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REACTIONS OF π-CYCLOPENTADIENYLTRIPHENYLPHOSPHINEMETAL DIIODIDES AND π-CYCLOPENTADIENYLCARBONYLMETAL DIIODIDES (M = Co, Rh, Ir) WITH 1,4-DILITHIO-1,2,3,4-TETRAPHENYLBUTADIENE

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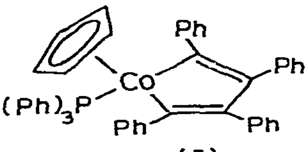
Summary

Reactions between π-cyclopentadienyltriphenylphosphinemetal diiodides (M = Rh and Ir) and 1,4-dilithio-1,2,3,4-tetraphenylbutadiene result in the formation of 1-(π-cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetraphenylrhodole and 1-(π-cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetraphenyliridole, respectively, in low yield. Reactions between π-cyclopentadienyltriphenylphosphinecobalt diiodide or π-cyclopentadienylcarbonylcobalt diiodide do not produce the expected cobaltacyclopentadiene complexes, but instead a low yield of π-cyclopentadienyl-(π-tetraphenylcyclobutadiene)cobalt. The trimeric rhodium complex $(\pi\text{-}C_5H_5Rh)_3(CO)(PhC{\equiv}CPh)$ has been isolated from a reaction between 1,4-dilithio-1,2,3,4-tetraphenylbutadiene and π-cyclopentadienylcarbonylrhodium diiodide. The importance of metallocyclic intermediates in the formation of polynuclear complexes of this type is discussed.

Introduction

The isolation of a number of metallocyclopentadiene complexes of cobalt, rhodium and iridium has been reported in the literature, and the common method of preparation of such complexes has been via a route involving reactions of mono- or di-acetylenes with organometallic carbonyls, phosphines or stilbenes [1—9]. Several workers also have discussed the role of such complexes for the specific case of catalysis by cobalt and/or rhodium carbonyls [10—11]. In view of the unique preparation of the metallocyclic complex I from a reaction between π-cyclopentadienyltriphenylphosphinecobalt diiodide, isopropylmagnesium bromide and diphenylacetylene [12], it was therefore of interest to attempt the formation of metallocyclopentadiene complexes by a different and hopefully more direct method involving reactions of the dilithium reagent 1,4-dilithio-1,2,3,4-tetra-

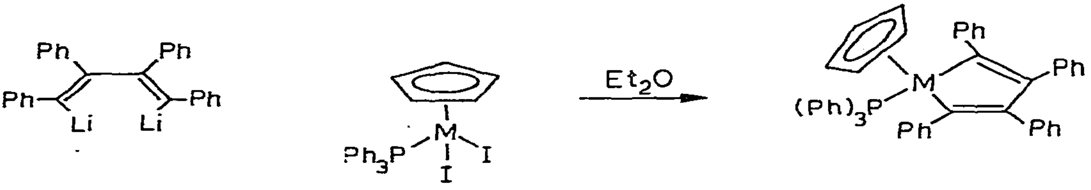


(I)

phenylbutadiene (II) with the organometallic diiodides IIIa-IIIc. We have previously reported on the reactions of π-cyclopentadienylcarbonylmetal diiodides (M = Co, Rh, Ir) with several other dilithium reagents to form metallofluorene complexes of the transition metals [13].

Discussion

We have found that reactions between 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (II) [14], and the rhodium and iridium diiodides IIIb and IIIc result in the formation of the rhoda- and irida-cyclopentadiene complexes IVa and IVb. Both compounds have been isolated in low yields as air-stable crystalline solids. The metallocyclic complexes IV were the only organometallic products isolated from these reactions, although appreciable amounts of metallic decomposition products and small amounts of 1,2,3,4-tetraphenylbutadiene, hexaphenylbenzene, and 1,2,3-triphenylnaphthalene [14] were also formed. The NMR and IR spectra of complexes IV compare favorably with those of the corresponding cobaltacycle I, which was prepared according to the method of Yamazaki and Hagihara [12] and it appears that complexes IVa and IVb are fully analogous in structure to the cobalt compound I. The mass spectra of IVa and IVb show major peaks assignable to M^+ (molecular ion), $(M - PPh_3)^+$, and $(C_5H_5MPhC{\equiv}CPh)^+$.



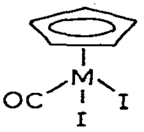
(II)

(IIIa, M = Co
IIIb, M = Rh
IIIc, M = Ir)

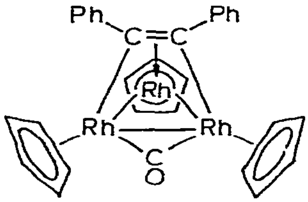
(IVa, R = Rh
IVb, R = Ir)

Unlike the rhodium and iridium reactions, the reaction of dilithium reagent II with π-cyclopentadienyltriphenylphosphinecobalt diiodide (IIIa) proceeds in an anomalous manner, giving π-cyclopentadienyl-π-tetraphenylcyclobutadienecobalt (V) [15—17]. Small amounts of 1,2,3,4-tetraphenylbutadiene, hexaphenylbenzene, and 1,2,3,-triphenylnaphthalene [14] were again obtained. The expected cobaltacycle I thus was not obtained in this reaction, although it is nevertheless a likely intermediate, in view of the isolation of IVa and IVb as described above.

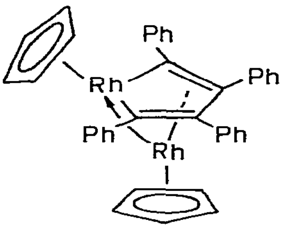
Reactions of the dilithium reagent II with both the cobalt and rhodium π-cyclopentadienylcarbonylmetal diiodides VIa and VIb have also been studied. As in the related reaction between the cobalt compound IIIa and II, the only identifiable organometallic product from the reaction of VIa and II was V. Assuming that the desired cobaltacycle is again an intermediate in this reaction, it could readily lose carbon monoxide under the reaction conditions employed and undergo a σ- to π-rearrangement to form V. Cobaltacycle I has already been reported to undergo a similar transformation when heated above its melting point [12] and it is reasonable to expect that the cobaltacycle formed by reaction of II and VIa could undergo this process even more readily than I. Other organic products were also formed in this reaction, including 1,2,3,4-tetraphenylbutadiene, 1,2,3-triphenylnaphthalene and tetraphenylcyclopentadienone.



(VIa, M = Co
VIb M = Rh)



(VII)



(VIII)

A similar reaction between dilithium reagent II and π-cyclopentadienylcarbonylrhodium diiodide (VIb) has resulted in the formation of the purple trinuclear rhodium complex VII. Complex VII has been isolated previously from the reaction between π-cyclopentadienyldicarbonylrhodium and diphenylacetylene [18]. The formation of VII from a reaction involving II and VIb is of special significance, since it lends support to the postulate that metallocyclic intermediates are plausible intermediates in the formation of products resulting from reactions of acetylenes with π-cyclopentadienyldicarbonylmetal compounds*. We have previously speculated on the formation of the metallocyclic complex VIII from the reaction between diphenylacetylene and π-cyclopentadienyldicarbonylrhodium [18]. It is reasonable to assume that VIII would gain added stability compared to the uncomplexed rhodacyclopentadiene intermediate proposed in the present study, because of the second coordinated (π-C_5H_5)Rh group incorporated into the molecule which would inhibit further reactions of the metallocyclic ring system.

Experimental

All operations including column chromatography were carried out using Schlenk tube techniques under a nitrogen atmosphere. Hexane and benzene were purified by distillation from calcium hydride under nitrogen, while ethyl ether was predried over sodium wire and then distilled from sodium-benzophenone. Diphenylacetylene [19], π-cyclopentadienylcarbonylcobalt diiodide [20], π-cyclopentadienylcarbonylrhodium diiodide [20] and π-cyclopentadienyltriphenylphosphinecobalt diiodide [20] were all prepared by published procedures. π-Cyclopentadienyltriphenylphosphinerhodium diiodide was prepared in 70% yield as brown crystals. m.p. 245-250°, in a manner analogous to that used for the cobalt com-

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* The diphenylacetylene ligand which is present in VII probably arises from unreacted diphenylacetylene used in the formation of II [14].

pound [20]. (Found: C, 40.43; H, 3.06; I, 37.18; P, 4.55; Rh, 15.00. $C_{23}H_{20}I_2PF$ calcd.: C, 40.38; H, 2.95; I, 37.10; P, 4.53; Rh, 15.04%). π-Cyclopentadienyltriphenylphosphineiridium diiodide was prepared by the method of Graham and Ol [21]. CAMAG neutral grade alumina was used for column chromatography and w deactivated with 5% water. Camag silica gel was used for preparative TLC; the plates were 20 × 20 cm and had an adsorbant thickness of 1.2 mm. NMR spectra were taken on a Varian A-60 spectrometer and were calibrated using the sideband technique. IR spectra were taken on a Beckman IR-10 spectrometer as KBr pellets. All melting points were taken under nitrogen and are uncorrected. Microanalyses were performed by the Office of Research Services, Microanalytical Laboratory, University of Massachusetts. All reactions were observed to proceed in low yield, with considerable amounts of decomposition products being trapped on the chromatography column. In each case, therefore, the column was extracte in order to recover the metallic residues and to achieve a more reasonable materia balance.

Reaction of π-cyclopentadienyltriphenylphosphinerhodium diiodide (IIIb) and 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (II)

The dilithium reagent was prepared by the addition of 1.0 g of lithium wire to a solution of diphenylacetylene (3.56 g, 20 mmol) in 30 ml of ethyl ether. The mixture was stirred at room temperature for 45 min until deep red in color, and then added dropwise with stirring to a slurry of IIIb (5.48 g, 8 mmol) in 100 ml of ethyl ether. After stirring at room temperature for 24 h, the reaction mixture was filtered, yielding a brown filtrate. The solution was evaporated to dryness, the residue was dissolved in a minimum amount of benzene mixed with alumina to form a moist packing, and dried under vacuum for 2 h. The treated alumina was placed on top of an alumina column (2.5 × 30 cm) which had been packed dry. Elution with 20% benzene in hexane removed a band from the column which was evaporated to dryness to yield a solid (0.27 g) found to contain small amounts of hexaphenylbenzene, 1,2,3,4-tetraphenylbutadiene, diphenylacetylene and 1,2,3-triphenylnaphthalene (TLC, mass spectrometry).

A second (brown) band was eluted using benzene. The solution was evaporated to dryness, and the impure residue was dissolved in a small amount of methylene chloride and placed on 3 preparative TLC plates. After one elution with 1/1 benzene/hexane, the major orange band was removed from the plates, extracted with ethyl ether, filtered and evaporated to dryness. The residue wa recrystallized twice from benzene/hexane to yield 1-(π-cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetraphenylrhodole (IVa) (0.020 g) as orange-brown crystals, m.p. 275—277°. (Found: C, 77.71; H, 5.29. $C_{51}H_{40}PRh$ calcd.: C, 77.86; H, 5.12%.) Mass spectrometry: *m/e* (molecular ion) 786 (calcd. 786). NMR ($CDCl_3$): τ 2.6-3.1 (m, C_6H_5) and 3.1-3.7 (m, C_6H_5), 4.83 ppm (s, π-C_5H_5), ratio 7/1. IR (KBr): 3050w, 1600m, 1480m, 1435m, 1265vw, 1180vw, 1160vw, 1090-1075m, 1030m, 910w, 790m, 750m, 730m, 700s cm^{-1}.

Reaction of π-cyclopentadienyltriphenylphosphineiridium diiodide (IIIc) and 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (II)

The dilithium reagent II (prepared from 1.0 g of lithium wire and diphenylacetylene (3.56 g, 20 mmol) in 30 ml of ethyl ether) was added dropwise to a slurry of IIIc (6.19 g, 8 mmol) in 100 ml of ethyl ether. The mixture was stirred at room temperature for 24 h and then filtered to yield a brown filtrate. The brown solution was evaporated to dryness, the residue was dissolved in a small amount of benzene and chromatographed on a dry column of alumina as described above. Elution with 25% benzene in hexane brought down a green band which was evaporated to dryness and recrystallized from benzene/hexane to yield 0.14 g of 1,2,3,4-tetraphenylbutadiene, m.p. 182-183° (lit. [14] 182.5-183°). The mother liquor contained small amounts of hexaphenylbenzene, diphenylacetylene and 1,2,3-triphenylnaphthalene.

Further elution of the column with benzene removed a second (brown) band. After evaporation to dryness, the residue was dissolved in a minimal amount of carbon tetrachloride and subjected to dry column chromatography as above. Elution with carbon tetrachloride separated the major yellow band from a leading minor impurity. The yellow band was extracted with ethyl ether, filtered and evaporated to dryness. Two recrystallizations of the residue from benzene/hexane yielded 0.02 g of 1-(π-cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetraphenyliridole (IVb) as a yellow solid. (Found: C, 69.83; H, 4.86. $C_{51}H_{40}IrP$ calcd.: C, 69.92; H, 4.60%.) Mass spectrometry: *m/e* (molecular ion) 874-876 (calcd. 874-876). NMR ($CDCl_3$): τ 2.5-3.8 (m, C_6H_5), 4.88 ppm (s, π-C_5H_5), ratio 7/1. IR (KBr): 3040m, 1590m, 1475m, 1430m, 1170m, 1085m, 1020w, 900w, 800m, 740m, 725m, 690s cm^{-1}.

Reaction of π-cyclopentadienyltriphenylphosphinecobalt diiodide (IIIa) and 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (II)

The dilithium reagent [from 1.0 g of lithium and diphenylacetylene (4.28 g, 24 mmol) in 40 ml of ethyl ether] was added dropwise to a slurry of IIIa (6.0 g, 9.4 mmol) in 120 ml of ethyl ether. Stirring was continued for 24 h at room temperature and the reaction mixture was then filtered to yield a dark brown filtrate. The ether solution was evaporated to dryness and the residue placed on top of an alumina column which had been packed dry. Hexane eluted 1.1 g of diphenylacetylene (TLC and IR).

Further elution with 10% benzene in hexane removed a yellow-green band from the column. The green solution was evaporated to dryness, and the residue dissolved in a small amount of benzene and placed on 4 preparative TLC plates. One elution with 10% benzene in hexane separated a top yellow band (A) and a lower yellow band (B). Both bands were removed from the plates, extracted with ethyl ether, filtered and evaporated to dryness.

Band A (0.14 g) was identified as a mixture of 1,2,3,4-tetraphenylbutadiene, hexaphenylbenzene and 1,2,3-triphenylnaphthalene (MS, TLC). Band B was recrystallized twice from benzene/hexane and identified as π-cyclopentadienyl-π-tetraphenylcyclobutadienecobalt (V) (0.11 g) by TLC and NMR, m.p. 260° (reported 262-264° [15], 256° [16], 264° [17]).

Reaction of π-cyclopentadienylcarbonylcobalt diiodide (VIa) and 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (II)

The dilithium reagent [from 1.2 g of lithium and diphenylacetylene (7.12 g, 40 mmol) in 60 ml of ether] was added dropwise to a slurry of π-cyclopentadienylcarbonylcobalt diiodide (VIa) (3.24 g, 8 mmol) in 60 ml of ethyl ether.

The reaction mixture was stirred at room temperature for 24 h. Filtration under nitrogen yielded a brown filtrate which was concentrated to a tar, treated with hexane to induce crystallization, filtered and dried. The resulting solid was dissolved in a minimal amount of benzene and chromatographed on an alumina column which had been packed in hexane. Benzene eluted a large brown band (A) which was shown by TLC to be a mixture. Further elution with 1/1 benzene/ether removed a red-brown band (B) which was also a mixture.

Band A was subjected to dry column chromatography. Hexane elution brought down two bands, the first of which was shown to contain 1.8 g of diphenylacetylene. The second hexane band was evaporated to dryness (85 mg) and was shown to consist of hexaphenylbenzene, 1,2,3-triphenylnaphthalene and 1,2,3,4-tetraphenylbutadiene (MS, TLC). Continued elution of the column with 10% benzene in hexane produced a third band which gave after recrystallization 0.21 g of π-cyclopentadienyl-π-tetraphenylcyclobutadienecobalt (V), m.p. 260°. Compound V was further identified by mass spectrometry, IR, NMR and TLC versus an authentic sample.

Band B was evaporated to dryness, dissolved in a minimal amount of benzene and chromatographed on a dry column of alumina as above. Benzene elution removed a very small purple band which produced a purple solid identified as tetraphenylcyclopentadienone by mass spectrometry and TLC.

Reaction of π-cyclopentadienylcarbonylrhodium diiodide (VIb) and 1,4-dilithiotetraphenylbutadiene (II)

The dilithium reagent [from 1.2 g of lithium and diphenylacetylene (7.12 g, 40 mmol) in 60 ml of ether] was added dropwise with stirring to a slurry of π-cyclopentadienylcarbonylrhodium diiodide (VIb) (7.2 g, 16 mmol) in 200 ml of ethyl ether. After stirring at room temperature for 24 h, the reaction mixture was filtered to yield a brown filtrate. Utilizing dry column chromatography, elution with hexane brought down a light yellow band which was evaporated to dryness and recrystallized from hexane to yield 2.0 g of diphenylacetylene. Further elution with 25% benzene in hexane removed a green band from the column, which was evaporated to dryness and recrystallized from benzene/hexane to yield 0.38 g of a yellow-white solid identified as 1,4-diiodo-1,2,3,4-tetraphenyl-butadiene, m.p. 198-200° (lit. [22] 203-204°). (Found: C, 55.34; H, 3.66; I, 40.9. $C_{28}H_{20}I_2$ calcd.: C, 55.11; H, 3.30; I, 41.59%.)

Continued elution with benzene removed a purple band. The solution was evaporated to dryness and the residue was recrystallized twice from benzene/hexane to yield a dark purple solid (0.13 g), identified as carbonyldiphenylacetylenetris(π-cyclopentadienylrhodium) (VII) by TLC, NMR, IR and mass spectral comparisons with an authentic sample [18].

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