Inorganica Chimica Acta Letters, 64 (1982) L267–L268

Synthesis of Rhodium(I) Acetylacetonato-bis-triphenylphosphite Complex and its Reactivity towards Carbon Monoxide

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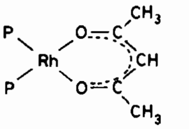
Received January 4, 1982

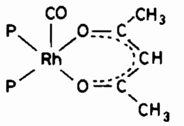
Rhodium(I) complex compounds with the phosphite ligands have been recently investigated but only a few were synthesized in the solid state. $\{HRh[P(OCH_3)]_2\}_3$, η^3-$C_3H_5Rh[P(OR)_3]$ [1] and $\{Rh[P(OCH_3)_3]_5\}BPh_4$ [2] were isolated and examined. It has been stated spectroscopically and calorimetrically that the trimethyl phosphite [P] used to substitute the olefin coordinated in $[Rh(COD)Cl]_2$, and CO in the $[Rh(CO)_2Cl]_2$ complexes [3]. The substitution process of olefins by the triphenyl phosphite in complexes $[RhCl(olefin)_n]_2$ and [Rh(acac)(olefin)] [4] has been examined calorimetrically and the formation of the $[Rh_2Cl_2P_2(olefin)_n]$, $[RhClP_2]_2$, $[RhClP_3]$ and $[Rh(acac)P_2]$ has been reported [4]. However, neither of these complexes have been isolated, nor have the proposed formulae been evidenced by physicochemical investigations.

We report the synthesis and structural investigations of two Rh(I) complexes with triphenyl phosphite:



(1)

P = P(OPh)$_3$



(2)

Complex (1) is formed immediately after addition of $P(OPh)_3$ to $Rh(acac)(CO)_2$. The reaction is accompanied by rapid liberation of CO. The infrared spectrum of the obtained complex presents bands at frequencies expected for the coordinated phosphite and acetylacetone, and no bands at about 2000 cm^{-1}, which may suggest the presence of coordinated CO. The ^1H NMR spectrum in C_6D_6 presents one line originating from CH_3 protons of acetylatone (at δ = 1.28 ppm), and the CH proton line (at δ = 4.79 ppm). Only one CH_3 acetylacetone line is indicative for equivalence of both CH_3 groups, and also is confirmative for the presence of plane of symmetry in a molecule.

The ^{31}P NMR spectrum of the pure compound (1) presents the doublet at $\delta = -123.1$ ppm (with respect to 85% H_3PO_4), with coupling constant JRh–P = 308.6 Hz. The presence of free phosphite has no influence on the NMR spectrum of complex (1), only the additional line at $\delta = -127.4$ ppm of the non-coordinated phosphite appears. Thus, in that system the exchange of free and coordinated phosphite does not occur or is very slow.

Complex (1) reacts with CO under mild conditions (p = 1 atm; t = 25 °C) to produce the complex (2). Passing CO through the solution of complex (1) in $CHCl_3$ or in C_6H_6 is accompanied by the appearance of a new infrared band at 2010 cm^{-1}, corresponding to the coordinated CO. That band was observed also in the spectrum of the compound isolated from the reaction mixture. Formation of the new compound on the passage of CO through the solution of complex (1) could be proved and confirmed by UV spectroscopy. In the electronic spectrum of complex (1) during CO uptake the intensive band at 31200 cm^{-1} disappeared, while a new band appeared at 27500 cm^{-1}. In the ^1H NMR spectrum of complex (2) in C_6D_6 the lines assigned to CH_3 and CH protons of acetylacetone are at 1.49 and 4.43 ppm, respectively.

Decrease of electron density on rhodium, resulting from the coordination of CO, is responsible for the downfield position of both lines compared with complex (1). However, the equivalence of both CH_3 groups of acetylacetone is preserved, which is indicative of CO coordination to complex (1) rather than for its substitution for the already coordinated phosphite. Measurements of the volume of the consumed CO show that one CO molecule was uptaken per complex molecule. Hence, the formed compound was pentacoordinated, with a square pyramid structure.

Experimental

Rhodium(I)acetylacetonato-bis-triphenylphosphite: Rh(acac)[P(OPh)$_3$]$_2$

To $Rh(acac)(CO)_2$ (0.1 g), $P(OPh)_3$ (0.3 ml) was slowly added. CO was liberated and the yellow precipitate settled down. The precipitate was filtered off, washed with ethanol and dried. The complex was purified on Al_2O_3 column, using $CHCl_3$ as an eluent. Yield: 0.22 g. Found: C = 59.3%; H = 5.0%. Calcd.: C = 59.9%; H = 4.5%. IR spectrum in KBr: 593m, 683s, 733s, 767vs, 883vs, 900vs, 930s, 1020s, 1067m, 1170s, 1193vs, 1387s, 1480vs, 1507s, 1570s, 1583vs. UV–VIS spectrum in $CHCl_3$: 27700 cm^{-1} (1600), 31200 cm^{-1} (10000), 38500 cm^{-1} (16600).

Rhodium(I) acetylacetonato-carbonyl-bis-triphenylphosphite: [Rh(acac)]P(OPh$_3$)]$_2$CO]

Solution of $Rh(acac)[P(OPh)_3]_2$ in $CHCl_3$ was saturated with CO for 1–2 h. Next the solvent was

0020-1693/82/0000-0000/$02.75

evaporated under reduced pressure and the residue was washed with ether.

IR spectrum in KBr: 753m, 767m, 900vs, 910vs, 1020m, 1070m, 1083m, 1160s, 1180vs, 1477s, 1580m, 2010vs.

UV–VIS spectrum in $CHCl_3$: 27500 cm^{-1} (4700), 37500 cm^{-1} (11100).

Rhodium(I) Acetylacetonato-dicarbonyl

$[Rh(acac)(CO)_2]$ was prepared following the method given in [5].

Measurements

^{31}P NMR measurements were made on a Jeol 40.5 MHz.

^{1}H NMR measurements were made on a Tesla 80 MHz; line positions were determined *versus* HMDSO.

Electronic absorption spectra and IR spectra were recorded on a Specord UV–VIS and a Specord 75 IR spectrometer, respectively.

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