A Novel Route to Formaldehyde and Thioformaldehyde Rhodium Complexes☆

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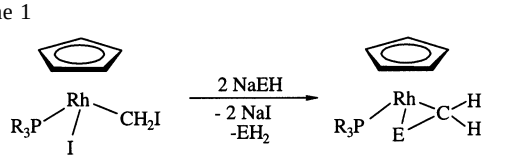
The acetoxymethyl rhodium compounds [(η^5-C_5R_5)Rh(CH_2OAc)(L)I] (**4**, **13**–**16**) which were prepared from the chloromethyl derivatives [(η^5-C_5R_5)Rh(CH_2Cl)(L)I] and sodium acetate in benzene/acetic acid as solvent, reacted with $AgPF_6$ to give the chelate complexes [(η^5-C_5R_5)Rh{κ^2-*C,O*-$CH_2OC(Me)O$}(L)]PF_6 (**19**–**23**) in excellent yields. Treatment of these complexes with KOH in methanol led to the elimination of the acetyl group and to the formation of the formaldehyde compounds [(η^5-C_5R_5)Rh(η^2-CH_2O)(L)] (**24**–**27**). The related thioformaldehyde complexes [(η^5-C_5Me_5)Rh(η^2-CH_2S)(L)] (**46**, **47**) and [(η^5-C_5H_5)Rh(η^2-CH_2S)(PMe_3)] (**50**) were obtained on a similar route. Studies on the reactivity of the formaldehyde derivatives revealed that the Rh–CH_2O bond is rather labile and the CH_2O ligand easily converted to a CO group.

In a series of papers we have recently shown[1] that cobalt and rhodium half-sandwich type complexes, which contain $MI(CH_2I)$ as a molecular unit, can be transformed to the corresponding thio-, seleno-, and telluroformaldehyde metal derivatives upon treatment with SH^-, SeH^-, and TeH^-, respectively (see Scheme 1). Due to the lone electron pairs at the chalcogen atom of the CH_2E ligand, these compounds behave as Lewis bases and react with in situ generated 16-electron fragments such as $[W(CO)_5]$ or [(η^5-C_5H_5)$Mn(CO)_2$] to give dinuclear hetero-metallic complexes with the aldehyde CH_2E in a bridging position.[1d][2] First attempts to complete the series of compounds [(η^5-C_5R_5)M(η^2-CH_2E)(L)] by those with E = O failed. The reaction of the respective precursor [(η^5-C_5R_5)M(L)(L′)] with monomeric formaldehyde was rather slow and in most cases led to a mixture of products among which the carbonyl complexes [(η^5-C_5R_5)M(CO)(L)] were the dominating species. Therefore, we had to develop a different synthetic route. The present paper describes that for M = Rh the key to success was the preparation of metalated acetic acid derivatives [Rh]$CH_2OC(O)CH_3$ as intermediates which could be converted in two steps to the coordinated formaldehyde ligand. Some related results to this work were already reported.[3]

Scheme 1

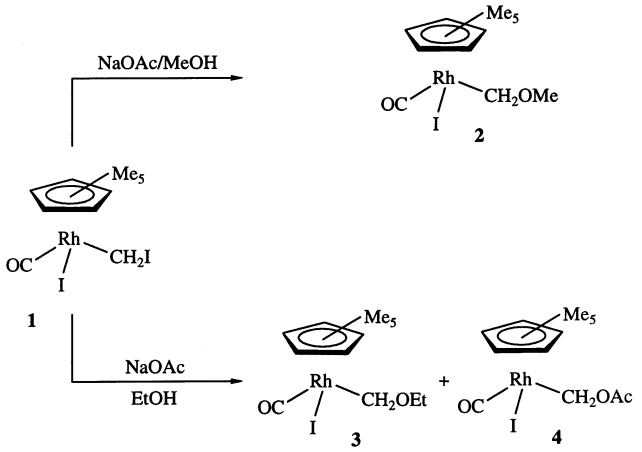


Results

Preparation of $RhCH_2OAc$ Precursors

The carbenoide rhodium complex **1**, which can easily be prepared from $[C_5Me_5Rh(CO)_2]$ and CH_2I_2,[4] reacts quite smoothly in polar solvents with sodium acetate. While in acetone a mixture of products is formed, the reaction of **1** with excess NaOAc in methanol leads to the methoxymethyl compound **2** in good yield. In contrast, the starting material **1** and NaOAc react in ethanol to give two products **3** and **4** (see Scheme 2), which could be separated by chromatographic techniques. Although the desired acetoxy derivative **4** is the dominating species provided that an excess of sodium acetate is used, the separation of the two compounds on Al_2O_3 results in the partial conversion of **4**

Scheme 2. [Ac = CH_3CO]



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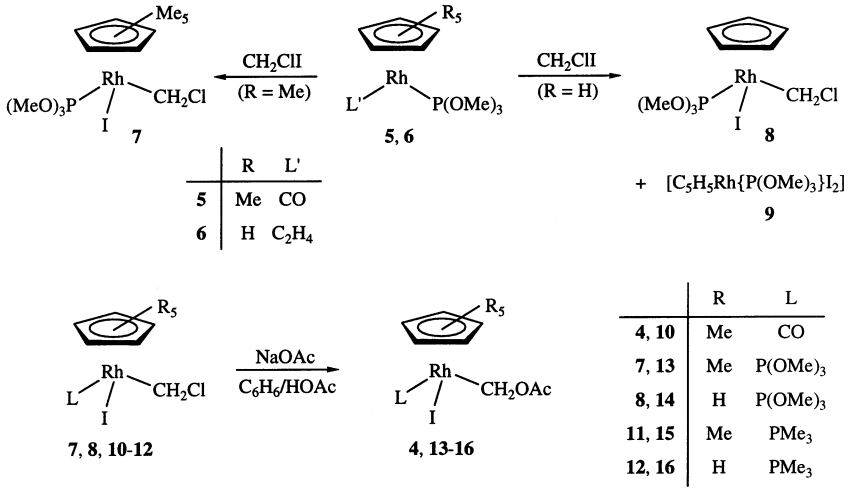
Scheme 3. [Ac = CH_3CO]

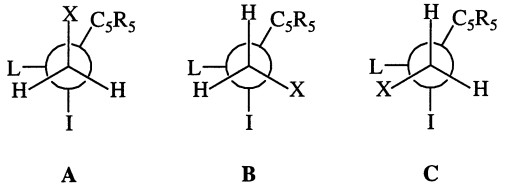


to the dinuclear complex [{(η^5-C_5Me_5)Rh(μ-CO)}$_2$]. Therefore, the isolated yield is rather low.

The method of choice for the preparation of **4** is the reaction of **7** with excess NaOAc in a mixture of benzene and glacial acetic acid as the solvent. Under these conditions, not only **4** but also the half-sandwich type Rh−CH_2OAc complexes **13**−**16** (Scheme 3) have been obtained in 80−85% yield. The synthesis of the formerly unknown chloromethyl rhodium(III) precursors **7** and **8** was achieved by oxidative addition (followed by elimination of CO or C_2H_4) of CH_2ClI to [(η^5-C_5Me_5)Rh(CO){$P(OMe)_3$}] and [(η^5-C_5H_5)Rh(C_2H_4){$P(OMe)_3$}], respectively. We note that the rate of formation of **15** from **11** is significantly higher than from [(η^5-C_5Me_5)Rh(CH_2I)(PMe_3)I][4] which can be understood by the HSAB concept: Substitution of the hard chloride by the hard nucleophile OAc^- is favoured compared to the displacement of the soft iodide by acetate.[5]

The acetoxymethyl derivatives **4** and **13**−**16** are yellow to red-brown microcrystalline solids, which are air-stable and soluble in common organic solvents. The most typical feature of the ^{1}H-NMR spectra of **4** and **13**−**16** is the appearance of two distinct signals for the methylene protons of the CH_2OAc group which due to Rh-H, H-H, and in some cases P-H coupling are split into doublets of doublets or appear as doublets of doublets of doublets. Since the size of ^3J(PH), which depends on the mutual orientation of the phosphorus and the hydrogen atoms of the $PRhCH_2$ unit,[6] differs considerably (e.g. between 0 Hz and 8.8 Hz for **15**), we assume that the rotation around the Rh−CH_2O axis is partially hindered and the conformations **A** or **B** (Figure 1) are preferred. A similar observation has already been made for compounds such as **12** and [(η^5-C_5H_5)Rh(CH_2X)(PMe_3)X] (X = Br, I)[7] as well as for related cyclopentadienyliron derivatives [(η^5-C_5H_5)Fe(CH_2R)(CO)(PR'_3)] (R = Ph, $SiMe_3$).[8]

Figure 1. Conformations of compounds [(η^5-C_5R_5)Rh(CH_2X)(L)I] (X = Cl, OAc) viewed along the Rh−C axis. Due to the formally octahedral geometry the bond angle P−Rh−I is assumed to be 90° (see also ref.[8])

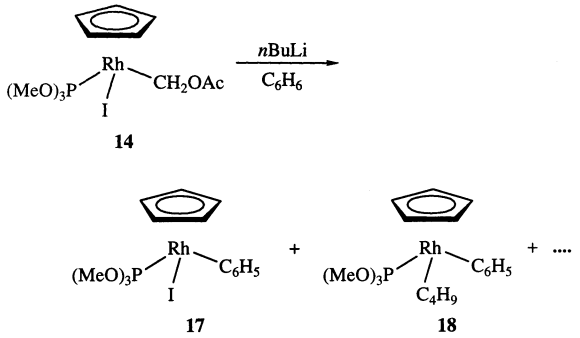


Conversion of $RhCH_2OAc$ to Rh(η^2-CH_2O) Complexes

Attempts to convert the acetoxymethyl compounds **4** and **13**−**16** to the corresponding formaldehyde complexes by using different nucleophiles failed.[9] Whereas treatment of **4** with NaOMe in methanol/benzene or with *n*BuLi in benzene led mainly to decomposition (and to the formation of small amounts of [{(η^5-C_5Me_5)Rh(μ-CO)}$_2$]), the reaction of **15** with NaOMe in methanol or with NaOH in water/benzene in the presence of [$PhCH_2NEt_3$]Cl (TEBA) as phase-transfer catalyst gave mainly the mononuclear compound [(η^5-C_5Me_5)Rh(CO)(PMe_3)].[10] Although the ^{1}H-NMR spectrum of the reaction mixture formed from **15** and NaOMe in CD_3OD showed that besides the carbonyl complex [(η^5-C_5Me_5)Rh(CO)(PMe_3)] the corresponding formaldehyde compound **26** (see Scheme 5) is probably formed, the attempts to separate the two C_5Me_5Rh species by chromatographic techniques failed. One noteworthy result is that from the mixture of products obtained upon treatment of the trimethylphosphite complex **14** with two equiv of *n*BuLi in benzene/hexane the half-sandwich type rhodium(III) derivatives **17** and **18** (Scheme 4) could be isolated in low yield. The ^{1}H NMR data as well as the mass spectra and (in the case of **17**) the elemental analysis revealed that both in **17** and **18** a Rh−C_6H_5 bond is present, the phenyl group originating either from benzene or from in situ generated LiPh, respectively.

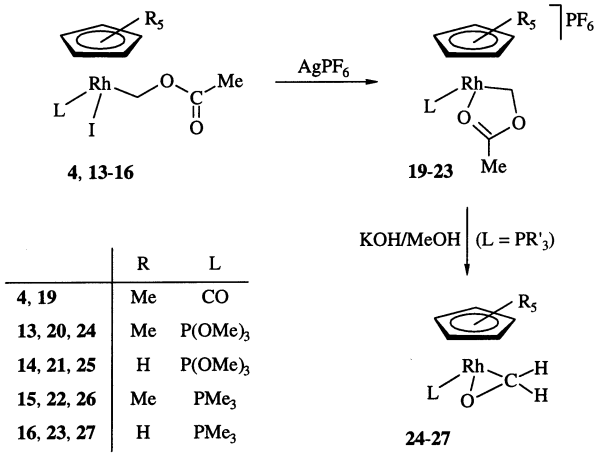
The methodology for the successful preparation of the formaldehyde rhodium complexes **24**−**27** is outlined in Scheme 5. Instead of an attack of a nucleophile to the carbon atom of the acetoxy unit of **4** and **13**−**16** the first step involves the cleavage of the Rh−I linkage by $AgPF_6$. This is followed by the formation of a five-membered chelate

Scheme 4. [Ac = CH_3CO]



ring. Since the coordination of the carbonyl oxygen atom to the metal increases the δ+ charge at the C=O carbon atom, a subsequent nucleophilic attack at this carbon is preferred. Finally, the products **24**−**27** are obtained in moderate yield. It should be emphasized that even treatment of the highly reactive bis(trimethylphosphane) compounds $[(\eta^5\text{-}C_5H_5)Rh(PMe_3)_2]$ and $[(\eta^5\text{-}C_5Me_5)Rh(PMe_3)_2]$[11] with formaldehyde does not lead to **26** and **27** but instead gives the carbonyl derivatives $[(\eta^5\text{-}C_5H_5)Rh(CO)(PMe_3)]$ and $[(\eta^5\text{-}C_5Me_5)Rh(CO)(PMe_3)]$.

Scheme 5

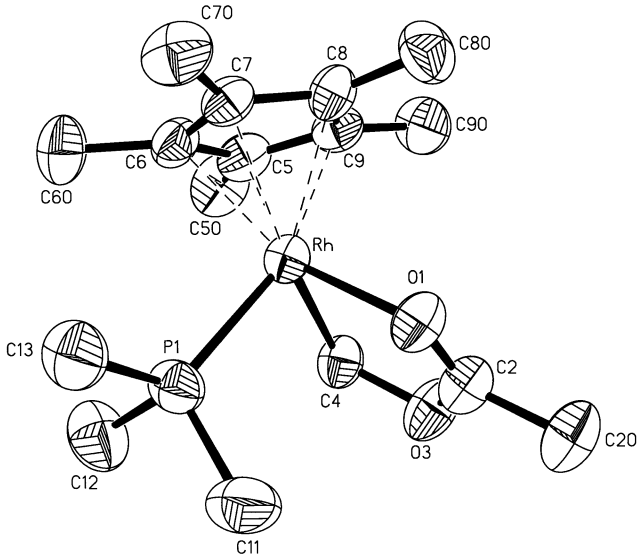


	R	L
4, 19	Me	CO
13, 20, 24	Me	$P(OMe)_3$
14, 21, 25	H	$P(OMe)_3$
15, 22, 26	Me	PMe_3
16, 23, 27	H	PMe_3

The chelate complexes **19**−**23** are yellow to orange-yellow air-stable solids which in nitromethane display the conductivity expected for 1:1 electrolytes. The spectroscopic data of **19**−**23** and of the non-ionic precursors **4** and **13**−**16** differ insofar, as in the ^{13}C NMR spectra of **19**−**23** the signal of the C=O carbon atom is shifted significantly (16−20 ppm) to lower field due to the interaction of the acetyl moiety with the metal. In the IR spectra of the chelate compounds the C=O stretching frequency is also reduced and appears at 1600−1610 cm^{-1} compared with 1700−1720 cm^{-1} for **4** and **13**−**16**, respectively. For the dicyclopentadienylvanadium complexes $[(\eta^5\text{-}C_5H_5)_2V\{\eta^1\text{-}CH_2OC(O)R\}Cl]$ and $[(\eta^5\text{-}C_5H_5)_2V\{\kappa^2\text{-}C,O\text{-}CH_2OC(R)O\}]BPh_4$ an almost identical trend has been observed.[12]

The result of the X-ray crystal structure analysis of **22** is shown in Figure 2. The acetoxymethyl unit acts as a bidentate ligand and forms a nearly planar five-membered ring with the rhodium center. The distance C2−O1 [1.240(8) Å] indicates significant double bond character which is in agreement with the bonding pattern shown for **19**−**23** in Scheme 5. The corresponding C=O bond length in the vanadium complex $[(\eta^5\text{-}C_5H_5)_2V\{\kappa^2\text{-}C,O\text{-}CH_2OC(Me)O\}]^+$ is 1.236(4) Å[12] and thus almost identical to that in **22**. Compared with C2−O1, the distance C2−O3 [1.307(8) Å] is considerably longer and quite similar to the C−O(W) distance found in $[(\eta^5\text{-}C_5H_5)W(CO)_3(OAc)]$.[13] The Rh−C4 bond length [2.067(6) Å] is somewhat shorter than in related cationic cyclopentadienylrhodium compounds such as $[(\eta^5\text{-}C_5H_5)Rh(CH_2NC_5H_5)(PMe_3)I]^+$ [14] and $[(\eta^5\text{-}C_5H_5)\text{-}RhCH_3(CO)(PPh_2R)]^+$ [R = NHCH(Me)Ph][15] which could be due to the electronic effect caused by the OAc group. The Rh−C4−O3 bond angle is 109.7(4)° which is consistent with the sp^3 hybridization of the CH_2 carbon atom. The distances between rhodium and the carbon atoms of the C_5Me_5 ring are in the usual range for complexes containing the $C_5Me_5Rh(PMe_3)$ unit.[16] However, as has previously been observed for those half-sandwich type compounds with π-donating ligand,[7][17] the metal−carbon bond lengths [Rh−C5 and Rh−C6] *trans* to this ligand are shorter than the other Rh−C(ring) distances.

Figure 2. Molecular structure of **22**[a] (thermal elipsoids with 50% probability)



[a] Selected bond lengths [Å] and angles [°]: Rh−P1 2.300(2), Rh−O1 2.112(4), Rh−C4 2.067(6), Rh−C5 2.170(6), Rh−C6 2.179(6), Rh−C7 2.254(6), Rh−C8 2.230(7), Rh−C9 2.198(6), O1−C2 1.240(8), C2−O3 1.307(8), C2−C20 1.501(9), O3−C4 1.471(7); P1−Rh−O1 91.3(1), P1−Rh−C4 87.7(2), O1−Rh−C4 77.9(2), Rh−O1−C2 113.9(4), O1−C2−O3 122.2(6), O1−C2−C20 122.6(6), O3−C2−C20 115.2(6), C2−O3−C4 116.0(5), Rh−C4−O3 109.7(4).

The second step of the synthesis of compounds **24**−**27** (see Scheme 5) proved to be difficult. Treatment of the acetoxymethyl complexes **20**−**23** with NaOMe or KOH in methanol at room temperature gave in each case a mixture of products with the carbonyl and the formaldehyde compounds $[(\eta^5\text{-}C_5R_5)Rh(CO)(L)]$ and $[(\eta^5\text{-}C_5R_5)Rh(\eta^2\text{-}CH_2O)(L)]$ as the dominating species. Attempts to separate

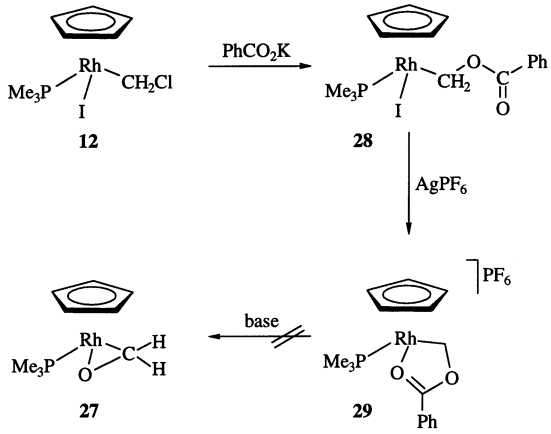
these mixtures by chromatographic techniques led mainly to the isolation of the Rh−CO complexes. However, the rate of the decomposition of the formaldehyde derivatives to $[(\eta^5\text{-}C_5R_5)Rh(CO)(L)]$ could be considerably reduced if the reaction of **20**−**23** with base was carried out at low temperature. After the reaction mixture was worked up at 0°C, oily products were obtained which could partly be converted to yellow-brown microcrystalline solids. Since the formaldehyde compounds **24**−**27** are not only labile (and air-sensitive) but also readily soluble in pentane, the yield of the isolated solids did not exceed 30%.

Even more labile than the trimethylphosphite and trimethylphosphane complexes **24**−**27** is the corresponding carbonyl derivative $[(\eta^5\text{-}C_5Me_5)Rh(\eta^2\text{-}CH_2O)(CO)]$. Addition of excess NaOMe to a solution of **19** in methanol at −78°C led initially to the formation of a clear yellow solution which rapidly turned blue if the same work-up procedure was used as applied for **24**−**27**. The isolated product consisted of both $[(\eta^5\text{-}C_5Me_5)Rh(CO)_2]$ and the dinuclear compound $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}CO)\}_2]$. However, the ^{1}H-NMR spectrum of the reaction mixture in CD_3OD at −40°C displayed two doublets of doublets at δ 5.67 [J(RhH) = 4.4, J(HH) = 6.1 Hz] and 5.46 [J(RhH) = 0.6, J(HH) = 6.1 Hz] and one doublet at δ 1.66 [J(RhH) = 0.4 Hz] which can be assigned to the CH_2 and C_5Me_5 protons of $[(\eta^5\text{-}C_5Me_5)Rh(\eta^2\text{-}CH_2O)(CO)]$, respectively.

With regard to the spectroscopic data of the isolated formaldehyde complexes, we note that at least in the case of **25**, **26**, and **27** for the methylene protons of the coordinated CH_2O ligand two distinct signals (both doublets of doublets of doublets) have been observed. The ^2J(HH) coupling of 18.2−21.5 Hz lies between that of free formaldehyde (42.2 Hz) and ethylenoxide (5.5 Hz)[18] and indicates some double bond character for the C−O bond. The H-H coupling constant of **25**−**27** is quite similar to that of the cationic rhenium compound $[(\eta^5\text{-}C_5H_5)Re(\eta^2\text{-}CH_2O)(NO)(PPh_3)]^+$ (16.6 Hz)[19] for which according to the structural data also a partial C−O double bond character has been postulated. We note that a three-membered MCO ring as shown in Scheme 6 dominates the structural chemistry of formaldehyde complexes containing the $Zr(C_5H_5)_2$ unit which is probably due to the higher oxophilicity of electron-poor transition-metal centres.[12][20]

To find out whether complexes that are structurally related to **19**−**23** are also suitable starting materials for the generation of formaldehyde rhodium derivatives, compounds **28** and **29** (Scheme 6) have been prepared. Both were obtained via the same route as **16** and **23** and characterized by elemental analysis and spectroscopic means. However, treatment of **29** with various bases led to a mixture of products among which **27** could not be exactly identified.

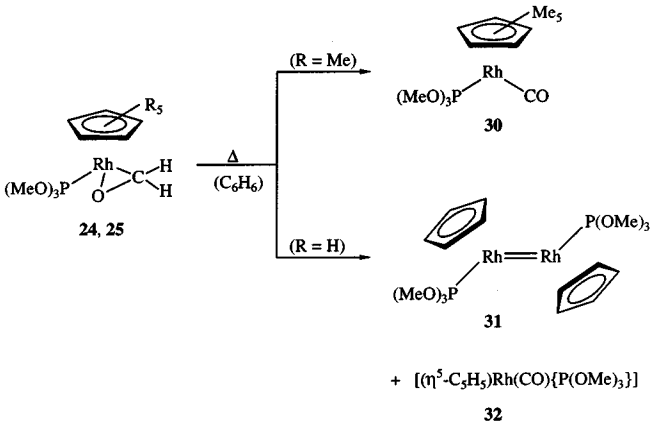
Scheme 6



Reactions of Rh(η^2-CH_2O) Complexes

The striking lability of the formaldehyde rhodium complexes $[(\eta^5\text{-}C_5R_5)Rh(\eta^2\text{-}CH_2O)(L)]$ initiated a series of experiments aimed to find out whether during the decomposition besides the carbonyl derivatives other compounds are formed too. If the course of the thermal decomposition of **24**, **26**, and **27** in C_6D_6 is studied in an NMR tube at room temperature, the complexes $[(\eta^5\text{-}C_5R_5)Rh(CO)(L)]$ indeed are the most dominating species among the observed products. After completion of the reaction the spectroscopically determined yield of the carbonyl compounds is 80−90%. Hydrido complexes such as $[(\eta^5\text{-}C_5Me_5)RhH_2(PMe_3)]$[21] could not be detected. The most surprising discovery was that in contrast to the thermolysis of **24** which gave almost quantitatively $[(\eta^5\text{-}C_5Me_5)Rh(CO)\{P(OMe)_3\}]$,[22] the corresponding reaction of **25** led to a mixture of **31** and **32** (Scheme 7) in the ratio of ca. 70:30 under the same conditions (benzene, 25°C). If a somewhat higher concentration of **25** is used, the relative amount of the dinuclear complex increases and, after fractional crystallization, the isolated yield of **31** (which is a green moderately air-sensitive solid) is about 40%.

Scheme 7



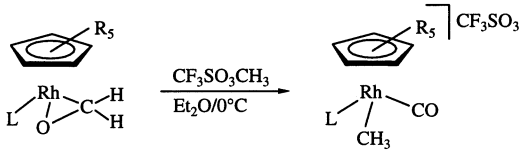
The structural proposal for **31** is mainly supported by the mass spectrum and the NMR spectroscopic data. In the mass spectrum peaks for M^+, $M^+ - P(OMe)_3$, and $M/2^+$ are observed, which is in agreement with the presence of a dinuclear framework. The ^{1}H-NMR spectrum displays two signals for the protons of the C_5H_5 and $P(OMe)_3$ ligands,

while the ^{31}P-NMR spectrum displays only a single resonance, its splitting being consistent with a spectrum of an AA′XX′ type (A,A′ = ^{31}P; X, X′ = ^{103}Rh). Since compound **31** is formally an analogue of the well-known carbonyl complex [{(η^5-C_5Me_5)Rh(μ-CO)}$_2$] (the structural data of which indicate the presence of a metal−metal double bond),[23] we tentatively assign a similar bonding pattern also to **31**. The spectroscopic data are of course not conclusive as to the *cis* or *trans* disposition of the two cyclopentadienyl (and equally the two phosphite) ligands.

The question of why compound **25** but not the related complexes **24**, **26**, and **27** decomposes by loss of formaldehyde and formation of a dinuclear product can not be answered definitively. It should be noted, however, that only in the mass spectra of **24**, **26**, and **27** the peak of the molecular ion M^+ appears, while the corresponding peak (m/z = 322) is missing in the mass spectrum of **25**. On the other hand, only in the latter the ion CH_2O^+ is observed with relatively high intensity. A plausible explanation of these results is that due to the less pronounced donor character of C_5H_5 compared to C_5Me_5 and of $P(OMe)_3$ compared to PMe_3, the metal-to-formaldehyde bond of compound **25** is the weaker and can be cleaved more easily than in the C_5Me_5Rh and $Rh(PMe_3)$ counterparts. The loss of formaldehyde from **25** would generate the 16-electron species [(η^5-C_5H_5)Rh{$P(OMe)_3$}] which dimerizes preferentially and does not react with CH_2O or benzene. The carbonyl complexes [(η^5-C_5R_5)Rh(CO)(L)] as the preferred products of the thermal decomposition of **24**, **26**, and **27** (and in part also of **25**) are probably formed via the formyl(hydrido)metal intermediates [(η^5-C_5R_5)RhH(CHO)(L)] which eliminate H_2 to give the final products. There is ample evidence for this pathway, particular due to the work by Thorn[24] and Roper et al.[25]

The reactions of **24**, **26**, and **27** with methyltriflate follow an unexpected course. In contrast to several other formaldehyde metal complexes which react with HX or RX by attack of the electrophile to the CH_2O oxygen atom,[12][25b][26] on treatment of **24**, **26**, or **27** with $CF_3SO_3CH_3$ no $RhCH_2OCH_3$ species could be detected. Instead the triflates of the cationic complexes **33**−**35** were formed. While the isolated yield of **33** and **34** was high, that of **35** was rather low which could be due to the lability of the Rh−CO bond in the rhodium(III) species. The PF_6 salts of the cations [(η^5-C_5R_5)Rh(CH_3)(CO)(PMe_3)]$^+$ (R = H, Me) were previously prepared in our laboratory either from the acyl derivative [(η^5-C_5Me_5)Rh{$C(O)CH_3$}(PMe_3)I] and $AgPF_6$[10] or by salt metathesis from [(η^5-C_5H_5)Rh(CH_3)(CO)(PMe_3)]I and NH_4PF_6[27]. We assume that compounds **33**−**35** are formed via the carbonyl complexes [(η^5-C_5R_5)Rh(CO)(L)] and that the electrophile $CF_3SO_3CH_3$ strongly facilitates the conversion of **24**, **26**, and **27** to [(η^5-C_5R_5)RhH(CHO)(L)] and subsequently to [(η^5-C_5R_5)Rh(CO)(L)]. This mechanistic proposal is supported by the observation that upon addition of methyltriflate to solutions of the starting material a rapid evolution of gas (H_2) is observed.

Scheme 8



24, 26, 27 **33-35**

	R	L
33	Me	$P(OMe)_3$
34	Me	PMe_3
35	H	PMe_3

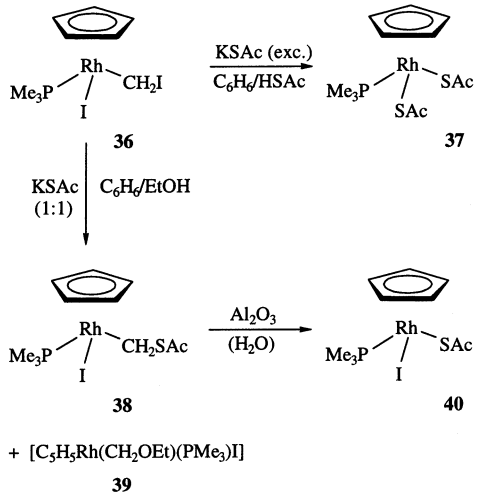
The formaldehyde complexes **26** and **27** react with CF_3SO_3H in a less straightforward manner and afford a mixture of products. Among those the cations [(η^5-C_5R_5)RhH(CO)(PMe_3)]$^+$ could be identified by ^{1}H-NMR spectroscopy.[10][27] Treatment of **26** and **27** with CH_2I_2 leads to the fast displacement of CH_2O (detected by ^{1}H NMR) and to the formation of [(η^5-C_5Me_5)Rh(CH_2I)(PMe_3)I][4] and [(η^5-C_5H_5)Rh(CH_2I)(PMe_3)I],[7] respectively. Compounds **26** and **27** behave thus analogously to the carbonyl and ethene derivatives [(η^5-C_5Me_5)Rh(CO)(PMe_3)] and [(η^5-C_5H_5)Rh(C_2H_4)(PMe_3)]. The noteworthy difference is, however, that the reactions of **26** and **27** with CH_2I_2 proceed much faster than those of the corresponding carbonyl and ethene complexes which is probably due to the weaker Rh−CH_2O compared to the Rh−CO and Rh−C_2H_4 bond.

Thioacetate− and Thioformaldehyde−Rhodium Complexes

The methodology used for the preparation of [(η^5-C_5R_5)Rh(η^2-CH_2O)(L)] (**24**−**27**) could also be applied for the synthesis of the corresponding thioformaldehyde complexes [(η^5-C_5R_5)Rh(η^2-CH_2S)(L)]. The investigations, which were carried out to obtain the respective precursors, are summarized in Schemes 9 and 10. Reaction of the starting material **36** with excess CH_3COSK in benzene/thioacetic acid led not only to cleavage of the CH_2−I but also to that of the Rh−I and Rh−C bonds and gave the bis(thioacetato)rhodium(III) compound **37** in nearly 80% yield. In contrast, treatment of **36** with one equiv of CH_3COSK in benzene/ethanol afforded a mixture of **38** and the known ethoxymethyl complex **39**,[3] which could be separated by fractional crystallization from pentane. The isolated yield of **38** was about 60%. If the separation of **38** and **39** was attempted by column chromatography using deactivated Al_2O_3, loss of the CH_2 fragment of the CH_2SAc ligand of **38** occurred and the half-sandwich rhodium(III) compound **40** was obtained. Both **37** and **38** as well as **40** were characterized by elemental analyses, mass spectra and IR and NMR spectroscopic techniques.

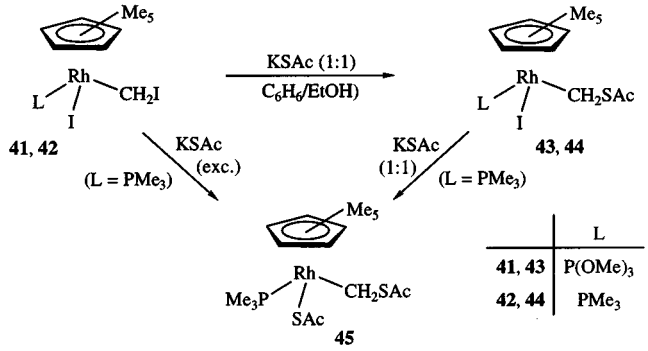
The preparation of the pentamethylcyclopentadienyl complexes **43** and **44** from the $RhCH_2I$ precursors **41** and **42** and CH_3COSK in benzene/ethanol proceeded in a clear manner and gave the expected products almost quantita-

Scheme 9. [Ac = CH_3CO]



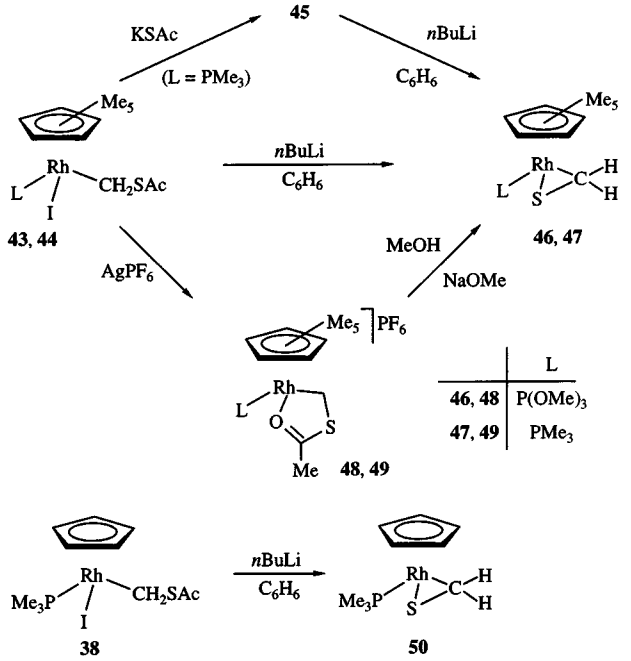
tively. In this case, no byproducts such as [(η^5-C_5Me_5)Rh(CH_2OEt)(L)I] [L = $P(OMe)_3$, PMe_3] were observed. The reaction of **42** with an excess of potassium thioacetate led both to the cleavage of the CH_2-I and the Rh−I bond and produced the thioacetatorhodium(III) derivative **45**. The same compound was obtained from **44** and an equimolar amount of CH_3COSK. The ^{1}H-NMR spectra of complexes **38**, **43**, and **44**, each containing a $RhCH_2SAc$ unit, display two distinct signals for the diastereotopic CH_2 protons which are well separated (by 0.2 to 0.7 ppm) and due to Rh-H, P-H, and H-H coupling appear as doublets of doublets of doublets.

Scheme 10. [Ac = CH_3CO]



The thioformaldehyde complexes **46** and **47** can be prepared in two different ways (see Scheme 11) using either the neutral derivatives **43** and **44** or the cationic compounds **48** and **49** as starting materials. The latter were prepared similar to the above mentioned chelate complexes **19**−**23** from **43** or **44** and $AgPF_6$ in acetone. The conversion of **48** and **49** to the thioformaldehyde compounds **46** and **47** proceeded then analogously as described for the Rh(η^2-CH_2O) counterparts.

Scheme 11. [Ac = CH_3CO]



However, in contrast to **24**−**27** the Rh(η^2-CH_2S) complexes **46** and **47** can also be prepared directly from **43** and **44** upon treatment with *n*BuLi in benzene/hexane. After the reaction mixture was worked up by column chromatography using Al_2O_3, the isolated yield of **46** and **47** was 75%. The (η^5-C_5H_5)Rh derivative **50**, which had previously been prepared from **36** and two molar equivalents of NaSH,[1a][1d] was obtained on the same route. In this context it should be reminded that treatment of **14** (a related species to **38** with a $RhCH_2OAc$ linkage) did not yield the corresponding formaldehyde complex **25**, probably due to the lability of the Rh−CH_2O bond toward the organolithium reagent. We note that the ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra of **46** and **47** are quite similar to those of the cyclopentadienyl complexes [(η^5-C_5H_5)Rh(η^2-CH_2E)(L)] (E = S, Se, Te; L = PMe_3, PMe_2Ph, P*i*Pr_3)[1d] and thus deserve no further comment.

Discussion

The present investigation has shown that carbenoide rhodium compounds containing $Rh(CH_2X)I$ as a molecular fragment are not only useful starting materials for the synthesis of thio-, seleno-, and telluroformaldehyde complexes[1] but also open up a preparative route to corresponding formaldehyde metal derivatives. Although several examples are known which prove that compounds of the general composition [M(η^2-CH_2O)L_n] can be obtained from an appropriate precursor and free formaldehyde,[12][25][28] this method of synthesis failed for complexes such as [(η^5-C_5R_5)Rh(η^2-CH_2O)(L)]. The main reason for this is the lability of the Rh−CH_2O bond which is

illustrated by our studies concerned to the reactivity of the isolated compounds **24**−**27**. The preferred pathway of decomposition seems to be the conversion of [Rh](CH_2O) to [Rh](CO) and H_2 ([Rh] = [(η^5-C_5R_5)Rh(L)]) which is noteworthy insofar as the reverse reaction, i.e. the formation of [M](CH_2O) from [M](CO) and hydrogen, is described as an important step in the metal-assisted hydrogenation of carbon monoxide.[29] Presently the state of the art is that electron-poor transition metal centers are more suitable to stabilize the M−CH_2O bond than electron-rich counterparts which is probably due to the well-known oxophilicity of d^o-d^4 systems.[30] Electron-rich transition metal centers prefer to coordinate thio- and selenoformaldehyde instead of CH_2O, which has first been shown by Roper et al.[31] and has also been confirmed by this work as well as by previous studies from our laboratory.[1]

We acknowledge the support for this work by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. Moreover, we are also grateful to Mrs. *R. Schedl* and Mr. *C. P. Kneis* for elemental analyses and DTA measurements as well as to Mrs. *M. L. Schäfer* and Dr. *W. Buchner* for recording the NMR spectra.

Experimental Section

All operations were carried out in an inert gas atmosphere with the Schlenk technique. The starting materials **1**,[4] **5**,[22] **6**,[32] **10**−**12**,[4][7] **36**,[32] and **41**, **42**[4] were prepared as described in the literature. CH_3COSK (KSAc) was prepared as a white microcrystalline solid from equimolar amounts of KOH and thioacetic acid in ethanol and used without further purification. − MS: Varian MAT CH7. − IR: Perkin-Elmer 397. − NMR: Varian EM 360 L, Bruker WH 90, AC 200, and WM 400. − Melting points: DTA. − Conductivity measurements (in CH_3NO_2) with conductometer Schott CG 851; Λ in $cm^2\Omega^{-1}mol^{-1}$.

1. Preparation of [(η^5-C_5Me_5)Rh(CH_2OMe)(CO)I] (**2**): A suspension of 85.1 mg (0.16 mmol) of **1** in 5 ml of methanol was treated with 13.5 mg (0.25 mmol) of CH_3CO_2Na and stirred for 3 h at room temp. The solvent was removed and the residue was extracted with 10 ml of ether. The extract was brought to dryness in vacuo and the residue was dissolved in 1 ml of pentane. After the solution was stored for 12 h at −78°C, a red-brown microcrystalline solid precipitated which was filtered, washed with small portions of pentane (−20°C) and dried; yield 45 mg (64%); m. p. 77°C (dec.). − IR (C_6H_6): $\tilde{\nu}$ = 2007 cm^{-1} [ν(CO)]. − ^{1}H NMR (200 MHz, C_6D_6): δ = 5.30 [dd, *J*(RhH) = 2.0, *J*(HH) = 3.8 Hz, 1 H, one H of C*H*$_2$OMe], 5.15 [dd, *J*(RhH) = 5.1, *J*(HH) = 3.8 Hz, 1 H, one H of C*H*$_2$OMe], 3.03 (s, 3 H, OCH_3), 1.68 [d, *J*(RhH) = 0.5 Hz, 15 H, C_5Me_5]. MS (70 eV); *m*/*z* (%) = 438 (10) [M^+], 393 (10) [M^+ − CH_2OMe], 365 (100) [$C_5Me_5RhI^+$], 266 (2) [$C_5Me_5Rh(CO)^+$], 238 (10) [$C_5Me_5Rh^+$]. − $C_{13}H_{20}IO_2Rh$ (438.1): calcd. C 35.64, H 4.60; found C 34.97, H 4.88.

2. Reaction of **1** *with CH_3CO_2Na in Ethanol:* A solution of 135.3 mg (0.25 mmol) of **1** in 5 ml of ethanol was treated with 20.9 mg (0.26 mmol) of CH_3CO_2Na and stirred for 15 h at room temp. The solvent was removed, the residue was extracted with 10 ml of benzene and after the extract was concentrated to ca. 2 ml in vacuo, it was chromatographed on Al_2O_3 (neutral, activity grade IV, height of column 5 cm). With benzene/pentane (1:1), a brown-yellow fraction was eluted which after removal of the solvent and recrystallization of the residue from ether/pentane gave red-brown crystals of **3**; yield 68 mg (60%). Subsequently with benzene, first a deep blue fraction containing [(η^5-$C_5Me_5Rh)_2$(μ-$CO)_2$] and then a yellow fraction was eluted. The latter was brought to dryness in vacuo, the residue was washed with pentane (0°C) and dried. A yellow solid of **4** was obtained; yield 19 mg (16%). − **3**: m. p. 96°C (dec.). − IR (C_6H_6): $\tilde{\nu}$ = 2010 cm^{-1} [ν(CO)]. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.26 [dd, *J*(RhH) = 2.0, *J*(HH) = 3.7 Hz, 1 H, one H of C*H*$_2$OEt], 5.06 [dd, *J*(RhH) = 5.0, *J*(HH) = 3.7 Hz, 1 H, one H of C*H*$_2$OEt], 3.44, 3.22, 1.20 [ABX_3 spin system, $J(H_AH_X)$ = 7.2, $J(H_BH_X)$ = −7.2, $J(H_AH_B)$ = 9.5 Hz, 5 H, $OCH_AH_BC(H_X)_3$], 1.96 [d, *J*(RhH) = 0.5 Hz, 15 H, C_5Me_5]. − MS (70 eV); *m*/*z* (%) = 452 (10) [M^+], 393 (9) [M^+ − CH_2OEt], 365 (100) [$C_5Me_5RhI^+$], 266 (3) [$C_5Me_5Rh(CO)^+$], 238 (14) [$C_5Me_5Rh^+$]. − $C_{14}H_{22}IO_2Rh$ (452.1): calcd. C 37.19, H 4.90; found C 37.45, H 5.03.

3. Preparation of [(η^5-C_5Me_5)Rh(CH_2OAc)(CO)I] (**4**): A solution of 152.3 mg (0.34 mmol) of **10** in 2 ml of benzene was treated with a solution of 258 mg (3.16 mmol) of CH_3CO_2Na in 2 ml of acetic acid (100%) and stirred for 3 h at 50°C. After cooling to room temp., the solvent was removed, the oily residue was extracted with 15 ml of benzene and the extract was brought to dryness in vacuo. A yellow solid was obtained which was washed with small portions of pentane (0°C) and dried; yield 103 mg (65%); m. p. 116°C (dec.). − IR (KBr): $\tilde{\nu}$ = 2020 cm^{-1} [ν(CO)], 1715 cm^{-1} [ν(C=O)]. − ^{1}H NMR (200 MHz, C_6D_6): δ = 6.20 [dd, *J*(RhH) = *J*(HH) = 2.2 Hz, 1 H, one H of C*H*$_2$OAc], 4.93 [dd, *J*(RhH) = 4.4, *J*(HH) = 2.2 Hz, 1 H, one H of C*H*$_2$OAc], 1.70 (s, 3 H, OCH_3), 1.53 [d, *J*(RhH) = 0.5 Hz, 15 H, C_5Me_5]. − ^{13}C NMR (22.5 MHz, $CDCl_3$): δ = 188.7 [d, *J*(RhC) = 78.0 Hz, Rh(CO)], 170.3 [s, *C*(O)CH_3], 104.5 [d, *J*(RhC) = 4.4 Hz, *C*$_5$Me$_5$], 55.6 [d, *J*(RhC) = 22.8 Hz, $RhCH_2$], 21.3 [s, C(O)*C*H_3], 10.1 [br. s, $C_5(CH_3)_5$]. − $C_{14}H_{20}IO_3Rh$ (465.1): calcd. C 36.06, H 4.32, Rh 22.09; found C 36.01, H 4.24, Rh 21.80.

4. Preparation of [(η^5-C_5Me_5)Rh(CH_2Cl){P($OMe)_3$}I] (**7**): A solution of 236.1 mg (0.61 mmol) of **5** in 8 ml of ether was treated under continuous stirring dropwise with 80 μl (1.10 mmol) of CH_2ClI. Evolution of gas (CO) was observed. The solution was stirred for 2 h at room temp. and then concentrated to ca. 2 ml in vacuo. After pentane (ca. 5 ml) was added, the solution was stored for 12 h at −78°C. Orange-red crystals precipitated which were filtered, washed with small quantities of pentane (−20°C) and dried; yield 203 mg (62%); m. p. 106°C (dec.). − ^{1}H NMR (200 MHz, C_6D_6): δ = 5.17 [ddd, *J*(RhH) = 8.0, *J*(PH) = 1.9, *J*(HH) = 6.0 Hz, 1 H, one H of C*H*$_2$OAc], 4.49 [ddd, *J*(RhH) = 1.6, *J*(PH) = 4.4, *J*(HH) = 6.0 Hz, 1 H, one H of C*H*$_2$OAc], 3.64 [d, *J*(PH) = 11.5 Hz, 9 H, P$(OMe)_3$], 1.79 [dd, *J*(RhH) = 0.3, *J*(PH) = 4.3 Hz, 15 H, C_5Me_5]. − ^{13}C NMR (22.5 MHz, C_6D_6): δ = 101.5 [dd, *J*(RhC) = *J*(PC) = 4.4 Hz, *C*$_5$Me$_5$], 54.2 [d, *J*(PC) = 6.6 Hz, P$(OMe)_3$], 35.5 [dd, *J*(RhC) = 30.2, *J*(PC) = 19.1 Hz, $RhCH_2$], 9.6 [d, *J*(RhC) = 2.2 Hz, $C_5(CH_3)_5$]. − ^{31}P NMR (36.2 MHz, C_6D_6): δ = 133.1 [d, *J*(RhP) = 253.1 Hz]. − MS (70 eV); *m*/*z* (%) = 538 (2) [M^+], 489 (66) [M^+ − CH_2Cl], 365 (100) [$C_5Me_5RhI^+$], 362 (2) [$C_5Me_5RhP(OMe)_3^+$], 238 (8) [$C_5Me_5Rh^+$]. − $C_{14}H_{26}ClIO_3PRh$ (538.6): calcd. C 31.22, H 4.87; found C 31.21, H 4.92.

5. Preparation of [(η^5-C_5H_5)Rh(CH_2Cl){P($OMe)_3$}I] (**8**) *and [(η^5-C_5H_5)Rh{P($OMe)_3$}I_2]* (**9**): A solution of 219.5 mg (0.69 mmol) of **6** in 3 ml of benzene was treated dropwise with 85 μl (1.17 mmol) of CH_2ClI and stirred for 28 h at room temp. A red-violet solid **9** precipitated. After addition of 10 ml of benzene to the reaction mixture, the solid was separated from the mother liquor, washed with acetone and ether, and dried; yield 38 mg (10%). The mother liquor was concentrated to 2−3 ml in vacuo and treated dropwise with 15 ml of pentane. A red-brown solid **8**

was formed which was filtered, repeatedly washed with small portions of ether (0°C), and dried; yield 188 mg (58%).

8: m. p. 89°C (dec.). − ^{1}H NMR (200 MHz, C_6D_6): δ = 5.47 [ddd, *J*(RhH) = 4.0, *J*(PH) = 1.4, *J*(HH) = 5.6 Hz, 1 H, one H of CH_2Cl], 5.27 [dd, *J*(RhH) = 0.3, *J*(PH) = 3.2 Hz, 5 H, C_5H_5], 4.73 [ddd, *J*(RhH) = 1.8, *J*(PH) = 9.8, *J*(HH) = 5.6 Hz, 1 H, one H of CH_2Cl], 3.53 [d, *J*(PH) = 11.8 Hz, 9 H, $P(OMe)_3$]. − ^{13}C NMR (22.5 MHz, C_6D_6): δ = 92.4 [dd, *J*(RhC) = *J*(PC) = 3.7 Hz, C_5H_5], 54.0 [d, *J*(PC) = 5.9 Hz, $P(OMe)_3$], 27.3 [dd, *J*(RhC) = 26.5, *J*(PC) = 17.2 Hz, $RhCH_2$]. − ^{31}P NMR (36.2 MHz, C_6D_6): δ = 133.4 [d, *J*(RhP) = 245.6 Hz]. − MS (70 eV); *m*/*z* (%) = 468 (2) [M^+], 419 (31) [$M^+ - CH_2Cl$], 341 (8) [$M^+ - I$], 295 (26) [$C_5H_5RhI^+$], 292 (9) [$C_5H_5RhP(OMe)_3^+$], 168 (28) [$C_5H_5Rh^+$]. − $C_9H_{16}ClIO_3PRh$ (468.5): calcd. C 23.08, H 3.44, Rh 21.97; found C 23.33, H 3.57, Rh 22.15.

9: m. p. 96°C (dec.). − ^{1}H NMR (60 MHz, CD_3NO_2): δ = 5.97 [dd, *J*(RhH) = 0.4, *J*(PH) = 1.3 Hz, 5 H, C_5H_5], 4.34 [d, *J*(PH) = 10.8 Hz, 9 H, $P(OMe)_3$]. − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 116.0 [d, *J*(RhP) = 211.4 Hz]. − MS (70 eV); *m*/*z* (%) = 546 (21) [M^+], 419 (100) [$M^+ - I$], 295 (83) [$C_5H_5RhI^+$], 168 (60) [$C_5H_5Rh^+$]. − $C_8H_{14}I_2O_3PRh$ (545.9): calcd. C 17.60, H 2.58; found C 17.82, H 2.62.

6. Preparation of [(η^5-C_5Me_5)Rh(CH_2OAc){$P(OMe)_3$}I] (**13**): A solution of 165.5 mg (0.31 mmol) of **7** in 6 ml of benzene was treated with a solution of 194.9 mg (1.60 mmol) of CH_3CO_2Na in 4 ml of acetic acid (100%) and stirred for 6 h at room temp. The solvent was removed, the residue was extracted with 20 ml of ether, and after the extract was filtered, the filtrate was concentrated to ca. 5 ml in vacuo. Pentane (ca. 5 ml) was added and the solution was stored for 12 h at −78°C. Orange-red crystals precipitated which were separated from the mother liquor, washed twice with 2 ml portions of pentane (−20°C) and dried; yield 134 mg (77%); m. p. 70°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1712 cm^{-1} [ν(C=O)]. − ^{1}H NMR (200 MHz, C_6D_6): δ = 5.92 [ddd, *J*(RhH) = 8.2, *J*(PH) = 2.2, *J*(HH) = 6.0 Hz, 1 H, one H of CH_2OAc], 5.10 [ddd, *J*(RhH) = 0.7, *J*(PH) = 4.4, *J*(HH) = 6.0 Hz, 1 H, one H of CH_2OAc], 3.53 [d, *J*(PH) = 10.5 Hz, 9 H, $P(OMe)_3$], 1.78 (s, 3 H, OCH_3), 1.70 [dd, *J*(RhH) = 0.4, *J*(PH) = 4.2 Hz, 15 H, C_5Me_5]. − ^{13}C NMR (22.5 MHz, C_6D_6): δ = 170.4 [s, *C*(O)CH_3], 101.4 [dd, *J*(RhC) = *J*(PC) = 4.4 Hz, C_5Me_5], 57.2 [dd, *J*(RhC) = 27.2, *J*(PC) = 17.7 Hz, $RhCH_2$], 54.0 [d, *J*(PC) = 5.9 Hz, $P(OMe)_3$], 21.2 [s, C(O)*C*H$_3$], 9.7 [d, *J*(RhC) = 1.5 Hz, $C_5(CH_3)_5$]. − ^{31}P NMR (36.2 MHz, C_6D_6): δ = 136.4 [d, *J*(RhP) = 256.1 Hz]. − MS (70 eV); *m*/*z* (%) = 562 (1) [M^+], 489 (58) [$M^+ - CH_2OAc$], 365 (100) [$C_5Me_5RhI^+$], 362 (1) [$C_5Me_5RhP(OMe)_3^+$], 238 (9) [$C_5Me_5Rh^+$]. − $C_{16}H_{29}IO_5PRh$ (562.2): calcd. C 34.18, H 5.20, Rh 18.31; found C 34.48, H 5.39, Rh 18.13.

7. Preparation of [(η^5-C_5H_5)Rh(CH_2OAc){$P(OMe)_3$}I] (**14**): Compound **14** was prepared analogously to **13** by using 210.2 mg (0.45 mmol) of **8** (in 6 ml of benzene) and 250 mg (3.05 mmol) of CH_3CO_2Na (in 2 ml of 100% acetic acid) as starting materials; time of reaction 90 min at 25°C. Red-brown microcrystalline solid; yield 173 mg (78%); m. p. 76°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1700 cm^{-1} [ν(C=O)]. − ^{1}H NMR (200 MHz, C_6D_6): δ = 6.70 [ddd, *J*(RhH) = *J*(HH) = 4.8, *J*(PH) = 1.4 Hz, 1 H, one H of CH_2OAc], 5.83 [ddd, *J*(RhH) = 2.4, *J*(PH) = 8.5, *J*(HH) = 4.8 Hz, 1 H, one H of CH_2OAc], 5.23 [dd, *J*(RhH) = 0.5, *J*(PH) = 3.1 Hz, 5 H, C_5H_5], 3.47 [d, *J*(PH) = 10.5 Hz, 9 H, $P(OMe)_3$], 1.72 (s, 3 H, OCH_3). − ^{13}C NMR (22.5 MHz, C_6D_6): δ = 169.9 [s, *C*(O)CH_3], 91.0 [dd, *J*(RhC) = *J*(PC) = 4.2 Hz, C_5H_5], 53.9 [d, *J*(PC) = 5.9 Hz, $P(OMe)_3$], 49.3 [dd, *J*(RhC) = 25.0, *J*(PC) = 15.4 Hz, $RhCH_2$], 21.6 [s, C(O)*C*H$_3$]. − ^{31}P NMR (36.2 MHz, C_6D_6): δ = 135.8 [d, *J*(RhP) = 248.6 Hz]. − MS (70 eV); *m*/*z* (%) = 492 (1) [M^+], 419 (100) [$M^+ - CH_2OAc$], 365 (50) [$M^+ - I$], 295 (70) [$C_5H_5RhI^+$], 292 (18) [$C_5H_5RhP(OMe)_3^+$], 168 (58) [$C_5H_5Rh^+$]. − $C_{11}H_{19}IO_5PRh$ (492.1): calcd. C 26.85, H 3.89, Rh 20.92; found C 27.06, H 3.98, Rh 21.35.

8. Preparation of [(η^5-C_5Me_5)Rh(CH_2OAc)(PMe_3)I] (**15**): Compound **15** was prepared analogously to **4** by using 321.3 mg (0.47 mmol) of **11** (in 5 ml of benzene) and 308.3 mg (3.76 mmol) of CH_3CO_2Na (in 5 ml of 100% acetic acid) as starting materials; time of reaction 5 h at 25°C. An orange-yellow oil was obtained which upon addition of 0.5 ml of pentane gave an orange-yellow microcrystalline solid; yield 190 mg (78%); m. p. 83°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1708 cm^{-1} [ν(C=O)]. − ^{1}H NMR (200 MHz, C_6D_6): δ = 5.57 [ddd, *J*(RhH) = 2.1, *J*(PH) = 8.8, *J*(HH) = 6.5 Hz, 1 H, one H of CH_2OAc], 5.23 [dd, *J*(RhH) = 5.1, *J*(HH) = 6.5 Hz, 1 H, one H of CH_2OAc], 1.70 (s, 3 H, OCH_3), 1.59 [dd, *J*(RhH) = 0.3, *J*(PH) = 2.7 Hz, 15 H, C_5Me_5], 1.35 [dd, *J*(RhH) = 0.7, *J*(PH) = 10.3 Hz, 9 H, PMe_3]. − ^{13}C NMR (22.5 MHz, C_6D_6): δ = 170.3 [s, *C*(O)CH_3], 99.3 [dd, *J*(RhC) = 4.4, *J*(PC) = 2.9 Hz, C_5Me_5], 60.1 [dd, *J*(RhC) = 30.2, Hz, *J*(PC) = 15.4, $RhCH_2$], 21.1 [s, C(O)*C*H$_3$], 17.4 [d, *J*(PC) = 32.4 Hz, PMe_3], 10.0 [br. s, $C_5(CH_3)_5$]. − ^{31}P NMR (36.2 MHz, C_6D_6): δ = 4.8 [d, *J*(RhP) = 157.8 Hz]. − MS (70 eV); *m*/*z* (%) = 514 (6) [M^+], 441 (100) [$M^+ - CH_2OAc$], 365 (83) [$C_5Me_5RhI^+$], 314 (2) [$C_5Me_5Rh(PMe_3)^+$], 238 (5) [$C_5Me_5Rh^+$]. − $C_{16}H_{29}IO_2PRh$ (514.2): calcd. C 37.37, H 5.70; found C 37.28, H 6.07.

9. Preparation of [(η^5-C_5H_5)Rh(CH_2OAc)(PMe_3)I] (**16**): Compound **16** was prepared analogously to **4** by using 140.1 mg (0.33 mmol) of **12** (in 2 ml of benzene) and 270 mg (3.30 mmol) of CH_3CO_2Na (in 1 ml of 100% acetic acid) as starting materials; time of reaction 6 h at 25°C. After recrystallization from ether (25°C to −78°C) orange-red crystals were obtained; yield 125 mg (85%); m. p. 106°C (dec.). − IR (KBr): $\tilde{\nu}$ = 1720 cm^{-1} [ν(C=O)]. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.60 [dd, *J*(RhH) = 4.9, *J*(HH) = 5.7 Hz, 1 H, one H of CH_2OAc], 5.42 [dd, *J*(RhH) = 0.4, *J*(PH) = 1.4 Hz, 5 H, C_5H_5], 4.97 [ddd, *J*(RhH) = 2.6, *J*(PH) = 8.3, *J*(HH) = 5.7 Hz, 1 H, one H of CH_2OAc], 1.78 [dd, *J*(RhH) = 0.8, *J*(PH) = 11.1 Hz, 9 H, PMe_3], 1.70 (s, 3 H, OCH_3). − ^{13}C NMR (22.5 MHz, C_6D_6): δ = 169.5 [s, *C*(O)CH_3], 89.9 [dd, *J*(RhC) = *J*(PC) = 3.7 Hz, C_5H_5], 51.5 [dd, *J*(RhC) = 27.2, *J*(PC) = 13.4, $RhCH_2$], 19.6 [d, *J*(PC) = 33.8 Hz, PMe_3], 18.9 [s, C(O)C*H*$_3$]. − ^{31}P NMR (36.2 MHz, C_6D_6): δ = 10.3 [d, *J*(RhP) = 160.0 Hz]. − MS (70 eV); *m*/*z* (%) = 444 (3) [M^+], 371 (100) [$M^+ - CH_2OAc$], 295 (23) [$C_5H_5RhI^+$], 244 (73) [$C_5H_5Rh(PMe_3)^+$], 168 (35) [$C_5H_5Rh^+$]. − $C_{11}H_{19}IO_2PRh$ (444.0): calcd. C 29.75, H 4.31, Rh 23.18; found C 30.01, H 4.40, Rh 23.53.

10. Reaction of Compound **14** *nBuLi:* A solution of 276.5 mg (0.56 mmol) of **14** in 20 ml of benzene was treated under continuous stirring with 0.8 ml of a 1.41 M solution (1.12 mmol) of *n*BuLi in hexane at room temp. After the reaction mixture was stirred for 1 h, the solvent was removed and the residue was extracted with 20 ml of ether. The extract was brought to dryness in vacuo, the oily residue was dissolved in 2 ml of benzene and the solution was chromatographed on Al_2O_3 (neutral, activity grade IV, height of column 5 cm). With hexane, a yellow fraction was eluted from which upon evaporation of the solvent a light yellow oil **18** was obtained; yield 8 mg (3%). Further elution with benzene gave a red fraction which was brought to dryness in vacuo. The residue was dissolved in 10 ml of ether, the extract was concentrated to ca. 1 ml and then stored for 12 h at −20°C. A red-brown microcrystalline solid **17** precipitated which was washed with small portions of pentane and dried; yield 21 mg (8%).

17: ^{1}H NMR (60 MHz, $CDCl_3$): δ = 8.20, 7.07 (both m, 5 H, C_6H_5), 5.03 [dd, *J*(RhH) = 0.5, *J*(PH) = 3.2, 5 H, C_5H_5], 3.32 [d, *J*(PH) = 11.7 Hz, 9 H, $P(OMe)_3$]. − MS (70 eV); *m*/*z* (%) = 496 (7) [M^+], 419 (11) [$M^+ - C_6H_5$], 292 (100) [$C_5H_5RhP(OMe)_3^+$], 168 (69) [$C_5H_5Rh^+$]. − $C_{14}H_{19}IO_3PRh$ (496.1): calcd. C 33.90, H 3.86; found C 33.56, H 3.98.

18: ^{1}H NMR (60 MHz, C_6D_6): δ = 7.64, 7.37 (both m, 5 H, C_6H_5), 5.17 [dd, *J*(RhH) = 0.4, *J*(PH) = 2.2 Hz, 5 H, C_5H_5], 3.28 [d, *J*(PH) = 11.4 Hz, 9 H, $P(OMe)_3$] 1.1 (br. m, 9 H, C_4H_9). − MS (70 eV); *m*/*z* (%) = 462 (2) [M^+], 292 (100) [$C_5H_5RhP(OMe)_3^+$], 168 (56) [$C_5H_5Rh^+$].

11. Preparation of [(η^5-C_5Me_5)Rh{κ^2-C,O-$CH_2OC(Me)O$}(CO)]PF_6 (**19**): A solution of 81.2 mg (0.17 mmol) of **4** in 5 ml of acetone was treated under continuous stirring with a solution of 42.9 mg (0.17 mmol) of $AgPF_6$ in 2 ml of acetone at room temp. A pale yellow precipitate of AgI was rapidly formed. After the reaction mixture was stirred for 20 min, it was filtered and the filtrate was concentrated to ca. 2 ml in vacuo. Upon addition of 20 ml of ether, the solution was rigorously stirred until a yellow microcrystalline solid precipitated. This was filtered, washed twice with 5 ml portions of ether and dried; yield 69 mg (83%); dec. temp. 109°C. − Λ = 66 $cm^2\Omega^{-1}mol^{-1}$. − IR (nujol): $\tilde{\nu}$ = 2030 cm^{-1} [ν(CO)], 1605 [ν(C=O)]. − ^{1}H NMR (200 MHz, CD_3NO_2): δ = 6.23 [dd, *J*(RhH) = 0.5, *J*(HH) = 6.0 Hz, 1 H, one H of $RhCH_2$], 5.63 [dd, *J*(RhH) = 4.0, *J*(HH) = 6.0 Hz, 1 H, one H of $RhCH_2$], 2.23 (s, 3 H, CH_3), 1.92 [d, *J*(RhH) = 0.4 Hz, 15 H, C_5Me_5]. − ^{13}C NMR (22.5 MHz, CD_3NO_2): δ = 190.7 [d, *J*(RhC) = 70.5 Hz, Rh(CO)], 187.9 (s, C=O), 107.6 [d, *J*(RhC) = 5.2 Hz, C_5Me_5], 81.0 [d, *J*(RhC) = 23.5 Hz, $RhCH_2$], 18.6 [s, C(O)CH_3], 9.3 [br. s, $C_5(CH_3)_5$]. − $C_{14}H_{20}F_6O_3PRh$ (484.2): calcd. C 37.74, H 4.17; found C 37.44, H 4.31.

12. Preparation of [(η^5-C_5Me_5)Rh{κ^2-C,O-$CH_2OC(Me)O$}{P(OMe)$_3$}]PF_6 (**20**): Compound **20** was prepared analogously to **19** by using 131.7 mg (0.24 mmol) of **13** and 59.9 mg (0.24 mmol) of $AgPF_6$ as starting materials. Yellow microcrystalline solid; yield 131 mg (94%); dec. temp. 66°C. − Λ = 80 $cm^2\Omega^{-1}mol^{-1}$. − IR (nujol): $\tilde{\nu}$ = 1600 cm^{-1} [ν(C=O)]. − ^{1}H NMR (200 MHz, CD_3NO_2): δ = 5.91, 5.77 [both part of an ABPX spin system; from $^1H\{^{31}P\}$: *J*(RhH) = 0.3 and 4.2, *J*(HH) = 6.4 Hz, 1H each, $RhCH_2$], 3.77 [d, *J*(PH) = 11.8 Hz, 9 H, $P(OMe)_3$], 2.14 (s, 3 H, CH_3), 1.76 [dd, *J*(RhH) = 0.4, *J*(PH) = 4.4 Hz, 15 H, C_5Me_5]. − ^{13}C NMR (50.3 MHz, CD_3NO_2): δ = 186.3 (s, C=O), 103.2 [dd, *J*(RhC) = 5.3, *J*(PC) = 3.4 Hz, C_5Me_5], 82.1 [dd, *J*(RhC) = 25.9, *J*(PC) = 23.1 Hz, $RhCH_2$], 53.8 [d, *J*(PC) = 4.7 Hz, $P(OMe)_3$], 18.5 [s, C(O)CH_3], 9.2 [br. s, $C_5(CH_3)_5$]. − ^{31}P NMR (36.2 MHz, CD_3NO_2): δ = 129.4 [d, *J*(RhP) = 256.1 Hz]. − $C_{16}H_{29}F_6O_5P_2Rh$ (580.3): calcd. C 33.12, H 5.04; found C 33.38, H 5.26.

13. Preparation of [(η^5-C_5H_5)Rh{κ^2-C,O-$CH_2OC(Me)O$}{P(OMe)$_3$}]PF_6 (**21**): Compound **21** was prepared analogously to **19** by using 90.2 mg (0.18 mmol) of **14** and 45.4 mg (0.18 mmol) of $AgPF_6$ as starting materials. Yellow microcrystalline solid; yield 87 mg (94%); dec. temp. 112° C. − Λ = 65 $cm^2\Omega^{-1}mol^{-1}$. − IR (nujol): $\tilde{\nu}$ = 1600 cm^{-1} [ν(C=O)]. − ^{1}H NMR (200 MHz, CD_3NO_2): δ = 7.37 [ddd, *J*(RhH) = 4.5, *J*(PH) = 1.4, *J*(HH) = 6.2 Hz, 1 H, one H of $RhCH_2$], 5.88 [ddd, *J*(RhH) = 0.3, *J*(PH) = 28.3, *J*(HH) = 6.2 Hz, 1 H, one H of $RhCH_2$], 5.85 [dd, *J*(RhH) = 0.6, *J*(PH) = 2.8 Hz, 5 H, C_5H_5], 3.80 [d, *J*(PH) = 12.0 Hz, 9 H, $P(OMe)_3$], 2.17 (s, 3 H, CH_3). − ^{13}C NMR (22.5 MHz, CD_3NO_2): δ = 188.1 (s, C=O), 91.4 [dd, *J*(RhC) = *J*(PC) = 4.4 Hz, C_5H_5], 73.0 [dd, *J*(RhC) = 23.5, *J*(PC) = 20.6 Hz, $RhCH_2$], 54.3[d, *J*(PC) = 4.4 Hz, $P(OMe)_3$], 17.9 [s, C(O)CH_3]. − ^{31}P NMR (36.2 MHz, CD_3NO_2): δ = 128.2 [d, *J*(RhP) = 242.7 Hz]. − $C_{11}H_{19}F_6O_5P_2Rh$ (510.1): calcd. C 25.90, H 3.75, Rh 20.17; found C 25.81, H 3.91, Rh 19.78.

14. Preparation of [(η^5-C_5Me_5)Rh{κ^2-C,O-$CH_2OC(Me)O$}(PMe_3)]PF_6 (**22**): Compound **22** was prepared analogously to **19** by using 67.0 mg (0.13 mmol) of **15** and 36.1 mg (0.14 mmol) of $AgPF_6$ as starting materials. Orange-yellow microcrystalline solid; yield 59 mg (85%); dec. temp. 60°C. − Λ = 84 $cm^2\Omega^{-1}mol^{-1}$. − IR (nujol): $\tilde{\nu}$ = 1608 cm^{-1} [ν(C=O)]. − ^{1}H NMR (200 MHz, CD_3NO_2): δ = 5.86 [ddd, *J*(RhH) = 4.0, *J*(PH) = 0.3, *J*(HH) = 7.4 Hz, 1 H, one H of $RhCH_2$], 5.55 [ddd, *J*(RhH) = *J*(HH) = 7.4, *J*(PH) = 27.7 Hz, 1 H, one H of $RhCH_2$], 2.16 (s, 3 H, CH_3), 1.73 [dd, *J*(RhH) = 0.3, *J*(PH) = 2.6 Hz, 15 H, C_5Me_5], 1.48 [dd, *J*(RhH) = 0.8, *J*(PH) = 10.4 Hz, 9 H, PMe_3]. − ^{13}C NMR (50.3 MHz, CD_3NO_2): δ = 186.1 (s, C=O), 101.4 [dd, *J*(RhC) = *J*(PC) = 3.0 Hz, C_5Me_5], 84.6 [dd, *J*(RhC) = 28.5 Hz, $RhCH_2$], 18.8 [s, C(O)CH_3], 13.8 [d, *J*(PC) = 31.0 Hz, PMe_3], 9.5 [br. s, $C_5(CH_3)_5$]. − ^{31}P NMR (36.2 MHz, CD_3NO_2): δ = 2.3 [d, *J*(RhP) = 159.3 Hz]. − $C_{16}H_{29}F_6O_2P_2Rh$ (532.3): calcd. C 36.11, H 5.49, Rh 19.34; found C 36.05, H 5.31, Rh 19.70.

15. Preparation of [(η^5-C_5H_5)Rh{κ^2-C,O-$CH_2OC(Me)O$}(PMe_3)]PF_6 (**23**): Compound **23** was prepared analogously to **19** by using 96.2 mg (0.22 mmol) of **16** and 58.0 mg (0.23 mmol) of $AgPF_6$ as starting materials. Orange-yellow microcrystalline solid; yield 83 mg (81%); dec. temp. 68°C. − Λ = 78 $cm^2\Omega^{-1}mol^{-1}$. − IR (nujol): $\tilde{\nu}$ = 1605 cm^{-1} [ν(C=O)]. − ^{1}H NMR (200 MHz, CD_3NO_2): δ = 7.37 [ddd, *J*(RhH) = 4.2, *J*(PH) = 0.8, *J*(HH) = 6.8 Hz, 1 H, one H of $RhCH_2$], 5.60 [ddd, *J*(RhH) = 0.3, *J*(PH) = 19.7, *J*(HH) = 6.8 Hz, 1 H, one H of $RhCH_2$], 5.57 [dd, *J*(RhH) = 0.6, *J*(PH) = 1.3 Hz, 5 H, C_5H_5], 2.18 (s, 3 H, CH_3), 1.63 [dd, *J*(RhH) = 0.8, *J*(PH) = 11.5 Hz, 9 H, PMe_3]. − ^{13}C NMR (22.5 MHz, CD_3NO_2): δ = 187.5 (s, C=O), 90.6 [dd, *J*(RhC) = 5.2, *J*(PC) = 2.9 Hz, C_5H_5], 75.4 [dd, *J*(RhC) = 25.7, *J*(PC) = 14.7 Hz, $RhCH_2$], 17.0 [s, C(O)CH_3], 16.2 [d, *J*(PC) = 33.1 Hz, PMe_3]. − ^{31}P NMR (36.2 MHz, CD_3NO_2): δ = 12.5 [d, *J*(RhP) = 150.3 Hz]. − $C_{11}H_{19}F_6O_2P_2Rh$ (462.1): calcd. C 28.59, H 4.15, Rh 22.27; found C 28.42, H 4.11, Rh 22.00.

16. Preparation of [(η^5-C_5Me_5)Rh(η^2-CH_2O){P(OMe)$_3$}] (**24**): A suspension of 89.7 mg (0.15 mmol) of **20** in 5 ml of methanol was treated at 0°C under continuous stirring with 98.1 mg (1.40 mmol) of KOH. A yellow-brown solution was formed of which after it was stirred for 10 min at 0°C, the solvent was removed in vacuo. The residue was extracted twice with 5 ml of cold ether (0°C) and the combined extracts were brought by cooling with an ice bath to dryness in vacuo. The remaining yellow-brown oil was dissolved in 2 ml of pentane (0°C) and the solution was stored for 10 h at −78°C. A yellow-brown microcrystalline solid precipitated which was filtered, washed twice with small quantities of pentane (−20°C) and dried; yield of oily product 38 mg (62%), yield of solid material 15 mg (26%); m. p. 36°C (dec.). − IR (C_6H_6): $\tilde{\nu}$ = 2805 cm^{-1} [ν(CH_2)], 1220 [ν(C−O)]. − ^{1}H NMR (200 MHz, C_6D_6): δ = 4.62 (m, 2 H, CH_2O), 3.52 [d, *J*(PH) = 12.2 Hz, 9 H, $P(OMe)_3$], 1.89 [dd, *J*(RhH) = 0.5, *J*(PH) = 3.4 Hz, 15 H, C_5Me_5]. − ^{13}C NMR (50.3 MHz, C_6D_6): δ = 97.6 [dd, *J*(RhC) = *J*(PC) = 4.4 Hz, C_5Me_5], 78.1 [dd, *J*(RhC) = 12.0, *J*(PC) = 5.9 Hz, CH_2O], 51.1 [br. s, $P(OMe)_3$], 10.0 [s, $C_5(CH_3)_5$]. − ^{31}P NMR (36.2 MHz, C_6D_6): δ = 149.2 [d, *J*(RhP) = 311.1 Hz]. − MS (70 eV); *m*/*z* (%) = 392 (2) [M^+], 390 (32) [$M^+ - 2$ H], 362 (100) [$M^+ - CH_2O$], 238 (49) [$C_5Me_5Rh^+$], 30 (2) [CH_2O^+]. − $C_{14}H_{26}O_4PRh$ (392.2): calcd. C 42.87, H 6.68; found C 42.59, H 6.70.

17. Preparation of [(η^5-C_5H_5)Rh(η^2-CH_2O){P(OMe)$_3$}] (**25**): Compound **25** was prepared analogously to **24** by using 95.3 mg (0.19 mmol) of **21** and 88.7 mg (1.26 mmol) of KOH as starting

materials. Yellow-brown solid; yield of oily product 43 mg (71%), yield of solid material 13 mg (22%); m. p. 43°C (dec.). – IR (C_6H_6): $\tilde{\nu}$ = 2825 cm^{-1} [$\nu(CH_2)$], 1232 [$\nu(C-O)$]. – ^1H NMR (200 MHz, C_6D_6): δ = 5.56 [ddd, J(RhH) = 2.5, J(PH) = 0.5, J(HH) = 21.5 Hz, 1 H, one H of CH_2O], 5.29 [dd, J(RhH) = 0.8, J(PH) = 2.6 Hz, 5 H, C_5H_5], 4.60 [ddd, J(RhH) = 2.0, J(PH) = 5.1, J(HH) = 21.5 Hz, 1 H, one H of CH_2O], 3.80 [d, J(PH) = 12.4 Hz, 9 H, $P(OMe)_3$]. – ^{13}C NMR (100.6 MHz, C_6D_6): δ = 86.1 [dd, J(RhC) = J(PC) = 3.1 Hz, C_5H_5], 72.6 [dd, J(RhC) = 13.6, J(PC) = 4.9 Hz, CH_2O], 51.6 [br. s, $P(OMe)_3$]. – ^{31}P NMR (36.2 MHz, C_6D_6): δ = 150.1 [d, J(RhP) = 299.2 Hz]. – $C_9H_{16}O_4PRh$ (322.1): calcd. C 33.56, H 5.01; found C 33.54, H 4.81.

18. Preparation of $[(\eta^5\text{-}C_5Me_5)Rh(\eta^2\text{-}CH_2O)(PMe_3)]$ (**26**): Compound **26** was prepared analogously to **24** by using 105.6 mg (0.20 mmol) of **22** and 85.9 mg (1.22 mmol) of KOH as starting materials. Brownish microcrystalline solid; yield of oily product 39 mg (56%), yield of solid material 20 mg (29%); m. p. 25°C (dec.). – IR (C_6H_6): $\tilde{\nu}$ = 2800 cm^{-1} [$\nu(CH_2)$], 1210 [$\nu(C-O)$]. – ^1H NMR (200 MHz, C_6D_6): δ = 4.48 [ddd, J(RhH) = 3.0, J(PH) = 0.6, J(HH) = 18.2 Hz, 1 H, one H of CH_2O], 4.15 [ddd, J(RhH) = 2.4, J(PH) = 6.1, J(HH) = 18.2 Hz, 1 H, one H of CH_2O], 1.87 [dd, J(RhH) = 0.4, J(PH) = 2.2 Hz, 15 H, C_5Me_5], 0.99 [dd, J(RhH) = 0.9, J(PH) = 8.9 Hz, 9 H, PMe_3]. – ^{13}C NMR (50.3 MHz, C_6D_6): δ = 96.5 [dd, J(RhC) = J(PC) = 3.3 Hz, C_5Me_5], 74.4 [dd, J(RhC) = 14.0, J(PC) = 6.6 Hz, CH_2O], 15.8 [d, J(PC) = 25.7 Hz, PMe_3], 10.7 [s, $C_5(CH_3)_5$]. – ^{31}P NMR (36.2 MHz, C_6D_6): δ = 2.8 [d, J(RhP) = 190.3 Hz]. – MS (70 eV); m/z (%) = 344 (2) [M^+], 342 (23) [M^+ – 2 H], 314 (100) [M^+ – CH_2O], 238 (25) [$C_5Me_5Rh^+$], 30 (2) [CH_2O^+]. – $C_{14}H_{26}OPRh$ (344.3): calcd. C 48.85, H 7.61 Rh 29.83; found C 48.34, H 7.55, Rh 29.50.

19. Preparation of $[(\eta^5\text{-}C_5H_5)Rh(\eta^2\text{-}CH_2O)(PMe_3)]$ (**27**): Compound **27** was prepared analogously to **24** by using 98.7 mg (0.21 mmol) of **23** and 103.6 mg (1.48 mmol) of KOH as starting materials. Brownish microcrystalline solid; yield of oily product 39 mg (56%), yield of solid material 20 mg (29%); m. p. 39°C (dec.). – IR (C_6H_6): $\tilde{\nu}$ = 2790 cm^{-1} [$\nu(CH_2)$], 1215 [$\nu(C-O)$]. – ^1H NMR (60 MHz, C_6D_6): δ = 5.70 [ddd, J(RhH) = 2.8, J(PH) = 0.5, J(HH) = 19.8 Hz, 1 H, one H of CH_2O], 5.07 [dd, J(RhH) = 0.3, J(PH) = 1.2 Hz, 5 H, C_5H_5], 4.03 [ddd, J(RhH) = 2.1, J(PH) = 5.0, J(HH) = 19.8 Hz, 1 H, one H of CH_2O], 0.90 [dd, J(RhH) = 0.8, J(PH) = 10.4 Hz, 9 H, PMe_3]. – ^{13}C NMR (100.6 MHz, C_6D_6): δ = 85.0 [br. s, C_5H_5], 67.9 [m, CH_2O], 17.7 [d, J(PC) = 28.4 Hz, PMe_3]. – ^{31}P NMR (36.2 MHz, C_6D_6): δ = 8.0 [d, J(RhP) = 193.5 Hz]. – MS (70 eV); m/z (%) = 274 (4) [M^+], 272 (30) [M^+ – 2 H], 244 (100) [M^+ – CH_2O], 168 (50) [$C_5H_5Rh^+$], 30 (4) [CH_2O^+]. – $C_9H_{16}OPRh$ (274.1): calcd. C 39.44, H 5.88, Rh 37.54; found C 39.73, H 6.16, Rh 38.09.

20. Preparation of $[(\eta^5\text{-}C_5H_5)Rh\{CH_2OC(O)Ph\}(PMe_3)I]$ (**28**): A solution of 87.1 mg (0.21 mmol) of **12** in 4 ml acetone/benzene (1:1) was treated with 79.3 mg (0.49 mmol) of $PhCO_2K$ and stirred for 20 h at 50–60°C. After the reaction mixture was cooled to room temp., the solvent was removed and the residue was extracted with 15 ml of ether. The extract was concentrated to ca. 3 ml in vacuo and upon storing for 6 h at –78°C gave orange-red crystals. The crystals were separated from the mother liquor, washed twice with pentane (0°C) and dried; yield 59 mg (56%); m. p. 142°C (dec.). – IR (KBr): $\tilde{\nu}$ = 1712 cm^{-1} [$\nu(C=O)$]. – ^1H NMR (200 MHz, C_6D_6): δ = 8.1, 7.2 (both m, 5 H, C_6H_5), 7.00 [ddd, J(RhH) = 4.8, J(PH) = 0.3, J(HH) = 5.6 Hz, 1 H, one H of $RhCH_2$], 5.33 [ddd, J(RhH) = 1.4, J(PH) = 8.4, J(HH) = 5.6 Hz, 1 H, one H $RhCH_2$], 5.05 [dd, J(RhH) = 0.6, J(PH) = 1.4 Hz, 5 H, C_5H_5], 1.37 [dd, J(RhH) = 0.8, J(PH) = 11.2 Hz, 9 H, PMe_3]. – ^{31}P NMR (36.2 MHz, C_6D_6): δ = 10.0 [d, J(RhP) = 153.3 Hz]. – $C_{16}H_{21}IO_2PRh$ (506.1): calcd. C 37.97, H 4.18; found C 37.67, H 4.61.

21. Preparation of $[(\eta^5\text{-}C_5H_5)Rh\{\kappa^2\text{-}C,O\text{-}CH_2OC(Ph)O\}(PMe_3)]PF_6$ (**29**): A solution of 60.7 mg (0.12 mmol) of **28** in 3 ml of acetone was treated dropwise with a solution of 30.4 mg (0.12 mmol) of $AgPF_6$ in 2 ml of acetone. The reaction mixture was stirred for 10 min at room temp. and then filtered. The filtrate was concentrated to ca. 2 ml in vacuo and under vigorous stirring 15 ml of ether was added. An orange-yellow precipitate was formed which was separated from the mother liquor, washed twice with ether and dried; yield 52 mg (83%); dec. temp. 75°C. – IR (nujol): $\tilde{\nu}$ = 1602 cm^{-1} [$\nu(C=O)$]. – ^1H NMR (60 MHz, $(CD_3)_2CO$): δ = 8.1, 7.7 (both m, 5 H, C_6H_5), 6.17 (m, 1 H, one H of $RhCH_2$), 5.80 [dd, J(RhH) = 0.6, J(PH) = 1.2 Hz, 5 H, C_5H_5], 1.73 [dd, J(RhH) = 0.8, J(PH) = 11.8 Hz, 9 H, PMe_3], signal of one H of $RhCH_2$ partly covered by signal of C_5H_5. – ^{31}P NMR (36.2 MHz, CD_3NO_2): δ = 12.8 [d, J(RhP) = 150.4 Hz]. – $C_{16}H_{21}F_6O_2P_2Rh$ (524.2): calcd. C 36.66, H 4.04; found C 36.73, H 4.29.

22. Thermal Decomposition of **24**: A solution of 36.4 mg (0.09 mmol) of **24** in 0.5 ml of benzene was stored for 5 h at room temp. The reaction was controlled by measuring the ^1H-NMR spectrum in time intervals of ca. 20 min. After 5 h, the signals of **24** disappeared and new signals corresponding to **30**[22] were observed; yield ca 85%.

23. Thermal Decomposition of **25**: A solution of 50.6 mg (0.16 mmol) of **25** in 0.5 ml of benzene was stored for 6 d at room temp. The reaction was controlled by measuring the ^1H-NMR spectrum in time intervals of ca. 2–3 h. After 6 d, the signals of **25** disappeared and new signals corresponding to **31** and **32**[33] were observed; yield almost quantitative; ratio **31**/**32** = 70:30.

24. Preparation of $[\{(\eta^5\text{-}C_5H_5)RhP(OMe)_3\}_2]$ (**31**): A solution of 88.2 mg (0.27 mmol) of **25** in 0.6 ml of benzene was stored for 7 d at room temp. A characteristic change of color from yellow-brown to deep green occurred. The solvent was removed, the residue was washed twice with 2 ml portions of pentane and then extracted with 10 ml of ether . The extract was concentrated to ca. 1 ml in vacuo and stored for 12 h at –78°C. A green microcrystalline solid precipitated which was repeatedly washed with small quantities of pentane and dried; yield 30.5 mg (39%). – ^1H NMR (60 MHz, C_6D_6): δ = 5.57 [dd, J(RhH) = 0.6, J(PH) = 2.2 Hz, 5 H, C_5H_5], 3.57 [d, J(PH) = 13.1 Hz, 9 H, $P(OMe)_3$]. – ^{31}P NMR (36.2 MHz, C_6D_6): δ = 161.8 [pseudo-quartet, spectrum of AA′XX′ type, N = J(AX) + J(AX′) = 277.6 Hz]. – MS (70 eV); m/z (%) = 584 (8) [M^+], 460 (6) [M^+ – $P(OMe)_3$], 292 (88) [$M/2^+$], 233 (100) [$(C_5H_5)_2Rh^+$], 168 (67) [$C_5H_5Rh^+$]. – $C_{16}H_{28}O_6P_2Rh_2$ (584.2): calcd. C 32.90, H 4.83; found C 32.96, H 4.82.

25. Preparation of $[(\eta^5\text{-}C_5Me_5)Rh(CH_3)(CO)\{P(OMe)_3\}]CF_3SO_3$ (**33**): A solution of 47.1 mg (0.12 mmol) of **24** in 3 ml of ether was treated dropwise with 14 µl (0.12 mmol) of $CF_3SO_3CH_3$ at 0°C. Evolution of gas was observed and a pale yellow solid precipitated. After the cooling vessel was removed, the solid was separated from the mother liquor, repeatedly washed with ether and dried; yield 37 mg (55%). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2060 cm^{-1} [$\nu(CO)$]. – ^1H NMR (60 MHz, CD_2Cl_2): δ = 3.78 [d, J(PH) = 11.8 Hz, 9 H, $P(OMe)_3$], 1.86 [dd, J(RhH) = 0.4, J(PH) = 5.0 Hz, 15 H, C_5Me_5], 0.75 [dd, J(RhH) = 2.2, J(PH) = 6.1 Hz, 3 H, $RhCH_3$]. – ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 120.2 [d, J(RhP) = 218.8 Hz]. – $C_{16}H_{27}F_3O_7PRhS$ (554.3): calcd. C 34.67, H 4.91; found C 34.31, H 5.00.

26. Preparation of $[(\eta^5\text{-}C_5Me_5)Rh(CH_3)(CO)(PMe_3)]CF_3SO_3$ (**34**): Compound **34** was prepared analogously to **33** by using 44.6

mg (0.13 mmol) of **26** and 15 µl (0.13 mmol) of $CF_3SO_3CH_3$ as starting materials. Pale yellow solid; yield 45 mg (69%). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2045 cm^{-1} [ν(CO)]. − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.85 [dd, *J*(RhH) = 0.3, *J*(PH) = 3.1 Hz, 15 H, C_5Me_5], 1.55 [dd, *J*(RhH) = 0.8, *J*(PH) = 11.0 Hz, 9 H, PMe_3], 0.51 [dd, *J*(RhH) = 2.2, *J*(PH) = 5.7 Hz, 3 H, $RhCH_3$]. − ^{31}P NMR (36.2 MHz, $CDCl_3$): δ = 4.8 [d, *J*(RhP) = 126.5 Hz]. − $C_{16}H_{27}F_3O_4PRhS$ (506.3): calcd. C 37.95 H 5.38; found C 37.56, H 5.23.

27. Preparation of [(η^5-C_5H_5)Rh(CH_3)(CO)(PMe_3)]CF_3SO_3 (**35**): Compound **35** was prepared analogously to **33** by using 60.3 mg (0.22 mmol) of **27** and 25 µl (0.22 mmol) of $CF_3SO_3CH_3$ as starting materials. The crude product (dark oil) was dissolved in 8 ml of CH_2Cl_2, the solution was filtered and the filtrate was brought to dryness in vacuo. The residue was dissolved in 1 ml of methanol and the solution was layered with 10 ml of ether. Light brown crystals precipitated which were separated from the mother liquor, washed with ether and dried; yield 16 mg (16%). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2055 cm^{-1} [ν(CO)]. − ^{1}H NMR (200 MHz, CD_3NO_2): δ = 5.73 [dd, *J*(RhH) = 0.3, *J*(PH) = 1.4 Hz, 5 H, C_5H_5], 1.85 [dd, *J*(RhH) = 0.9, *J*(PH) = 10.8 Hz, 9 H, PMe_3], 1.03 [dd, *J*(RhH) = 2.3, *J*(PH) = 5.2 Hz, 3 H, $RhCH_3$]. − ^{31}P NMR (36.2 MHz, $(CD_3)_2CO$): δ = 12.8 [d, *J*(RhP) = 125.1 Hz]. − $C_{11}H_{17}F_3O_4PRhS$ (436.2): calcd. C 30.29 H 3.91; found C 29.80, H 4.08.

28. Preparation of [(η^5-C_5H_5)Rh(PMe_3)($SAc)_2$] (**37**): A solution of 146 mg (0.35 mmol) of **36** in 1 ml of benzene and 2 ml of thioacetic acid was treated with 302.9 mg (2.65 mmol) of KSAc at room temp. After the reaction mixture was stirred for 1 h, the solvent was removed and the residue was extracted with 10 ml of benzene. The extract was brought to drynesss in vacuo and upon addition of 1 ml of ether and 1 ml of pentane the oily residue was crystallized to give an orange solid; yield 105 mg (76%); m. p. 150°C (dec.). − IR (C_6H_6): $\tilde{\nu}$ = 1625 cm^{-1} [ν(C=O)]. − ^{1}H NMR (60 MHz, C_6D_6): δ = 5.40 [dd, *J*(RhH) = 0.4, *J*(PH) = 2.0 Hz, 5 H, C_5H_5], 2.57 (s, 6 H, $SCCH_3$), 1.32 [dd, *J*(RhH) = 0.9, *J*(PH) = 11.7 Hz, 9 H, PMe_3]. − ^{31}P NMR (36.2 MHz, C_6D_6): δ = 12.2 [d, *J*(RhP) = 120.0 Hz]. − MS (70 eV); *m/z* (%) = 394 (7) [M^+], 319 (100) [M^+ − SAc], 244 (65) [$C_5H_5Rh(PMe_3)^+$], 168 (16) [$C_5H_5Rh^+$]. − $C_{12}H_{20}O_2PRhS_2$ (394.3): calcd. C 36.58, H 5.11; found C 36.18, H 5.09.

29. Preparation of [(η^5-C_5H_5)Rh(CH_2SAc)(PMe_3)I] (**38**): A solution of 104.2 mg (0.25 mmol) of **36** in 4 ml C_6H_6/EtOH (1:1) was treated with 28.3 mg (0.25 mmol) of KSAc and stirred for 1 h at room temp. The solvent was removed, the residue was extracted with 10 ml of benzene and the extract was brought to dryness in vacuo. The residue was now extracted with 5 ml of pentane and the dark red extract was worked up as described below. The remaining solid was dissolved in 2 ml of ether and then 2 ml of pentane was added. After the solution was stored for 12 h at −78°C orange-red crystals of **38** were formed which were separated from the mother liquor, washed twice with pentane and dried; yield 67 mg. The pentane extract was also brought to dryness in vacuo, the residue was dissolved in 1 ml of benzene and the solution was chromatographed on Al_2O_3 (neutral, activity grade IV, height of column 4 cm). With benzene, a red fraction was eluted which upon work up gave red-brown needles of **39**[3]; yield 23 mg (21%). − **38**: m. p. 142°C (dec.). − IR (C_6H_6): $\tilde{\nu}$ = 1670 cm^{-1} [ν(C=O)]. − ^{1}H NMR (200 MHz, C_6D_6): δ = 4.87 [dd, *J*(RhH) = 0.5, *J*(PH) = 1.6 Hz, 5 H, C_5H_5], 4.10 [ddd, *J*(RhH) = 4.8, *J*(PH) = 3.8, *J*(HH) = 9.2 Hz, 1 H, one H of $RhCH_2$], 3.44 [ddd, *J*(RhH) = 2.2, *J*(PH) = 6.9, *J*(HH) = 9.2 Hz, 1 H, one H of $RhCH_2$], 2.14 (s, 3 H, $SCCH_3$), 1.34 [dd, *J*(RhH) = 0.7, *J*(PH) = 11.1 Hz, 9 H, PMe_3]. − ^{31}P NMR (36.2 MHz, C_6D_6): δ = 7.3 [d, *J*(RhP) = 150.0 Hz]. − MS (70 eV); *m/z* (%) = 371 (95) [M^+ − CH_2SAc], 333 (88) [M^+ − I], 295 (27) [$C_5H_5RhI^+$], 244 (100) [$C_5H_5Rh(PMe_3)^+$], 168 (57) [$C_5H_5Rh^+$]. − $C_{11}H_{19}IOPRhS$ (460.1): calcd. C 28.71, H 4.16; found C 28.48, H 3.84.

30. Preparation of [(η^5-C_5H_5)Rh(PMe_3)(SAc)I] (**40**): a) A solution of 50.3 mg (0.11 mmol) of **38** in 1.5 ml of benzene was chromatographed on Al_2O_3 (neutral, activity grade IV, height of column 4 cm). With benzene, an orange-yellow fraction was eluted from which the solvent was removed in vacuo. To the oily residue 1 ml of pentane was added and after the mixture was stirred for 1 h an orange solid was obtained; yield 45 mg (91%). − b) A solution of 131.8 mg (0.25 mmol) of **36** in 1.5 ml of benzene and 3 ml of thioacetic acid was treated with 30.1 mg (0.26 mmol) of KSAc and stirred for 2 h at room temp. The solvent was removed, the residue was extracted with 10 ml of benzene and the extract was concentrated to ca. 2 ml in vacuo. The ^{1}H-NMR spectrum of the solution revealed that the major component of the crude product was **38**. The solution was chromatographed on Al_2O_3 (neutral, activity grade IV, height of column 4 cm) and with benzene two fractions were eluted. The first fraction contained a mixture of products among which **37** could be detected. The second fraction was worked up analogously as described for a) to give an orange microcrystalline solid; yield 80 mg (72%); m. p. 118°C (dec.). − IR (C_6H_6): $\tilde{\nu}$ = 1620 cm^{-1} [ν(C=O)]. − ^{1}H NMR (200 MHz, C_6D_6): δ = 5.20 [dd, *J*(RhH) = 0.3, *J*(PH) = 1.9 Hz, 5 H, C_5H_5], 2.57 (s, 3 H, $SCCH_3$), 1.50 [dd, *J*(RhH) = 0.7, *J*(PH) = 11.9, 9 H, PMe_3]. − MS (70 eV); *m/z* (%) = 446 (1) [M^+], 371 (50) [M^+ − SAc], 319 (17) [M^+ − I], 295 (16) [$C_5H_5RhI^+$], 244 (60) [$C_5H_5Rh(PMe_3)^+$], 168 (36) [$C_5H_5Rh^+$]. − $C_{10}H_{17}IOPRhS$ (446.1): calcd. C 26.93, H 3.84; found C 27.24, H 3.81.

31. Preparation of [(η^5-C_5Me_5)Rh(CH_2SAc){$P(OMe)_3$}I] (**43**): A solution of 87.9 mg (0.14 mmol) of **41** in 3 ml of benzene was treated under stirring with a solution of 16.0 mg (0.14 mmol) of KSAc in 1.5 ml of ethanol. After the reaction mixture was continuously stirred for 1 h at room temp., the solvent was removed and the residue was extracted with 10 ml of ether. The extract was brought to dryness in vacuo, the oily residue was washed with 0.5 ml of ethanol and 3 ml of pentane was added. Upon storing for 12 h at −78°C an orange-red solid precipitated which was washed twice with pentane and dried; yield 61 mg (75%). − IR (C_6H_6): $\tilde{\nu}$ = 1670 cm^{-1} [ν(C=O)]. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.77 [d, *J*(PH) = 11.2 Hz, 9 H, $P(OMe)_3$], 3.20 [ddd, *J*(RhH) = 5.2, *J*(PH) = 2.6, *J*(HH) = 8.4 Hz, 1 H, one H of $RhCH_2$], 2.99 [ddd, *J*(RhH) = 3.2, *J*(PH) = 5.0, *J*(HH) = 8.4 Hz, 1 H, one H of $RhCH_2$], 2.23 (s, 3 H, $SCCH_3$), 1.87 [dd, *J*(RhH) = 0.3, *J*(PH) = 4.5 Hz, 15 H, C_5Me_5]. − ^{13}C NMR (22.5 MHz, C_6D_6): δ = 198.9 (s, C=O), 101.0 [dd, *J*(RhC) = *J*(PC) = 4.4 Hz, C_5Me_5], 54.2 [d, *J*(PC) = 6.6 Hz, $P(OMe)_3$], 29.7 (s, $SCCH_3$), 9.6 [d, *J*(RhC) = 1.5 Hz, $C_5(CH_3)_5$], 5.3 [dd, *J*(RhC) = 27.2, *J*(PC) = 19.1 Hz, $RhCH_2$]. − ^{31}P NMR (36.2 MHz, C_6D_6): δ = 133.6 [d, *J*(RhP) = 248.6 Hz]. − MS (70 eV); *m/z* (%) = 489 (24) [M^+ − CH_2SAc], 365 (41) [$C_5Me_5RhI^+$], 362 (100) [M^+ − CH_2SAc − I], 238 (46) [$C_5Me_5Rh^+$]. − $C_{16}H_{29}IO_4PRhS$ (578.3): calcd. C 33.23, H 5.06; found C 33.47, H 5.18.

32. Preparation of [(η^5-C_5Me_5)Rh(CH_2SAc)(PMe_3)I] (**44**): Compound **44** was prepared analogously to **43** by using 87.1 mg (0.15 mmol) of **42** and 17.1 mg (0.15 mmol) of KSAc as starting materials. The ether extract was concentrated to ca. 1 ml in vacuo and then stored for 12 h at −78°C. Orange microcrystalline solid; yield 58 mg (73%); m. p. 137°C (dec.) − IR (C_6H_6): $\tilde{\nu}$ = 1665 cm^{-1} [ν(C=O)]. − ^{1}H NMR (200 MHz, C_6D_6): δ = 3.60 [ddd, *J*(RhH) =

2.4, J(PH) = 5.0, J(HH) = 8.2 Hz, 1 H, one H of $RhCH_2$], 3.17 [ddd, J(RhH) = J(PH) = 4.1 Hz, J(HH) = 8.2 Hz, 1 H, one H of $RhCH_2$], 2.19 (s, 3 H, $SCCH_3$), 1.72 [dd, J(RhH) = 0.3, J(PH) = 2.8 Hz, 15 H, C_5Me_5], 1.30 [dd, J(RhH) = 0.9, J(PH) = 10.1 Hz, 9 H, PMe_3]. – ^{13}C NMR (22.5 MHz, C_6D_6): δ = 198.7 (s, C=O), 98.8 [dd, J(RhC) = 5.2, J(PC) = 3.7 Hz, C_5Me_5], 29.6 (s, $SCCH_3$), 17.4 [d, J(PC) = 32.4 Hz, PMe_3], 10.0 [br. s, $C_5(CH_3)_5$], 5.9 [dd, J(RhC) = 28.7, J(PC) = 15.4, $RhCH_2$]. – ^{31}P NMR (36.2 MHz, C_6D_6): δ = 2.1 [d, J(RhP) = 140.1 Hz]. – MS (70 eV); m/z (%) = 441 (93) [$M^+ - CH_2SAc$], 365 (100) [$C_5Me_5RhI^+$], 314 (7) [$M^+ - CH_2SAc - I$], 238 (8) [$C_5Me_5Rh^+$]. – $C_{16}H_{29}IOPRhS$ (530.3): calcd. C 36.24, H 5.51; found C 35.83, H 5.53.

33. Preparation of [(η^5-C_5Me_5)Rh(CH_2SAc)(PMe_3)SAc] (**45**): a) A solution of 131.2 mg (0.25 mmol) of **42** in 2 ml of benzene was treated with a solution of 98.5 mg (0.86 mmol) of KSAc in 1 ml of ethanol and stirred for 30 min at room temp. The solvent was removed, the residue was extracted with 10 ml of ether and the extract was concentrated to ca. 1 ml in vacuo. Upon addition of 2 ml of pentane, the solution was stored for 12 h at −78°C. Yellow crystals precipitated which were separated from the mother liquor and dried; yield 80 mg (67%). – b) A solution of 56.6 mg (0.10 mmol) of **44** in 1 ml of benzene was treated with a solution of 12.2 mg (0.11 mmol) of KSAc in 0.5 ml of ethanol. After the reaction mixture was worked up as described for a), a yellow solid was obtained; yield 28 mg (58%); m. p. 163°C (dec.). – IR (C_6H_6): $\tilde{\nu}$ = 1660, 1609 cm^{-1} [ν(C=O)]. – ^{1}H NMR (200 MHz, C_6D_6): δ = 2.70 [ddd, J(RhH) = 2.5, J(PH) = 7.2, J(HH) = 8.5 Hz, 1 H, one H of $RhCH_2$], 2.55, 2.15 (both s, 3 H each, $SCCH_3$), 1.63 [dd, J(RhH) = 0.3, J(PH) = 2.9 Hz, 15 H, C_5Me_5], 1.24 [dd, J(RhH) = 0.9, J(PH) = 10.2 Hz, 9 H, PMe_3], signal of one H of $RhCH_2$ not exactly located. – ^{31}P NMR (36.2 MHz, C_6D_6): δ = 2.2 [d, J(RhP) = 140.0 Hz]. – MS (70 eV); m/z (%) = 478 (0.1) [M^+], 389 (44) [$M^+ - CH_2SAc$], 313 (88) [$C_5Me_5Rh(SAc)^+$], 314 (22) [$C_5Me_5Rh(PMe_3)^+$], 238 (13) [$C_5Me_5Rh^+$]. – $C_{18}H_{32}O_2PRhS_2$ (478.5): calcd. C 45.19, H 6.74; found C 45.35, H 6.46.

34. Preparation of [(η^5-C_5Me_5)Rh(η^2-CH_2S){$P(OMe)_3$}] (**46**): a) A solution of 81.7 mg (0.14 mmol) of **43** in 8 ml of benzene was treated with 85 μl of a 1.6 M solution (0.14 mmol) of *n*BuLi in hexane and stirred for 10 min at room temp. The solvent was removed and the residue was extracted with 10 ml of pentane. The extract was brought to dryness in vacuo, the oily residue was dissolved in 2 ml of benzene and the solution was chromatographed on Al_2O_3 (neutral, activity grade IV, height of column 5 cm). With benzene, an orange fraction was eluted from which the solvent was removed. The oily residue was dissolved in 8 ml of pentane, the solution was filtered, the filtrate was concentrated to ca. 2 ml and then stored for 12 h at −78°C. Orange-yellow crystals precipitated which were separated from the mother liquor and dried; yield 42 mg (75%). – b) A solution of 85.7 mg (0.14 mmol) of **48** in 5 ml of methanol was treated at room temp. with an excess (ca. 50 mg) of $NaOCH_3$. After the reaction mixture was stirred for 10 min, the solvent was removed and the residue was extracted with 15 ml of pentane. The extract was concentrated to ca. 2 ml in vacuo and then stored for 12 h at −78°C. Orange-yellow crystals; yield 42 mg (73%); m. p. 76°C (dec.). – ^{1}H NMR (90 MHz, C_6D_6): δ = 3.91 [ddd, J(RhH) = 2.7, J(PH) = 0.9, J(HH) = 8.6 Hz, 1 H, one H of CH_2S], 3.34 [d, J(PH) = 12.0 Hz, 9 H, $P(OMe)_3$], 1.77 [dd, J(RhH) = 0.7, J(PH) = 3.9 Hz, 15 H, C_5Me_5], signal of one H of CH_2S partly covered by signal of $P(OMe)_3$. – ^{13}C NMR (50.3 MHz, C_6D_6): δ = 98.5 [dd, J(RhC) = J(PC) = 4.5 Hz, C_5Me_5], 51.5 [d, J(PC) = 6.3 Hz, $P(OMe)_3$], 49.5 [dd, J(RhC) = 18.9, J(PC) = 7.4 Hz, CH_2S], 9.7 [s, $C_5(CH_3)_5$]. – ^{31}P NMR (36.2 MHz, C_6D_6): δ = 143.4 [d, J(RhP) = 290.3 Hz]. – MS (70 eV); m/z (%) = 408 (52) [M^+], 362 (100) [$M^+ - CH_2S$], 238 (40) [$C_5Me_5Rh^+$]. – $C_{14}H_{26}O_3PRhS$ (408.3): calcd. C 41.18, H 6.42; found C 41.50, H 6.55.

35. Preparation of [(η^5-C_5Me_5)Rh(η^2-CH_2S)(PMe_3)] (**47**): Compound **47** was prepared analogously to **46** either by using 68.1 mg (0.15 mmol) of **44** and 90 μl of a 1.6 M solution (0.15 mmol) of *n*BuLi in hexane or 78.4 mg (0.14 mmol) of **49** and ca. 50 mg of $NaOCH_3$ as starting materials. Orange-brown microcrystalline solid; yield 41 mg (76%) from **44** and 34 mg (68%) from **49** as starting material; m. p. 81°C (dec.). – ^{1}H NMR (200 MHz, C_6D_6): δ = 3.87 (m, 2 H, CH_2S), 1.87 [dd, J(RhH) = 0.5, J(PH) = 2.4 Hz, 15 H, C_5Me_5], 1.07 [dd, J(RhH) = 0.9, J(PH) = 9.0 Hz, 9 H, PMe_3]. – ^{13}C NMR (50.3 MHz, C_6D_6): δ = 96.6 [dd, J(RhC) = J(PC) = 4.4 Hz, C_5Me_5], 46.6 [dd, J(RhC) = 19.9, J(PC) = 5.5 Hz, CH_2S], 15.9 [d, J(PC) = 28.5 Hz, PMe_3], 10.1 [s, $C_5(CH_3)_5$]. – ^{31}P NMR (36.2 MHz, C_6D_6): δ = 4.9 [d, J(RhP) = 184.6 Hz]. – MS (70 eV); m/z (%) = 360 (55) [M^+], 314 (100) [$M^+ - CH_2S$], 238 (21) [$C_5Me_5Rh^+$]. – $C_{14}H_{26}PRhS$ (360.3): calcd. C 46.67, H 7.27; found C 46.48, H 7.52.

36. Preparation of [(η^5-C_5Me_5)Rh{κ^2-C,O-$CH_2SC(Me)O$}{$P(OMe)_3$}]PF_6 (**48**): Compound **48** was prepared analogously to **19** by using 130.0 mg (0.22 mmol) of **43** and 56.5 mg (0.22 mmol) of $AgPF_6$ as starting materials. Orange-yellow solid; yield 117 mg (89%); dec. temp. 69°C. – Λ = 82 $cm^2\Omega^{-1}mol^{-1}$. – IR (nujol): $\tilde{\nu}$ = 1565 cm^{-1} [ν(C=O)]. – ^{1}H NMR (60 MHz, $(CD_3)_2CO$): δ = 3.83 [d, J(PH) = 11.6 Hz, 9 H, $P(OMe)_3$], 3.37 (m, 2 H, $RhCH_2$), 2.40 (s, 3 H, $SCCH_3$), 1.77 [dd, J(RhH) = 0.3, J(PH) = 4.5 Hz, 15 H, C_5Me_5]. – ^{13}C NMR (22.5 MHz, CD_3NO_2): δ = 226.4 (s, C=O), 103.0 [dd, J(RhC) = 5.9, J(PC) = 4.2 Hz, C_5Me_5], 54.0 [d, J(PC) = 5.9 Hz, $P(OMe)_3$], 27.1 [s, $C(O)CH_3$], 21.5 [dd, J(RhC) = 27.9, J(PC) = 22.8 Hz, $RhCH_2$], 9.2 [d, J(RhC) = 2.2 Hz, $C_5(CH_3)_5$]. – ^{31}P NMR (36.2 MHz, CD_3NO_2): δ = 126.7 [d, J(RhP) = 251.6 Hz]. – $C_{16}H_{29}F_6O_4P_2RhS$ (596.3): calcd. C 32.23, H 4.90; found C 32.10, H 5.11.

37. Preparation of [(η^5-C_5Me_5)Rh{κ^2-C,O-$CH_2SC(Me)O$}(PMe_3)]PF_6 (**49**): Compound **49** was prepared analogously to **19** by using 159.4 mg (0.30 mmol) of **44** and 78.2 mg (0.31 mmol) of $AgPF_6$ as starting materials. Orange-yellow solid; yield 54 mg (96%); dec. temp. 96°C. – Λ = 73 $cm^2\Omega^{-1}mol^{-1}$. – IR (nujol): $\tilde{\nu}$ = 1552 cm^{-1} [ν(C=O)]. – ^{1}H NMR (200 MHz, $(CD_3)_2CO$): δ = 3.29 [ddd, J(RhH) = 2.9, J(PH) = 0.3, J(HH) = 9.5 Hz, 1 H, one H of $RhCH_2$], 3.07 [ddd, J(RhH) = 9.5, J(PH) = 18.9 J(HH) = 9.5 Hz, 1 H, on H of $RhCH_2$], 2.36 (s, 3 H, $SCCH_3$), 1.71 [dd, J(RhH) = 0.3, J(PH) = 2.7 Hz, 15 H, C_5Me_5], 1.52 [dd, J(RhH) = 0.7, J(PH) = 10.5 Hz, 9 H, PMe_3]. – ^{13}C NMR (22.5 MHz, CD_3NO_2): δ = 226.1 (s, C=O), 100.8 [dd, J(RhC) = 5.9, J(PC) = 2.9 Hz, C_5Me_5], 27.3 [s, $C(O)CH_3$], 21.7 [dd, J(RhC) = 30.2, J(PC) = 15.4 Hz, $RhCH_2$], 13.6 [d, J(RhC) = 30.9 Hz, PMe_3], 9.3 [br. s, $C_5(CH_3)_5$]. – ^{31}P NMR (36.2 MHz, CD_3NO_2): δ = 4.0 [d, J(RhP) = 156.3 Hz]. – $C_{16}H_{29}F_6OP_2RhS$ (548.3): calcd. C 35.05, H 5.33; found C 34.66, H 5.45.

38. Preparation of [(η^5-C_5H_5)Rh(η^2-CH_2S)(PMe_3)] (**50**): Compound **50** was prepared analogously to **46** by using 68.1 mg (0.15 mmol) of **38** and 90 μl of a 1.6 M solution (0.15 mmol) of *n*BuLi in hexane as starting materials. The yellow microcrystalline solid **50** was identified by comparison of the NMR spectroscopic data with those of an authentic sample;[1d] yield 34 mg (79%).

39. X-ray Structure Determination of Compound **27**[34]: Single crystals of **27** were grown by slow diffusion of ether to a solution of **27** in nitromethane at room temp. Crystal data: orthorhombic, space group *Pbca*, a = 16.857(5), b = 23.538(6), c = 11.048(3) Å, Z = 8, $d_{calcd.}$ = 1.613 g cm^{-3}, μ(Mo-K_α) = 0.98 mm^{-1}; crystal size

0.9 × 1.35 × 0.2 mm; Nicolet P3 diffractometer, Mo-K_α radiation, graphite monochromator; ω scan, $2\Theta_{max} = 55°$; 4276 reflections scanned, 4053 unique reflections, 3919 reflections with $F > 3\sigma(F)$. Intensity data were corrected for Lorentz and polarization effects and a geometrical absorption correction was applied. The structure was solved by the Patterson method. Atomic coordinates and the anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least- squares. The positions of all hydrogen atoms were calculated according to ideal geometry (distance C−H = 0.95 Å). $R = 0.065$, $R_w = 0.070$ [weighting scheme $1/\sigma^2(F)$]; reflections-to-parameter ratio 16.00; residual electron density 2.31 eÅ^{-3}.

☆ Dedicated to Professor *Warren R. Roper* on the occasion of his 60th birthday.

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[34] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101821. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44(1223)336−033; e-mail: deposit@chemcrys.cam.ac.uk].

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