

In memory of T. A. Stephenson

Isometallocenes. Part 1. Polymethylated Isocobaltocenium Salts; a General Route to $[\text{Co}(\text{C}_4\text{Me}_4)(\text{arene})]^+$

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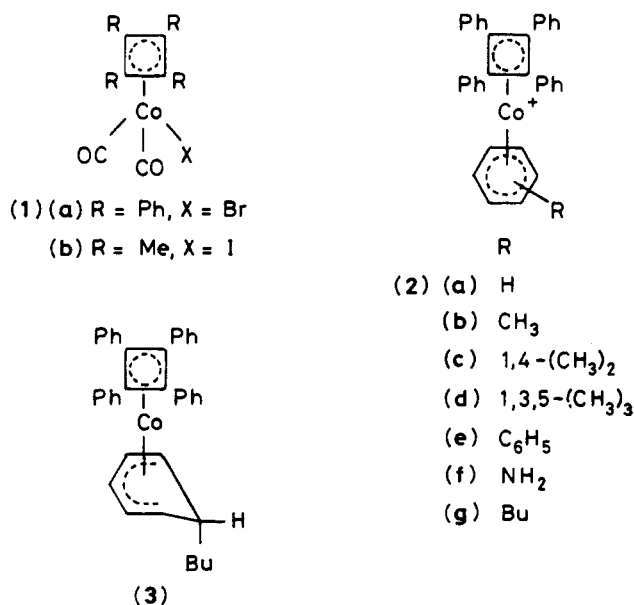
The formation of tricarbonyl(tetramethylcyclobutadiene)cobalt hexafluorophosphate and its conversion into the neutral complexes $[\{\text{Co}(\text{CO})_2(\text{C}_4\text{Me}_4)\}_2]$ and $[\text{Co}(\text{CO})_2(\text{C}_4\text{Me}_4)\text{I}]$ are described. Reaction of the latter with arenes in the presence of aluminium chloride provides a general route to the cations $[\text{Co}(\text{C}_4\text{Me}_4)(\text{arene})]^+$ of which seven new examples are described. Some carbonyl substitutions of the cation $[\text{Co}(\text{CO})_3(\text{C}_4\text{Me}_4)]^+$ are also reported.

We refer to isometallocenes as the series of complexes in which, in place of two cyclopentadienyl residues, the metal is π -bonded to one cyclobutadiene and one benzene ring. The aim of our work is to develop routes to a range of such complexes and to study their reactivities. The first members of this class were described by Maitlis and Efraty in 1965.¹ They treated bromodicarbonyl(tetraphenylcyclobutadiene)cobalt (**1a**) with benzene, methylbenzenes, biphenyl, or aniline in the presence of aluminium chloride to obtain salts of the cations (**2a**)—(**2f**) and used the same method to prepare the benzene(tetra-*p*-tolylcyclobutadiene)cobalt cation. They also added butyllithium to the benzene cation (**2a**) to give the cyclohexadienyl complex (**3**) and showed that *N*-bromosuccinimide would convert this into the cation (**2g**), thus developing a second route to such isocobaltocenium salts.

Only a few other isocobaltocenium salts have been described in the intervening twenty years. Hughes and co-workers² have described a benzene complex bearing aryl as well as alkoxy groups on the cyclobutadiene ring which they were able to obtain from the corresponding tricarbonyl(cyclobutadiene)cobalt salt (**4a**) and benzene, without a catalyst. We have shown³ that the tetramethylcyclobutadiene complex (**4b**) does not react under these conditions. Herberich and Naithani⁴ have obtained the benzene, (**5a**), and toluene complexes, (**5b**), by an intriguing method which involves treatment of the acylborabenzene complexes (**6**) with boron trifluoride and trifluoroacetic acid. The permethylated nickel dication $[\text{Ni}(\text{C}_4\text{Me}_4)(\text{C}_6\text{Me}_6)]^{2+}$, isoelectronic with the cobalt complex (**5f**) has also been described.⁵

Discussion

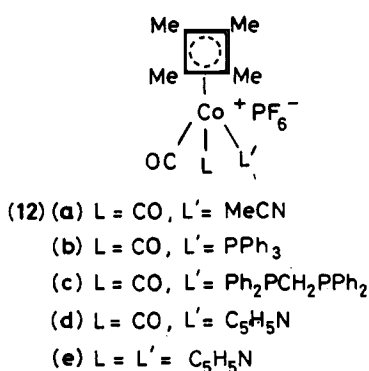
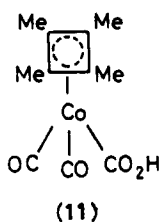
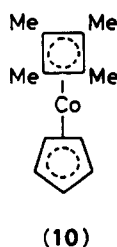
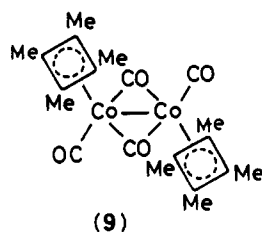
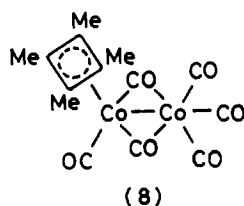
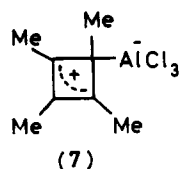
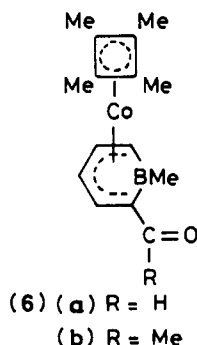
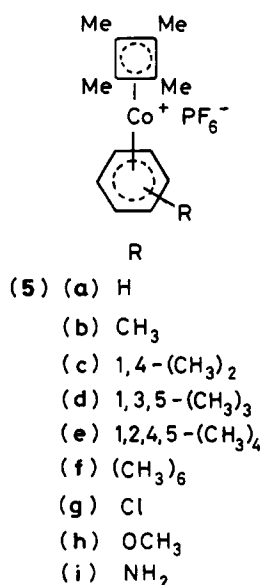
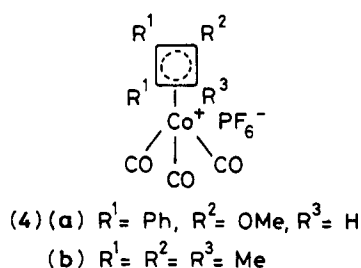
As briefly reported³ the tricarbonyl(tetramethylcyclobutadiene)cobalt salt (**4b**) forms smoothly on treating octacarbonyldicobalt with the aluminium compound (**7**) (*cf.* ref. 5). Although, unlike the above-mentioned aryl-alkoxy derivative (**4a**),² salt (**4b**) is unreactive towards arenes, reaction occurs when trimethylamine *N*-oxide is added in order to abstract one carbonyl group. Yields by this route are low and better conversion into the arene complexes (**5**) is achieved *via* the iodide⁶ (**1b**), which like the tetraphenylcyclobutadiene complex (**1a**) reacts with arenes in the presence of aluminium chloride. This two stage process requires conversion of the tricarbonyl salt (**4b**) into the halide (**1b**) by treatment with tetra-*n*-butylammonium iodide. This reaction is efficient on a small scale but yields were found to diminish rapidly when larger quantities were used. Addition of water accelerates the



reaction but the problem of scale persists. However, addition of 1 mol of trimethylamine *N*-oxide solves this problem also (*cf.* ref. 7).

By reaction of the iodide (**1b**) with the appropriate arene we have obtained all the complexes (**5a**)—(**5i**), generally in yields of 30–35% but reaching 63% for the durene (1,2,4,5-tetramethylbenzene) complex (**5e**). Liquid arenes are simultaneously used as reaction solvents, while a small quantity of iso-octane serves that function for the solid arenes (durene and hexamethylbenzene). The cations of the salts (**5**) arise as tetrachloroaluminates but in most cases are more conveniently isolated as hexafluorophosphates. In the ^1H n.m.r. spectra of complexes (**5b**)—(**5f**) the methyl groups on the cyclobutadiene ring resonate at substantially higher field ($\delta < 1.67$ p.p.m.) than those on the benzene ring (δ 2.48–2.32 p.p.m.) with a particularly large shift (to δ 1.35 p.p.m.) in the case of the hexamethylbenzene complex (**5f**).

Dicarbonyliodo(tetramethylcyclobutadiene)cobalt(i) (**1b**) has previously been obtained⁶ in high yield from either bis[diiodo(tetramethylcyclobutadiene)nickel] or from the neutral carbonyl (**8**), but neither of these starting compounds is as conveniently available as the salt (**4b**). As expected it also forms cleanly from di- μ -carbonyl-bis[carbonyl(tetramethylcyclobut-



adiene)cobalt] (9). We have obtained the latter, albeit in modest yield, by sodium amalgam reduction of the salt (4b). This product was observed as a minor by-product in the preparation of cyclopentadienyl(tetramethylcyclobutadiene)cobalt (10) from the cation (4b) with (cyclopentadienyl)sodium; a product with similar spectral characteristics was observed but not isolated pure⁶ when the same complex (10) was prepared from

the iodide (1b). Both these methods give poor yields of the cyclopentadienyl complex (10), as does the reaction of the salt (4b) with (cyclopentadienyl)thallium.

In the presence of aqueous bases (e.g. K_2CO_3) the cation (4b) loses one carbonyl group, possibly as CO_2 from the initially formed acid (11). An unstable product, thought to be of this type (11), was observed spectroscopically and small amounts of the dimers (8) and (9) isolated under differing conditions from such systems may result from thermal decomposition of this intermediate. In the presence of electron donors (acetonitrile, phosphines, pyridine) base treatment leads to the substituted salts (12a)–(12e), the last two as a mixture which has not been separated.

Studies on the reactions of cationic complexes (4b), (5), and (12) with nucleophiles are in progress.

Experimental

All reactions were carried out under nitrogen. Column chromatography was carried out on neutral alumina (Spence's grade UG1 100 mesh, which had been treated with ethyl acetate, washed with ethanol and with water, and oven-dried at 150°C for 12 h). Light petroleum refers to the fraction of b.p. 30 – 40°C . Evaporation of solutions was effected with a rotary evaporator operating under water-pump vacuum below 40°C .

Tricarbonyl(tetramethylcyclobutadiene)cobalt Hexafluorophosphate (4b).—To a suspension of anhydrous aluminium chloride (13.4 g, 0.10 mol) in dichloromethane (40 cm^3) contained in a three-necked, round-bottomed flask equipped with a pressure-equalising dropping funnel, condenser, thermometer, and magnetic stirrer and cooled to -30°C , a solution of but-2-yne (5.0 g, 93 mmol) in dichloromethane (25 cm^3) was added dropwise with vigorous stirring over 30 min. A further 35 cm^3 of dichloromethane were then added and the mixture allowed to warm and stirred for 30 min at 0°C , then 1 h at 20°C . Octacarbonyldicobalt (7.92 g, 23 mmol) was then added, all at once, and stirring continued for 70 h. The mixture was poured into diethyl ether (500 cm^3), the resultant precipitate filtered off, washed with diethyl ether, and dried *in vacuo*. To this dry solid was added a solution of ammonium hexafluorophosphate (9.6 g, 59 mmol) in water (150 cm^3). The product was collected by filtration, washed with a little water, and purified in 2–3 g portions by dissolving in acetone and reprecipitation with diethyl ether; yield 10.7–12.4 g (59–68%). The very pale yellow (almost colourless) salt shows $\nu_{\text{CO}}(\text{KBr})$ at 2110m and 2065s cm^{-1} ; $\delta[(\text{CD}_3)_2\text{CO}]$ 2.075 p.p.m. (Found: C, 33.25; H, 3.1. $\text{C}_{11}\text{H}_{12}\text{CoF}_6\text{O}_3\text{P}$ requires C, 33.4; H, 3.05%).

Dicarbonyliodo(tetramethylcyclobutadiene)cobalt (1b).—(a) *Using potassium carbonate.* To a magnetically stirred solution of the salt (4b) (790 mg, 2 mmol) in dichloromethane (20 cm^3) was added anhydrous potassium carbonate (280 mg, 2 mmol) followed by tetra-n-butylammonium iodide (740 mg, 2 mmol) and the mixture stirred at 20°C for 18 h. The mixture was then filtered, the solids washed thoroughly with dichloromethane, and the combined filtrates evaporated; the residue was dissolved in light petroleum, filtered, and again evaporated. The product was purified by column chromatography using dichloromethane as eluant to give dark brown crystals (500 – 600 mg ; 71–85%), m.p. 138 – 144°C (decomp.), $\nu_{\text{CO}}(\text{KBr})$ at 2016 and 2055 cm^{-1} , $\delta[(\text{CD}_3)_2\text{CO}]$ 1.925 p.p.m. [lit.⁶ m.p. 140°C , ν_{CO} 2016 and 2055 cm^{-1} , $\delta(\text{CDCl}_3)$ 1.81 p.p.m.] (Found: C, 33.9; H, 3.15; I, 36.4. $\text{C}_{10}\text{H}_{12}\text{CoIO}_2$ requires C, 34.3; H, 3.5; I, 36.25%).

Reaction was complete in 2 h when water (1 cm^3) was added to the above reaction mixture (yield: 67%) but the yield (with or without water) dropped to 47–51% on a 5-mmol and 41% on a 10-mmol scale.

(b) *Using trimethylamine N-oxide.* A mixture of the salt (**4b**) (3.96 g, 10 mmol), trimethylamine *N*-oxide (0.75 g, 10 mmol), and tetrabutylammonium iodide (3.70 g, 10 mmol) in dichloromethane (100 cm³) was stirred at 0–5 °C for 2 h, then filtered, the residual solids well washed with dichloromethane, and the combined filtrates evaporated. Dissolution of the residue in light petroleum, filtration, and evaporation left a product (2.67 g, 76%), m.p. 139–143 °C (decomp.), of sufficient purity for all further work.

General Procedure for the Preparation of (Arene)(tetramethylcyclobutadiene)cobalt Hexafluorophosphates (5) using Liquid Arenes.—A stirred mixture of the iodo-complex (**1b**) (350 mg, 1 mmol), the arene (15 cm³), and anhydrous resublimed aluminium chloride (400 mg, 3 mmol) was heated under reflux for 1–1.5 h. After cooling to 20 °C ammonium hexafluorophosphate (330 mg, 2 mmol) dissolved in water (15 cm³) was added and stirring continued for 1–1.5 h. The precipitated product was filtered off, and washed with benzene and water. It was then dissolved in acetone, filtered and evaporated, and the residue purified by column chromatography, eluting with acetone, dichloromethane, or a mixture of these. Diethyl ether precipitated the yellow salts (**5**) from their acetone solutions.

The following products were obtained in this way (individual yields have not been optimised): benzene complex (**5a**) (98 mg, 25%), decomp. 224–234 °C, $\delta[(\text{CD}_3)_2\text{CO}]$ 6.68 (C₆H₆) and 1.67 (CH₃) p.p.m. (lit.:⁴ 6.61 and 1.67 p.p.m.) (Found: C, 42.9; H, 4.6. C₁₄H₁₈CoF₆P requires C, 43.1; H, 4.65%); toluene complex (**5b**) (137 mg, 34%), decomp. 236–246 °C, $\delta[(\text{CD}_3)_2\text{CO}]$ 6.58 (C₆H₅), 2.48 (PhCH₃), and 1.66 (C₄H₃) p.p.m. (lit.:⁴ 6.60, 2.48, and 1.67 p.p.m.) (Found: C, 44.3; H, 5.0. C₁₅H₂₀CoF₆P requires C, 44.3; H, 5.0%); *p*-xylene (1,4-dimethylbenzene) complex (**5c**) (146 mg, 35%), decomp. 252–262 °C $\delta[(\text{CD}_3)_2\text{CO}]$ 6.48 (4 H, C₆H₄), 2.45 (6 H, CH₃), and 1.62 p.p.m. (12 H, CH₃) (Found: C, 47.25; H, 5.5. C₁₆H₂₂CoF₆P requires C, 47.2; H, 5.6%); mesitylene (1,3,5-trimethylbenzene) complex (**5d**) (138 mg, 32%), decomp. 267–277 °C, $\delta[(\text{CD}_3)_2\text{CO}]$ 6.38 (3 H, C₆H₃), 2.45 (9 H, CH₃), and 1.60 p.p.m. (12 H, CH₃) (Found: C, 46.1; H, 5.2. C₁₇H₂₄CoF₆P requires C, 45.95; H, 5.3%); chlorobenzene complex (**5g**) (136 mg, 32%), decomp. 230–240 °C, $\delta[(\text{CD}_3)_2\text{CO}]$ 6.85 (5 H, m, Ph) and 1.75 p.p.m. (12 H, CH₃) (Found: C, 39.2; H, 3.85. C₁₄H₁₇ClCoF₆P requires C, 39.6; H, 4.0%).

Complexes (5e) and (5f).—The above general procedure was adapted by using the solid arene (5–10 mmol) dissolved or partially dissolved in iso-octane (10 cm³). (Greater dilution lowers the yield.) Durene (1.34 g, 10 mmol) yielded the complex (**5e**) (282 mg, 63%), decomp. 288–298 °C, $\delta[(\text{CD}_3)_2\text{CO}]$ 6.36 (2 H, C₆H₂), 2.32 (12 H, CH₃), and 1.51 p.p.m. (12 H, CH₃) (Found: C, 48.0; H, 5.9. C₁₈H₂₆CoF₆P requires C, 48.4; H, 5.9%). Hexamethylbenzene (1.62 g, 10 mmol) yielded the tetrachloroaluminate (**5f**; AlCl₄ in place of PF₆) (101 mg, 20%), decomp. 187–197 °C, $\delta[(\text{CD}_3)_2\text{CO}]$ 2.33 (18 H, CH₃) and 1.35 p.p.m. (12 H, CH₃) (Found: C, 48.4; H, 5.3. C₂₀H₃₀AlCl₄Co requires C, 48.2; H, 6.1%).

Anisole(tetramethylcyclobutadiene)cobalt Hexafluorophosphate (5h).—Reaction of (**1b**) and the arene under reflux led to partial demethylation and a low yield of impure complex (**5h**). The iodo-complex (**1b**) (350 mg, 1 mmol) and sublimed aluminium chloride (400 mg, 3 mmol) were therefore stirred in redistilled anisole (10 cm³) at 80 °C for 1 h. Work-up by the above general procedure then yielded the salt (**5h**) (126 mg, 30%), decomp. 264–274 °C, $\delta[(\text{CD}_3)_2\text{CO}]$ 6.5 (5 H, m, Ph), 4.03 (3 H, s, OCH₃), and 1.65 p.p.m. (12 H, s, CH₃) (Found: C, 42.85; H, 4.6. C₁₅H₂₀CoF₆OP requires C, 42.9; H, 4.8%).

Aniline(tetramethylcyclobutadiene)cobalt Hexafluorophosphate (5i).—The complex (**5i**) (199 mg, 25%) was obtained by the same procedure as above from the iodo complex (**1b**) (700 mg, 2 mmol), aluminium chloride (800 mg, 6 mmol), and aniline (10 cm³), decomp. 209–219 °C, ν_{NH} at 3400 and 3640 cm^{−1}, $\delta[(\text{CD}_3)_2\text{CO}]$ 6.2 (5 H, m, Ph), 3.5 (br, NH₂ + H₂O from solvent), and 1.60 p.p.m. (12 H, s, CH₃) (Found: C, 41.8; H, 4.5; N, 3.4. C₁₄H₁₉CoF₆NP requires C, 41.5; H, 4.7; N, 3.5%).

Formation of Arene Complexes from Tricarbonyl(tetramethylcyclobutadiene)cobalt Hexafluorophosphate (4b).—(a) *The benzene complex (5a).* The salt (**4b**) (790 mg, 2 mmol) and anhydrous trimethylamine *N*-oxide (450 mg, 6 mmol) in benzene (10 cm³) were heated under reflux for 18 h. After cooling ammonium hexafluorophosphate (660 mg, 4 mmol) was added and the mixture stirred for 1 h. Work-up then followed the above general procedure, yielding the benzene complex (**5a**) (23 mg, 3%) identical with the sample described above. On one occasion an 8% yield was obtained after only 1 h reflux.

(b) *The anisole complex (5h).* The salt (**4b**) (790 mg, 2 mmol), trimethylamine *N*-oxide dihydrate (670 mg, 6 mmol), and anisole (10 cm³) were heated to 80 °C and stirred at this temperature for 1.5 h. After cooling to 20 °C ammonium hexafluorophosphate (660 mg, 4 mmol) in water (10 cm³) was added and stirring continued for 1 h. The salt (**5h**) (169 mg, 20%) was isolated as before and identified by comparison of i.r. and n.m.r. spectra with the sample described above.

Di-μ-carbonyl-bis[carbonyl(tetramethylcyclobutadiene)-cobalt] (9).—To an excess (1.5 mmol) of a 1.5% sodium amalgam under tetrahydrofuran the hexafluorophosphate (**4b**) (390 mg, 1 mmol) was added and the mixture stirred at 20 °C overnight. The organic phase was filtered through Kieselguhr, the solvent evaporated, and the residue separated on an ice-water cooled alumina column. Light petroleum, followed by its mixture with 10% of toluene, were used as solvents, the latter eluting the product (138 mg, 31%) as brown crystals; a purer product was obtained by chromatography on silica gel, at −14 °C, eluting with pentane–toluene (2:1); ν_{CO} (light petroleum) at 1978s and 1785s cm^{−1}, $\delta(\text{C}_6\text{D}_6)$ 1.5 p.p.m. Principal peaks in the mass spectrum at *m/z* 446.0325 (*M*⁺, C₂₀H₂₄Co₂O₄ calc.: 446.0338), 418.0377 [(*M* − CO)⁺, C₁₉H₂₄Co₂O₃: 418.0389], 390.0420 [(*M* − 2CO)⁺, C₁₈H₂₄Co₂O₂: 390.0440], 362.0491 [(*M* − 3CO)⁺, C₁₇H₂₄Co₂O: 362.0491], 334.0553 [(*M* − 4CO)⁺, C₁₆H₂₄Co₂: 334.0542], 332.0412 (C₁₆H₂₂Co₂: 332.0385), 330.0209 (C₁₆H₂₀Co₂: 330.0229), 273.1072 (C₁₆H₂₂Co: 273.1053), and 195.0214 (C₉H₁₂CoO: 195.0220) (Found: C, 54.2; H, 5.4. C₂₀H₂₄Co₂O₄ requires C, 53.8; H, 5.4%).

Oxidation of this complex (**9**) (200 mg) by dissolving in diethyl ether (20 cm³) followed, at −60 °C, by dropwise addition of iodine (55 mg) in diethyl ether (10 cm³) yielded, after warming to room temperature, removal of solvent, and recrystallisation, the iodo-complex (**1b**) (150 mg, 60%) identical with the samples described above.

Acetonitriledicarbonyl(tetramethylcyclobutadiene)cobalt Hexafluorophosphate (12a).—Potassium carbonate (140 mg, 1 mmol) was added to a solution of the salt (**4b**) (390 mg, 1 mmol) in acetonitrile (10 cm³) and the mixture stirred overnight at 20 °C, then filtered and evaporated. The residue was extracted with light petroleum to remove neutral products; these included complex (**8**) but were not further examined. The residue was then dissolved in dichloromethane, filtered, and the product (**12a**) (94 mg, 23%) precipitated with diethyl ether as a yellow powder, ν_{CO} (Nujol) at 2064 and 2020 cm^{−1}, $\delta(\text{CDCl}_3)$ 2.4 (3 H, CH₃CN) and 1.64 p.p.m. (12 H, CH₃) (Found: C, 35.05; H, 3.7; N, 2.7. C₁₂H₁₅CoF₆NO₂P requires C, 35.2; H, 3.7; N, 3.4%).

Dicarbonyl(tetramethylcyclobutadiene)(triphenylphosphine)-cobalt Hexafluorophosphate (12b).—The tricarbonyl salt (**4b**) (390 mg, 1 mmol), triphenylphosphine (262 mg, 1 mmol), and potassium carbonate (140 mg, 1 mmol) were stirred in dichloromethane (10 cm³) at 20 °C overnight. After filtration diethyl ether was added to precipitate the yellow product (**12b**) (450 mg, 72%), ν_{CO} (Nujol) at 2 060 and 2 020 cm⁻¹, δ (CDCl₃) 7.35 (15 H, m, Ph) and 1.66 p.p.m. (12 H, d, J_{HP} 6 Hz, CH₃) (Found: C, 53.6; H, 4.3. C₂₈H₂₇CoF₆O₂P₂ requires C, 53.35; H, 4.3%).

[Bis(diphenylphosphino)methane]dicarbonyl(tetramethylcyclobutadiene)cobalt Hexafluorophosphate (12c).—Using bis(diphenylphosphino)methane (384 mg, 1 mmol) in place of triphenylphosphine and 4 h reaction time the above procedure gave the salt (**12c**) (425 mg, 56%), ν_{CO} (CH₂Cl₂) at 2 063 and 2 030 cm⁻¹ (Found: C, 55.85; H, 4.6. C₃₅H₃₄CoF₆O₂P₃ requires C, 55.85; H, 4.55%).

Cyclopentadienyl(tetramethylcyclobutadiene)cobalt (10).—The salt (**4b**) (400 mg) was added to a solution of (cyclopentadienyl)sodium (100 mg) in tetrahydrofuran (20 cm³) and the mixture stirred at 0 °C overnight. After evaporation of the solvent the residue was extracted with diethyl ether, the extract filtered and evaporated, and the resulting oil chromatographed on silica gel. Pentane–dichloromethane (2:1) eluted the product (**10**) (75 mg, 32%) identified by its spectra.⁶ The same product has been obtained (26%) using (cyclopentadienyl)thallium; these yields have not been optimised.

Reaction of the Salt (4b) with Pyridine.—The salt (700 mg) was warmed in pyridine at 80 °C until reaction was complete as

judged by i.r. monitoring (1 h). Evaporation of pyridine left a red residue which was taken up in dichloromethane (10 cm³); addition of diethyl ether precipitated a product which was shown by its i.r. and n.m.r. spectra to be the bis(pyridine) complex (**12e**) (410 mg, 56%) but which was not obtained analytically pure. At 20 °C the same reaction produced a 2:1 mixture of the same compound (**12e**) and the monopyridine complex (**12d**).

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