The Reaction of \(h^5\text{-Cyclopentadienyl}\)carbonyl(triphenylphosphine)iridium and Bis(pentafluorophenyl)acetylene

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The reaction between \(h^5\text{-cyclopentadienyl}\)carbonyl(triphenylphosphine)iridium and bis(pentafluorophenyl)acetylene has been investigated in detail. As in earlier studies involving the analogous cobalt and rhodium complexes, the metalloycylic product 1-(\(h^5\text{-cyclopentadienyl}\))-1-triphenylphosphine-2,3,4,5-tetrakis(pentafluorophenyl)iridole (3) has been obtained, although in very low yield. A variety of highly fluorinated organic products have also been isolated and identified, including hexakis(pentafluorophenyl)benzene (5), trans-1,2-bis(pentafluorophenyl)ethene (6) and 1,2,3,4-tetrakis(pentafluoro phenyl)naphthalene (4). The latter product has been synthesized by an independent method. Reaction mechanisms to account for the formation of 4 under these conditions are discussed.

Introduction

There are currently many known metalloyclopentadienyl complexes of the cobalt triad metals, and mononuclear metalloycles of these metals have frequently been implicated as intermediates in the cyclotrimerization of acetylenes as well as in the formation of \(h^5\text{-cyclobutadienemetal complexes}\) [1-8]. In earlier studies, we have described reactions of \((h^5\text{-C}_5\text{H}_5)\text{M(CO)(PPh}_3\text{)}\) complexes, where M = Co [4] or Rh [5], with bis(pentafluorophenyl)acetylene. These reactions produce the metalloycles (1) and (2), respectively, as the principal products, and their structures have been conclusively established by means of spectroscopic and X-ray diffraction techniques.

\[
\text{C}_6\text{H}_5\text{} \quad \text{C}_6\text{H}_5
\]

In an effort to synthesize and study the corresponding iridacyle, 1-(\(h^5\text{-cyclopentadienyl}\))-1-triphenylphosphine-2,3,4,5-tetrakis(pentafluorophenyl)iridole (3), the reaction of bis(pentafluorophenyl)acetylene with \((h^5\text{-C}_5\text{H}_5)\text{Ir(CO)(PPh}_3\text{)}\) has been investigated, and our results are reported herein.

Results

The reaction of \((h^5\text{-C}_5\text{H}_5)\text{Ir(CO)(PPh}_3\text{)}\) and \(\text{C}_6\text{F}_5\text{C=CCF}_6\) was carried out under two different sets of conditions: (1) in a sealed tube at 160 °C for 96 hours using benzene as the solvent; (2) in refluxing mesitylene for 88.5 hours. In both cases, very complex reaction mixtures resulted. By a combination of column and thin layer chromatographic methods, however, a number of products could be isolated and identified.

In the case of the sealed tube reaction, only one product could be separated and identified. A white crystalline compound 4 was obtained whose spectral data and elemental analysis suggested the molecular formula \((\text{C}_6\text{F}_5\text{C}_6\text{H}_4)_2\text{C}_6\text{H}_4\). The UV spectrum of 4 was found to be analogous to that of 1,2,3,4-tetraphenylnaphthalene [9]. Based on this data, the structure shown below, i.e., 1,2,3,4-tetrakis(pentafluorophenyl)naphthalene (4), was proposed for this compound.

\[
\text{OC} \quad \text{PPH}_3 \quad \text{C}_6\text{F}_5 \quad \text{C=CCF}_6
\]

In order to verify the structural formulation of 4, an independent synthesis of 4 was carried out. It is known that the reaction of tetraphenylocyclopentadienone with the benzene precursor diphenyl iodonium-2-carboxylate results in the formation of 1,2,3,4-tetraphenylnaphthalene [10, 11]. We find that an analogous reaction using tetrakis(pentafluorophenyl)cyclopentadienone yields the desired fluorinated naphthalene, 1,2,3,4-tetrakis(penta-
fluorophenyl)naphthalene (4), in 27% yield. This compound was shown to be identical to 4 obtained from the reaction of \((h^5-C_5H_5)Ir(CO)(PPh_3)\) and \(C_6F_3C=CC_6F_5\).

The reaction of \((h^5-C_5H_5)Ir(CO)(PPh_3)\) and \(C_6F_3C=CC_6F_5\) when conducted in refluxing mesitylene also yielded many products, several of which could be separated and characterized. Not surprisingly, a very small amount of hexakis(pentafluorophenyl)benzene (5) was obtained. Iridium complexes have previously been found to be effective acetylene trimerization catalysts [12, 15]. An 8% yield of \(\text{trans-1,2-bis(pentafluorophenyl)ethene}\) (6) was also isolated and was identified by spectral data and elemental analysis. This compound has been prepared earlier by the reaction of \(\text{trans-1,2-diodoethylene}\) and \(C_6F_3MgBr\) in the presence of \(\text{CoCl}_2\) [13]. In addition to 5 and 6 a 3.3% yield of the naphthalene derivative 4 was likewise obtained from this reaction.

Two other white crystalline compounds, 7 and 8, were also isolated from the reaction mixture in very small amounts. The mass spectrum of 7 showed a very strong parent ion at \(m/e\) 416. The IR spectrum of 7 indicated the presence of fluorinated aromatic groups [14] and its proton NMR spectrum showed peaks at \(\tau\) 1.76 and 2.14 in the ratio of 1:4. A possible structure for this product is shown below.

The mass spectrum of 8 gave a very strong parent ion at \(m/e\) 1150, which when coupled with the elemental analysis data suggested a molecular formula of \((C_6F_5C_6F_5)_3C_6H_4\). The IR spectrum of 8 indicated the presence of perfluorinated aromatic rings and the proton NMR spectrum gave a multiplet centered at \(\tau\) 2.16. A possible structure for this compound is shown above.

Three organometallic compounds were isolated from the reaction mixture, although only one product could be fully characterized. This product was the desired iridacycle 3, however, the yield of 3 after separation and purification was only 1%. Mass, proton NMR, and IR spectroscopic data as well as elemental analysis are in agreement with the metallocyclic formulation. Moreover, the IR spectrum of 3 is virtually identical with those of the cobalt and rhodium complexes 1 and 2 when taken under similar conditions.

Two other organometallic complexes, 9 and 10, were also isolated but were difficult to characterize. The mass spectra of both 9 and 10 exhibited peaks at very high mass units (> 1000). Although the spectra were reproducible, very high operating temperatures were required and the observed peaks could be the result of recombination ions. Complex 9 was a red crystalline solid whose proton NMR indicated the presence of two distinct \(h^5-C_5H_5\) resonances in the ratio of 2:1. The IR spectrum of 9 indicated the presence of \(C_6F_3\) groups. This product therefore likely has an acetylenic as well as \(h^5-C_5H_5\)Ir cluster units as components [15]. Complex 10 was a yellow crystalline compound whose proton NMR spectrum showed only aromatic protons, while the IR spectrum indicated the presence of a terminal carbonyl group \((\nu CO = 2030 \text{ cm}^{-1})\) as well as \(C_6F_3\) moieties. The two complexes 9 and 10 are under further investigation.

**Discussion**

The isolation and characterization of the iridacycle 3 completes the series of these highly fluorinated metallocyclopentadienes of the cobalt triad. A corresponding series of metallocycles in which the metallocyclic ring bears phenyl substituents has been obtained earlier by different procedures [2, 3]. The synthetic procedure for each metallocycle 1–3 was the same, i.e., the reaction of \((h^5-C_5H_5)M(CO)(PPh_3)\) (\(M = \text{Co}, \text{Rh}, \text{Ir}\)) with bis(pentafluorophenyl)acetylene. The yields of 1–3, however, decreased significantly in going from the first to the third row elements, ranging from 49% for \(M = \text{Co}\) in refluxing benzene to 8% for \(M = \text{Rh}\) in refluxing xylene to 1% for \(M = \text{Ir}\) in refluxing mesitylene. It can also be seen that progressively more severe conditions were required to promote these reactions in progressing from the cobalt to the iridium analogs.

While the reactions of the cobalt and rhodium complexes gave relatively simple product mixtures [4, 5], in the case of the iridium analog the condi-
tions employed, although adequate to permit the formation and isolation of 3, also gave rise to many other reaction pathways and resulted in a very complex reaction mixture. This result could be due to the higher temperatures involved as well as the chemical versatility of iridium in such systems.

Although the number of organic products formed in this reaction is high, the yield of any given product is generally quite low. To a great extent, this precludes their use to support any mechanistic considerations. Two exceptions are compounds 4 and 6 whose yields were modest.

The reduction of acetylenes by organotransition metal complexes is a well-known phenomenon [16-18]. Moreover, the isolation of 6 suggests the existence of Ir–H bonds at some time during the reaction. These bonds could arise by oxidative addition of a C–H bond to iridium under the reaction conditions involved, the most likely source being the ortho-hydrogens of a coordinated triphenylphosphine substituent. Such ortho-metallation reactions are known for iridium complexes [19]. Other sources such as the solvent [20] cannot be specifically ruled out at the present time, however.

The naphthalene derivative 4 which was isolated from both reactions contains two acetylene units as well as an ortho-phenylene (C₆H₄) moiety. This ortho-phenylene fragment also probably results originally from a coordinated triphenylphosphine ligand in both reactions, since when reaction (1) was repeated using C₅D₅ as the solvent, a completely non-deuterated product 4 was obtained, and since in reaction (2) triphenylphosphine is the only possible source. These results therefore suggest not only ortho-metallation of a triphenylphosphine substituent, but also cleavage of a carbon-phosphorus bond during these reactions. There are at present a number of examples of such P–C bond cleavages in the literature [21-25], however, none has yet been shown to lead to purely organic products.

Several mechanistic pathways could account for the formation of 4 and related products in this reaction. Two such possibilities are outlined in the Scheme. In one such process, intramolecular oxidative addition of a P–C bond of a coordinated triphenylphosphine ligand could occur at an early stage of the reaction. Such a transformation has been postulated previously for reactions of (h⁵-C₅H₅)Ir(CO)(PPh₃) [21]. Subsequent insertion of an acetylene into the resulting iridium-phenyl bond followed by insertion of another molecule of acetylene could lead to an intermediate which upon oxidative addition of an ortho C–H bond of the terminal phenyl group would give rise to an iridacycloheptatriene. Reductive elimination of the organic moiety from this metallocycle would then yield 4.

Alternatively, oxidative addition of an ortho C–H bond of a coordinated triphenylphosphine ligand could occur, followed by cleavages of both C–P and C–Ir bonds under the severe reaction conditions involved. Subsequent intramolecular Diels–Alder type addition of the resulting phenylene moiety to the iridacyclic ring followed by reductive elimination from iridium would then produce 4. Unfortunately, 3 was not obtained in sufficient quantity to test this latter mechanistic possibility.

**Experimental**

Tetrakis(pentafluorophenyl)cyclopentadienone [13], diphenyliodonium-2-carboxylate [10, 11], (h⁵-C₅H₅)Ir(CO)(PPh₃) [26] and bis(pentafluorophenyl)acetylene [27] were prepared according to literature methods. Mesitylene, benzene and hexane were distilled under nitrogen from calcium hydride before use. All other solvents were used as obtained commercially. Alumina was deactivated with water (5%). Preparative TLC plates were prepared using CAMAG Silica Gel for Thin Layer Chromatography (5% CaSO₄ and UV indicator) and were 20 x 20 cm with an absorbent thickness of 1.2 mm. The plates
were activated by heating to 100 °C for 12 h prior to use. NMR spectra were recorded on a Perkin-Elmer R-12A instrument, IR spectra were determined on a Beckman IR-10 instrument and mass spectra were obtained with a Perkin-Elmer-Hitachi RMU 6L instrument. UV spectra were recorded on a Perkin-Elmer 202 spectrophotometer. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts. Mass spectra of organoiridium compounds are referenced to $^{199}$Ir; all peaks containing iridium displayed the proper isotope pattern.

Reaction of (h$^5$-cyclopentadienyl)carbonyl-(triphenylphosphine)iridium and bis(pentafluorophenyl)acetylene in a sealed tube

To a thick-walled (3 mm) Pyrex tube (2 x 15 cm) was added [h$^5$-cyclopentadienyl]carbonyl(triphenylphosphine)iridium (500 mg, 0.914 mmol), bis(pentafluorophenyl)acetylene (655 mg, 1.83 mmol) and 5 ml of benzene. The tube was sealed under vacuum and heated to 160 °C for 96 h. The tube was then cooled, opened, and the contents filtered and washed with benzene. To the filtrate was added 10 g of silica gel under nitrogen and the solvent was removed. This coated silica gel was added to a silica gel column (2 x 50 cm) packed dry under nitrogen.

Elution with 6/1 hexane/benzene brought down a light yellow band. Removal of the solvent followed by recrystallization from methylene chloride-heptane gave 39 mg of 1,2,3,4-tetrakis(pentafluorophenyl)naphthalene (4) (5.4% yield). The product was identified by comparison with a known sample (vide infra).

Repetition of this experiment using CeDe as the solvent also yielded the naphthalene derivative 4. A mass spectrum of this product indicated no decomposition of CeDe.

Synthesis of 1,2,3,4-tetrakis(pentafluorophenyl)-naphthalene (4)

To a small test tube (1 x 7 cm) was added tetrakis(pentafluorophenyl)cyclopentadienone (200 mg, 0.134 mmol) diphenyliodonium-2-carboxylate (200 mg, 5.59 mmol) and 1 ml of triglyme. A thermowater was placed into this mixture and the tube heated with a microburner. The temperature rose slowly and much effervescence was apparent. After 5 min the temperature had reached 200 °C. The tube was cooled, an additional 5 mg of diphenyliodonium-2-carboxylate was added and the heating process was repeated. The addition of diphenyliodonium-2-carboxylate was repeated once again and the temperature was maintained at 200 °C for 5 min. The test tube was cooled and the reaction mixture was dissolved in methylene chloride. Alumina (0.5 g) was then added, the solvent removed and the coated alumina was added to an alumina column (2 x 36 cm).

Elution of the column with 11/1 Skelly B/ether gave an orange band which upon solvent removal yielded 26 mg (26% recovery) of unreacted tetrakis(pentafluorophenyl)cyclopentadienone. Further elution with this solvent brought down a colorless band which upon solvent removal and recrystallization from methylene chloride-heptane followed by drying at 50 °C in vacuo for 12 h yielded 29 mg (27%) of 1,2,3,4-tetrakis(pentafluorophenyl)naphthalene (4), m.p. 319-321 °C (with sublimation).

Analysis for C$_{34}$H$_4$F$_{20}$

Caled C 51.54 H 0.51
Found C 51.19 H 0.59

NMR (acetone-de$_2$) δ 2.05 (broad s); IR (KBr) 1525 (s), 1495 (s), 985 (s) cm$^{-1}$; MS (m/e, rel. abundance, assignment) 792 (100, M$^+$), 773 (17, M$^+$F$^+$), 626 (24, M$_2$CeF$_5$), 396 (21, M$^+$); UV (C$_6$H$_{12}$)$\lambda_{max}$(A$_m$) 216 (Sh), 243 (68,000), 297 nm (11,600).

Reaction of (h$^5$-cyclopentadienyl)carbonyl-(triphenylphosphine)iridium and bis(pentafluorophenyl)acetylene in mesitylene

A solution of (h$^5$-cyclopentadienyl)carbonyl-triphenylphosphine)iridium (1.56 g, 2.79 mmol) and bis(pentafluorophenyl)acetylene (2.00 g, 5.59 mmol) in 20 ml of mesitylene was heated to reflux for 88.5 h under nitrogen with magnetic stirring. The reaction mixture was cooled, filtered under nitrogen and the residue was washed with ca. 25 ml of benzene. The residue was dried and sublimed at 200-205 °C/10$^{-3}$ mm to give 20 mg (1%) of hexakis(pentafluorophenyl)benzene (5) [15]. The filtrate was added to an alumina column (4 x 20 cm) packed in hexane under nitrogen. Elution of this column with hexane brought down a colorless band (Band 1). Further elution with hexane and then benzene gave a brown zone (Band 2). The solvent was removed from each band and the residues were dried.

Separation of Band 1

TLC analysis of this band indicated the presence of several components. The residue (0.35 g) was added to preparative TLC plates. After two elutions with hexane, nine separate bands plus the original band were observed. Each band was scraped from the plates, extracted with ether, filtered and dried. The characterization of these bands is reported in order of decreasing R$_f$ value.

The band of highest R$_f$ (83 mg) was recrystallized from methylene chloride-heptane to give white crystals of trans-1,2-bis(pentafluorophenyl)ethene (6). The yield was 4.1% based on the acetylene and 8.3% based on iridium, m.p. 105-105.5 °C (lit. 13 m.p. 96.5-97.5 °C).

Analysis for C$_{14}$H$_2$F$_{10}$

Caled C 46.69 H 0.56
Found C 46.89 H 0.72.
IR (KBr) 1650 (w), 1530 (s), 1495 (s), 1420 (m), 1330 (m), 1145 (m), 965 (s) cm\(^{-1}\). MS (m/e, rel. abundance, assignment) 360 (100, M\(^+\)), 341 (21, M-C\(_\text{CF}_5\)\(^+\)), 291 (85, M-C\(_\text{CF}_3\)\(^+\)), 192 (25, M-C\(_6\text{F}_{5}\)H\(^+\)), 180 (23, M\(^+\)), UV (C\(_6\text{H}_{12}\)) \(\lambda_{\text{max}}(A_m)\) 306 (11,000), 292 (19,000), 282 (20,000), 213 nm (10,000).

The band of second highest \(R_f\) (24 mg) was recrystallized twice from methylene chloride-heptane and dried in vacuo at 45 °C for 48 h to give white crystals of 7. NMR (acetone-d\(_6\)) \(\delta 1.76\) (m, 1H), 2.14 (m, 4H); IR (KBr) 1650 (w), 1485 (s), 1435 (m), 1325 (w), 1050 (w), 1025 (w), 975 (s), 890 (w), 850 (w), 765 (w), 750 (w) cm\(^{-1}\). MS (m/e, rel. abundance, assignment) 416 (100, M\(^+\)), 396 (70, M-C\(_{13}\)F\(_{20}\)H\(^-\)), 292 (19,000), 282 (20,000), 213 nm (10,000).

The next five bands were not characterized either because of their minute quantities or the fact that TLC showed they were complex mixtures themselves.

The band of eighth highest \(R_f\) (47 mg) was shown to be 1,2,3,4-tetrakis(pentafluorophenyl)naphthalene (4) by comparison with a known sample (vide supra).

The final two bands were not characterized.

Separation of Band 2

Analysis of this band by TLC also indicated the presence of several components. The residue (1.05 g) was applied to preparative TLC plates and eluted twice with 8/1/1 Skelly B/benzene/ether. Five distinct bands were observed. These bands were removed from the plates, extracted with ether or methylene chloride, filtered, and dried. The band of highest \(R_f\) proved to be 1,2,3,4-tetrakis(pentafluorophenyl)naphthalene (27 mg). The total yield of this compound was therefore 3.3%.

The band of second highest \(R_f\) (244 mg) proved to be a complex mixture which required further preparative TLC using two elutions of 8/2 Skelly B/benzene. Isolation of this band from the plates gave a red oil which was identical to that from the mother liquor of the recrystallization of 3. The red oils were combined and crystallized from methylene chloride-heptane to give 38 mg of a red crystalline solid (9), m.p. 328-329 °C.

\textit{Analysis for C\(_{33}\)H\(_{20}\)F\(_{20}\)IrP}

Calcd C 49.56 H 1.63.
Found C 49.80 H 1.56.

NMR (CDCl\(_3\)) \(\delta 4.87\) (s, 5H, C\(_5\)H\(_5\)), 2.56-2.92 (m, 15H, C\(_5\)H\(_5\)). IR (KBr) 2910 (w), 1620 (w), 1475 (s), 1435 (m), 1085 (m), 977 (s), 940 (s), 810 (w), 740 (w), 685 (w), 527 (w), 500 (w) cm\(^{-1}\). MS (m/e, rel. abundance, assignment) 1234 (20, M\(^+\)), 1215 (1, M-F\(^+\)), 974 (3, M-PPh\(_3\)\(^+\)), 616 (19, C\(_5\)H\(_4\)IrC\(_6\text{F}_{5}\)C\(_2\)C\(_6\text{F}_{5}\)\(^+\)), 358 (70, C\(_6\text{F}_{5}\)C\(_6\)F\(_3\)C\(_2\)C\(_6\text{F}_{5}\)\(^+\)), 262 (100, PPh\(_3\)\(^+\)). Evaporation of the mother liquor at this point gave a red oil (9) (vide infra).

The band of fourth highest \(R_f\) also was found to be a mixture, but contained one yellow component which was purified by preparative TLC using two elutions of 7/3 Skelly B-benzene. Isolation of this band from the plates gave a red oil which was identical to that from the mother liquor of the recrystallization of 3. The red oils were combined and crystallized from methylene chloride-heptane to give 38 mg of a red crystalline solid (9), m.p. 328-329 °C.

\textit{Anal. Found} C 48.69 H 1.27.

NMR (acetone-d\(_6\)) \(\delta 4.96\) (s, 10H, C\(_5\)H\(_5\)), 4.98 (s, 5H, C\(_5\)H\(_5\)). IR (KBr) 1595 (w), 1580 (s), 1315 (w), 980 (s) cm\(^{-1}\). MS (m/e, rel. abundance, assignment) 1234 (100, M\(^+\)), 1055 (63, M-C\(_6\text{F}_{5}\)\(^+\)), 560 (20, M\(^++\)), 358 (10, C\(_6\text{F}_{5}\)C\(_6\)F\(_3\)C\(_2\)C\(_6\text{F}_{5}\)\(^+\)).

The fifth highest band (yellow) was recrystallized from methylene chloride-heptane to give 30 mg of a yellow crystalline solid (10), m.p. 262-264 °C.

\textit{Anal. Found} C 55.29 H 2.35.

NMR (acetone-d\(_6\)) \(\delta 2.6\) (m, 8H). IR (KBr) 2930 (w), 2030 (s), 1485 (s), 1435 (m), 1060 (m), 985 (s), 740 (w), 690 (w), 515 (w) cm\(^{-1}\). MS (m/e, rel. abundance, assignment) 1124 (2, M\(^+\)), 1096 (33, M-CO\(^+\)), 548 (15, M-CO\(^++\)).

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[1] For a summary, see refs. 2–8 and references cited therein.