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THE FORMATION AND ACETYLATION OF π-CYCLOPENTADIENYL-π-CYCLOBUTADIENERHODIUM

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SUMMARY

The photolysis of π-cyclopentadienyldicarbonylrhodium and photo-α-pyrone in benzene solution has produced the first unsubstituted π-cyclobutadiene derivative of rhodium, π-cyclopentadienyl-π-cyclobutadienerhodium. The product has been characterized by elemental, IR, NMR and mass spectral analyses. π-Cyclopentadienyl-π-cyclobutadienerhodium undergoes Friedel–Crafts acetylation with acetic anhydride and stannic chloride on the π-cyclobutadiene ring to form π-cyclopentadienyl-π-acetylcyclobutadienerhodium in 25% yield.

The formation and chemistry of π-cyclobutadiene derivatives of the transition metals has been a very active area of organic and organometallic chemistry since the first discoveries of these types of compounds in 1959[1-2]. Although many varieties of substituted and unsubstituted π-cyclobutadiene complexes of cobalt are now known[3-7], no corresponding derivatives of rhodium or iridium have yet been reported*. In this note, we report the synthesis and properties of the first unsubstituted π-cyclobutadiene derivative of rhodium, π-cyclopentadienyl-π-cyclobutadienerhodium (I).

Rosenblum and coworkers have recently described an elegant method for the formation of π-cyclobutadiene complexes of iron[9] and cobalt[4]. Since all attempts in our laboratory to produce π-cyclobutadiene complexes of rhodium from reactions of π-cyclopentadienyldicarbonylrhodium and acetylenes have thus far failed (the products instead are π-cyclopentadienone–rhodium compounds, rhodiacyclopentadiene complexes, trinuclear rhodium cluster complexes, etc.)[7,10], it occurred to us that Rosenblum's method might also prove useful for the synthesis of π-cyclobutadienerhodium derivatives. This has proved to be the case.

When photo-α-pyrone and π-cyclopentadienyldicarbonylrhodium were photolyzed in benzene solution for 36 h, column chromatography of the reaction products produced two organorhodium compounds. The first band to be eluted was purified by vacuum sublimation, and gave a low yield of π-cyclopentadienyl-π-cyclobutadienerhodium (I). Complex (I) is a white crystalline material of m.p. 129.5–130°. Like

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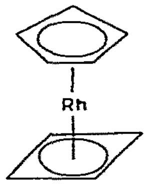
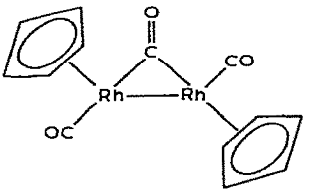
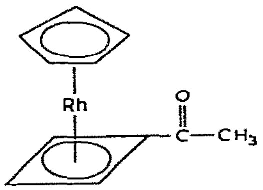
* π-Cyclopentadienyl-π-tetraphenylcyclobutadienerhodium has recently been prepared and characterized by Helling and coworkers[8].


(I)


(II),


(III)

its cobalt analog[4] (I) is very soluble in common organic solvents, can be readily sublimed, and appears to be indefinitely stable in air. The NMR spectrum of (I), taken in CCl_4, exhibits two resonances at τ 4.75 and 5.95 with the expected relative intensities of 5/4. Both resonances are actually doublets, due to coupling of the respective ring protons with the ^{103}Rh nucleus ($I = 1/2$, 100% relative abundance)[11]. The π-cyclobutadiene proton–rhodium coupling (J 1.6 Hz) is slightly greater than coupling between the protons of the π-cyclopentadienyl ring and rhodium (J 1.0 Hz). It is of further interest to note that the extent of deshielding of protons of both rings in (I) compared to its cobalt analog[4] is very nearly equal to deshielding observed in the NMR spectrum of ruthenocene relative to ferrocene[12]. The mass spectrum of (I) is also consistent with the proposed structure, exhibiting intense peaks at m/e 220 (molecular ion), 194 ($C_5H_5RhC_2H_2$), 168 (C_5H_5Rh) and 141 (C_3H_2Rh).

The second band to be eluted from the column produced a small amount of μ-carbonylbis(π-cyclopentadienylcarbonylrhodium) (II). The dinuclear complex (II) is known to be a reaction product from the photolysis of π-cyclopentadienyldicarbonylrhodium[13,14], and was characterized by its IR, NMR and mass spectra. No other reaction products could be detected under the reaction conditions employed.

Rosenblum *et al.*[4] as well as Amiet and Pettit[3] have shown that the π-cyclobutadiene ring in π-cyclopentadienyl-π-cyclobutadienecobalt is more reactive toward electrophilic reagents than is the π-cyclopentadienyl ring. When (I) was treated with a mixture of acetic anhydride and stannic chloride under the Friedel–Crafts conditions employed for the cobalt analog[4], pale-yellow crystals of π-cyclopentadienyl-π-acetylcyclobutadienerhodium (III) were obtained in 25% yield. No other acetylation products could be detected, indicating that in (I) as well as in the cobalt analog, the π-cyclobutadiene ring is more reactive towards acetylation than is the π-cyclopentadienyl ring. The apparently greater reactivity of the π-cyclobutadiene ring in (I) compared to its cobalt analog (as measured by the yields of acetylated products) is striking, but may be due simply to the enhanced relative stabilities of (I) and/or (III) to decomposition by the Lewis acid employed*. Further studies on the stability and chemistry of (I), and its comparative reactivity, are in progress.

EXPERIMENTAL

α-Pyrone was prepared according to the procedure of Zimmerman *et al.*[17], but with the following modifications: (1) The coumalic acid was heated in an oil bath

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* π-Cyclopentadienyl-π-cyclobutadienecobalt is known to be sensitive to Lewis acids and is rapidly decomposed by these reagents even at low temperatures[4]. The lower relative reactivity of ruthenocene compared to ferrocene under electrophilic conditions is well-established[15,16].

at 200–215°; (2) ground glass connections between the sublimation flask and the Vycor tube were wrapped with heating tape maintained at ca. 190–200°; (3) the product was trapped in a U-tube immersed in an ice-salt bath at −10°. Yields of α-pyrone after vacuum distillation ranged from 35 to 43%. (π-Cyclopentadienyl)dicarbonylrhodium was prepared according to a literature procedure[10]. Melting points are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

Reaction of α-pyrone and π-cyclopentadienyldicarbonylrhodium

The photolysis was carried out using a medium pressure quartz mercury vapor lamp (Hanovia Type L, 450 watts) with a Corex filter.

A solution of α-pyrone (1.92 g, 20 mmol) in 800 ml of benzene was photolyzed for 12 h. Stirring was effected by constant bubbling of nitrogen through the solution. π-Cyclopentadienyldicarbonylrhodium (2.24 g, 10 mmol) was added to the reaction flask and the solution was photolyzed for an additional 24 h. The red-brown solution was evaporated to dryness, and the residue was dissolved in ca. 50 ml of benzene, filtered, and chromatographed on an alumina column (2.5 × 35 cm) which had been packed in hexane. Hexane elution removed a light yellow band from the column. The yellow solution was evaporated to dryness and allowed to stand uncovered in the air for several days. The residue was dissolved in hexane and chromatographed on an alumina column (2 × 10 cm) which had been packed dry. Elution with hexane brought down a colorless band which was evaporated to dryness. The residue was purified by vacuum sublimation at 80°/20 mm Hg, yielding white crystals of π-cyclopentadienyl π-cyclobutadienerhodium (I) (0.11 g, 5%), m.p. 129.5–130°. (Found: C, 49.45; H, 4.34. C_9H_9Rh calcd.: C, 49.12; H, 4.13%). IR spectrum (KBr): major bands at 1410 w; 1310 w, 1210 m, 1100 w, 990 m, 925 m, and 780 s (cm^{-1}).

A second band (red) was eluted from the column using benzene. The red solution was evaporated to dryness to yield 0.060 g (3%) of μ-carbonylbis(π-cyclopentadienylcarbonylrhodium) (II). Mass spectrometry: *m/e* 420 (molecular ion), 392 $[(C_5H_5RhCO)_2]^+$, 364 $[(C_5H_5Rh)_2CO]^+$, 336 $[(C_5H_5Rh)_2]^+$, 233 $[(C_5H_5)_2Rh]^+$, 196 $[C_5H_5RhCO]^+$, 168 $[C_5H_5Rh]^+$. NMR ($CDCl_3$): τ 4.48 (s, π-C_5H_5). IR (KBr): 1960 s, 1810 s, 1400 m, 1010 m, 795–775 s (cm^{-1}).

Acetylation of π-cyclopentadienyl-π-cyclobutadienerhodium (I)

A solution of π-cyclopentadienyldicarbonylrhodium (0.15 g, 0.682 mmol) in 10 ml of methylene chloride was placed in a flask which had previously been flamed out under vacuum and flushed with dry nitrogen. The solution was cooled to −78° using a Dry Ice–acetone bath. A mixture of acetic anhydride (1.4 ml, 15 mmol), stannic chloride (0.14 ml, 1.22 mmol) and 5 ml of methylene chloride was added dropwise to this solution over a period of 5 min. The color of the reaction mixture immediately turned from clear to red-orange. The reaction was stirred at −78° for 1 h. At the end of this period, the reaction mixture was poured into an ice-cold solution of 20 ml of 2 *M* HCl. The aqueous layer was extracted twice with methylene chloride, and the combined organic phase was extracted with 0.01 *M* NaOH and then water. The methylene chloride solution was dried over anhydrous sodium sulfate and evaporated to dryness. The residue was dissolved in a small amount of benzene and chromatographed on an alumina column (2 × 5 cm) which had been packed in hexane.

Elution with benzene and then ether removed a colorless band from the column which was collected and evaporated to dryness. The yellow-white product was identified as π-cyclopentadienyl-π-acetylcyclobutadienerhodium (III) (0.045 g, 25%), m.p. 85°. (Found: C, 50.11; H, 4.52. $C_{11}H_{11}ORh$ calcd.: C, 50.40; H, 4.23%). Mass spectrometry: *m/e* 262 (molecular ion), 247 $[M-CH_3]^+$, 233 $[(C_5H_5)_2Rh]^+$, 219 $[M-COCH_3]^+$, 168 $[C_5H_5Rh]^+$, 103 $[Rh]^+$. NMR (CCl_4): τ 4.77 (d, π-C_5H_5, J(H–Rh) 1.0 Hz), τ 5.40 (d, π-C_4H_3, J(H–Rh) 1.6 Hz), τ 5.82 (d, π-C_4H_3, J(H–Rh) 1.8 Hz), τ 8.15 (s, $COCH_3$). The relative intensity ratio is 5/2/1/3. IR (KBr): 1650 s, 1440–1390 m, 1255 s, 1110–990 vs, 790 s cm^{-1}.

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