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REACTIONS OF PARTIALLY AND TOTALLY HALOGENATED DIPHENYLACETYLENES WITH π-CYCLOPENTADIENYLDICARBONYL-COBALT AND -RHODIUM

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Summary

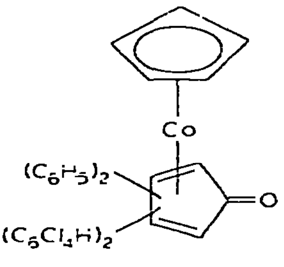
When $(\pi\text{-}C_5H_5)Co(CO)_2$ (I) is caused to react with bis(pentafluorophenyl)acetylene, the major product is the cyclopentadienone complex $(\pi\text{-}C_5H_5)Co[C_5(C_6F_5)_4O]$. A reaction between pentafluorophenylphenylacetylene and complex I produces a variety of products, including the cyclobutadiene complex $(\pi\text{-}C_5H_5)Co[C_4(C_6H_5)_2(C_6F_5)_2]$, the trimerized product $C_6(C_6H_5)_3(C_6F_5)_3$, all three isomers of $(\pi\text{-}C_5H_5)Co[C_5(C_6H_5)_2(C_6F_5)_2O]$, and several complexes of possible polynuclear nature. A reaction of pentachlorophenylphenylacetylene with complex I produces two cyclopentadienone-cobalt complexes exhibiting loss of one and two chlorine atoms, respectively. Likewise, a reaction between this acetylene and $(\pi\text{-}C_5H_5)Rh(CO)_2$ (II) gives a rhodium-complexed cyclopentadienone exhibiting loss of two chlorine atoms as the major product, although the trimerized product $C_6(C_6H_5)_3(C_6Cl_5)_3$ and a trinuclear complex were also obtained. The reaction between II and bis(pentachlorophenyl)acetylene produced a trinuclear rhodium complex in low yield.

Introduction

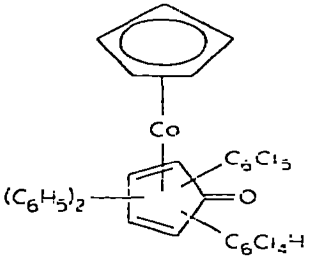
While reactions of π-cyclopentadienyldicarbonylcobalt (I) with disubstituted acetylenes have been described extensively in the literature [1-12], the analogous reactions of π-cyclopentadienyldicarbonylrhodium(II) have received considerably less attention. Dickson et al. have reported on the reactions of complex II with but-2-yne and hexafluorobut-2-yne [12-14], and have also described sealed tube reactions of bis(pentafluorophenyl)acetylene and pentafluorophenylphenylacetylene with II [6]. In a recent paper, we have discussed the reaction of II with diphenylacetylene [15]. It was therefore of interest to extend these studies of reactions of both cobalt complex I and rhodium complex II with a series of different substituted acetylenes. Our first report in this regard described the reaction of II with bis(pentafluorophenyl)-acetylene in refluxing xylene or toluene [16]. We now describe a comparative study of reactions between the π-cyclopentadienyldicarbonylmetal complexes I, M = Co; II, M = Rh) and the partially and also totally halogenated diarylacetylenes — pentachlorophenylphenylacetylene (III), bis(pentachlorophenyl)acetylene (IV), pentafluorophenylphenylacetylene (V) and bis(pentafluorophenyl)-acetylene (VI).

Results and discussion

When (π-C_5H_5)Co$(CO)_2$ (I) was caused to react with pentachlorophenylphenylacetylene (III), two major products (VII and VIII) were isolated from the reaction mixture using a combination of column chromatography, preparative TLC and fractional crystallization techniques. When the crude reaction mixture was placed upon an alumina column, the first band to be eluted consisted of the starting acetylene III which was isolated in 73% yield. Further elution of the column then produced an orange-amber band which was purified by preparative TLC and which yielded π-cyclopentadienyl-π-[bis(tetrachlorophenyl)diphenylcyclopentadienone]cobalt (VII) as fine rust-colored crystals in 9% yield. An infrared spectrum of VII verified the presence of an organic carbonyl group from its absorbance at 1601 cm^{-1}. The NMR spectrum of VII exhibited a singlet at τ 1.98 (s, 2H) which was indicative of the presence of two unique aromatic protons. The assigned structure was further verified by total elemental analysis and mass spectrometry which confirmed a molecular weight of 784 (calcd. 784) and established the presence of 8 chlorine atoms. The theoretical isotope pattern which would be observed for 8 chlorine atoms per molecule was calculated by use of the binomial expansion equation.



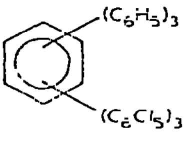
(VII)



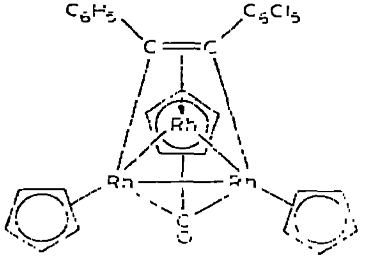
(VIII)

The second major product of this reaction, π-cyclopentadienyl-π-[tetrachlorophenylpentachlorophenyldiphenylcyclopentadienone]cobalt (VIII), was eluted from the column after compound VII, and was obtained as red crystals after recrystallization from benzene/hexane. The infrared spectrum of VIII also contained a strong organic carbonyl absorption at 1601 cm^{-1}. An NMR spectrum exhibited a peak at τ 2.1 assignable to the unique aromatic proton, and peaks at 4.88 (s, π-C_5H_5) and 2.5-3.0 (m, C_6H_5). The mass spectrum confirmed a molecular weight of 819 (calcd. 819) and the array of peaks surrounding the parent ion corresponded to the expected isotope pattern for the presence of 9 chlorine atoms in the molecule.

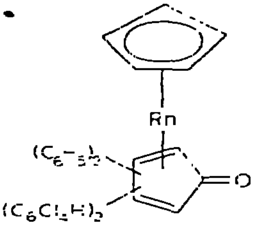
Three principal products (IX-XI) were isolated from the reaction of (π-C_5H_5)Rh(CO)$_2$ (II) and acetylene III, and these are illustrated below:



(IX)



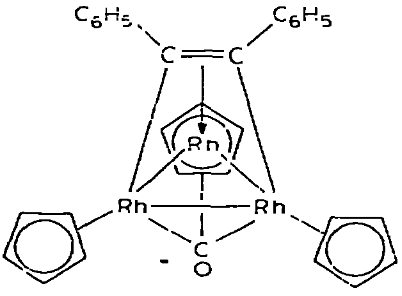
(X)



(XI)

The cyclotrimerization product IX was obtained as an extremely insoluble precipitate, following cooling of the reaction mixture to room temperature and filtration of the yellow solid. The mass spectrum of IX exhibited a cluster of peaks for the parent ion at *m/e* 1044-1074, corresponding to the presence of 15 chlorine atoms in the molecule. We have already reported on the use of hexakis-(pentafluorophenyl)benzene as a mass marking agent in the high mass region [16], and the prospect of utilizing trimerization product IX in a similar manner was investigated. It was felt that the lower volatility of IX as compared to $C_6(C_6F_5)_6$ would possibly provide a more effective marker when used with a high molecular weight unknown of comparable low volatility. Such a use, however, proved impractical due to the extreme involatility of IX in the mass spectrometer.

Complex X, carbonyl(pentachlorophenylphenylacetylene)tris(π-cyclopentadienylrhodium), was isolated as dark green crystals in the form of a benzene solvate*. The low value for the carbonyl stretching frequency (1680 cm^{-1}) and the presence of two C_5H_5 peaks in the NMR spectrum (τ 4.71 and 4.95, ratio 2/1) of X indicated that this compound is similar in structure to complex XII, a product of the reaction between II and diphenylacetylene [15]. The structure as



(XII)

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* Trinuclear rhodium complexes of this type (e.g., XII) are known to form benzene solvates readily [15]. A singlet at τ 2.63 in the NMR spectrum of X is also attributable to the presence of benzene.

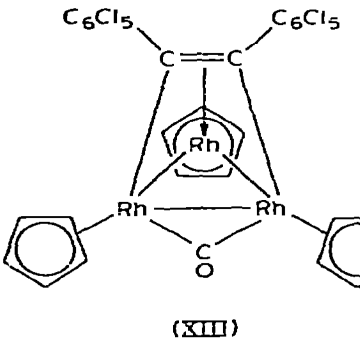
shown for XII has been confirmed by X-ray crystallography [17]. Like cluster complex XII, X shows a parent ion (*m/e* 882) and loss of CO (*m/e* 854) in the mass spectrum.

The final product of the reaction of II with III was complex XI, π-cyclopentadienyl[bis(tetrachlorophenyl)diphenylcyclopentadienone] rhodium. While the isolation of cyclopentadienone complexes is common from reactions of II with disubstituted acetylenes, this particular complex, like VII and VIII, is of special interest in that it exhibits loss of chlorine atoms in the formation of the product. This loss of two chlorines is verified not only by the mass spectrum (*m/e* 828) but also by the NMR spectrum of XI. π-C_5H_5 and phenyl peaks are observed in common positions (τ 4.63 and 2.77, ratio 5/10); however, a single sharp peak at τ 2.22 of intensity 2 was also observed and is assignable to the single proton on each of the tetrachlorophenyl rings.

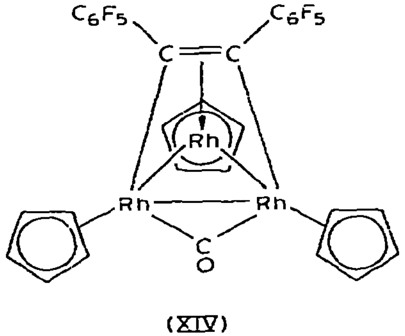
The mechanism by which dehalogenation occurs in the formation of the cyclopentadienone complexes VII, VIII, XI and XIX is presently unknown. Possibly either nucleophilic displacement of an *ortho*-halogen atom by the metal or oxidative addition of a carbon—*ortho*-halogen bond to the metal occurs [18-20]. In either case, protonolysis by the solvent under the reaction conditions employed could result in replacement of an *ortho*-halogen atom by hydrogen*.

The second acetylene to be investigated was bis(pentachlorophenyl)acetylene (IV). The reaction of IV with (π-C_5H_5)Co(CO)$_2$ (I) for 24 h in refluxing xylene resulted in a myriad of products and a 75% recovery of IV. Unfortunately, the very low yields of so many products coupled with the difficulties of separation and purification precluded their isolation and identification.

When (π-C_5H_5)Rh(CO)$_2$ (II) was caused to react with acetylene IV in refluxing xylene for 24 h, several products were obtained in low yield. The black filtrate containing these products was separated from unreacted starting acetylene (17% recovery) by filtration and placed on an alumina column. The only identifiable organometallic product from this reaction was then eluted from the column and isolated as a dark green solid (XIII). Compound XIII exhibited a carbonyl stretching frequency at 1810 cm^{-1}, and showed several peaks in the π-C_5H_5 region of the NMR spectrum between τ 4.5-5.0. The mass spectrum of



(XIII)



(XIV)

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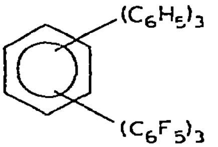
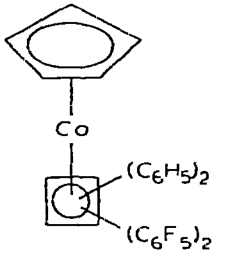
[*] X-ray studies to confirm the position of dehalogenation in these complexes are in progress and will be reported in a subsequent publication.

XIII showed strong peaks at *m/e* 168 ($C_5H_5Rh^+$) and *m/e* 233 [$(C_5H_5)_2Rh^+$], both of which are commonly observed in π-cyclopentadienylrhodium compounds. In addition, a cluster of peaks was observed at *m/e* 1050 ± 10, indicating that a highly chlorinated species was present. These data, coupled with the knowledge gained from previous rhodium—acetylene reactions, suggests that XIII is the trinuclear compound as shown. It is similar in structure to complex XIV, a product from the reaction of II and bis(pentafluorophenyl)acetylene (VI), whose structure has been verified by X-ray crystallography [17]. It is interesting that the carbonyl stretching frequencies in complexes X and XII suggest that they are triply-bridging, whereas the carbonyl frequencies in complexes XIII and XIV indicate doubly-bridging substituents. Unfortunately, the NMR spectrum of XIII was of poor quality, due to lack of sufficient sample and poor solubility. Nevertheless, on the basis of the above data, complex XIII is tentatively identified as carbonyl[bis(pentachlorophenyl)acetylene]tris(π-cyclopentadienylrhodium).

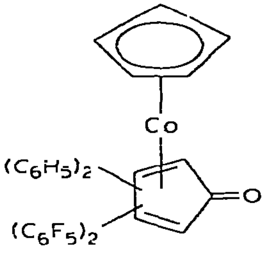
The reaction of (π-C_5H_5)$Co(CO)_2$ with pentafluorophenylphenylacetylene (V) produced several isolable products (XV-XVIII). Compound XV was eluted from the column and recrystallized to yield colorless crystals, which were identified as tris(pentafluorophenyl)triphenylbenzene by mass spectrometry and by elemental analysis.



(XV)



(XVII)



(XVIII)

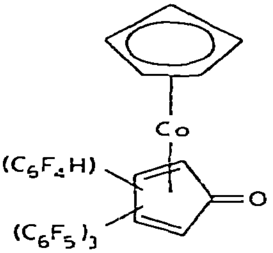
Complex XVI was eluted from the column and purified by preparative TLC to yield a red solid. The product has not yet been identified, although NMR data indicate the presence of phenyl and π-cyclopentadienyl substituents, while mass spectrometry suggests a polynuclear structure. More detailed structural studies are in progress and will be described at a later date.

Preparative TLC and recrystallization yielded a third product from this reaction, complex XVII, identified as π-cyclopentadienyl-π-[diphenylbis(pentafluorophenyl)cyclobutadiene]cobalt. An NMR spectrum of XVII exhibited a π-C_5H_5 peak at τ 5.29 and a mass of peaks in the phenyl region from 2.6-3.3. A mass spectrum of XVII indicated a molecular weight of 660 (calcd. 660).

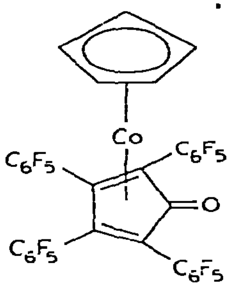
The fourth and final product from this reaction was identified as a mixture of π-cyclopentadienyl-π[diphenylbis(pentafluorophenyl)cyclopentadienone]-cobalt isomers (XVIII). Recrystallization techniques produced one of these isomers in pure form. Relative to cyclobutadienecobalt complex XVII, this product has a characteristic shift of the π-C_5H_5 protons to lower field in its NMR spectrum (τ 4.95). A mass spectrum of XVIII established a molecular weight of 688 (calcd. 688) and an infrared spectrum of the complex showed a strong peak at 1610 cm^{-1} indicative of an organic carbonyl group.

The reaction of acetylene V with (π-C_5H_5)Rh(CO)$_2$ (II) has not yet been investigated.

Two major products were isolated when cobalt complex I was caused to react with bis(pentafluorophenyl)acetylene (VI), and these are illustrated below as complexes XIX and XX. The first product (XIX) was isolated as a red solid and identified as π-cyclopentadienyl-π-[tetrafluorophenyltris(pentafluorophenyl)-cyclopentadienone]cobalt. Its infrared spectrum showed a strong organic carbonyl absorption at 1615 cm^{-1} and the NMR spectrum exhibited a strong π-C_5H_5 peak at τ 4.9. The presence of the unique aromatic proton was not detectable in this case by NMR spectroscopy, perhaps due to multiple splitting as a result of the various fluorine atoms present. The molecular weight was observed to be 850 (calcd. 850) by mass spectrometry.



(XIX)



(XX)

A second red product was isolated and identified from this reaction as π-cyclopentadienyl-π-tetrakis(pentafluorophenyl)cyclopentadienonecobalt (XX). An infrared spectrum of XX showed a strong absorption at 1620 cm^{-1}, assigned to the carbonyl stretching frequency. The NMR spectrum of XX exhibited a broad π-C_5H_5 peak at τ 4.79, while the mass spectrum established the molecular weight as 868 (calcd. 868).

The reaction of complex II with acetylene VI has already been described [15,16].

Experimental

All operations were carried out under nitrogen using Schlenk tube techniques. Pentane, hexane, heptane, benzene, toluene and xylene were purified by distillation from calcium hydride under nitrogen. Ethyl ether was pre-dried over sodium wire and then distilled under nitrogen from sodium/benzophenone. Pentachlorophenylphenylacetylene [21], bis(pentachlorophenyl)acetylene [22], pentafluorophenylphenylacetylene [21], bis(pentafluorophenyl)acetylene [22], and π-cyclopentadienyldicarbonylcobalt [4] were prepared using published procedures. π-Cyclopentadienyldicarbonylrhodium was prepared in ca. 85% yield from a reaction between excess freshly sublimed cyclopentadienylthallium and [Rh(CO)$_2$Cl]$_2$ in hexane [15]. CAMAG neutral grade alumina was used for column chromatography, and was deactivated with 5% water. CAMAG silica gel was used for preprarative TLC; the plates were 20 × 20 cm and had an absorbant thickness of 1.2 mm. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. Mass spectra were recorded on a Perkin—Elmer RMU-6L instrument. NMR and IR spectra were recorded on Varian A-60 and Beckman IR-10 spectrometers, respectively.

Reaction of π-cyclopentadienyldicarbonylcobalt (I) and pentachlorophenylphenylacetylene (III)

Pentachlorophenylphenylacetylene (III) (2.67 g, 7.6 mmol) and π-cyclopentadienyldicarbonylcobalt (I) (0.68 g, 4 mmol) were mixed with 200 ml of dry xylene in a 500 ml 3-necked flask which was equipped with a condenser, a nitrogen inlet and a bubbler. The flask was covered with aluminum foil in order to minimize exposure to the light, and was degassed several times under nitrogen. The reaction mixture was heated at reflux for 7 d, cooled to room temperature, filtered, and concentrated. The concentrate was chromatographed on an alumina column (20" X 1") which had been packed in 1/1 benzene—heptane.

The first band (grey-brown) was eluted with 1/1 benzene—heptane and was identified as the starting acetylene (III) (total recovery = 1.95 g, 73%), after evaporation to dryness and recrystallization from benzene—heptane.

A second band (orange-amber) was eluted with benzene, and TLC of this solution indicated the presence of several products. The solution was therefore concentrated and placed on 6 preparative TLC plates which were eluted with a 5/1 benzene—ether solution. The major red band (lowest R_F) was removed from the plates, extracted with ether, and evaporated to dryness, yielding 270 mg (8.6%) of rust-colored crystals identified as π-cyclopentadienyl-π-[bis(tetrachlorophenyl)diphenylcyclopentadienone]cobalt (VII), m.p. 275-277°C. An analytical sample was prepared by recrystallization from benzene—heptane and drying in vacuo at 150°C. (Found: C, 52.56; H, 2.47; Cl, 36.14; Co, 7.25; 0, 1.94. $C_{34}H_{17}Cl_8CoO$ calcd.: C, 52.08; H. 2.19; Cl, 36.17; Co, 7.52; O, 2.04%.) The molecular weight was 784 as determined by mass spectrometry (calcd. 784). The following major bands were exhibited in the IR (KBr) spectrum: 3100 m, 1710 w, 1601 s, 1450 m, 1400-1300 m, 1100-1000 w and 860-670 cm^{-1}. The NMR spectrum ($CDCl_3$) consisted of the following peaks: τ 5.1 (s, 5H, π-C_5H_5), 1.98 (s, 2H), and 2.5-2.9 (m, 10H, C_6H_5).

A third small band (red) was eluted from the column with benzene and a TLC indicated the presence of a number of products. Due to the complex nature of the band, no further effort was made to separate and identify these minor products.

Band four (red-orange) was eluted from the column with a 4/1 benzene—chloroform solution, and evaporation of the solvent yielded 50 mg of red crystals which were identified as π-cyclopentadienyl-π-(tetrachlorophenylpentachlorophenyldiphenylcyclopentadienone)cobalt (VIII), m.p. 315.5-316°C. An analytical sample was prepared by recrystallization from benzene—heptane and drying in vacuo at 150°C. (Found: C, 49.91; H, 2.05; Cl, 38.47; Co, 7.20; O, 1.90. $C_{34}H_{16}Cl_9CoO$ calcd.: C, 49.89; H, 1.97; Cl, 38.98; Co, 7.21; O, 1.95%.) The molecular weight was 819 as determined by mass spectrometry (calcd. 819). The IR spectrum (KBr) exhibited the following major peaks: 3100 w, 1710 m, 1601 s, 1400-1310 m, 1180 w and 875-670 m cm^{-1}. The NMR spectrum ($CDCl_3$) consisted of the following peaks: τ 4.88 (s, 5H, π-C_5H_5), 2.1 (m, 1H), and 2.5-3.0 (m, 10H, C_6H_5).

Reaction of π-cyclopentadienyldicarbonylrhodium (II) and pentachlorophenylphenylacetylene (III)

Pentachlorophenylphenylacetylene (III) (1.4 g, 4 mmol) and π-cyclopentadienyldicarbonylrhodium (II) (0.45 g, 2 mmol) were mixed with 25 ml of dry xylene in a flask which had previously been flamed out under vacuum and flushed with nitrogen. The flask was covered with aluminum foil, and the contents were heated at reflux for 24 h. After cooling to room temperature, filtration of the dark reaction mixture yielded 1.0 g (71%) of a yellow solid, tris(pentachlorophenyl)triphenylbenzene (IX), m.p. 310-315°C. The molecular weight was 1044-1074 as determined by mass spectrometry (calcd. 1044-1074). The IR spectrum (KBr) exhibited the following major peaks: 1620 s, 1495 w, 1410 w, 1330 s, 1105 w, 905 w, 810 m, 760 m, 730 m and 690 m cm^{-1}.

The dark green filtrate was chromatographed on an alumina column (2.5 × 35 cm) which had been packed in hexane. Hexane elution removed an orange-red band from the column, which was shown by TLC to contain the starting materials. An increase in solvent polarity to 25% benzene in ethyl ether brought down a blue-green band, which was evaporated to dryness. The green residue was recrystallized from benzene—hexane and dried in vacuo at 165°C, yielding 20 mg of carbonyl(pentachlorophenylphenylacetylene)tris(π-cyclopentadienylrhodium) (X) as dark green crystals, m.p. 270-271°C. The product was isolated as a benzene solvate in spite of drying in vacuo at 165°C for 24 h. (Found: C, 42.94; H, 3.20; Cl, 18.89; Rh, 33.6. $C_{30}H_{20}Cl_5ORh_3 \cdot 1/2\ C_6H_6$ calcd.: C, 43.00; H, 2.52; Cl, 19.23; Rh, 33.48%.) The molecular weight was 882 as determined by mass spectrometry (calcd. 882). The following major bands were present in the IR spectrum (KBr): 1805 w, 1680 s, 1475 w, 1410 w, 1320 m, 1100 w, 995 w, 785 s and 680 m cm^{-1}. The NMR spectrum ($CDCl_3$) consisted of the following peaks: τ 4.71 (s, 10H, π-C_5H_5), 4.95 (s, 5H, π-C_5H_5), 2.95 (m, 5H, C_6H_5) and 2.63 (s, C_6H_6).

A third band (yellow) was eluted from the column with ethyl ether. The solution was evaporated to dryness and the residue was recrystallized from benzene—hexane to yield 20 mg of yellow π-cyclopentadienyl[bis(tetrachlorophenyl)diphenylcyclopentadienone]rhodium (XI), m.p. 299-300°C. An analytical sample was prepared by drying the sample in vacuo at 165°C. (Found: C, 49.61; H, 2.28. $C_{34}H_{17}Cl_8ORh$ calcd.: C, 49.32; H, 2.07%.) The molecular weight was 828 as determined by mass spectrometry (calcd. 828). The IR spectrum exhibited the following major bands: 3070 w, 1615 s, 1445 w, 1410 w, 1330 m, 810 m and 695 m cm^{-1}. The NMR spectrum ($CDCl_3$) contained the following peaks: τ 2.22 (s, 2H, C_6HCl_4), 2.77 (m, 10H, C_6H_5) and 4.63 (d, 5H, C_5H_5, J(H—Rh) = 1.0 Hz).

Reaction of π-cyclopentadienyldicarbonylrhodium (II) and bis(pentachlorophenyl)-acetylene (IV)

Bis(pentachlorophenyl)acetylene (IV) (1.4 g, 2.68 mmol) and π-cyclopentadienyldicarbonylrhodium (II) (0.30 g, 1.34 mmol) were mixed with 50 ml of dry xylene in a flask which had previously been flamed out under vacuum, and flushed with nitrogen. The flask was covered with aluminum foil and the contents were heated at reflux for 24 h. After cooling to room temperature, the reaction mixture was filtered to yield 1.3 g of a grey solid. This material was extracted for 9 d in a Soxhlet extractor with 100 ml of toluene, yielding 1.0 g (71% recovery) of the starting acetylene (IV), m.p. 362-364°C (reported [22] 359°C.)

The black filtrate obtained from the reaction mixture was chromatographed on an alumina column (2.5 × 35 cm) which had been packed in hexane. Elution with benzene brought down an unidentified small brown band. Further elution with benzene removed a green band from the column, which was evaporated to dryness and recrystallized from benzene—hexane to yield 20 mg of a dark green solid identified as bis(pentachlorophenyl)acetylenecarbonyltris(π-cyclopentadienylrhodium) (XIII). An analytical sample was prepared by drying in vacuo at 165°C. (Found: C, 35.88; H, 2.17; Cl, 31.65; Rh, 26.6. $C_{30}H_{15}Cl_{10}ORh_3 \cdot 1/2\ C_6H_6$ calcd.: C, 36.23; H, 1.66; Cl, 32.41; Rh, 28.22%.) The molecular weight was approximately 1050 as determined by mass spectrometry (calcd.: 1050-1070). The following major peaks were observed in the IR spectrum (KBr): 1810 s, 1400 m, 1310 m, 1105 w, 990 w and 800 s cm^{-1}. The NMR spectrum ($CDCl_3$) consisted of a multiplet at τ 4.5-5.0 (m, C_5H_5).

Further elution with benzene removed two additional very minor green bands which remain unidentified.

Reaction of π-cyclopentadienyldicarbonylcobalt (I) and pentafluorophenylphenylacetylene (V)

Pentafluorophenylphenylacetylene (V) (2.11 g, 7.86 mmol) and π-cyclopentadienyldicarbonylcobalt (I) (0.756 g, 4.2 mmol) were mixed with 120 ml of dry xylene in a 250 ml, 3-necked flask equipped with a condenser, nitrogen inlet and bubbler. The flask was covered with aluminum foil and the contents were degassed several times with nitrogen. The reaction mixture was heated at reflux for 24 h, cooled to room temperature, and concentrated to ca. 20 ml. Alumina (8 g) was added to this solution, and the resulting slurry was dried under vacuum before being placed on top of an alumina column (20" by 1") which had been packed dry.

Elution with pentane brought down a colorless band which was identified by TLC as a small amount of the starting acetylene (V).

Further elution with pentane brought down a second band (yellow) which formed colorless crystals on concentration. These crystals were recrystallized from benzene—heptane and dried in vacuo at 90°C, yielding 8 mg of tris(pentafluorophenyl)triphenylbenzene (XV), m.p. 211-213°C. (Found: C, 63.13; H, 2.33. $C_{42}H_{15}F_{15}$ calcd.: C, 62.68; H, 1.88%.) The molecular weight was 804 as determined by mass spectrometry (calcd. 804).

The remaining portion of band two after evaporation of the pentane was dissolved in methylene chloride and placed on 4 preparative TLC plates. Multiple elution with a solution of 1/9 benzene—hexane separated two products, a red band of higher R_F and a yellow band of lower R_F. The red band was removed from the plates, extracted with benzene and evaporated to dryness to yield 62 mg of an unidentified red solid.

The lower yellow band was removed from the plates, extracted with benzene, and evaporated to dryness, yielding 85 mg of π-cyclopentadienyl[π-diphenylbis(pentafluorophenyl)]cyclobutadienecobalt (XVII). An analytically pure sample was obtained as yellow crystals after recrystallization from benzene—heptane and drying in vacuo at 100°C, m.p. 203-205°C. (Found: C, 60.16; H, 2.35. $C_{33}H_{15}F_{10}Co$ calcd.: C, 60.01; H, 2.29%.) The molecular weight was 660 as determined by mass spectrometry (calcd. 660). The IR spectrum (KBr) contained the following major bands: 3000-2800 m, 1730 w, 1650 w, 1600 s, 1550-1450 s, 1255 s, 1200-950 s, 910 m and 900-690 m cm^{-1}. The NMR spectrum ($CDCl_3$) exhibited the following peaks: τ 5.29 (s, π-C_5H_5), and 2.6-3.3 (m, C_6H_5).

A third band (red-orange) was eluted from the original column with a solution of 3/1 benzene—ether. Evaporation of the solvent yielded 438 mg (15%) of the three isomers of π-cyclopentadienyl-π-diphenylbis(pentafluorophenyl)cyclopentadienonecobalt (XVIII), as evidenced by TLC. An analytical sample was obtained as red-orange crystals by recrystallization from benzene—heptane and drying in vacuo at 105°C, m.p. 234-236°C. (Found: C, 59.79; H, 2.34; F, 27.58; Co, 8.83. $C_{34}H_{15}F_{10}CoO$ calcd.: C, 59.32; H, 2.20; F, 27.60; Co, 8.56%.) The molecular weight was 688 as determined by mass spectrometry (calcd. 688). The IR spectrum (KBr) exhibited the following major peaks: 2090 m, 1610 s, 1520 m, 1490 m, 1100 m, 990 s, 720 m and 875-650 m cm^{-1}. The NMR spectrum ($CDCl_3$) contained the following peaks: τ 4.95 (s, π-C_5H_5) and 2.1-3.1 (m, C_6H_5).

Continued elution with ethyl ether removed a blue, air-sensitive band which has not yet been identified.

Reaction of π-cyclopentadienyldicarbonylcobalt (I) and bis(pentafluorophenyl)acetylene (VI)

Bis(pentafluorophenyl)acetylene (VI) (2.03 g, 5.66 mmol) and π-cyclopentadienyldicarbonylcobalt (I) (0.509 g, 2.83 mmol) were mixed with 150 ml of dry xylene in a 300 ml, 3-necked flask equipped with a condenser, nitrogen inlet and bubbler. The flask was covered with aluminum foil and the contents were degassed several times with nitrogen. The reaction mixture was heated at reflux for 48 h, cooled to room temperature and filtered. Alumina (6 g) was added to the solution and the slurry was dried under vacuum before being placed on top of an alumina column (12" × 1.75") which had been packed dry.

The first band was eluted from the column with 7/1 pentane—ether and was shown by TLC to contain the starting acetylene I. Continued elution with the pentane—ether solution brought down a small second band (green-brown), shown to contain many products. These remain unidentified.

A third band (red-orange) was eluted from the column with 1/1 pentane—ether and was collected in three 100 ml fractions. A solution of fraction one was placed on a preparative TLC plate which was eluted several times with 5/1 benzene—ether. The red band of highest R_F was removed from the plate, extracted with ether and evaporated to yield 10 mg of red crystals, identified as π-cyclopentedienyl-π-[tetrafluorophenyltris(pentafluorophenyl)cyclopentadienone]-cobalt (XIX). An analytical sample was prepared by recrystallization from benzene—heptane and drying in vacuo at 100°C, m.p. 274-275°C. (Found: C, 49.23; H, 1.53. $C_{33}H_6F_{19}CoO \cdot 1/2\ C_6H_6$ calcd.: C, 49.98; H, 1.02%.) The molecular weight was 850 as determined by mass spectrometry (calcd. 850). The IR spectrum (KBr) contained the following major bands: 3100 w, 2960 m, 1715 m, 1615 s, 1470-1400 s, 1360 m, 1220 m, 1200-950 s, 920 s, 840 m, 735 m, 710 m cm^{-1}. The NMR spectrum ($CDCl_3$) consisted of a singlet at τ 4.9 (π-C_5H_5).

The second fraction of band three was evaporated to dryness and recrystallized from benzene—heptane to yield 616 mg (25%) of red crystals identified as π-cyclopentadienyl-π-[tetrakis(pentafluorophenyl)cyclopentadienone]cobalt (XX). The complex was dried in vacuo at 100°C, m.p. 315-317°C (reported [6] m.p. 328-329°C). (Found: C, 47.10; H, 0.60; Co, 6.85; F, 43.8; O, 1.86. $C_{34}H_5F_{20}CoO$ calcd.: C, 47.03; H, 0.58; Co, 6.74; F, 43.76; O, 1.84%.) The IR spectrum (KBr) contained the following major peaks: 3100 m, 1620 s, 1480 s, 1370 m, 1300 s, 1100 m, 990 s, 920 s, 840 s, 740 s and 700 s cm^{-1}. The NMR spectrum ($CDCl_3$) consisted of a singlet at τ 4.79 (π-C_5H_5).

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