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NOTE

NEW σ-BONDED RHODIUM(I) COMPLEXES CONTAINING THE LIGANDS TRIPHENYLPHOSPHINE, BUTADIENE, 1,5-CYCLOOCTADIENE, NORBORNADIENE, AND DIPHENYLACETYLENE. II

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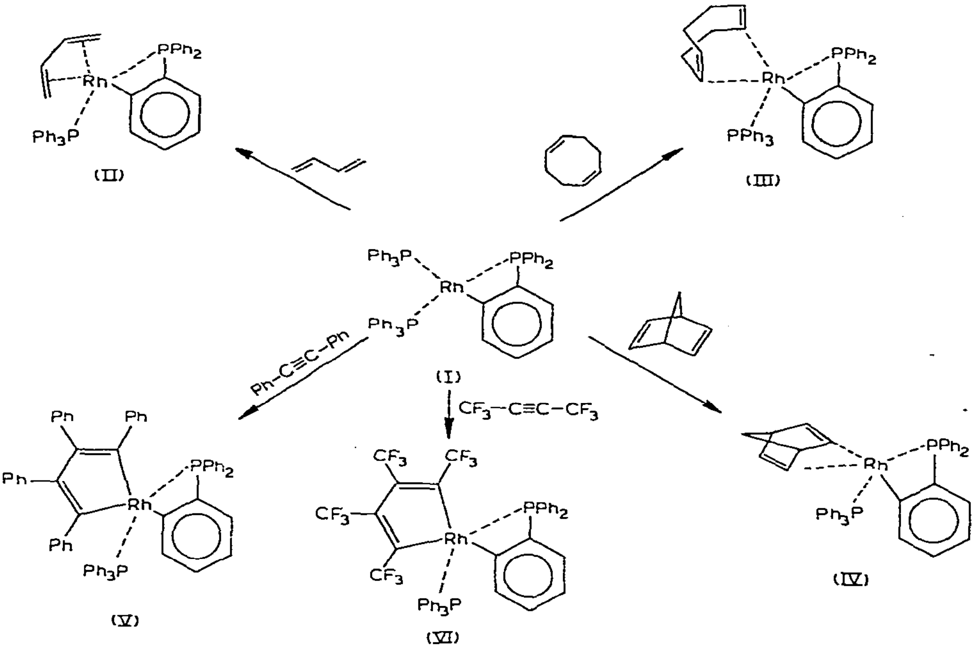
Within the framework of our investigations concerning low-valent rhodium compounds we became interested in the potentiality of forming olefin and acetylene complexes with $(Ph_3P)_2(Ph_2PC_6H_4)Rh$ (I), whose characterization and properties have been described in paper I[1]. Therefore we reacted (I) with butadiene, 1,5-cyclooctadiene, norbornadiene, and diphenylacetylene thus forming pentacoordinated rhodium complexes, whose proposed trigonal bipyramidal structures (II), (III), (IV), (V) are shown in Fig. 1. Magnetic susceptibility measurement of these compounds confirm the expected diamagnetism for rhodium(I) complexes. The cryoscopic determination of the molecular weight in benzene gave values much lower than for the



calculated monomeric species, which suggests that dissociation occurs in solution[2,3].

The IR spectra are mainly determined by absorptions due to Ph_3P. Both double bonds of the diolefins are coordinated to the rhodium, as is evicenced by the absence of stretching frequencies in the region of uncoordinated double bonds. The proposed structures in which one hydrogen in the *ortho*-position is abstracted to form a σ-rhodium–carbon bond is supported by the intense shoulder at 745–755 cm^{-1} assigned to the C–H out of plane deformation mode of an *ortho*-disubstituted benzene. The rhodium–carbon band is attributed to the absorption at 320–330 cm^{-1}.

BUTADIENE

Butadiene readily reacts with (I), yielding the light-yellow complex (II). The NMR spectrum is in agreement with the proposed configuration, in which the ligand butadiene is π-bonded to the metal. Three absorptions of equal intensity (at 4.9, 2.3, and 0.4 ppm from TMS, respectively) are found. The peaks are complicated owing to splittings induced by ^{103}Rh and ^{31}P. Comparison with other butadiene complexes of established structures, for example $C_4H_6Fe(CO)_3$[4], suggests assigning the low field pattern at 4.9 ppm to the two equivalent protons on the central carbon atoms. The absorptions at 2.3 and 0.4 ppm can be attributed to the four terminal protons. Chemical evidence supporting the composition of this complex has been obtained by the reaction with hydrogen. Mass spectral analysis of the formed gas confirmed the presence of 53% of the calculated amount of n-butane.

1,5-CYCLOOCTADIENE

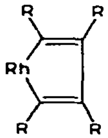
Upon heating (I) with an excess of 1,5-cyclooctadiene, a yellow complex of analytical composition (III) was formed. The NMR spectrum (Varian HR 100) shows three groups of protons at 7.0, 4.5, and 2.7 ppm, which can be assigned to the phenyl, the "olefinic", and the "aliphatic" protons, respectively. A similar pattern for the 1,5-cyclooctadiene ligand has been observed for $[C_8H_{12}RhCl]_2$[5] for which X-ray analysis has confirmed that the 1,5-cyclooctadiene is present in the tub conformation. Accordingly, we like to discuss the structure as shown for (III). The presence of 1,5-cyclooctadiene in this compound could also be supported by the reaction with an aqueous solution of NaCN which liberated the complexed 1,5-cyclooctadiene. In addition, the hydrogenation of (III) yielded 70% [calculated for $(Ph_3P)_2(Ph_2PC_6H_4)(C_8H_{12})Rh$] cyclooctane.

NORBORNADIENE

The reaction of (I) with norbornadiene in boiling benzene resulted upon cooling to the precipitation of a lemon-yellow complex whose elemental analysis, IR and NMR spectra are in agreement with the proposed structure (IV). The NMR spectrum exhibits three groups of resonances. The absorptions at 7 ppm can be assigned to the phenyl protons. The signals at 3.2 ppm and 1.1 ppm can be attributed to the olefinic-tertiary and bridging CH_2 protons, respectively. Wilkinson *et al.*[5] have reported an analogous pattern for the complex norbornadienerhodium chloride. The ligand norbornadiene is liberated upon reacting (IV) with an aqueous solution of KCN (51% based on the empirical formula). The hydrogenation of (IV) yielded 79% of the calculated amount of bicyclo[2.2.1]heptane.

DIPHENYLACETYLENE

A dark-red complex of empirical formula $(Ph_2C_2)_2(Ph_3P)(Ph_2PC_6H_4)Rh$ is formed upon direct reaction of (I) with diphenylacetylene in boiling toluene. This complex appears to be thermally stable up to 180°. The mass spectral analysis of the decomposition products showed no fragmentations corresponding to tolane, indicating that the complex probably does not contain two coordinated diphenylacetylenes. However, the fragmentation pattern shows the presence of an ion due to $(PhC{\equiv}CPh)_2$. The NMR spectrum shows a complexed multiplet at $\sim$7 ppm attributable to the differently bonded phenyl rings. The IR spectrum exhibits no bands in the 1600–2000 cm^{-1} region which can be assigned to a coordinated acetylene moiety[7]. There is, however, a sharp strong band at 1598 cm^{-1} which can be attributed to a C=C stretching frequency adjacent to rhodium[6,7]. All of the evidence presented is consistent with the proposed structure (V), which contains a tetraphenylrhodiacyclopentadiene ring with the metal formally in the rhodium(III) state. Similar compounds have been described recently and have been proposed as intermediates in the trimerization of acetylenes[8-10]. It should be noted, however, that at present we cannot unambiguously exclude the possibility of a structure containing a complexed tetraphenylcyclobutadiene ring, and final determination of the structure must be done by X-ray analysis.

In order to gain additional proof for the presence of a  system in this type of complex, we tried to synthesize the analogous complex of (V) in which the phenyl ring is substituted by a CF_3 group. It might be expected that a ^{19}F NMR analysis would permit one to distinguish between a cyclobutadiene and a rhodiacyclopentadiene structure. By reacting (I) with hexafluoro-2-butyne we obtained a dark-red complex of empirical formula $(Ph_3P)(Ph_2PC_6H_4)(C_8F_{12})Rh$. The infrared spectrum shows a sharp band of medium intensity at 1560 cm^{-1} which can be assigned to a double-bond stretching frequency adjacent to the rhodium[6,11]. The ^{19}F NMR spectrum consists of a very complex multiplet centered at -31 ppm and is not consistent with a cyclobutadiene structure, and therefore the structure (VI) is proposed for this complex.

EXPERIMENTAL

All complexes were handled under an argon atmosphere by dry-box techniques. Infrared spectra were obtained on Nujol mulls or KBr films via a Beckman IR-5 spectrophotometer. NMR spectra were taken on a Varian HR-60 spectrometer in deuterobenzene solutions unless otherwise stated. The resonances are referred to tetramethylsilane. Melting points were determined on a conventional hot-stage microscope and are uncorrected.

$(Ph_3P)(Ph_2PC_6H_4)(C_4H_6)Rh$

Butadiene was condensed into an evacuated, thick glass tube containing $(Ph_3P)_2(Ph_2PC_6H_4)Rh$ (1.8 g) which had been suspended in dry toluene (10 ml). The tube was sealed and held at 70° for 24 h. Upon cooling, a yellow complex precipitated which was filtered and washed with cooled n-hexane (0.6 g, 53%); m.p. 155–165° (dec.). (Found: C, 69.7; H, 5.3; P, 9.6; Rh, 14.3. $C_{40}H_{35}P_2Rh$ calcd.: C, 70.5; H, 5.3; P, 9.1; Rh, 15.1%.)

Reaction of this complex with 20 psig hydrogen at 100° produced 53% of the calculated amount of n-butane based on mass spectral analysis.

$(Ph_3P)(Ph_2PC_6H_4)(C_8H_{12})Rh$

A toluene (10 ml) suspension of $(Ph_3P)_2(Ph_2PC_6H_4)Rh$ (2.1 g) was heated with 1,5-cyclooctadiene (10 ml) for 10 h at 70–80°. At this temperature complete solution of the complex occurred. Upon cooling, a yellow complex precipitated which was washed with n-hexane and dried (1.4 g, 82%); m.p. 165–175° (dec.). (Found: C, 71.5; H, 5.8; P, 8.2; Rh, 14.4; mol.wt. in benzene, 435. $C_{44}H_{41}P_2Rh$ calcd.: C, 71.8; H, 5.8; P, 8.4; Rh, 14.0%; mol.wt., 734.)

A suspension (978 mg) of (III) in H_2O/CCl_4 was stirred for 24 h with an aqueous solution of NaCN. GLC analysis of the CCl_4 phase revealed the presence of 48% of the calculated amount of 1,5-cyclooctadiene. The hydrogenation of 1.4 g complex in benzene at 100° and 400 psig hydrogen pressure gave 70% cyclooctane [calculated for $(Ph_3P)(Ph_2PC_6H_4)(C_8H_{12})Rh$].

$(Ph_3P)(Ph_2PC_6H_4)(C_7H_8)Rh$

Treatment of a toluene suspension (10 ml) of $(Ph_3P)_2(Ph_2PC_6H_4)Rh$ (3.2 g) with norbornadiene (10 ml) for 20 h at 80–90° led to a yellow solution. Upon cooling, a lemon-yellow complex precipitated (1.8 g, 69%); m.p. 180–190° (dec.). (Found: C, 71.3; H, 5.1; P, 8.7; Rh, 13.2; mol.wt., 511. $C_{43}H_{37}P_2Rh$ calcd. C, 71.8; H, 5.3; P, 8.6; Rh, 14.3%; mol.wt., 718.)

The complex, 719 mg, was suspended in a mixture H_2O/CCl_4 and treated for 20 h with an aqueous solution of NaCN. GLC analysis of the organic phase yielded 51% (calculated for the empirical formula) of norbornadiene. The hydrogenation of $(Ph_3P)(Ph_2PC_6H_4)(C_7H_8)Rh$ (458 mg) resulted in the formation of 79% of the calculated amount of norbornane.

$(Ph_3P)(Ph_2PC_6H_4)(Ph_4C_4)Rh$

A toluene suspension of $(Ph_3P)_2(Ph_2PC_6H_4)Rh$ (4.8 g) and tolane (3.4 g) in toluene (30 ml) was refluxed for 8 h. The solution turned dark-red, and upon cooling, a dark-red complex separated (4.0 g, 79%) which was filtered, washed in n-hexane, and dried; m.p. 175–177°. (Found: C, 78.3; H, 5.4; P, 5.8; Rh, 10.2. $C_{64}H_{49}P_2Rh$ calcd.: C, 78.1; H, 5.1; P, 6.3; Rh, 10.5%.)

$(Ph_3P)(Ph_2PC_6H_4)(C_8F_{12})Rh$

A toluene solution of $(Ph_3P)_2(Ph_2PC_6H_4)Rh$ (2.6 g) was heated to 70–80° and hexafluoro-2-butyne was bubbled in. Upon cooling, a dark-red complex precipitated (1.6 g, 57%). (Found: C, 55.1; H, 3.0; F, 25; Rh, 9.7. $C_{44}H_{29}F_{12}P_2Rh$ calcd.: C, 55.6; H, 3.1; F, 24; Rh, 10.8%.)

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