL′ = $Rh(CO)_2$; **40**, RhLL′ = $Rh(\eta^2\text{-}CH_2{=}C{=}CHMe)(PiPr_3)$] are prepared on a similar route.

Following our research on compounds of the general composition $\{[CH_2(C_5H_4)_2][ML_n]_2\}$, where M is Co,[2] Rh,[3] and Ir,[3b,4] we became interested in learning whether complexes of this type but with either different *metal centers* or different *coordination spheres* can be prepared. The general aim of this work is to study the chemistry of dinuclear molecules in which the two metal atoms are held in close proximity by one or two bridging ligands and according to this possibility show a cooperative behavior. The considerable potential of this objective as far as bridging units such as $[CH_2(C_5H_4)_2]^{2-}$, $[Me_2Si(C_5H_4)_2]^{2-}$, $[C_2H_4(C_5Me_4)_2]^{2-}$, etc. are concerned has recently been demonstrated by Watts,[5] Katz,[6] Müller-Westerhoff,[7] Bitterwolf,[8] Bergman,[9] Schrock,[10] and Heck et al.[11]

For the synthesis of the *unsymmetrical* complexes $\{[CH_2(C_5H_4)_2][ML_n][M'L'_n]\}$, which were the target of this work, the main difficulty certainly is to find a preparative route that avoids—at least to a larger extent—the formation of the symmetrical analogues $\{[CH_2(C_5H_4)_2][ML_n]_2\}$ and $\{[CH_2(C_5H_4)_2][M'L'_n]_2\}$. Two general strategies have recently been developed. Härter and co-workers used a cyclopentadienyl metal compound such as $[C_5H_5Mn(CO)_3]$ which can be lithiated at the five-membered ring and then treated the metalated derivative with (dimethylamino)fulvene to generate a manganese complex with a π-bonded $C_5H_4CH_2C_5H_5$ ligand.[12] With this as a starting material, heterometallic compounds such as $\{[CH_2(C_5H_4)_2][Mn(CO)_3][C_5H_5TiCl_2]\}$ were obtained. We preferred a more simple procedure which started with $CH_2(C_5H_5)_2$, converted this substrate with *n*BuLi or $NaNH_2$ to $(C_5H_5CH_2C_5H_4)Li$ and $(C_5H_5CH_2C_5H_4)Na$, respectively, and prepared from these intermediates the mononuclear dicarbonylmetal compounds $[(C_5H_5CH_2C_5H_4)M(CO)_2]$ (M = Co, Rh, Ir).[13] These molecules behave similarly to $[(C_5H_5CH_2C_5H_4)Mn(CO)_3]$[12] and, after lithiation, react with carbonylmetal halides to form the mixed-metal complexes $\{[CH_2(C_5H_4)_2][Co(CO)_2][M(CO)_2]\}$ (M = Rh, Ir), etc.[13]

In this paper we describe an extension of this work with the particular emphasis on the preparation of mono- and dinuclear complexes containing a rhodium–vinylidene, rhodium–alkyne, or rhodium–allene unit. Some preliminary results have already been communicated.[14]

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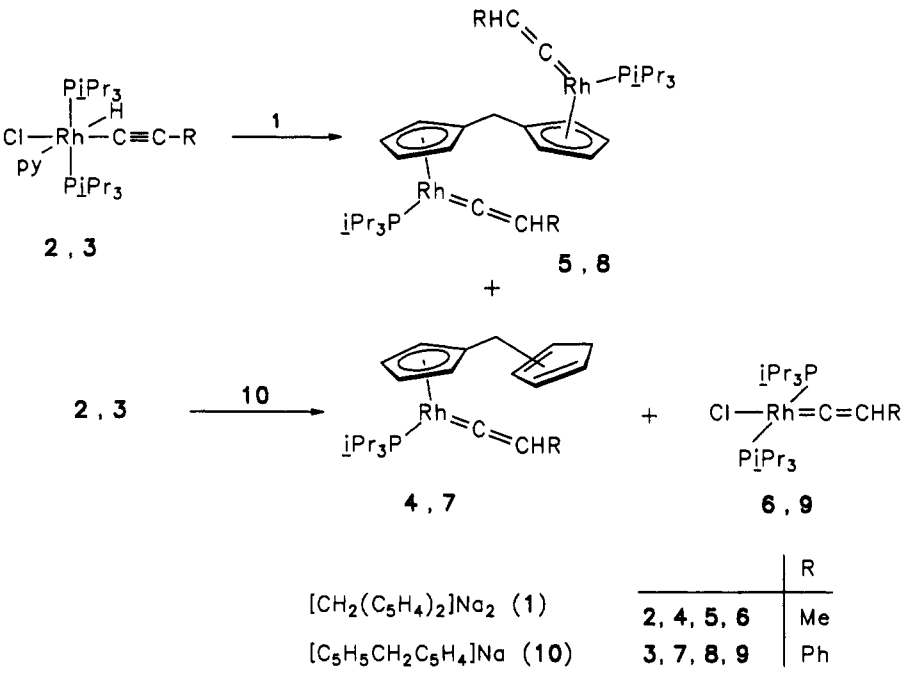
Scheme I



	R
$[CH_2(C_5H_4)_2]Na_2$ (1)	
2, 4, 5, 6	Me
$[C_5H_5CH_2C_5H_4]Na$ (10)	
3, 7, 8, 9	Ph

$$[RhH(C{\equiv}C\underline{t}Bu)Cl(py)(P\underline{i}Pr_3)_2] \xrightarrow{10} [(C_5H_5CH_2C_5H_4)Rh(=C=CH\underline{t}Bu)(P\underline{i}Pr_3)]$$

11 12

Results

Preparation of the Vinylidene Complexes $[(C_5H_5CH_2C_5H_4)Rh(=C=CHR)(PiPr_3)]$ and $[CH_2(C_5H_4)_2][Rh(=C=CHR)(PiPr_3)]_2$. In contrast to most of the earlier work[2-9] on the synthesis of the binuclear complexes $\{[CH_2(C_5H_4)_2][ML_n]_2\}$, where the dilithium derivative $[CH_2(C_5H_4)_2]Li_2$ was used as the source of the bridging unit, we have found that the related disodium compound $[CH_2(C_5H_4)_2]Na_2$ (1) equally is suitable. 1 is formed quantitatively on treatment of a suspension of $NaNH_2$ at −70 °C with a solution of $CH_2(C_5H_5)_2$ in THF, followed by warming to room temperature and irradiation of the reaction mixture in an ultrasonic bath. 1 reacts with $[RhH(C{\equiv}CMe)Cl(py)(PiPr_3)_2]$ (2), which is the preferred starting material for $[C_5H_5Rh(=C=CHMe)(PiPr_3)]$,[15] to give not only $\{[CH_2(C_5H_4)_2][Rh(=C=CHMe)(PiPr_3)]_2\}$ (5) but also in an approximate ratio of 1:1 a mixture of $[(C_5H_5CH_2C_5H_4)Rh(=C=CHMe)(PiPr_3)]$ (4) and 5. The reaction of 1 with $[RhH(C{\equiv}CPh)Cl(py)(PiPr_3)_2]$ (3) proceeds similarly (Scheme I) and also gives $[(C_5H_5CH_2C_5H_4)Rh(=C=CHPh)(PiPr_3)]$ (7) and $\{[CH_2(C_5H_4)_2][Rh(=C=CHPh)(PiPr_3)]_2\}$ (8), respectively. In both cases, the ring-free square-planar vinylidene complexes *trans*-$[RhCl(=C=CHMe)(PiPr_3)_2]$ (6) and *trans*-$[RhCl(=C=CHPh)(PiPr_3)_2]$ (9)[16] are formed as byproducts in ca. 5–7% yield. The three compounds (4–6 and 7–9) can be separated by chromatographic techniques using hexane and hexane/ether mixtures as eluants.

A more convenient procedure for the preparation of the mononuclear complexes 4, 7, and $[(C_5H_5CH_2C_5H_4)Rh(=C=CH\,tBu)(PiPr_3)]$ (12) consists in the reaction of 2, 3, or $[RhH(C{\equiv}C\,tBu)Cl(py)(PiPr_3)_2]$ (11) with $[C_5H_5CH_2C_5H_4]Na$ (10) in THF. After the displaced triisopropylphosphine is trapped by addition of CH_3I, the products are isolated in 70–80% yield. Compounds 4, 7, and 12 as well as the dinuclear complexes 5 and 8 are yellow oils which readily dissolve in all common organic solvents and spontaneously decompose in the presence of air. They have been characterized by elemental analysis and (with the exception of 8) also by mass spectrometry.

The structural proposal depicted in Scheme I for the mono- and the dinuclear species is strongly supported by the ^1H and the ^{13}C NMR spectroscopic data. For the symmetrical molecules 5 and 8, two proton resonances for the ring hydrogens H(2,5) and H(3,4) are observed which in some cases show virtual coupling. In contrast to the NMR spectra of 4 and 7 which display only one set of signals, the spectra of the *tert*-butylvinylidene complex are indicative of the presence of two isomers formed in a 1:1 ratio. We assume that the uncoordinated C_5H_5 ring in 12 is linked either at C(2) or at C(3) to the $[CH_2C_5H_4$-

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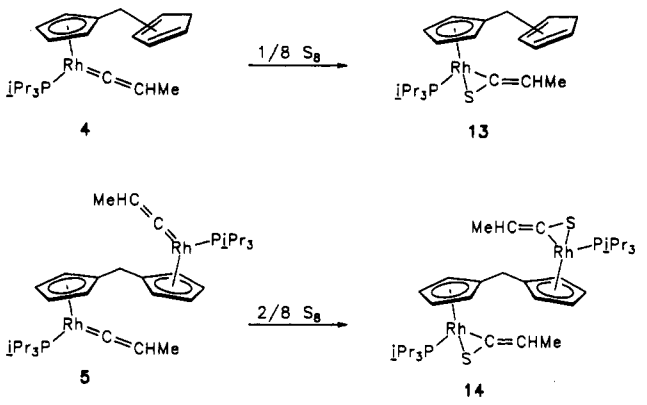
Scheme II



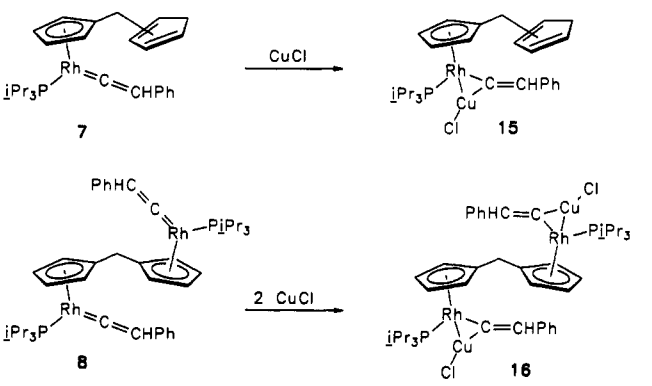
Rh(=C=CH*t*Bu)(P*i*Pr$_3$)] moiety, and thus a similar situation as that found for the dicarbonyl compounds [($C_5H_5CH_2C_5H_4$)M(CO)$_2$] (M = Co, Rh, Ir) would exist.[13] The assignment for the ^{13}C resonances of the C_5H_4 ring carbon atoms follows the rule proposed by Coville that C(1) (*ipso*-C) is less shielded than C(2) and C(5) and these are less so than C(3) and C(4).[17] The chemical shift of the bridging CH_2 carbons of the $C_5H_5CH_2C_5H_4$ and $CH_2(C_5H_4)_2$ ligands corresponds to that of CH_2Ph_2, which is in full agreement with the increment tables for disubstituted methane derivatives.[18]

Both the mononuclear and the dinuclear vinylidene-rhodium complexes behave in a similar way toward electrophiles as the cyclopentadienyl derivatives [C_5H_5-Rh(=C=CHR)(P*i*Pr$_3$)]. Compounds **4** and **5** react with stoichiometric amounts of sulfur (Scheme II) to give the corresponding thioketene–rhodium complexes [(C_5H_5-$CH_2C_5H_4$)Rh(η^2-S=C=CHMe)(P*i*Pr$_3$)] (**13**) and {[CH_2-(C_5H_4)$_2$][Rh(η^2-S=C=CHMe)(P*i*Pr$_3$)]$_2$} (**14**), respectively. Whereas **13** is a red oil at room temperature, **14** is a red solid which for a short period of time can be handled in air. Since only one set of signals is observed in the NMR spectra of **13** and **14**, we assume that the addition of sulfur leads stereoselectively to one diastereomer. If the kinetically preferred product is formed, the attack of the electrophile presumably occurs at that side of the Rh=C bond which is less shielded and, therefore, the *Z* isomer should be obtained. In the case of the cyclopentadienyl complexes [C_5H_5Rh(η^2-S=C=CHR)(P*i*Pr$_3$)], the NMR data have also been interpreted as being in support of this mechanistic proposal.[19]

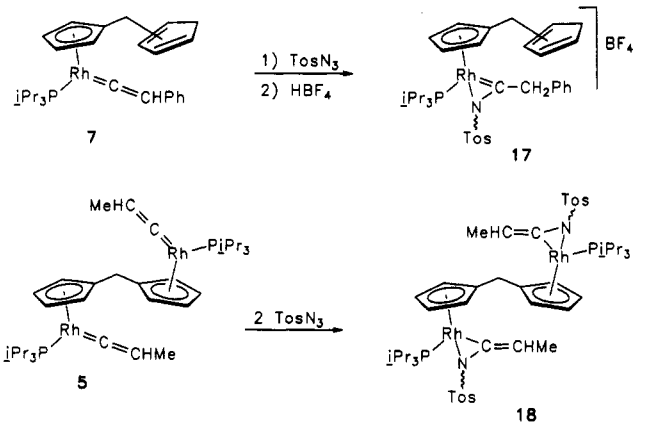
The reaction of **7** and **8** with anhydrous CuCl in THF affords the heterometallic complexes **15** and **16** (Scheme III) in which the α-carbon atom of the vinylidene unit bridges the two different metal centers. The composition of the red crystalline solids has been substantiated by elemental analysis and in the case of **15** also by mass spectrometry. In contrast to [C_5H_5(P*i*Pr$_3$)Rh(μ-C=CH_2)-CuCl][20] and the related osmium compounds [C_6H_6(PR_3)-Os(μ-C=CHPh)CuCl],[21] there is no indication that for **15** and **16** an oligomer or polymeric form exists besides the monomeric one formulated here.

The nucleophilicity of the Rh=C bond in **7** is also illustrated in the reaction with tosyl azide (Scheme IV).

Scheme III



Scheme IV



In analogy to previous work[22] it is conceivable that in the initial step a [2 + 3] cycloaddition between the Rh=C unit and $TosN_3$ occurs to give an intermediate with a five-membered ring RhC(=CHPh)NNNTos which subsequently loses N_2 and forms a η^2-N,C-bonded ketenimine–rhodium complex. As the attempts to purify the crude reaction product by column chromatography failed, the oily substance was dissolved in ether and treated with an equimolar amount of HBF_4. An orange solid was isolated which, owing to conductivity measurements, is a 1:1 electrolyte and analyzes as [($C_5H_5CH_2C_5H_4$)(P*i*Pr$_3$)-RhC(CH_2Ph)NTos]BF_4 (**17**). The NMR data for the cationic compound leave no doubt that the proton attacks not the nitrogen but the β-C atom of the ketenimine ligand. In the ^1H NMR spectrum, the benzylic CH_2 protons (AB system) give rise to two well separated doublets at δ 5.38 and 5.12 with a H–H coupling of 16.4 Hz.

A clean reaction occurs between **5** and tosyl azide to give the crystalline dinuclear ketenimine complex **18** in ca. 70% yield. Also in this case, the NMR spectra indicate that only one diastereomer is formed with the tosyl groups probably pointing away from the rhodium centers. We note that the formally "bisected" relative of **18**, [C_5H_5-Rh(η^2-TosN=C=CHPh)(P*i*Pr$_3$)], has already been described and characterized by an X-ray structural analysis.[22]

Finally, as far as the reactivity of the vinylidene compounds [($C_5H_5CH_2C_5H_4$)Rh(=C=CHR)(P*i*Pr$_3$)] and

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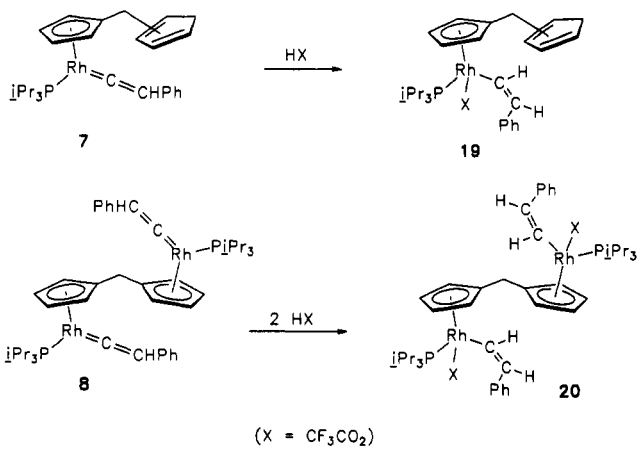
Scheme V



$\{[CH_2(C_5H_4)_2][Rh(=C=CHR)(PiPr_3)]_2\}$ is concerned, it should be mentioned that the tendency to add electrophiles at the Rh=C bond is also confirmed by the reaction of **7** and **8** with CF_3CO_2H (Scheme V). Under mild conditions (25 °C, 15 min) the mono- and dinuclear vinyl trifluoroacetates **19** and **20** are formed and isolated as brown air-sensitive solids. Owing to the extreme lability of **20** in solution, no reliable NMR data could be obtained and thus the compound has been characterized by elemental analysis and the IR data. The proposed structure for **19** with the *Z* configuration of the RhCH=CHPh unit is mainly supported by the ^1H NMR spectrum in which the signals of the vinylic protons show a relatively small H–H coupling of 5.9 Hz.

Mono- and Dinuclear Alkyne, Allene, and Olefin Complexes with $[C_5H_5CH_2C_5H_4]^-$ and $[CH_2(C_5H_4)_2]^{2-}$ as Ligands. Following the synthesis of the mono- and dinuclear vinylidenerhodium complexes **4**, **5**, **7**, and **8**, we tried to find out whether related alkyne compounds with PhC≡CPh and MeC≡CMe as ligands can be prepared on a similar route. The reaction of *trans*-[RhCl(PhC≡CPh)$(PiPr_3)_2$][23] with **10** proceeds smoothly and gives the mononuclear complex $[(C_5H_5CH_2C_5H_4)Rh(PhC{\equiv}CPh)(PiPr_3)]$ (**23**) (Scheme VI) as a yellow air-sensitive oil in 80% yield. Due to the fact that during the preparation of **10** small amounts of the disodium salt **1** are also formed, the dinuclear compound $\{[CH_2(C_5H_4)_2][Rh(PhC{\equiv}CPh)(PiPr_3)]_2\}$ (**24**) is obtained as a byproduct in 4% yield. **23** and **24** are separated by column chromatography and characterized by spectroscopic means. In particular, the NMR data for **23** leave no doubt that as in the case of **12** two isomeric species with a different linkage of the $RhC_5H_4CH_2$ unit to the cyclopentadiene ring are present. The assignment (for details see Experimental Section) of the ^1H and ^{13}C NMR signals is supported both by DEPT, H,H-COSY, and H,C-COSY measurements and also by spectral simulation.[24] It is interesting to note that the formation of two isomers is indicated not only by doubling of the resonances for the C_5H_5, the bridging CH_2, and *ipso*-C_5H_4 carbon atoms but also by the appearance of two sets of signals for the acetylene carbons of the PhC≡CPh ligand, the ^{31}P phosphorus of the coordinated phosphine, and even for the CH_3 protons of the P-bound isopropyl groups.

The reaction of *trans*-[RhCl(MeC≡CMe)$(PiPr_3)_2$] with **10** probably takes the expected course and initially leads to the alkyne complex $[(C_5H_5CH_2C_5H_4)Rh(MeC{\equiv}CMe)(PiPr_3)]$ (^1H NMR, in C_6D_6: δ 2.38 with the intensity of 6H). However, this compound rearranges quantitatively during chromatographic workup on Al_2O_3 to give the isomeric allene rhodium(I) compound $[(C_5H_5CH_2C_5H_4)Rh(\eta^2\text{-}CH_2{=}C{=}CHCH_3)(PiPr_3)]$ (**25**). There is some precedent for such an arrangement insofar as we have found that *trans*-[IrCl(MeC≡CMe)$(PiPr_3)_2$] isomerizes to *trans*-$[IrCl(\eta^2\text{-}CH_2{=}C{=}CHMe)(PiPr_3)_2]$[25] and that the reaction of $[C_5H_5Rh(MeC{\equiv}CMe)(PiPr_3)]$ with acids HX leads to the methallylmetal cation $[C_5H_5Rh(\eta^3\text{-}CH_2CHCHMe)(PiPr_3)]^+$ via the hydrido(methylallene) derivative $[C_5H_5RhH(\eta^2\text{-}CH_2{=}C{=}CHMe)(PiPr_3)]^+$ as an intermediate.[26] Furthermore, Richards et al.[27] have reported the formation of $[ReCl(\eta^2\text{-}CH_2{=}C{=}CHPh)(diphos)_2]$ from $[ReCl(N_2)(diphos)_2]$ (diphos = $Ph_2PCH_2CH_2PPh_2$) and MeC≡CPh, while we recently observed that *trans*-$[RhCl(C_2H_4)(AsiPr_3)_2]$ reacts with HC≡CMe, MeC≡CMe, and MeC≡C*t*Bu to yield the corresponding allene complexes *trans*-$[RhCl(\eta^2\text{-}CH_2{=}C{=}CHR)(AsiPr_3)_2]$ (R = H, Me, *t*Bu), respectively.[28] Compound **25** is an oily air-sensitive substance which has been characterized by NMR spectroscopy. The *trans* disposition of Rh and CH_3 at the uncoordinated C=C bond of the allene ligand is supported by comparison of the ^1H NMR data with those of $[C_5H_5Rh(\eta^2\text{-}CH_2{=}C{=}CHMe)(PiPr_3)]$ where the configuration of the $Rh(CH_2{=}C{=}CHMe)$ unit has been confirmed by deuteration studies.[26]

The synthesis of the (cyclooctene)iridium(I) complexes **27** and **30** with $[C_5H_5CH_2C_5H_4]^-$ as the ring ligand is outlined in Scheme VII. The preparative procedure is similar to that for $[C_5H_5Ir(C_8H_{14})_2]$ and $[C_5H_5Ir(C_8H_{14})(PiPr_3)]$.[29] As has been mentioned in the case of **24**, the formation of traces of **1** during the preparation of **10** explains why minor amounts of $\{[CH_2(C_5H_4)_2][Ir(C_8H_{14})_2]_2\}$ (**28**)[3b] have also been isolated. Both **27** and **30** are oily materials which are moderately air-stable and readily soluble in all common organic solvents.

Unsymmetrical Dirhodium and Dinuclear Mixed-Metal Complexes. After we had observed that the dicarbonyl derivatives $[(C_5H_5CH_2C_5H_4)M(CO)_2]$ (M = Rh, Ir) after lithiation react with $[Co(CO)_4I]$ and $[Rh(CO)_2Cl]_2$ to give the heterodinuclear compounds $\{[CH_2(C_5H_4)_2][M(CO)_2][M'(CO)_2]\}$ in reasonable yields,[13] we tried to prepare a dirhodium complex containing two different vinylidene ligands in the same molecule on a similar route. Unfortunately, the reactions of both **4** with *trans*-[Rh(C≡CPh)(py)$(PiPr_3)_2$] (**31**) and **7** with *trans*-[Rh(C≡CMe)(py)$(PiPr_3)_2$] (**32**) lead to the formation of a mixture of products from which an analytically pure sample of $\{[CH_2(C_5H_4)_2][Rh(=C=CHMe)(PiPr_3)][Rh(=C=CHPh)(PiPr_3)]\}$ could not be isolated.[30] We succeeded, however, in the synthesis of $\{[CH_2(C_5H_4)_2][Rh(=C=CHPh)(PiPr_3)][Rh(PhC{\equiv}CPh)(PiPr_3)]\}$ (**33**) and $\{[CH_2(C_5H_4)_2][Rh(=C=CHMe)(PiPr_3)][Ir(C_8H_{14})$-

(23) Werner, H.; Wolf, J.; Schubert, U.; Ackermann, K. *J. Organomet. Chem.* **1986**, *317*, 327–356.
(24) Schneider, D. Dissertation, University of Würzburg, 1992.
(25) (a) Werner, H.; Höhn, A. *J. Organomet. Chem.* **1984**, *272*, 105–113. (b) Höhn, A. Dissertation, University of Würzburg, 1986.
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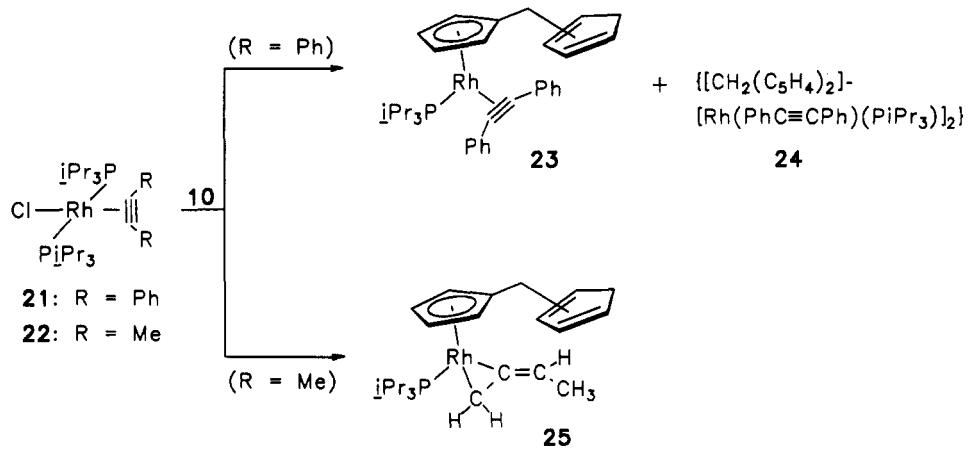
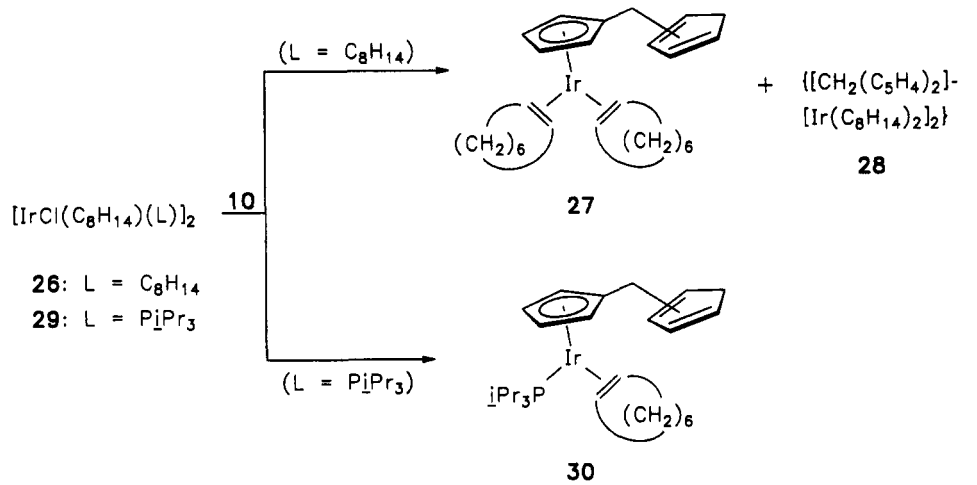
(30) For the discussion of the spectroscopic data see ref 24.

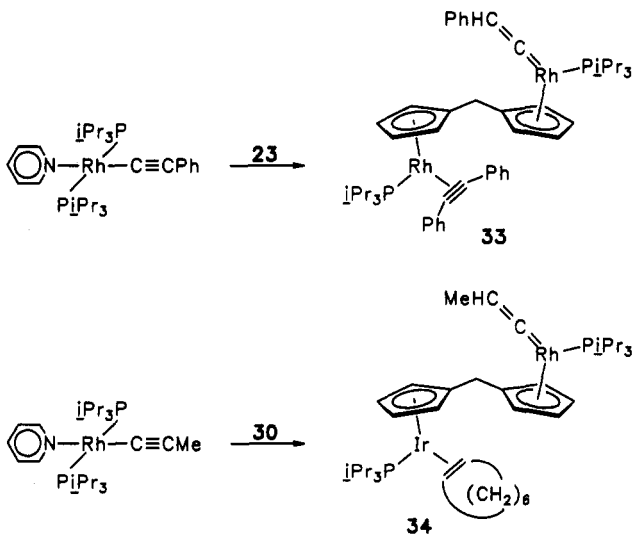
Scheme VI



Scheme VII



Scheme VIII

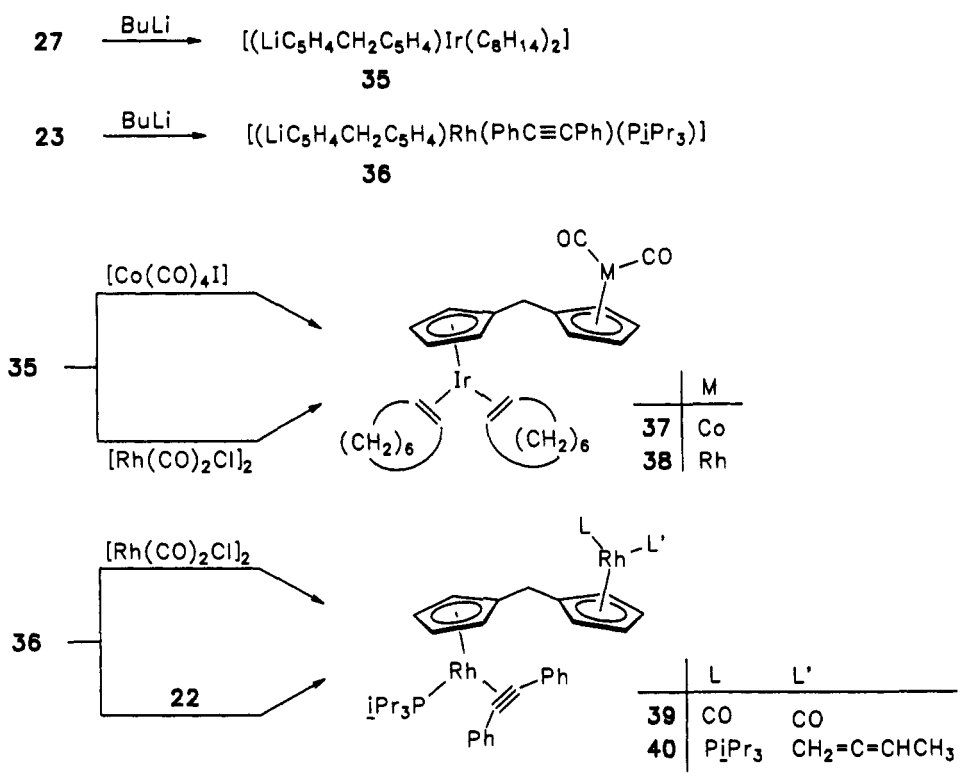


(P*i*Pr$_3$)]} (**34**) (see Scheme VIII) from **23** and **30** using again the square-planar alkynylrhodium complexes **31** and **32** as substrates. Although the yield is rather low in these reactions (10–15%), correct elemental analyses have been obtained for both compounds **33** and **34**. The ^{1}H and ^{31}P NMR data for **33** and **34** prove that indeed the unsymmetrical molecules and not 1:1 mixtures of the symmetrical analogues, e.g. {[CH$_2$(C$_5$H$_4$)$_2$][Rh(=C=CHPh)(P*i*Pr$_3$)]$_2$} (**8**) and {[CH$_2$(C$_5$H$_4$)$_2$][Ir(C$_8$H$_{14}$)(P*i*Pr$_3$)]$_2$}, are present. Although solutions of **33** and **34** are not indefinitely stable, there is no evidence that a conproportionation to give the symmetrical counterparts occurs.

As far as the mechanism of formation of **33** and **34** is concerned, we assume that in the initial step a proton transfer from the substituted cyclopentadiene moiety of **23** or **30** to the metal center of **31** and **32** takes place. The generation of a L$_n$RhH(C≡CMe) intermediate in the reaction of **30** and *trans*-[Rh(C≡CMe)(py)(P*i*Pr$_3$)$_2$] (**32**) is shown in the ^{1}H NMR spectrum by a hydride resonance in the high-field region at δ −13.3 (dd, J(RhH) = 22, J(PH) = 32 Hz) which after stirring the solution for 2 h at room temperature disappears and gives rise to the signals of **34**. In agreement with previous studies[15] we note that the alkynyl(hydrido)rhodium intermediate is relatively labile and this may explain why the yield of the final product (**33** and **34**) is rather low.

A second method to prepare unsymmetrical or mixed-metal dinuclear complexes with [CH$_2$(C$_5$H$_4$)$_2$]$^{2-}$ as a bridging ligand is based on the metalation of precursors such as **23** or **27** with *n*BuLi followed by treatment of the lithium derivatives with a mononuclear carbonyl or (alkyne)metal compound. On this route, complexes **37**–**40** (see Scheme IX) are obtained. For [(LiC$_5$H$_4$CH$_2$C$_5$H$_4$)-Rh(PhC≡CPh)(P*i*Pr$_3$)] (**36**), which can be isolated as an extremely air- and moisture-sensitive solid, the conversion of an uncoordinated C$_5$H$_5$ to a metalated C$_5$H$_4$ ring fragment is clearly confirmed by the NMR data. The ^{13}C NMR spectrum (in THF-d_8) displays one doublet for the *ipso*-C (J(RhC) = 2.9 Hz) and two singlets for the C(2,5) and C(3,4) carbon atoms of the lithiated unit instead of

Scheme IX



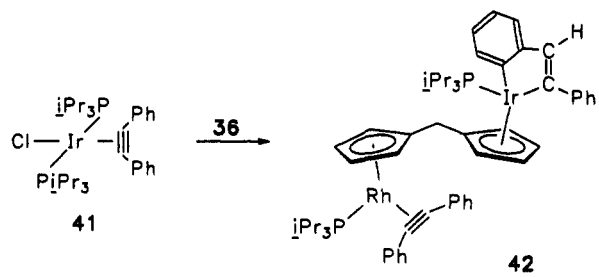
the resonances for the ring CH_2 and CH carbon atoms of **23**. Another characteristic feature is that, in contrast to **23**, the spectrum of **36** shows only one set of signals for the bridging CH_2, the *ipso*-C of C_5H_4Rh, and the Rh-(PhC≡CPh) carbon atoms.

For the dinuclear complexes **37–39**, which are isolated in 40–65% yields, the structural proposal is not only supported by elemental analyses and mass spectra but, in particular, by the IR data. In all cases, two CO stretching vibrations at 2024, 1964 cm^{-1} (**37**) and ca. 2040, 1980 cm^{-1} (**38**, **39**) are observed which have almost the same frequencies as those of the parent $C_5H_5M(CO)_2$ molecules. In contrast to **39**, where both C_5H_4 rings are bonded to rhodium, an unambiguous assignment of the ring carbon resonances in the ^{13}C NMR spectrum is possible for the mixed-metal compound **38** because those signals which belong to the C_5H_4Rh unit are split into a doublet due to Rh–C coupling.

It has already been mentioned that the reaction of **10** with **22** leads to the allene complex **25**, and thus the formation of the unsymmetrical dinuclear compound {$[CH_2(C_5H_4)_2][Rh(\eta^2\text{-}CH_2{=}C{=}CHMe)(PiPr_3)][Rh(PhC{\equiv}CPh)(PiPr_3)]$} (**40**) from **22** and **36** deserves no further comment. With regard to the ^{13}C NMR data for **40**, we note two interesting features, namely (1) the appearance of two doublets-of-doublets-of-doublets for the *ipso*-C atoms of the two five-membered rings which therefore show coupling with *both* rhodium nuclei and (2) the observation of *two* signals for the PhC≡CPh carbons and of *five* signals for the eight CH carbons of the two C_5H_4 units which could be explained by an unsymmetrical coordination of the alkyne to rhodium. The latter may also be due to an unsymmetrical arrangement of the [Rh-(PhC≡CPh)(PiPr3)] fragment to one of the rings possibly caused by steric strain.

Finally, the synthesis of the rhodium–iridium complex {$[CH_2(C_5H_4)_2][Rh(PhC{\equiv}CPh)(PiPr_3)][Ir(C_6H_4CH{=}CPh)(PiPr_3)]$} (**42**) (Scheme X) from *trans*-$[IrCl(PhC{\equiv}CPh)(PiPr_3)_2]$ (**41**) and **36** illustrates once more that in mixed-metal compounds the conversion of a particular ligand is strongly influenced by the respective metal center. Even after prolonged stirring, a second metalation at one of the phenyl groups of the Rh(PhC≡CPh) unit in **42** does not occur and also in the symmetrical molecule **24** (see Scheme VI) no analogous rearrangement takes place. We note that the mononuclear cyclopentadienyl complexes $[C_5H_5Rh(PhC{\equiv}CPh)(PiPr_3)]$ and $[C_5H_5Ir(PhC{\equiv}CPh)(PiPr_3)]$ can also be converted to the isomeric metallacycles $[C_5H_5M(C_6H_4CH{=}CPh)(PiPr_3)]$,[23,25] but in both cases the presence of a strong acid such as CF_3CO_2H or HBF_4 is necessary.

Scheme X



Concluding Remarks

The results described in this article reveal that the recently found preparative route which consists in the stepwise coordination of two metal–ligand fragments to the ring units of the $[CH_2(C_5H_4)_2]^{2-}$ dianion can be used for the synthesis of both unsymmetrical homo- and heterodinuclear complexes. Alkynes, vinylidenes, olefins, and allenes are among the ligands which are tolerated at least at one of the metal centers in the $[CH_2(C_5H_4)_2]$-bridged compounds. The crucial intermediates in the

preparation of the dinuclear complexes are the mononuclear compounds $[(C_5H_5CH_2C_5H_4)MLL']$ (M = Rh, Ir) which react either by direct means or via the lithium derivatives $[(LiC_5H_4CH_2C_5H_4)MLL']$ to give the final products. However, to attain cooperative behavior between the two metal centers, it is probably necessary to introduce a second bridging unit which could be either a dialkyl phosphide, a diphosphine, or a hydride ligand.[2,3] The serendipitous finding that the reaction of the polymeric precursor $\{[CH_2(C_5H_4)_2][IrBr_2]_2\}_n$ with Na_2CO_3/EtOH in the presence of $CH_2{=}CHtBu$ affords the doubly vinyl-bridged dinuclear iridium complex $\{[CH_2(C_5H_4)_2][Ir_2(\mu\text{-}CH{=}CHtBu)_2]\}$[4] by activation of a terminal olefin C—H bond could be considered as an indication that, equally, compounds such as **33**, **34**, or **37–40** in which an unsaturated hydrocarbon ligand is already coordinated to one or both metal atoms may be useful in achieving the final goal.

Experimental Section

General Data. All reactions were carried out under an atmosphere of argon by Schlenk tube techniques. The starting materials $CH_2(C_5H_5)_2$,[31] $(C_5H_5CH_2C_5H_4)Na$ (**10**),[13] *trans*-$[RhCl(RC{\equiv}CR)(PiPr_3)_2]$ (**21**, **22**),[23] $[IrCl(C_8H_{14})_2]_2$ (**26**),[33] $[IrCl(C_8H_{14})(PiPr_3)]_2$ (**29**),[29] *trans*-$[Rh(C{\equiv}CR)(py)(PiPr_3)_2]$ (**31**, **32**),[15] $[Co(CO)_4I]$,[34] $[Rh(CO)_2Cl]_2$,[35] and *trans*-$[IrCl(PhC{\equiv}CPh)(PiPr_3)_2]$ (**41**)[25a] were prepared as described previously. IR spectra were recorded on a Perkin-Elmer 1420 infrared spectrometer and NMR spectra on a Varian EM 360 L, a JEOL FX 90 Q, and Bruker AC 200 and WM 400 instruments. Mass spectra were measured with a Varian MAT CH7 spectrometer.

Preparation of $[CH_2(C_5H_4)_2]Na_2$ (1). A suspension of $NaNH_2$ (43 mg, 1.1 mmol) in 6 mL of tetrahydrofuran (THF) was treated under stirring at −78 °C with a solution of $CH_2(C_5H_5)_2$ (75 mg, 0.52 mmol) in 2 mL of THF. After warming to room temperature, the suspension was put into an ultrasonic bath and irradiated as long as a precipitate was present. The solution was again cooled to −78 °C and left in a modest vacuum (ca. 50–100 Torr) until all of the ammonia had disappeared. The suspension containing a finely divided light-yellow precipitate of **1** was used without further purification. Yield: quantitative.

Reaction of 1 with $[RhH(C{\equiv}CMe)Cl(py)(PiPr_3)_2]$ (2). A suspension of **1** (85 mg, 0.45 mmol) in 6 mL of THF was treated at −20 °C with a solution of **2** (375 mg, 0.65 mmol) in 5 mL of THF, and the resulting solution was stirred for 3 h at room temperature. The solvent was removed and the residue extracted three times with 8 mL of pentane. To remove free triisopropylphosphine, the combined extracts were treated with 1 mL of methyl iodide and the mixture was stirred for 30 min. The precipitate was filtered off, the solvent was removed, and the yellow oily residue was dissolved in a small quantity (ca. 1 mL) of hexane. The solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 15 cm). With hexane, a yellow fraction was eluted which contained the mononuclear compound **4**, yield 78 mg (27%). (For an improved preparation of **4**, see below). With hexane/ether (10:1) a second yellow fraction was obtained which was brought to dryness in vacuum to give yellow air-sensitive oil **5**, yield 80 mg (33%). By increasing the amount of ether, a third fraction was eluted which according to the ^1H and ^{31}P NMR spectra contained the vinylidene complex **6**,[16] yield ca. 5%. Anal. Calcd for $C_{35}H_{60}P_2Rh_2$ (**5**) (mol weight 748.63) C, 56.15; H, 8.08. Found (mol weight 748 (MS)): C, 56.54; H, 8.40. IR (hexane): ν(C=C) 1666 cm^{-1}. ^1H NMR (C_6D_6, 90 MHz): δ 5.49 (m, 4H, H(2) and H(5) of C_5H_4), 4.85 (vt, N = 4.2 Hz, 4H, H(3) and H(4) of C_5H_4), 4.03 (s, br, 2H, CH_2), 3.25 (ddq, J(RhH) = 1.5, J(PH) = 4.4, J(HH) = 7.4 Hz, 2H, =C*H*CH$_3$), 1.98 (m, 6H, PC*H*CH$_3$), 1.90 (ddd, J(RhH) = 0.5, J(PH) = 1.6, J(HH) = 7.4 Hz, 6H, =CHC*H*$_3$), 1.09 (dd, J(PH) = 13.5, J(HH) = 7.3 Hz, 36H, PCHC*H*$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 312.57 (dd, J(RhC) = 65.9, J(PC) = 28.3 Hz, Rh=*C*=CHCH$_3$), 107.94 (dd, J(RhC) = J(PC) = 4.7 Hz, *ipso*-carbons of C_5H_4), 102.96 (dd, J(RhC) = 15.5, J(PC) = 4.2 Hz, Rh=C=*C*HCH$_3$), 86.40 (s, br, C(2,5) of C_5H_4), 83.80 (s, br, C(3,4) of C_5H_4), 29.37 (s, CH_2), 26.48 (d, J(PC) = 21.6 Hz, P*C*HCH$_3$), 19.99 (s, PCH*C*H$_3$), 5.54 (d, J(RhC) = 2.6 Hz, =CH*C*H$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 73.68 (d, J(RhP) = 208.1 Hz, P*i*Pr$_3$).

Reaction of 1 with $[RhH(C{\equiv}CPh)Cl(py)(PiPr_3)_2]$ (3). A suspension of **1** (131 mg, 0.7 mmol) in 8 mL of THF was treated at −20 °C with a solution of **3** (700 mg, 1.1 mmol) in 10 mL of THF, and the mixture was stirred for 3 h at room temperature. The reaction mixture was worked up as described above for **4–6**. The yield was 140 mg (25%) for **7**, 200 mg (42%) for **8**, and ca. 7% for the known vinylidene complex **9**.[16] (For an improved preparation of **7**, see below). Compound **8**, which was isolated as an oil, can be converted into a yellow low-melting solid by storing a highly concentrated solution in pentane at −78 °C, but this procedure is accompanied by a significant decrease in the yield. Anal. Calcd for $C_{45}H_{64}P_2Rh_2$ (**8**): C, 61.93; H, 7.39. Found: C, 62.03; H, 7.50. ^1H NMR (C_6D_6, 90 MHz): δ 6.95 (m, 10H, C_6H_5), 5.22 (m, 4H, H(2) and H(5) of C_5H_4), 4.59 (vt, N = 4.2 Hz, H(3) and H(4) of C_5H_4), 4.19 (dd, J(RhH) = 1.5, J(PH) = 4.6 Hz, 2H, =C*H*C$_6$H$_5$), 3.80 (s, br, 2H, CH_2), 1.58 (m, 6H, PC*H*CH$_3$), 0.74 (dd, J(PH) = 13.8, J(HH) = 6.9 Hz, 36H, PCHC*H*$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 317.59 (dd, J(RhC) = 68.0, J(PC) = 27.9 Hz, Rh=*C*=CHPh), 132.85 (d, J(RhC) = 3.0 Hz, *ipso*-carbon of C_6H_5), 128.34 and 125.11 (both s, *ortho*- and *meta*-carbons of C_6H_5), 124.34 (s, *para*-carbon of C_6H_5), 115.78 (dd, J(RhC) = 14.7, J(PC) = 4.0 Hz, Rh=C=*C*HPh), 108.19 (dd, J(RhC) = J(PC) = 4.3 Hz, *ipso*-carbons of C_5H_4), 86.61 (s, br, C(2,5) of C_5H_4), 84.40 (s, br, C(3,4) of C_5H_4), 29.28 (s, CH_2), 26.77 (d, J(PC) = 22.9 Hz, P*C*HCH$_3$), 19.93 (s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 72.18 (d, J(RhP) = 205.1 Hz, P*i*Pr$_3$).

Alternative Procedure for the Preparation of 8. A solution of **7** (50 mg, 0.1 mmol) in 5 mL of hexane was treated dropwise at −78 °C with 0.4 mL (0.1 mmol) of a 0.25 M solution of *n*BuLi in hexane. An orange, extremely air-sensitive solid precipitated which after 10 min was filtered off, washed twice with 3 mL of pentane and dried in vacuum. The solid was then treated with a solution of **3** (64 mg, 0.1 mmol) in 5 mL of THF, and the mixture was stirred for 2 h at room temperature. The solvent was removed, and the oily residue was extracted three times with 5 mL of pentane/ether (3:1). The combined extracts were brought to dryness in vacuum, and the residue was dissolved in ca. 0.5 mL of hexane and chromatographed on Al_2O_3 (neutral, activity grade V, height of column 10 cm). With hexane/ether (7:1) two yellow fractions were eluted of which the first contained **7** (ca. 10 mg) and the second **8**, yield 23 mg (26%).

Preparation of $[(C_5H_5CH_2C_5H_4)Rh(=C{=}CHCH_3)(PiPr_3)]$ (4). A suspension of **10**, prepared from $CH_2(C_5H_5)_2$ (288 mg, 2.0 mmol) and $NaNH_2$ (47 mg, 1.2 mmol) in 10 mL of THF, was treated at −78 °C with a solution of **2** (340 mg, 0.60 mmol) in 10 mL of THF. After warming to room temperature, the reaction mixture was stirred for 3 h, and then the solvent was removed. The residue was extracted three times with 10 mL of pentane, and the combined extracts were treated with 1 mL of methyl iodide to remove excess P*i*Pr$_3$. After 30 min the solution was filtered, the filtrate was brought to dryness in vacuum, and the oily yellow residue was dissolved in 1 mL of hexane. The solution was chromatographed on Al_2O_3 (neutral, activity grade III, height of column 15 cm). With hexane a yellow fraction was eluted which after evaporation of the solvent gave a yellow air-sensitive oil, yield 214 mg (80%). Anal. Calcd for $C_{23}H_{38}PRh$ (mol weight 446.43): C, 61.88; H, 8.13. Found (mol weight 446 (MS)): C, 62.19; H, 8.22. ^1H NMR (C_6D_6, 90 MHz): δ 6.42 (m, 3H, olefin protons of C_5H_5), 5.52 (m, 2H, H(2) and H(5) of C_5H_4), 4.77 (m,

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2H, H(3) and H(4) of C_5H_4), 3.71 (s, br, 2H, $C_5H_5CH_2C_5H_4$), 3.21 (m, 1H, =CHCH$_3$), 2.99 and 2.76 (both m, 1H each, CH_2 of C_5H_5), 2.10 (m, 3H, PCHCH$_3$), 1.85 (d, J(HH) = 6.8 Hz, 3H, =CHCH$_3$), 1.05 (dd, J(PH) = 13.4, J(HH) = 7.1 Hz, 18H, PCHCH$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 73.60 (d, J(RhP) = 208.1 Hz, P*i*Pr$_3$).

Preparation of [($C_5H_5CH_2C_5H_4$)Rh(=C=CHPh)(P*i*Pr$_3$)] (7) was analogous to that described for **4**, using **10** (prepared from $CH_2(C_5H_5)_2$ and $NaNH_2$, see above) and **3** (382 mg, 0.60 mmol) as starting materials, yielding a yellow air-sensitive oil, 231 mg (76%). Anal. Calcd for $C_{28}H_{38}PRh$ (mol weight 508.49): C, 66.13; H, 7.53. Found (mol weight 508 (MS)): C, 66.06; H, 7.73. ^{1}H NMR (C_6D_6, 90 MHz): δ 6.89 (m, 5H, C_6H_5), 6.24 (m, 3H, olefin protons of C_5H_5), 5.09 (m, 2H, H(2) and H(5) of C_5H_4), 4.53 (m, 2H, H(3) and H(4) of C_5H_4), 4.06 (d, J(PH) = 5.1 Hz, 1H, =CHPh), 3.49 (s, br, 2H, $C_5H_5CH_2C_5H_4$), 2.63 and 2.49 (both m, 1H each, CH_2 of C_5H_5), 1.70 (m, 3H, PCHCH$_3$), 0.73 (dd, J(PH) = 13.9, J(HH) = 7.1 Hz, 18H, PCHCH$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 72.35 (d, J(RhP) = 205.1 Hz, P*i*Pr$_3$).

Preparation of [($C_5H_5CH_2C_5H_4$)Rh(=C=CH*t*Bu)(P*i*Pr$_3$)] (12) was analogous to that described for **4**, using **10** (prepared from $CH_2(C_5H_5)_2$ and $NaNH_2$, see above) and **11** (372 mg, 0.60 mmol) as starting materials, yielding a yellow air-sensitive oil, 193 mg (66%). Anal. Calcd for $C_{26}H_{42}PRh$ (mol weight 488.51): C, 63.93; H, 8.67. Found (mol weight 488 (MS)): C, 64.27; H, 8.84. The spectroscopic data indicate that the two isomers **12a** and **12b** (see results) are formed in a ca. 50:50 ratio. ^{1}H NMR (C_6D_6, 200 MHz): δ 6.76, 6.45, 6.33, 6.22, and 6.11 (all m, 3H, olefin protons of C_5H_5), 5.38 and 5.33 (both s, br, 2H, H(2) and H(5) of C_5H_4), 4.79 (m, 2H, H(3) and H(4) of C_5H_4), 3.78 and 3.75 (both s, br, 2H, $C_5H_5CH_2C_5H_4$), 3.13 (dd, J(RhH) = 1.8, J(PH) = 4.5 Hz, 1H, =CH*t*Bu), 2.95 and 2.78 both m, 2H, CH_2 of C_5H_5), 2.07 (m, 3H, PCHCH$_3$), 1.22 (s, 9H, C(CH$_3$)$_3$), 1.09 (dd, J(PH) = 13.5, J(HH) = 7.1 Hz, 18H, PCHCH$_3$). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 313.07 and 313.00 (both dd, J(RhC) = 66.5, J(PC) = 27.3 Hz, Rh=C=CH*t*Bu), 149.68 and 147.17 (both s, *ipso*-carbon of C_5H_5), 135.58, 133.31, 132.64, 131.05, 127.73, and 127.03 (all s, sp^2-carbons of C_5H_5), 122.39 (dd, J(RhC) = 14.1, J(PC) = 2.1 Hz, Rh=C=CH*t*Bu), 105.64 and 104.79 (both dd, J(RhC) = 7.1, J(PC) = 3.8 Hz, *ipso*-carbon of C_5H_4), 86.68 (s, br, C(2,5) of C_5H_4), 84.04 (s, br, C(3,4) of C_5H_4), 43.68 and 41.27 (both s, CH_2 of C_5H_5), 32.47 and 30.94 (both s, C(CH$_3$)$_3$), 30.11 and 28.06 (both s, $C_5H_5CH_2C_5H_4$), 26.73 (d, J(PC) = 21.9 Hz, PCHCH$_3$), 20.06 (s, PCHCH$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 72.83 and 72.79 (both d, J(RhP) = 208.4 Hz, P*i*Pr$_3$).

Preparation of [($C_5H_5CH_2C_5H_4$)Rh(η^2-S=C=CHMe)(P*i*Pr$_3$)] (13). A solution of **4** (60 mg, 0.13 mmol) in 5 mL of benzene was treated with sulfur (4.5 mg, 0.14 mmol), and the mixture was stirred for 30 min at room temperature. After removal of the solvent, the oily residue was extracted three times with 4 mL of CH_2Cl_2. The combined extracts were brought to dryness in vacuum, the residue was dissolved in a small amount (ca. 0.5 mL) of hexane/ether (5:1), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 8 cm) with hexane/ether (5:1). A red fraction was eluted which after evaporation of the solvent gave a red air-sensitive oil, yield 30 mg (48%). Anal. Calcd for $C_{23}H_{36}PRhS$: C, 57.73; H, 7.58. Found: C, 58.17; H, 7.81. ^{1}H NMR (C_6D_6, 90 MHz): δ 6.30 (m, 3H, olefin protons of C_5H_5), 5.65 (dq, J(PH) = 1.2, J(HH) = 6.6 Hz, 1H, =CHCH$_3$), 5.36 (m, 2H, H(2) and H(5) of C_5H_4), 4.95 (m, 2H, H(3) and H(4) of C_5H_4), 3.29 (s, br, 2H, $C_5H_5CH_2C_5H_4$), 2.75 (m, 2H, CH_2 of C_5H_5), 2.17 (d, J(HH) = 6.6 Hz, 3H, =CHCH$_3$), 1.85 (m, 3H, PCHCH$_3$), 1.03 and 0.93 (both dd, J(PH) = 13.5, J(HH) = 7.0 Hz, 18H, PCHCH$_3$).

Preparation of {[$CH_2(C_5H_4)_2$][Rh(η^2-S=C=CHMe)(P*i*Pr$_3$)]$_2$} (14). A solution of **5** (140 mg, 0.17 mmol) in 5 mL of benzene was treated with sulfur (11 mg, 0.34 mmol), and the mixture was stirred for 45 min at room temperature. After removal of the solvent the residue was extracted three times with 6 mL of ether. The further workup was the same as described for **13**. Red, moderately air-stable crystals were obtained, yield 67 mg (47%); mp 98 °C dec. ^{1}H NMR (C_6D_6, 90 MHz): δ 5.55 (dq, J(PH) = 1.2, J(HH) = 6.4 Hz, 2H, =CHCH$_3$), 5.09 (m, 4H, H(2) and H(5) of C_5H_4), 4.81 (vt, N = 4.6 Hz, 4H, H(3) and H(4) of C_5H_4), 3.73 (s, br, 2H, CH_2), 2.28 (d, J(HH) = 6.4 Hz, 6H, =CHCH$_3$), 1.90 (m, 6H, PCHCH$_3$), 1.05 and 0.95 (both dd, J(PH) = 13.3, J(HH) = 6.9 Hz, 36H, PCHCH$_3$).

Preparation of [($C_5H_5CH_2C_5H_4$)(P*i*Pr$_3$)Rh(μ-C=CHPh)-CuCl] (15). A solution of **7** (110 mg, 0.22 mmol) in 10 mL of THF was treated with CuCl (22 mg, 0.22 mmol, vacuum dried), and the resulting solution was stirred for 30 min at room temperature. The solvent was removed, the residue was extracted with 4 mL of CH_2Cl_2, and the combined extracts were concentrated to ca. 0.5 mL in vacuum. To complete the precipitation, 2 mL of pentane was added and the solution cooled to −78 °C. After 12 h the mother liquor was removed, and the remaining red solid was repeatedly washed with pentane (0 °C) and dried, yield 72 mg (53%); mp 79 °C dec. Anal. Calcd for $C_{28}H_{38}ClCuPRh$ (mol weight 607.52): C, 55.35; H, 6.30. Found (mol weight 607 (MS)): C, 55.31; H, 6.53. IR (KBr): ν(C=C) 1587 cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 7.39 (m, 5H, C_6H_5), 6.34 (m, 3H, olefin protons of C_5H_5), 6.04 (m, 1H, =CHPh), 5.71 and 5.38 (both s, br, 2H, H(2) and H(5) of C_5H_4), 5.23 (vt, N = 4.2 Hz, 2H, H(3) and H(4) of C_5H_4), 3.58 (m, 2H, $C_5H_5CH_2C_5H_4$), 2.95 (m, 2H, CH_2 of C_5H_5), 2.19 (m, 3H, PCHCH$_3$), 1.32 and 1.19 (both dd, J(PH) = 13.8, J(HH) = 7.0 Hz, 18H, PCHCH$_3$). ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 58.10 (d, J(RhP) = 181.1 Hz, P*i*Pr$_3$).

Preparation of {[$CH_2(C_5H_4)_2$][(P*i*Pr$_3$)Rh(μ-C=CHPh)-CuCl]$_2$} (16). A solution of **8** (110 mg, 0.13 mmol) in 10 mL of THF was treated with CuCl (25 mg, 0.26 mmol, vacuum dried), and the resulting solution was stirred for 45 min at room temperature. The further workup was as described for **15**. Red, moderately air-stable crystals were obtained, yield 79 mg (57%); mp 96 °C dec. Anal. Calcd for $C_{45}H_{64}Cl_2Cu_2P_2Rh_2$: C, 50.47; H, 6.02; Cu, 11.87; Rh, 19.22. Found: C, 50.97; H 6.20; Cu, 11.32; Rh, 18.78. IR (CH_2Cl_2): ν(C=C) 1585 cm^{-1}. ^{1}H NMR ($CDCl_3$, 60 MHz): δ 7.31 (m, 10H, C_6H_5), 5.79 (m, 4H, H(2) and H(5) of C_5H_4), 5.43 (m, 2H, =CHPh), 5.03 (m, 4H, H(3) and H(4) of C_5H_4), 3.75 (s, br, 2H, CH_2), 1.97 (m, 6H, PCHCH$_3$), 1.11 and 0.97 (both dd, J(PH) = 13.7, J(HH) = 7.1 Hz, 36H, PCHCH$_3$). ^{31}P NMR ($CDCl_3$, 36.2 MHz): δ 66.85 (d, J(RhP) = 180.1 Hz, P*i*Pr$_3$).

Preparation of [($C_5H_5CH_2C_5H_4$)(P*i*Pr$_3$)Rh(C(CH_2Ph)-NTos)]BF_4 (17). A solution of **7** (125 mg, 0.25 mmol) in 8 mL of pentane was treated dropwise at −78 °C with a solution of tosyl azide (49 mg, 0.25 mmol) in 2 mL of pentane, and the mixture was stirred for 10 min at the same temperature. After warming to 25 °C, the solvent was removed, the oily residue was dissolved in 3 mL of ether, and the solution was treated with 0.5 mL of 50% HBF_4 in ether. An orange solid spontaneously precipitated which was filtered off, repeatedly washed with ether and pentane, and dried, yield 97 mg (51%). Anal. Calcd for $C_{35}H_{46}BF_4NO_2PRhS$: C, 54.92; H, 6.06; N, 1.83; Rh, 13.44. Found: C, 54.80; H, 6.03; N, 1.95; Rh, 13.21. Conductivity (in CH_3NO_2): Λ = 78.2 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(S=O) 1300 and 1145 cm^{-1}. ^{1}H NMR (CD_3NO_2, 90 MHz): δ 7.61 (m, 9H, C_6H_4-CH_3 and C_6H_5), 6.05 (m, 3H, olefin protons of C_5H_5), 5.38 and 5.12 (both d, J(HH) = 16.4 Hz, 2H, CH_2Ph), 4.91 and 4.77 (both s, br, 2H, H(2) and H(5) of C_5H_4), 4.32 (m, 2H, H(3) and H(4) of C_5H_4), 3.36 (m, 2H, $C_5H_5CH_2C_5H_4$), 2.92 (m, 2H, CH_2 of C_5H_5), 2.48 (s, 3H, $C_6H_4CH_3$), 2.20 (m, 3H, PCHCH$_3$), 1.43 and 1.27 (both dd, J(PH) = 14.0, J(HH) = 7.2 Hz, 18H, PCHCH$_3$). ^{31}P NMR (CD_3NO_2, 36.2 MHz): δ 58.69 and 57.00 (both d, J(RhP) = 140.6 Hz, P*i*Pr$_3$).

Preparation of {[$CH_2(C_5H_4)_2$][Rh(η^2-TosN=C=CHMe)(P*i*Pr$_3$)]$_2$} (18). A solution of **5** (172 mg, 0.23 mmol) in 8 mL of pentane was treated dropwise at −78 °C with a solution of tosyl azide (94 mg, 0.48 mmol) in 2 mL of pentane, and the mixture was stirred for 15 min at the same temperature. After warming to 25 °C, the orange precipitate was filtered off, repeatedly washed with pentane (0 °C), and dried, yield 167 mg (67%); mp 75 °C dec. Anal. Calcd for $C_{49}H_{74}N_2O_2P_2Rh_2S_2$: C, 54.14; H, 6.86; N, 2.58; Rh, 18.93. Found: C, 54.16; H, 6.99; N, 2.62; Rh, 19.28. IR (KBr): ν(S=O) 1298 and 1146 cm^{-1}. ^{1}H NMR (C_6D_6, 90 MHz): δ 7.89 and 6.93 (both m, 8H, C_6H_4), 5.13 (m, 4H, H(2) and H(5) of C_5H_4), 4.91 (ddq, J(RhH) = 0.5, J(PH) = 1.2, J(HH) = 6.6 Hz,

2H, =C*H*CH$_3$), 4.66 (vt, N = 4.4 Hz, 4H, H(3) and H(4) of C$_5$H$_4$), 1.93 (s, 6H, C$_6$H$_4$C*H*$_3$), 1.85 (m, 6H, PC*H*CH$_3$), 1.77 (dd, J(PH) = 0.7, J(HH) = 6.6 Hz, 6H, =CHC*H*$_3$), 1.03 and 0.95 (both dd, J(PH) = 13.5, J(HH) = 7.0 Hz, 36H, PCHC*H*$_3$); signal of C*H*$_2$-(C$_5$H$_4$)$_2$ not observed. ^{31}P NMR: (C$_6$D$_6$, 36.2 MHz): δ 63.67 (d, J(RhP) = 172.8 Hz, P*i*Pr$_3$).

Preparation of [(C$_5$H$_5$CH$_2$C$_5$H$_4$)Rh((*Z*)-CH=CHPh)-(OCOCF$_3$)(P*i*Pr$_3$)] (19). A solution of **7** (140 mg, 0.27 mmol) in 5 mL of ether was treated with an equimolar amount of CF$_3$-CO$_2$H; the mixture was stirred for 15 min at room temperature and then filtered. The filtrate was concentrated to ca. 1 mL in vacuum, and 2 mL of pentane was added. To complete the precipitation, the solution was stored for 12 h at −78 °C. A light-brown, air-sensitive solid was obtained which was washed twice with pentane (0 °C) and dried in vacuum, yield 97 mg (58%). Anal. Calcd for C$_{30}$H$_{39}$F$_3$O$_2$PRh: C, 57.88; H, 6.31. Found: C, 57.63; H, 5.98. IR (CH$_2$Cl$_2$): ν(C=O) 1689 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 90 MHz): δ 8.35 (dd, J(PH) = 4.0, J(HH) = 5.9 Hz, 1H, C*H*=CHPh), 7.30 (m, 5H, C$_6$H$_5$), 6.20 (m, 3H, olefin protons of C$_5$H$_5$), 5.22 (s, br, 2H, H(2) and H(5) of C$_5$H$_4$), 4.96 (s, br, 2H, H(3) and H(4) of C$_5$H$_4$), 3.29 (s, br, 2H, C$_5$H$_5$C*H*$_2$C$_5$H$_4$), 2.62 (m, 2H, CH$_2$ of C$_5$H$_5$), 2.20 (m, 3H, PC*H*CH$_3$), 0.98 and 0.86 ((both dd, J(PH) = 13.2, J(HH) = 7.2 Hz, 18H, PCHC*H*$_3$); signal of CH=C*H*Ph not exactly located.

Preparation of {[CH$_2$(C$_5$H$_4$)$_2$][Rh((*Z*)-CH=CHPh)-(OCOCF$_3$)(P*i*Pr$_3$)]$_2$} (20). A solution of **8** (134 mg, 0.15 mmol) in 5 mL of ether was treated with 30 μL of CF$_3$CO$_2$H and stirred for 15 min at room temperature. After the solvent was removed, the residue was recrystallized from THF/pentane (25 to −78 °C). A brown, very air-sensitive solid was formed which was filtered off, washed three times with pentane (0 °C), and dried in vacuum, yield 100 mg (61%); mp 57 °C dec. Anal. Calcd for C$_{49}$H$_{66}$F$_6$O$_4$P$_2$Rh$_2$: C, 53.46; H, 6.04; Rh, 18.70. Found: C, 53.74; H, 6.43; Rh, 18.29. IR (CH$_2$Cl$_2$): ν(C=O) 1692 cm^{-1}. As the compound is not stable in solution, no reliable NMR spectra could be obtained.

Preparation of [(C$_5$H$_5$CH$_2$C$_5$H$_4$)Rh(PhC≡CPh)(P*i*Pr$_3$)] (23) and {[CH$_2$(C$_5$H$_4$)$_2$][Rh(PhC≡CPh)(P*i*Pr$_3$)]$_2$} (24). A suspension of **10** (83 mg, 0.50 mmol) in 8 mL of THF was treated at −78 °C with a solution of **21** (159 mg, 0.25 mmol) in 7 mL of THF. After warming to room temperature, the reaction mixture was stirred for 3 h, and then the solvent was removed. The residue was extracted three times with 8 mL of pentane, the combined extracts were treated with 1 mL of methyl iodide (to remove excess P*i*Pr$_3$), and after 30 min the solution was filtered. The filtrate was brought to dryness in vacuum, the residue was dissolved in ca. 2 mL of hexane, and the solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V, height of column 10 cm). With hexane, first an intense yellow fraction was eluted which after evaporation of the solvent gave **23** as a yellow air-sensitive oil, yield 117 mg (80%). With more hexane, a second yellow fraction was obtained, which contained **24** also as a yellow oil, yield 20 mg (4%).

Anal. Calcd for C$_{34}$H$_{42}$PRh (**23**) (mol weight 584.59): C, 69.86; H, 7.24. Found (mol weight 584 (MS)): C, 70.01; H, 7.50. IR (hexane): ν(C≡C) 1823 cm^{-1}. ^{1}H NMR (C$_6$D$_6$, 400 MHz): (isomer A (see Figure 1)) δ 6.31 (ddt, J(H(2)/H(3)) = 5.2, J(H(1)/H(3)) = J(H(3)/H(4)) = 1.5 Hz, 1H, H(3) of C$_5$H$_5$), 6.16 (ddt, J(H(2)/H(3)) = 5.2, J(H(1)/H(2)) = J(H(2)/H(4)) = 1.7 Hz, 1H, H(2) of C$_5$H$_5$), 5.73 (ddtt, J(H(1)/H(2)) = J(H1)/H(4)) = 1.7, J(H(1)/H(3)) = 1.5, J(H(1)/H(5)) = 0.7 Hz, 1H, H(1) of C$_5$H$_5$), 3.24 (m, 2H, H(5)), 2.60 (dddt, J(H(1)/H(4)) = J(H(2)/H(4)) = 1.7, J(H(3)/H(4)) = J(H(4)/H(5)) = 1.5 Hz, 2H, H(4) of C$_5$H$_5$); (isomer B (see Figure 1)) δ 6.28 (ddt, J(H(3)/H(4)) = 5.4, J(H(1)/H(3)) = J(H(2)/H(3)) = 1.8 Hz, 1H, H(3) of C$_5$H$_5$), 6.04 (ddt, J(H(3)/H(4)) = 5.4, J(H(1)/H(4)) = J(H(2)/H(4)) = 1.4 Hz, 1H, H(4) of C$_5$H$_5$), 5.98 (ddtt, J(H(1)/H(2)) = J(H(1)/H(3)) = 1.8, J(H(1)/H(4)) = 1.4, J(H(1)/H(5)) = 0.7 Hz, 1H, H(1) of C$_5$H$_5$), 3.00 (m, 2H, H(5)), 2.52 (ddd, J(H(1)/H(2)) = J(H(2)/H(3)) = 1.8, J(H(2)/H(4)) = 1.4 Hz, 2H, H(2) of C$_5$H$_5$); (the other signals cannot be definitely assigned to one of the isomers) δ 8.09 (m, 4H, C$_6$H$_5$), 7.27 (m, 6H, C$_6$H$_5$), 5.60 and 5.54 (both m, 2H, H(2′) and H(5′) of C$_5$H$_4$), 5.27 (vt, N = 4.1 Hz, 2H, H(3′) and H(4)′ of C$_5$H$_4$), 1.60 (m, 3H, PC*H*CH$_3$), 0.89 and 0.88 (both dd, J(PH) = 13.0, J(HH) = 7.2 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): (isomer A (see Figure 1)) δ 135.16 (s, C(3) of C$_5$H$_5$), 133.26 (s, C(2) of C$_5$H$_5$), 126.82 (s, C(1) of C$_5$H$_5$), 41.18 (s, C(4) of C$_5$H$_5$), 28.97 (d, J(RhC) = 1.6 Hz, C(5)); (isomer B (see Figure 1)) δ 132.52 (s, C(3) of C$_5$H$_5$), 130.87 (s, C(4) of C$_5$H$_5$), 127.44 (s, C(1) of C$_5$H$_5$), 43.29 (s, C(2) of C$_5$H$_5$), 29.83 (d, J(RhC) = 1.6 Hz, C(5)); (the other signals cannot be definitely assigned to one of the isomers) δ 149.02 and 146.42 (both d, J(RhC) = 2.6 Hz, *ipso*-carbon of C$_5$H$_5$), 133.64 (s, *ipso*-carbon of C$_6$H$_5$), 131.50 and 128.18 (both s, ortho- and meta-carbons of C$_6$H$_5$), 125.86 (s, para-carbon of C$_6$H$_5$), 105.82 and 105.14 (both dd, J(RhC) = 11.6, J(PC) = 2.3 Hz, *ipso*-carbon of C$_5$H$_4$), 96.24 and 96.20 (both dd, J(RhC) = 16.8, J(PC) = 4.8 Hz, PhC≡*C*Ph), 87.70 and 87.64 (both dd, J(RhC) = J(PC) = 2.7 Hz, C(2′) and C(5′) of C$_5$H$_4$), 82.54 (d, J(RhC) = 3.9 Hz, C(3′) and C(4′) of C$_5$H$_4$), 26.54 (d, J(PC) = 20.7 Hz, P*C*HCH$_3$), 20.01 (s, PCH*C*H$_3$); signal of C$_5$H$_5$*C*H$_2$C$_5$H$_4$ not observed; assignment of the carbon atoms of C$_5$H$_5$ confirmed by DEPT measurements. ^{31}P NMR (C$_6$D$_6$, 36.2 MHz): δ 71.85 and 71.78 (both d, J(RhP) = 199.5 Hz, P*i*Pr$_3$).

24: IR (hexane) ν(C≡O) 1834 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ 8.01 (m, 8H, C$_6$H$_5$), 7.26 (m, 12H, C$_6$H$_5$), 5.33 (m, 4H, H(2) and H(5) of C$_5$H$_4$), 5.14 (vt, N = 3.6 Hz, 4H, H(3) and H(4) of C$_5$H$_4$), 2.91 (s, br, 2H, CH$_2$), 1.54 (m, 6H, PC*H*CH$_3$), 0.84 (dd, J(PH) = 13.0, J(HH) = 7.1 Hz, 36H, PCHC*H*$_3$).

Preparation of [(C$_5$H$_5$CH$_2$C$_5$H$_4$)Rh(η^3-CH$_2$=C=CHCH$_3$)-(P*i*Pr$_3$)] (25). A suspension of **10** (84 mg, 0.50 mmol) in 8 mL of THF was treated at −78 °C with a solution of **22** (128 mg, 0.25 mmol). After warming to room temperature, the reaction mixture was worked up as described for **23**. A yellow air-sensitive oil was obtained, yield 74 mg (63%). ^{1}H NMR (C$_6$D$_6$, 90 MHz): δ 6.31 (m, 3H, olefin protons of C$_5$H$_5$), 5.63 (m, 1H, =C*H*CH$_3$), 5.13 (m, 4H, C$_5$H$_4$), 3.27 (m, 2H, C$_5$H$_5$C*H*$_2$C$_5$H$_4$), 2.77 (m, 2H, CH$_2$ of C$_5$H$_5$), 2.17 (dt, J(HH) = 6.5 and 1.7 Hz, 3H, =CHC*H*$_3$), 2.04 (m, 1H, =CH$_2$; the signal of the second =CH$_2$ proton could not be localized), 1.53 (m, 3H, PC*H*CH$_3$), 1.01 (dd, J(PH) = 13.0, J(HH) = 6.6 Hz, 18H, PCHC*H*$_3$). ^{31}P NMR (C$_6$D$_6$, 36.2 MHz): δ 68.85 and 68.77 (both d, J(RhP) = 194.9 Hz, P*i*Pr$_3$).

Preparation of [(C$_5$H$_5$CH$_2$C$_5$H$_4$)Ir(C$_8$H$_{14}$)$_2$] (27) and {[CH$_2$-(C$_5$H$_4$)$_2$][Ir(C$_8$H$_{14}$)$_2$]$_2$} (28). A suspension of **10**, freshly prepared from CH$_2$(C$_5$H$_5$)$_2$ (288 mg, 2.0 mmol) and NaNH$_2$ (55 mg, 1.4 mmol), in 15 mL of THF was treated at −78 °C with **26** (365 mg, 0.41 mmol). After warming to room temperature, the reaction mixture was stirred for 3h. The solvent was removed, and the residue was extracted four times with 8 mL of pentane. The combined extracts were brought to dryness in vacuum, the residue

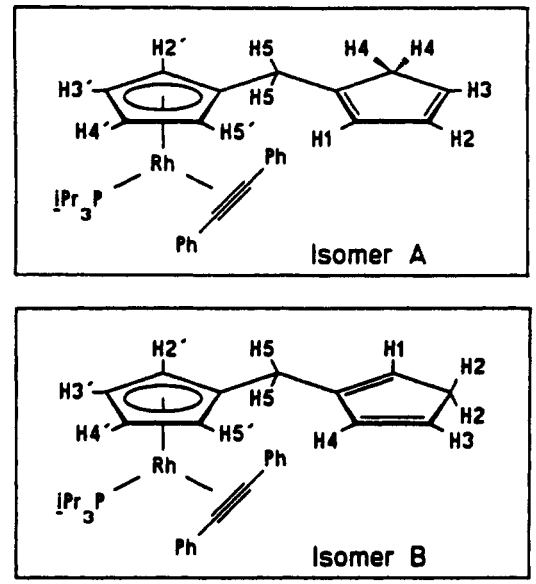

Figure 1. Numbering scheme for the protons and corresponding carbon atoms of isomers A and B of **23**.

was dissolved in 1 mL of hexane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade III, height of column 15 cm). With hexane a pale yellow fraction was eluted which after evaporation of the solvent gave **27** as an almost colorless, only moderately air-sensitive oil, yield 406 mg (89%). With hexane/benzene (10:1) a second fraction was eluted from which after removal of the solvent and recrystallization from pentane (25 to −78 °C) a colorless solid was isolated; yield of **28** 12 mg (3%). The compound was characterized by ^1H and ^{31}P NMR spectroscopic data (for comparison, see ref 3b). **27**: MS (70 eV) m/z (I_r) 556 (4.1; M^+), 446 (21.4; $M^+ - C_8H_{14}$), 336 (18.1; $M^+ - 2\,C_8H_{14}$); ^1H NMR (C_6D_6, 200 MHz) δ 6.61, 6.43, 6.34, 6.23, 6.18, and 5.97 (all m, 3H, olefin protons of C_5H_5, two isomers in approximately equimolar ratios), 4.85 and 4.84 (both vt, N = 3.8 Hz, 2H, H(2) and H(5) of C_5H_4), 4.38 and 4.33 (both vt, N = 3.8 Hz, 2H, H(3) and H(4) of C_5H_4), 3.45 and 3.41 (both m, 2H, $C_5H_5CH_2C_5H_4$), 2.85 and 2.79 (both m, 2H, CH_2 of C_5H_5), 2.20 (m, 4H, =CH of C_8H_{14}), 1.64 and 1.35 (both m, 24H, CH_2 of C_8H_{14}); ^{13}C NMR (C_6D_6, 50.3 MHz) δ 148.60 and 146.43 (both s, *ipso*-carbon of C_5H_5), 134.98, 133.72, 132.64, 131.30, and 127.24 (all s, sp^2-carbons of C_5H_5, one signal covered by the signal of C_6H_6), 102.22 and 101.50 (both s, *ipso*-carbon of C_5H_4), 86.87, 86.71, 86.61, and 86.49 (all s, C(2–5) of C_5H_4), 46.18 and 46.11 (both s, =CH of C_8H_{14}), 43.37 and 41.33 (both s, CH_2 of C_5H_5), 33.62, 33.31 and 26.88 (all s, CH_2 of C_8H_{14}), 26.04 and 23.06 (both s, $C_5H_5CH_2C_5H_4$).

Preparation of $[(C_5H_5CH_2C_5H_4)Ir(C_8H_{14})(PiPr_3)]$ (30). A solution of **29**, freshly prepared from **26** (168 mg, 0.19 mmol) and $PiPr_3$ (61 mg, 0.38 mmol), in 10 mL of hexane was treated at −20 °C with a suspension of **10** (83 mg, 0.50 mmol) in 7 mL of THF. After warming to 45 °C, the reaction mixture was stirred for 90 min and then the solvent was removed. The residue was extracted four times with 6 mL of pentane/benzene (1:1), and the combined extracts were brought to dryness in vacuum. The oily residue was dissolved in 1 mL of benzene, and the solution was chromatographed on Al_2O_3 (neutral, activity grade I, height of column 8 cm). With hexane/benzene (7:1) a red fraction was eluted from which after evaporation of the solvent a red air-sensitive oil was isolated, yield 85 mg (38%). ^1H NMR (C_6D_6, 60 MHz): δ 6.11 (m, 3H, olefin protons of C_5H_5), 4.97 (vt, N = 3.9 Hz, 2H, H(2) and H(5) of C_5H_4), 4.52 (m, 2H, H(3) and H(4) of C_5H_4), 3.59 (s, br, 2H, $C_5H_5CH_2C_5H_4$), 2.81 (m, 2H, CH_2 of C_5H_5), 2.34 (m, 2H, =CH of C_8H_{14}), 1.65 (m, 12H, CH_2 of C_8H_{14}), 1.01 (dd, J(PH) = 12.3, J(HH) = 6.2 Hz, 18H, PCHCH_3), signal of PCHCH$_3$ covered by other signals. ^{31}P NMR (C_6D_6, 36.2 MHz): δ 25.20 and 25.12 (both s, $PiPr_3$).

Preparation of $\{[CH_2(C_5H_4)_2][Rh(=C=CHPh)(PiPr_3)]$-$[Rh(PhC\equiv CPh)(PiPr_3)]\}$ (33). A solid sample of **31** (110 mg, 0.18 mmol) was treated at −10 °C with a solution of **23** (97 mg, 0.18 mmol) in 10 mL of THF. After warming to room temperature, the reaction mixture was stirred for 2 h, and then the solvent was removed. The oily residue was extracted three times with 5 mL of pentane, and the combined extracts were treated with 0.5 mL of methyl iodide. After 30 min, the solution was filtered and the solvent was evaporated in vacuum. The residue was dissolved in 1 mL of hexane and the solution was chromatographed on Al_2O_3 (neutral, activity grade IV, height of column 12 cm). With hexane a yellow fraction was eluted which contained nonreacted **23**. With hexane/ether (10:1) an orange fraction was obtained which after repeated chromatography and removal of the solvent gave an orange air-sensitive oil, yield 19 mg (11%). Anal. Calcd for $C_{51}H_{68}P_2Rh$: C, 64.56; H, 7.22. Found: C, 65.73; H, 7.53. IR (hexane): ν(C≡C) 1834 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 8.08 and 7.08 (both m, 15H, C_6H_5), 5.22 and 5.17 (both m, 4H, H(2) and H(5) of C_5H_4), 4.83 and 4.67 (both m, 4H, H(3) and H(4) of C_5H_4), 3.41 (m, 1H, =CHPh), 2.92 (s, br, 2H, CH_2), 1.59 (m, 6H, PCHCH$_3$), 0.88 and 0.67 (both dd, J(PH) = 12.8, J(HH) = 7.0 Hz, 36H, PCHCH_3).

Preparation of $\{[CH_2(C_5H_4)_2][Rh(=C=CHMe)(PiPr_3)]$-$[Ir(C_8H_{14})(PiPr_3)]\}$ (34). A solid sample of **32** (85 mg, 0.14 mmol) was treated with a solution of **30** (85 mg, 0.14 mmol) and stirred for 2 h at room temperature. The reaction mixture was worked up as described for **33**. After separation of nonreacted **30** by chromatography, with hexane/ether a second yellow fraction was eluted which after removal of the solvent gave a yellow air-sensitive oil, yield 16 mg (13%). Anal. Calcd for $C_{40}H_{70}IrP_2Rh$: C, 52.91; H, 7.77. Found: C, 54.17; H, 7.58. ^1H NMR (C_6D_6, 200 MHz): δ 5.45 and 5.04 (both m, 4H, H(2) and H(5) of C_5H_4), 4.83 and 4.75 (both m, 4H, H(3) and H(4) of C_5H_4), 3.93 (s, br, 2H, CH_2), 3.28 (m, 1H, =CHCH$_3$), 2.46 (m, 2H, =CH of C_8H_{14}), 1.80 (d, J(HH) = 7.0 Hz, 3H, =CHCH_3), 1.62 (m, 12H, CH_2 of C_8H_{14}), 1.09 and 1.03 (both dd, J(PH) = 13.0, J(HH) = 7.0 Hz, 36H, PCHCH_3), signal of PCHCH$_3$ obscured by signal of C_8H_{14} protons. ^{31}P NMR (C_6D_6, 36.2 MHz): δ 73.68 (d, J(RhP) = 208.2 Hz, $PiPr_3$ at Rh), 25.20 (s, $PiPr_3$ at Ir).

Preparation of $[(LiC_5H_4CH_2C_5H_4)Ir(C_8H_{14})_2]$ (35). A solution of **27** (165 mg, 0.30 mmol) in 15 mL of ether was treated at −78 °C under stirring dropwise with a 2 M solution of *n*BuLi (0.2 mL, 0.4 mmol) in hexane. After warming to room temperature, the solvent was removed and the residue repeatedly washed with pentane until the mother liquor remained colorless. A white, extremely air-sensitive solid was obtained which was directly used for the preparation of **37** and **38**, yield 163 mg (97%).

Preparation of $[(LiC_5H_4CH_2C_5H_4)Rh(PhC\equiv CPh)(PiPr_3)]$ (36) was analogous to that described for **35**, using **23** (176 mg, 0.30 mmol) as starting material. A yellow, very air-sensitive solid was obtained, yield 168 mg (95%). ^1H NMR (THF-d_8, 200 MHz): δ 7.93 (m, 4H, C_6H_5), 7.19 (m, 6H, C_6H_5), 5.48 (s, br, 2H, C_5H_4), 5.42 (vt, N = 5.1 Hz, 2H, C_5H_4), 5.35 (m, 2H, C_5H_4), 5.26 (m, 2H, C_5H_4), 3.02 (s, br, 2H, CH_2), 1.87 (m, 3H, PCHCH$_3$), 1.05 (dd, J(PH) = 12.9 Hz, J(HH) = 7.1 Hz, 18H, PCHCH_3). ^{13}C NMR (THF-d_8, 50.3 MHz): 134.75 (s, *ipso*-carbon of C_6H_5), 131.93 and 128.28 (both s, *ortho*- and *meta*-carbons of C_6H_5), 125.72 (s, *para*-carbon of C_6H_5), 120.18 (d, J(RhC) = 2.9 Hz, *ipso*-carbon of C_5H_4Li), 112.28 (dd, J(RhC) = 9.7, J(PC) = 2.6 Hz, *ipso*-carbon of C_5H_4Rh), 103.07 and 102.09 (both s, C(2–5) of C_5H_4Li), 97.46 (dd, J(RhC) = 17.1, J(PC) = 4.9 Hz, PhC≡CPh), 87.47 (s, br, C(2) and C(5) of C_5H_4Rh), 81.92 (d, J(RhC) = 3.8 Hz, C(3) and C(4) of C_5H_4Rh), 29.98 (s, br, CH_2), 26.80 (d, J(PC) = 20.2 Hz, PCHCH$_3$), 20.38 (s, PCHCH$_3$).

Reaction of 36 with MeOH. A solution of **36** (68 mg, 0.12 mmol) in 5 mL of THF was treated under stirring dropwise with 0.5 mL of methanol. After warming to room temperature, the same workup procedure was used as described for **23**. The ^1H NMR spectrum showed that again both isomers are present in a 1:1 ratio.

Preparation of $\{[CH_2(C_5H_4)_2][Co(CO)_2][Ir(C_8H_{14})_2]\}$ (37). A solid sample of **35** (191 mg, 0.34 mmol) was treated at −78 °C with a solution of freshly prepared $[Co(CO)_4I]$ (92 mg, 0.34 mmol) in 10 mL of ether. After warming to room temperature, the reaction mixture was stirred for 2 h, and then the solvent was removed. The brown residue was suspended in 5 mL of toluene, and the solution was filtered through Al_2O_3 (neutral, activity grade IV). The filtrate was brought to dryness in vacuum, the residue was dissolved in 1 mL of toluene, and the solution was chromatographed on Al_2O_3 (neutral, activity grade IV, height of column 12 cm). With hexane/toluene (12:1) a brown fraction was eluted which after evaporation of the solvent gave a brown air-sensitive oil, yield 87 mg (38%). Anal. Calcd for $C_{29}H_{38}CoIrO_2$ (mol weight 669.75): C, 52.01; H, 5.72. Found (mol weight 670 (MS)): C, 52.84; H, 6.32. IR (hexane): ν(CO) 2024, 1964 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 4.85 (vt, N = 3.8 Hz, 2H, C_5H_4), 4.70 (vt, N = 4.3 Hz, 2H, C_5H_4), 4.41 (vt, N = 4.3 Hz, 2H, C_5H_4), 4.36 (vt, N = 3.8 Hz, 2H, C_5H_4), 3.15 (s, 2H, $C_5H_4CH_2C_5H_4$), 2.16 (m, 4H, =CH of C_8H_{14}), 1.65 and 1.34 (both m, 24H, CH_2 of C_8H_{14}). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 107.07 (s, *ipso*-carbon of C_5H_4Co), 100.40 (s, *ipso*-carbon of C_5H_4Ir), 87.33, 86.41, 85.38, and 83.09 (all s, C(2–5) of C_5H_4), 46.49 (s, =CH of C_8H_{14}), 33.67, 33.26, and 26.90 (all s, CH_2 of C_8H_{14}), 26.11 (s, $C_5H_4CH_2C_5H_4$), signal of CoCO not exactly located.

Preparation of $\{[CH_2(C_5H_4)_2][Rh(CO)_2][Ir(C_8H_{14})_2]\}$ (38) was analogous to that described for **37**, using **35** (186 mg, 0.33 mmol) and a solution of $[Rh(CO)_2Cl]_2$ (74 mg, 0.19 mmol) in 7 mL of THF as starting materials. During chromatography with

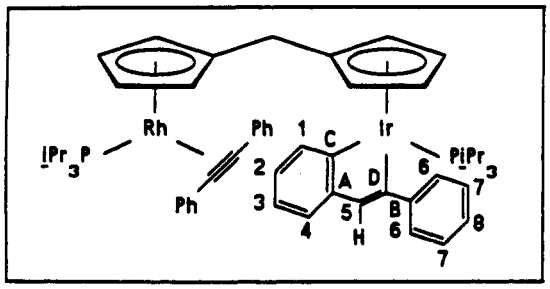

Figure 2. Assignment of the carbon atoms of the Ir(C_6H_4-CH=CPh) unit (confirmed by DEPT measurements).

hexane/toluene (12:1), an orange fraction was eluted which after evaporation of the solvent gave an orange oil. This was recrystallized from 2 mL of pentane (25 to −78 °C) to give an orange, moderately air-sensitive solid, yield 129 mg (53%); mp 85 °C dec. Anal. Calcd for $C_{29}H_{38}IrO_2Rh$ (mol weight 713.73): C, 48.80; H, 5.37. Found (mol weight 714 (MS)): C, 49.09; H, 5.36. IR (hexane): ν(CO) 2043, 1980 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 5.12 (vt, N = 4.3 Hz, 2H, C_5H_4), 4.85 (m, 4H, C_5H_4), 4.36 (vt, N = 3.6 Hz, 2H, C_5H_4), 3.21 (s, 2H, $C_5H_4CH_2C_5H_4$), 2.13 (m, 4H, =CH of C_8H_{14}), 1.51 and 1.30 (both m, 24H, CH_2 of C_8H_{14}). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 192.78 (d, J(RhC) = 83.8, CO), 112.61 (d, J(RhC) = 4.2 Hz, *ipso*-carbon of C_5H_4Rh), 101.22 (s, *ipso*-carbon of C_5H_4Ir), 88.62 (d, J(RhC) = 3.0 Hz, C(2) and C(5) of C_5H_4Rh), 87.23 (s, C(2) and C(5) of C_5H_4Ir), 86.34 (s, C(3) and C(4) of C_5H_4Ir), 86.14 (d, J(RhC) = 3.8 Hz, C(3) and C(4) of C_5H_4Rh), 46.39 (s, =CH of C_8H_{14}), 33.64, 33.24, and 26.81 (all s, CH_2 of C_8H_{14}), 27.00 (s, $C_5H_4CH_2C_5H_4$).

Preparation of {[$CH_2(C_5H_4)_2$][Rh(CO)$_2$][Rh(PhC≡CPh)(PiPr$_3$)]} (39). A solid sample of **36** (201 mg, 0.34 mmol) was treated at −78 °C under stirring with a solution of $[Rh(CO)_2Cl]_2$ (78 mg, 0.20 mmol) in 15 mL of THF. After warming to 45 °C, the reaction mixture was stirred for 2 h, and after cooling to room temperature, the solvent was removed. The residue was repeatedly extracted with pentane, and the combined extracts were brought to dryness in vacuum. The oily residue was dissolved in 1 mL of hexane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 15 cm). With hexane, an orange fraction was eluted which after removal of the solvent gave an orange oil. This was dissolved in 2 mL of warmed hexane (50 °C), and then the solution was cooled slowly to −78 °C and stored for 12 h. An orange, moderatley air-sensitive solid was obtained, yield 161 mg (64%); mp 81 °C dec. Anal. Calcd for $C_{36}H_{41}O_2PRh$: C, 58.23; H, 5.57. Found: C, 58.51; H, 5.46. IR (hexane): ν(CO) 2041, 1978, ν(C≡C) 1824 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 8.18 (m, 4H, C_6H_5), 7.17 (m, 6H, C_6H_5), 5.58 (m, 2H, C_5H_4), 5.26 (vt, N = 4.1 Hz, 2H, C_5H_4), 4.86 (vt, N = 3.8 Hz, 2H, C_5H_4), 4.67 (vt, N = 4.3 Hz, 2H, C_5H_4), 2.80 (m, 2H, CH_2), 1.57 (m, 3H, PCHCH$_3$), 0.87 (dd, J(PH) = 13.0 Hz, J(HH) = 7.1 Hz, 18H, PCHCH_3). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 192.99 (d, J(RhC) = 84.0 Hz, CO), 133.60 (s, *ipso*-carbon of C_6H_5), 131.44 and 128.30 (both s, *ortho*- and *meta*-carbons of C_6H_5), 126.06 (s, *para*-carbon of C_6H_5), 112.98 (dd, ^1J(RhC) = ^3J(RhC) = 3.8 Hz, *ipso*-carbon of $C_5H_4Rh(CO)_2$), 104.93 (dd, J(RhC) = 12.2, J(PC) = 3.4 Hz, *ipso*-carbon of $C_5H_4Rh(PiPr_3)L$), 95.73 (dd, J(RhC) = 17.6, J(PC) = 5.3 Hz, PhC≡CPh), 88.61 (d, J(RhC) = 2.8 Hz, two carbons of C_5H_4), 87.58 (s, br, two carbons of C_5H_4), 85.69 (d, J(RhC) = 3.8 Hz, two carbons of C_5H_4), 82.84 (d, J(RhC) = 4.0 Hz, two carbons of C_5H_4), 27.38 (s, CH_2), 26.15 (d, J(PC) = 21.0 Hz, PCHCH$_3$), 19.94 (s, PCHCH$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 71.81 (d, J(RhP) = 199.5 Hz, $PiPr_3$).

Preparation of {[$CH_2(C_5H_4)_2$][Rh(η^2-CH$_2$=C=CHCH$_3$)(PiPr$_3$)][Rh(PhC≡CPh)(PiPr$_3$)]} (40) was analogous to that described for **39**, using **36** (200 mg, 0.34 mmol) and **22** (205 mg, 0.40 mmol) as starting materials. During chromatography with hexane, a yellow fraction was eluted which after removal of the solvent and recrystallization of the oily residue from hexane (60 to −78 °C) gave a yellow solid, yield 156 mg (51%); mp 77 °C dec. Anal. Calcd for $C_{47}H_{68}P_2Rh$: C, 62.67; H, 7.61. Found: C, 62.84; H, 7.67. IR (KBr) ν(C≡C) 1824 cm^{-1}. ^{1}H NMR (C_6D_6, 90 MHz): δ 8.12 (m, 4H, C_6H_5), 7.22 (m, 6H, C_6H_5), 5.63 (m, 2H, C_5H_4), 5.42 (m, 1H, =CHCH$_3$), 5.28 (vt, N = 4.0 Hz, 2H, C_5H_4), 4.99 (m, 4H, C_5H_4), 2.96 (s, br, 2H, $C_5H_4CH_2C_5H_4$), 2.10 (dt, ^3J(HH) = 6.3, ^5J(HH) = 1.5 Hz, 3H, =CHCH_3), 2.00 (m, 1H, one proton of =CH$_2$, the signal of the second proton could not be localized), 1.53 (m, 6H, PCHCH$_3$), 0.96 and 0.91 (both dd, J(PH) = 12.6 Hz, J(HH) = 7.0 Hz, 36H, PCHCH_3). ^{13}C NMR (C_6D_6, 22.5 MHz): δ 161.10 (dd, J(RhC) = 23.4, J(PC) = 6.6 Hz, CH_2=C=CHCH$_3$), 134.02 (s, *ipso*-carbon of C_6H_5), 131.54 and 128.16 (both s, *ortho*- and *meta*-carbons of C_6H_5), 125.76 (s, *para*-carbon of C_6H_5), 109.66 (dd, J(RhC) = J(PC) = 1.8 Hz, CH_2=C=CHCH$_3$), 106.44 (ddd, ^1J(RhC) = 10.5, ^3J(RhC) = J(PC) = 2.2 Hz, *ipso*-carbon of C_5H_4-Rh(PhC≡CPh)($PiPr_3$), 105.66 (ddd, ^1J(RhC) = 6.6, ^3J(RhC) = J(PC) = 3.3 Hz, *ipso*-carbon of $C_5H_4Rh(\eta^2$-CH$_2$=C=CHCH$_3$)-($PiPr_3$)), 96.33 (dd, J(RhC) = 16.7, J(PC) = 5.1 Hz, one carbon of PhC≡CPh), 96.23 (dd, J(RhC) = 16.9, J(PC) = 5.1 Hz, one carbon of PhC≡CPh), 87.80 (m, C_5H_4), 86.33 (d, J(RhC) = 2.9 Hz, C_5H_4), 85.72 (d, J(RhC) = 3.7 Hz, C_5H_4), 84.56 (d, J(RhC) = 3.6 Hz, C_5H_4), 82.42 (d, J(RhC) = 2.9 Hz, C_5H_4), 26.69 (s, $C_5H_4CH_2C_5H_4$), 26.23 (d, J(PC) = 20.5 Hz, PCHCH$_3$), 25.88 (d, J(PC) = 19.1 Hz, PCHCH$_3$), 22.23 (s, br, =CHCH$_3$), 19.99 (s, PCHCH$_3$ of both phosphine ligands), 1.21 (dd, J(RhC) = 12.1, J(PC) = 2.6 Hz, CH$_2$=C=CHCH$_3$). ^{31}P NMR (C_6D_6, 36.2 MHz): δ 71.82 (d, J(RhP) = 199.3 Hz, $PiPr_3$), 68.69 (d, J(RhP) = 194.9 Hz, $PiPr_3$).

Preparation of {[$CH_2(C_5H_4)_2$][Rh(PhC≡CPh)(PiPr$_3$)][Ir(C_6H_4CH=CPh)(PiPr$_3$)]} (42) was analogous to that described for **39**, using **36** (200 mg, 0.34 mmol) and **41** (290 mg, 0.40 mmol) as starting materials. The workup procedure was the same as for **40**. A yellow, moderately air-sensitive solid was obtained, yield 216 mg (57%); mp 85 °C dec. Anal. Calcd for $C_{57}H_{72}IrP_2Rh$: C, 61.44; H, 6.51. Found: C, 61.80; H, 6.66. IR (hexane) ν(C≡C) 1811, ν(C=C) 1582 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.98 and 7.14 (both m, 19H, C_6H_5 and C_6H_4), 5.14 (m, 6H, C_5H_4), 4.93 (m, 1H, C_5H_4), 4.73 (s, br, 1H, C_5H_4), 2.60 (s, 2H, CH_2), 2.04 and 1.57 (both m, 6H, PCHCH$_3$), 0.85 (dd, J(PH) = 12.9, J(HH) = 7.1 Hz, 18H, PCHCH_3 from $PiPr_3$ on Rh), 0.67 and 0.60 (both dd, J(PH) = 13.0 Hz, J(HH) = 7.1 Hz, 18H, PCHCH_3 from $PiPr_3$ on Ir), signal of =CH proton not exactly located. ^{13}C NMR (C_6D_6, 50.3 MHz): δ 161.52 and 151.77 (both s, C(1) and C(9)), 152.58 and 146.10 (both d, J(PC) = 9.7 and 11.7 Hz, C(2) and C(8)), 142.53, 138.92, 128.75, 128.22, 127.52, 125.23, 122.75, 122.54 (all s, C(3–6) and C(10–12)), 134.03 (d, J(RhC) = 4.6 Hz, *ipso*-carbon of C_6H_5 groups on C≡C), 131.51 and 128.14 (both s, *ortho*- and *meta*-carbons of C_6H_5 groups on C≡C), 125.72 (s, *para*-carbon of C_6H_5 groups on C≡C), 104.67 (ddd, J(RhC) = 9.7, ^2J(PC) = ^4J(PC) = 2.5 Hz, *ipso*-carbon of C_5H_4Rh), 100.80 (dd, J(RhC) = 2.0, J(PC) = 10.4 Hz, *ipso*-carbon of C_5H_4Ir), 95.93 and 95.79 (both dd, J(RhC) = 17.1, J(PC) = 5.1 Hz, PhC≡CPh), 89.87 (d, J(RhC) = 4.2 Hz, one carbon of C_5H_4Rh), 87.48 (d, J(RhC) = 3.0 Hz, one carbon of C_5H_4Rh), 87.42 (d, J(RhC) = 2.6 Hz, one carbon of C_5H_4Rh), 85.84 (s, one carbon of C_5H_4Ir), 84.41 (s, one carbon of C_5H_4Ir), 82.58 (d, J(RhC) = 3.6 Hz, one carbon of C_5H_4Rh), 77.45 (s, two carbons of C_5H_4Ir), 25.79 (d, J(PC) = 20.7 Hz, PCHCH$_3$ from $PiPr_3$ on Rh), 25.28 (s, CH_2), 24.97 (d, J(PC) = 29.0 Hz, PCHCH$_3$ from $PiPr_3$ on Ir), 20.20 and 19.73 (both s, PCHCH$_3$ from $PiPr_3$ on Ir), 19.94 (s, PCHCH$_3$ from $PiPr_3$ on Rh); for assignment of C(1–12), see Figure 2. ^{31}P NMR (C_6D_6, 36.2 MHz): δ 71.68 (d, J(RhP) = 200.8 Hz, $PiPr_3$ on Rh), 12.88 (s, $PiPr_3$ on Ir).

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