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SOME REACTIONS OF π-CYCLOPENTADIENYL-BIS(TRIPHENYLPHOSPHINE) RHODIUM(I)

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Summary

Reactions of π-cyclopentadienylbis(triphenylphosphine)rhodium(I) (I) with alkyl halides, olefins, acetylenes, carbon disulfide and elementary sulfur have been investigated. Methyl iodide gives the oxidative-addition product [π-$C_5H_5Rh(PPh_3)_2CH_3$]I but isopropyl iodide produces the alkyl substituted-cyclopentadienyl complex (π-i-$C_3H_7C_5H_4$)$Rh(PPh_3)I_2$. Under a nitrogen atmosphere, olefins and acetylenes give compounds of the composition π-$C_5H_5Rh(PPh_3)(L)$ (L = CH_2=CHCN, CH_2=$CHCO_2CH_3$, $CH_3O_2CC{\equiv}CCO_2CH_3$). In the presence of air, however, complexes of the composition π-$C_5H_5Rh(L)_2$ (L = CH_2=CHCN, CH_2=$CHCO_2CH_3$, CH_2=$C(CH_3)CN$) and π-$C_5H_5Rh(L)_3$ (L = $CH_3O_2CC{\equiv}CCO_2CH_3$, $PhC{\equiv}CCO_2CH_3$) are formed. The reaction of carbon disulfide or sulfur with (I) also gives the compounds π-$C_5H_5Rh(PPh_3)(L)$ (L = CS_2, CS_3, S_5).

Introduction

In previous work, one of the authors reported the synthesis and reactions of π-cyclopentadienylbis(triphenylphosphine)cobalt, π-$C_5H_5Co(PPh_3)_2$ (II) [1]. It was observed that one of the triphenylphosphine molecules in this complex was readily replaced by various ligands. Synthesis of the rhodium analog, π-$C_5H_5Rh(PPh_3)_2$ (I) also was described [1].

In the present work, the reactions of (I) with some reagents have been studied to compare it with the cobalt analog and to examine a new route to rhodium complexes having a π-cyclopentadienyl group.

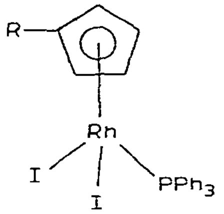
Results and discussion

Reactions with alkyl halides

It was reported previously that the cobalt complex (II) reacts with methyl iodide to give π-$C_5H_5Co(PPh_3)(CH_3)_2$ [2]. Oliver and Graham studied the reaction of alkyl halides (RX) with π-$C_5H_5Rh(PPh_3)(CH_2{=}CH_2)$ and obtained the rhodium—alkyl complex, π-$C_5H_5Rh(PPh_3)(R)X$ [3]. However, the oxidative addition reaction of methyl iodide with (I) at room temperature did not produce a similar compound but gave the ionic alkyl complex, [π-$C_5H_5Rh(PPh_3)_2CH_3$]I (III), in quantitative yield. More severe conditions (80°) did not give π-$C_5H_5Rh(PPh_3)(CH_3)I$ either. The closely related compound [π-$C_5H_5Rh(L)(CO)CH_3$]Br (L = PMe_2Ph) has been believed to be the intermediate in the reaction of π-$C_5H_5Rh(L)(CO)$ with CH_3Br which forms the acyl derivative π-$C_5H_5Rh(L)(COCH_3)Br$ [4].

On the other hand, treatment of (I) with isopropyl iodide afforded two complexes in almost equal amounts. One of the complexes was identified as the known complex, π-$C_5H_5Rh(PPh_3)I_2$ [5]. The proton NMR spectrum of the other complex in $CDCl_3$ showed methyl protons of the isopropyl group at 8.75 τ (doublet J 7Hz, 6H), methyne proton at 6.50 τ (multiplet, 1H), cyclopentadienyl ring protons at 5.30 τ (triplet J 2 Hz, 2H) and 4.50 τ (quartet J 2 Hz, 2H)[*], and phenyl protons at 2.2 - 2.8 τ (multiplet). On the basis of these data, together with the IR spectrum and elemental analysis, the complex was assigned the constitution π-isopropylcyclopentadienyl(triphenylphosphine)rhodium diiodide (IVb).

When (III) was heated in dichloromethane with isopropyl iodide at 80°, (π-$CH_3C_5H_4$)$Rh(PPh_3)I_2$ (IVa) was isolated in 18% yield, but (IVb) was not obtained at all. This fact suggests that the formation of the isopropyl-substituted cyclopentadienyl complex (IVb) described above proceeds not by a direct interaction of isopropyl iodide with the cyclopentadienyl ring but



(IVa), R = CH_3

(IVb), R = i-C_3H_7

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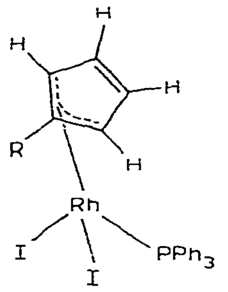
[*] The triplet signal of the two ring protons is further split by the phosphorus to give a quartet signal. The coupling with ^{31}P nucleus was confirmed by a decoupling study of (IVb) and the NMR spectrum of (π-$CH_3C_5H_4$)$Rh(CO)I_2$ or (π-$CH_3C_5H_4$)Rh(t-BuNC)I_2 in which each pair of the ring protons appeared as triplet. The methyne proton of the isopropyl group of (IVb) also couples with ^{31}P (J 3.5 Hz). From these facts it is reasonable to describe the structure of complexes (IV) as illustrated.



through an ionic σ-alkyl intermediate analogous to (III). Probably, owing to instability of the metal - isopropyl σ bond, the complex analogous to (III) was not obtained in the reaction of isopropyl iodide with (I).

Reactions with olefines and acetylenes

It has been shown in earlier work that one of the phosphines in (II) can be readily replaced by olefins or equimolar amounts of acetylenes at room temperature [1,2]. The same reaction occurred on heating (I) at 70° with acrylonitrile or methyl acrylate in benzene; π-$C_5H_5Rh(PPh_3)(CH_2{=}CHCN)$ (Va) and π-$C_5H_5Rh(PPh_3)(CH_2{=}CHCO_2CH_3)$ (Vb) were obtained, respectively. Similarly, dimethyl acetylenedicarboxylate gave π-$C_5H_5Rh(PPh_3)(CH_3O_2CC{\equiv}CCO_2CH_3)$ (VI) at room temperature although the yield was very low (2%)*.

Complex (II) also has been shown to give a cobaltacyclopentadiene complex by the reaction with 2 moles of acetylene [1], but complex (I) did not show this type of reaction.

Interestingly, both phosphines in (I) were replaced by olefins or acetylenes when the reactions were carried out in the presence of calculated amount of air [containing about 2 moles of oxygen per 1 mole of (I)]. Thus, on treatment of (I) at room temperature with acrylonitrile, methyl acrylate or methacrylonitrile in the presence of air, π-$C_5H_5Rh(CH_2{=}CHCN)_2$ (VIIa), π-$C_5H_5Rh(CH_2{=}CHCO_2CH_3)_2$ (VIIb), and π-$C_5H_5Rh[CH_2{=}C(CH_3)CN]_2$ (VIIc), respectively, were obtained along with triphenylphosphine oxide. Since complex (Va) did not react further with acrylonitrile in the presence of air, replacement of two phosphines as described above would proceed simultaneously and not stepwise. The IR spectra of these complexes showed absorptions at around 1450 cm^{-1} which are attributable to $\nu(C{=}C)$ of the coordinated olefins. The mass spectrum of (VIIa) showed a parent peak (*m/e* 274) and very intense peaks due to π-$C_5H_5Rh(CH_2{=}CHCN)^+$ (*m/e* 221) and π-$C_5H_5Rh^+$ (*m/e* 168). The same patern was observed in the mass spectrum of (VIIb) or (VIIc).

The proton NMR spectra of (VIIa) and (VIIb) were very complex, but that of (VIIc) was simple enough to allow speculation concerning the manner of coordination in this bis-olefin complex. Rotation of olefins in the complexes π-$C_5H_5Rh(CH_2{=}CH_2)_2$ and π-$C_5H_5Rh(CH_2{=}CHF)_2$ has been discussed by Cramer [6], but (VIIc) did not show any sign of olefin rotation in its high temperature NMR spectra in C_6D_6. Above 70°, decomposition occured. Complex (VIIc) was obtained as a mixture of three isomers. Isomer A was separated from isomer B and C by chromatography on alumina, but separation of isomer B from C was unsuccessful. Fig. 1 shows the proton NMR spectra of these isomers. A sharp singlet band at 4.62 τ, which was assigned to the cyclopentadienyl protons, was observed in the spectrum shown in Fig. 1a (isomer A). The cyclopentadienyl resonance is expected to be split by rhodium but in this case it seemed beyond the rèsolution of the spectrometer. The spectrum of Fig. 1a has also two non-equivalent methyl resonances at 8.32 and 8.83 τ, which are

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*Complex (VI) was obtained in better yield (56%) by reaction of tris(triphenylphosphine)rhodium chloride with dimethyl acetylenedicarboxylate and thallium cyclopentadienide.

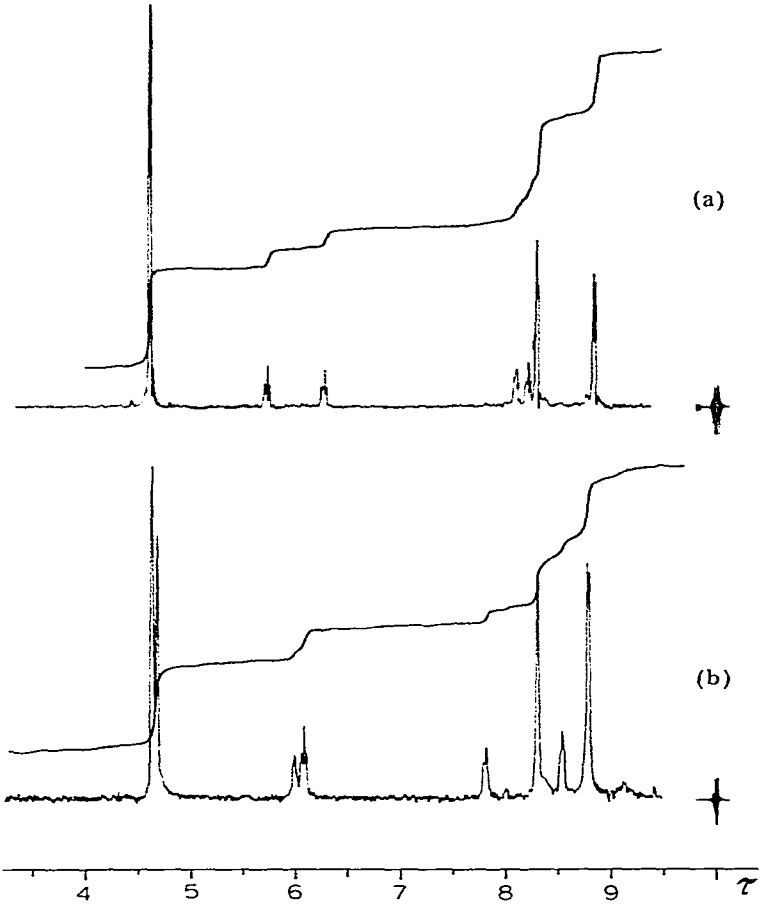


Fig. 1. ^1H NMR spectra of π-$C_5H_5Rh[CH_2{=}C(CH_3)CN]_2$ in $CDCl_3$. (a) Isomer A, (b) mixture of isomers B and C.

split by rhodium (J 1.3 and 1.8 Hz), and four non-equivalent proton resonances at 5.73, 6.26, 8.08 and 8.19 τ which consist of 1/2/1 triplets (J 2.0 Hz) by equal coupling with rhodium and the *gem*-proton. As shown in Fig. 2, there are six possible modes of coordination of the two methacrylonitrile molecules. Of these, (*iii*) or (*vi*) is attributed to isomer A since they have two non-equivalent methyl and four non-equivalent vinylidene protons, consistent with the spectrum shown in Fig. 1a. Considering the steric interaction between methyl and cyano groups in (*iii*), the authors prefer (*vi*) as a model for isomer A.

On the other hand, two cyclopentadienyl resonances (4.62 and 4.64 τ) with intensity ratio of 4/3 were observed in the spectrum shown in Fig. 1b, suggesting the presence of two compounds. Intensity ratio of the two methyl resonances and two pairs of proton resonances was also 4/3, respectively. This indicates that this is a spectrum of 4/3 mixture of two compounds (isomer B and C), each of which has two equivalent methyl and two pairs of equivalent vinylidene protons. The corresponding models are (*i*), (*ii*), (*iv*), and (*v*) in

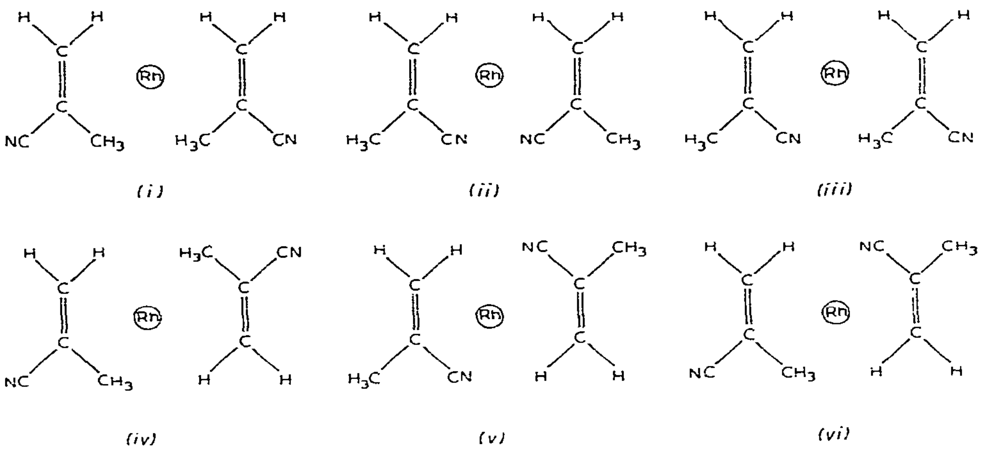
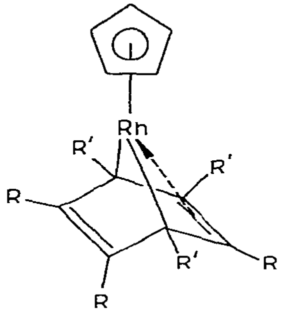


Fig. 2. Coordination models for π-$C_5H_5Rh[CH_2{=}C(CH_3)CN]_2$.

Fig. 2, but (*iv*) and (*v*) could well be favored over the other two in view of the steric interaction.

By the reaction of dimethyl acetylenedicarboxylate with (I) in the presence of air, a compound of the composition π-$C_5H_5Rh(CH_3O_2CC)_6$ (VIIIa) was obtained. The proton NMR spectrum of this complex proved the presence of three non-equivalent methyl groups. Its mass spectrum showed a parent peak (*m/e* 594) and an intense peak (*m/e* 426) due to hexacarbomethoxybenzene, and π-$C_5H_5Rh^+$ (*m/e* 168). These data and the obvious analogy to the 1,2,3,4-*tetrahapto*hexakis[(methoxycarbonyl)benzene](pentamethylcyclopentadienyl)-rhodium reported by Maitlis et al. [7] are consistent with the structure shown below.



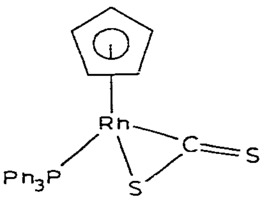
(VIII a), R = R' = CO_2CH_3
(VIII b), R = CO_2CH_3, R' = C_6H_5
(VIII c), R = R' = CF_3

By the similar reaction of (I) with methylphenylacetylenecarboxylate, (VIIIb) was obtained. Pyrolysis of (VIIIb) at 180° yielded 1,2,4-tri(methoxycarbonyl)-3,5,6-triphenylbenzene in 72% yield, but none of the 1,3,5-tri(methoxycarbonyl) isomer was detected. Complex (VIIIc) has been prepared by Dickson and Wilkinson [8] from dicarbonylcyclopentadienylrhodium and hexafluoro-2-butyne and the structure determined by Churchill and Mason [9].

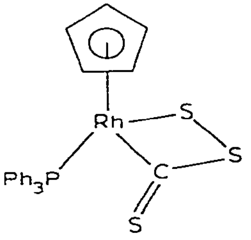
Reactions with carbon disulfide and elementary sulfur

It has been reported that complex (II) reacts with CS_2 very rapidly at room temperature to give π-$C_5H_5Co(PPh_3)(CS_2)$. Complex (I), however, reacted only at elevated temperatures. Thus, on heating (I) at 70° for 4 days with a large excess of CS_2, a 21% yield of dark cystalline π-$C_5H_5Rh(PPh_3)(CS_2)$ (IX) and a 17% yield of red crystalline π-$C_5H_5Rh(PPh_3)(CS_3)$ (X) were obtained. In the IR spectrum of (IX), a strong band assignable to ν(CS) appeared at 1180 cm^{-1}. The IR spectrum of (X) has bands, other than many bands due to cyclopentadienyl group and triphenylphosphine, at 1045 (very strong) and 870 cm^{-1} (medium) which seems to be the general pattern of absorption for —S—S—C(S)— ligand as a chelate [10]. The structure shown in the figure is proposed for (X). The preparation of an iridium complex with CS_3 as a ligand by the reaction of $(PPh_3)_2IrN_2Cl$ and CS_2 has been reported by Kubota and Carey [10].

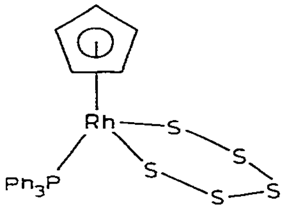
On treatment of (I) in benzene with sulfur, a complex of the composition π-$C_5H_5Rh(PPh_3)S_5$ (XI) was obtained in 22% yield. By analogy with the S_5 complex of titanium, $(\pi$-$C_5H_5)_2TiS_5$ [11], the structure illustrated may be assigned to (XI).



(IX)



(X)



(XI)

Experimental

All reactions were carried out in a nitrogen atmosphere unless otherwise stated. Melting points were determined on a Yanagimoto micro melting point apparatus. Proton NMR spectra were obtained using a Varian HA-100 spectrometer. IR spectra were obtained using a Perkin - Elmer model 521 spectrometer. Mass spectra were obtained using a Nippon Denshi model IS spectrometer at 75 eV.

Preparation of π-$C_5H_5Rh(PPh_3)_2$ (I)

This compound was prepared as described previously [1], but it can be obtained more conveniently by the reaction of $(PPh_3)_3RhCl$ with C_5H_5Na as described below. To a suspension of $(PPh_3)_3RhCl$ (3 g, 3.25 mmol) in benzene (20 ml) and tetrahydrofuran (20 ml), was added dropwise C_5H_5Na (5 mmol) in tetrahydrofuran (5 ml). The reaction mixture was stirred for 30 min at room temperature and then cooled to −20°. About 3 g of ice flakes were added and the mixture was stirred while being allowed to attain room temperature. The organic layer was separated and dried with sodium sulfate. After concentration under reduced pressure, the solution was chromatographed on alumina. The dark-green band of (I) was eluted with benzene and most of the solvent was removed from the eluate under reduced pressure. Addition of hexane to the residue gave dark-brown crystals of π-$C_5H_5Rh(PPh_3)_2 \cdot C_6H_6$ (1.87 g).

Reaction of (I) with CH_3I

Methyl iodide (1 ml) was added to a solution of (I) (300 mg) in benzene (15 ml) at room temperature. A yellow fine precipitate appeared within 10 min. This was separated by filtration and crystallized from dichloromethane/hexane to give yellow crystals of $[\pi\text{-}C_5H_5Rh(PPh_3)_2CH_3]I$ (III) (290 mg), decomp. 108 - 115°. (Found: C, 54.55; H, 4.30; halogen, 24.36. $C_{42}H_{38}IP_2$-$Rh \cdot 3/2CH_2Cl_2$ calcd.: C, 54.32; H, 4.30; halogen, 24.25%.) The proton NMR spectrum of (III) in $CDCl_3$ showed phenyl protons at 2.5 - 3.1τ (multiplet, 30H), CH_2Cl_2 protons at 4.18τ (singlet, 3H), cyclopentadienyl protons at 4.23τ (triplet J 3 Hz, 5H) and methyl protons at 8.56τ [1/1/2/2/1/1 sextet J(PH) 5 Hz, J(RhH) 3 Hz, 3H).

Reaction of (I) with i-C_3H_7I

Isopropyl iodide (1.7 ml) was added to a solution of (I) (500 mg) in benzene (40 ml) and the mixture was allowed to stand overnight. After concentration of the solution under reduced pressure, it was chromatographed on alumina. Two chocolate-brown bands were eluted with benzene/dichloromethane. From the second band, π-$C_5H_5Rh(PPh_3)I_2$ (81 mg) was obtained. From the first band, dark-brown crystals of $(\pi\text{-i-}C_3H_7C_5H_4)Rh(PPh_3)I_2$ (60 mg) (IVb) were obtained after concentration of the eluate and addition of hexane, decomp. 182 - 187°. (Found: C, 45.40; H, 3.72; I, 32.96. $C_{26}H_{25}I_2PRh \cdot 1/2C_6$-$H_6$ calcd.: C, 45.55; H, 3.82; I, 33.17%.) The presence of benzene as solvent of crystallization has been supported by the enhanced intensity of the NMR signals due to phenyl rings.

Reaction of $[\pi\text{-}C_5H_5Rh(PPh_3)_2CH_3]I$ (III) with i-C_3H_7I

To a solution of (III) (200 mg) in dichloromethane/benzene (1/1 mixture, 10 ml), i-C_3H_7I (1 ml) was added and the mixture was heated in a sealed tube at 80°. Within 2 h the yellow color of the solution turned chocolate-brown. Most of the solvent was removed under reduced pressure and the residue was chromatographed on alumina. Two brown bands and one yellow band separated on elution with benzene/dichloromethane. The first brown band was collected and concentrated. Addition of hexane to the residue yielded brown crystals of $(\pi\text{-}CH_3C_5H_4)Rh(PPh_3)I_2$ (IVa) (20 mg), decomp. 238 - 242°. (Found: C, 41.41; H, 3.39; I, 36.05. $C_{24}H_{22}I_2PRh$ calcd.: C, 41.29; H, 3.17; I, 36.36%.) The proton NMR spectrum of (IVa) in $CDCl_3$ showed cyclopentadienyl protons at 4.76τ (quartet J 2 Hz, 2H) and 5.04τ (triplet J 2 Hz, 2H), and methyl protons at 7.61τ (doublet J 3.5 Hz, 3H). From the second brown band and the yellow band, π-$C_5H_5Rh(PPh_3)I_2$ (42 mg) and unreacted (III) (68 mg), respectively, were obtained.

Reaction of (I) with olefins

To a solution of (I) (600 mg) in benzene (30 ml) was added acrylonitrile (6 ml) and the mixture was heated at 75° for 10 days. The solution was chromatographed on alumina, benzene/dichloromethane (1/1) being used as eluant. The yellow fraction was collected and evaporated almost to dryness. Crystallization from benzene/hexane gave orange crystals of π-$C_5H_5Rh(PPh_3)$-$(CH_2{=}CHCN)$ (Va) (200 mg), decomp. 170 - 175°. (Found: C, 64.11; H, 4.73; N, 2.99. $C_{26}H_{23}NPRh$ calcd.: C, 64.61; H, 4.80; N, 2.90%.) Similarly, orange crystalline π-$C_5H_5Rh(PPh_3)(CH_2{=}CHCO_2CH_3)$ (Vb) was obtained in 48% yield by the same procedure, decomp. 158 - 161°. (Found: C, 62.86; H, 5.03. $C_{27}H_{26}O_2PRh$ calcd.: C, 62.80; H, 5.08%.)

Reaction of (I) with dimethyl acetylenedicarboxylate

Dimethyl acetylenedicarboxylate (200 mg) was added to a solution of (I) (770 mg) in benzene (20 ml) and the mixture was allowed to stand overnight. The solution was concentrated under reduced pressure and then chromatographed on alumina. The green band and the yellow band were eluted with benzene and benzene/THF (20/1), respectively. From the green band, unreacted (I) (320 mg) was recovered. The yellow band was collected and concentrated under reduced pressure. Addition of hexane gave 11 mg of yellow π-C_5H_5Rh-$(PPh_3)(CH_3O_2CC{\equiv}CCO_2CH_3)$ (VI), decomp. 163 - 168°. (Found: C, 61.37; H, 4.84. $C_{29}H_{26}O_4PRh$ calcd.: C, 60.85; H, 4.58%.) This complex was obtained in better yield by the other route described below. $(PPh_3)_3RhCl$ (1 g) was suspended in a mixture of benzene (20 ml) and THF (20 ml). About 0.25 ml of dimethyl acetylenedicarboxylate was added with stirring. Then 600 mg of C_5H_5Tl was added and the mixture was stirred for 5 h. The undissolved material was removed by filtration and the dark-brown filtrate was chromatographed on silica-gel. The yellow band was eluted with benzene. Most of the solvent was removed from the eluate under reduced pressure. Addition of hexane to the residue gave 290 mg of (VI).

Reaction of (I) with olefins in the presence of air

In a 100 ml flask, (I) (200 mg) was dissolved in 5 ml of benzene and acrylonitrile (5 ml) was added. Then about 60 ml of air was bubbled in and the mixture was allowed to stand overnight. The solution was concentrated and chromatographed on alumina, benzene/dichloromethane being used as eluant. Concentration of the pale-yellow fraction and addition of hexane gave pale-yellow crystals of π-$C_5H_5Rh(CH_2{=}CHCN)_2$ (VIIa) (51 mg), decomp. 94 - 95°. (Found: C, 49.12; H, 4.03; N, 10.12; mol. wt. 274 (mass spectrum). $C_{11}H_{11}N_2Rh$ calcd.: C, 48.20; H, 4.04; N, 10.22%; mol.wt. 274.1.) By the similar treatment of (I) with methyl acrylate, π-$C_5H_5Rh(CH_2{=}CHCO_2CH_3)_2$ (VIIb) was obtained in 38% yield, decomp. 110 - 110.5°. (Found: C, 45.71; H, 4.92; mol.wt. 340 (mass spectrum). $C_{13}H_{17}O_4Rh$ calcd.: C, 45.68; H, 5.04%; mol.wt. 340.2.) Similar reaction of (I) (200 mg) with methacrylonitrile

(2.5 ml) and chromatography on alumina gave two yellow fractions. On concentration of the first fraction and addition of hexane, orange-yellow crystals of π-$C_5H_5Rh(CH_2{=}C(CH_3)CN)_2$ (VIIc, isomer A) (20 mg) was obtained, decomp. 103 - 106°. (Found: C, 51.92; H, 5.07; N, 9.18. $C_{13}H_{15}N_2Rh$ calcd.: C, 51.67; H, 5.00; N, 9.27%.) From the second fraction, yellow crystals of (VIIc, isomer B + C) were obtained (47 mg). These were recrystallized from dichloromethane/hexane. (Found: C, 51.92; H, 4.83; N, 9.21. $C_{13}H_{15}N_2Rh$ calcd.: C, 51.67; H, 5.00; N, 9.27%.)

Reaction of (I) with acetylenes in the presence of air

By the reaction of (I) with methyl phenylacetylenecarboxylate and according to a procedure similar to that described above, orange crystalline π-$C_5H_5Rh(C_6H_5C_2CO_2CH_3)_3$ (VIIIb) was obtained in 21% yield, decomp. 190 - 200°. (Found: C, 65.04; H, 4.71; mol. wt. 648 (mass spectrum). $C_{35}H_{29}O_6Rh$ calcd.: C, 64.82; H, 4.51%; mol. wt. 648.5.) The proton NMR spectrum showed three methyl resonances at 6.45, 6.46, and 6.92τ. Complex (VIIIb) was dissolved in *o*-dichlorobenzene in air and heated at 180° for 1 h. The reaction mixture was chromatographed on alumina, benzene being used as eluant. The *o*-dichlorobenzene fraction was discarded and then about 100 ml of eluate was collected. Evaporation of the solvent from the eluate gave white crystals of 1,2,4-tri(methoxycarbonyl)-3,5,6-triphenylbenzene in 72% yield, m.p. 200 - 201° (lit. 204 - 206° [12]). Similar treatment of (I) with dimethyl acetylenedicarboxylate in the presence of air gave red-brown crystals of π-$C_5H_5Rh(CH_3O_2CC)_6$ (VIIIa) in 24% yield, decomp. 173 - 180°. (Found: C, 46.40; H, 3.81; mol.wt. 594 (mass spectrum). $C_{23}H_{23}O_{12}Rh$ calcd.: C, 46.48; H, 3.90%; mol.wt. 594.3.) The proton NMR spectrum of (VIIIa) showed three methyl resonances at 6.10, 6.30, and 6.32τ.

Reaction of (I) with CS_2

Carbon disulfide (2 ml) was added to a solution of (I) (600 mg) in benzene (40 ml) and the mixture was heated at 70° in a sealed tube for 4 days. After concentration, the solution was chromatographed on silica gel to give a red zone followed by a yellow zone. The red zone was eluted with benzene. Most of the solvent was removed from the eluate under reduced pressure and hexane was added to give dark-red crystals of π-$C_5H_5Rh(PPh_3)(CS_2)$ (IX) (78 mg), decomp. 138 - 140°. (Found: C, 57.15; H, 3.99; S, 12.50. $C_{24}H_{20}S_2PRh$ calcd.: C, 56.92; H, 3.98; S, 12.66%.) The yellow zone was eluted with dichloromethane. After concentration of the eluate, hexane was added to give orange-red crystals of π-$C_5H_5Rh(PPh_3)(CS_3)$ (X) (71 mg), decomp. 222 - 226°. (Found: C, 53.59; H, 3.48; S, 17.76. $C_{24}H_{20}S_3PRh$ calcd: C, 53.53; H, 3.74; S, 17.86%.)

Reaction of (I) with sulfur

A mixture of (I) (250 mg) and sulfur (50 mg) in 15 ml of benzene was heated at 70° for 13 h. After concentration, the reaction mixture was chromatograhped on alumina. The light-brown band was eluted with benzene. Solvent was removed from the eluate under reduced pressure. The residue was crystallized with benzene/hexane to give dark-red crystals of π-$C_5H_5Rh(PPh_3)(S_5)$ (XI) (43 mg), decomp. 179 - 181°. (Found: C, 46.99; H, 3.46; S, 27.12. $C_{23}H_{20}S_5PRh$ calcd.: C, 46.77; H, 3.41; S, 27.14%.)

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