geneous colorless solution. After the system was cooled to −78 °C, an Et_2O solution (16 mL) of MeOH (42 mmol) was added. The resulting colorless solid of LiOMe was removed by filtration at −40 °C, and the filtrate was concentrated to dryness to give a colorless oily product. Addition of ca. 5 mL of pentane to the system at −78 °C yielded a pale red precipitate of *cis*-PdMePh($PMePh_2$)$_2$, which was filtered, washed with pentane (30 mL × 2), and dried in vacuo below −30 °C (78%). Formation of the complex was, however, confirmed by NMR spectroscopy: ^{1}H NMR (CD_2Cl_2, −50 °C) δ 0.19 (dd, J = 3 and 9 Hz, 3 H, PdCH_3); ^{31}P{^{1}H} NMR (CD_2Cl_2, −50 °C) δ 10.5 and 15.5 (AB, J = 23 Hz).

To a Schlenk tube containing *cis*-PdMePh($PMePh_2$)$_2$ (0.63 g, 1.0 mmol) and dppe (0.84 g, 2.1 mmol) were added Et_2O (16 mL), CH_2Cl_2 (7 mL), and styrene (100 μL) at −40 °C. The system was stirred at 0 °C for 2 h. The solution was concentrated to almost dryness, and 20 mL of hexane was added to −70 °C. The resulting white precipitate was filtered, washed with Et_2O (2 mL), and dried in vacuo. The crude product was dissolved in Et_2O (5 mL) and CH_2Cl_2 (12 mL) containing styrene (60 μL) at 10 °C, and the solution was allowed to stand at −20 °C for 2 days to yield white crystals of *cis*-PdMePh(dppe) (0.22 g, 35%): ^{1}H NMR (CD_2Cl_2, −30 °C) δ 0.36 (dd, J = 2 and 7 Hz, 3 H, PdCH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2, −30 °C) δ 2.1 (dd, J = 8 and 98 Hz, PdMe), 169.7 (dd, J = 12 and 115 Hz, PdPh); ^{31}P{^{1}H} NMR (CD_2Cl_2, −30 °C) δ 41.5 and 49.1 (AB, J = 12 Hz). Anal. Calcd for $C_{33}H_{32}P_2Pd$: C, 66.4; H, 5.4. Found: C, 66.9; H, 5.9.

Catalytic Cross-Coupling Reaction. To a Schlenk tube containing *trans*-PdPh(I)(PEt_2Ph)$_2$ (0.065 g, 0.10 mmol) and PhI (110 μL, 0.99 mmol) was added an Et_2O solution of MeMgI (1 mL, 1.24 mmol) at −20 °C. The system was sealed and stirred at 36 °C. After 20 h, 5 mL of an aqueous HCl solution (1 N) was added at −10 °C to quench the reaction. GLC analysis of the Et_2O layer revealed the formation of toluene (85%/PhI) and biphenyl (6%) at 97% conversion of PhI.

Reactions of Diorganopalladium Complexes with Organomagnesium Halides. A typical procedure to record the spectroscopic change as shown in Figure 2 is as follows. To a Schlenk tube containing *trans*-PdMePh(PEt_2Ph)$_2$ (2; 0.054 g, 0.10 mmol) and tolan (0.036 g, 0.20 mmol) was added an Et_2O solution of MeMgI (1.0 mL, 1.24 mmol) by means of a measuring pipette. The sample solution was transferred into an NMR sample tube below −10 °C. The sealed tube was placed in an NMR probe controlled to 35 ± 1 °C. The change in amounts of the palladium species with time was followed by measuring the relative area of the signals.

Kinetic Study on the Reductive Elimination of *cis*-PdMePh(PEt_2Ph)$_2$ (3). Complex 3 (~0.10 mmol) and Ph_2CH_2 (0.10 mmol) and the appropriate amounts of tolan, PEt_2Ph, and/or an organic iodide were placed in a Schlenk tube, and 1.0 mL of C_6D_6 was added by means of a measuring pipette. The sample solution was transferred into an NMR sample tube below +5 °C. The sealed tube was placed in a thermostated NMR probe (±1 °C). The amount of toluene produced on thermolysis with time was determined by measuring the ratio of the area of Ph_2CH_2 and $PhCH_3$ signals.

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Registry No. 1, 113530-53-3; 2, 113566-59-9; 3, 113530-48-6; 4, 77831-30-2; 5, 77881-04-0; *trans*-PdMe(*m*-tolyl)(PEt_2Ph)$_2$, 117339-69-2; *trans*-PdMePh(PEt_3)$_2$, 116244-36-1; *trans*-PdEtPh(PEt_3)$_2$, 117308-37-9; *cis*-PdMe(*p*-tolyl)(PEt_2Ph)$_2$, 113530-49-7; *cis*-PdMe(*p*-ClC_6H_4)(PEt_2Ph)$_2$, 113530-50-0; *cis*-PdMe(*p*-FC_6H_4)(PEt_2Ph)$_2$, 113530-51-1; *cis*-PdMe(*p*-$CF_3C_6H_4$)(PEt_2Ph)2, 113530-52-2; *cis*-PdMePh(PMe_2Ph)$_2$, 117308-38-0; *cis*-PdMePh(dmpe), 117308-39-1; *cis*-PdMePh(dppe), 117308-40-4; *trans*-PdPh(Br)(PEt_2Ph)$_2$, 115680-90-5; *trans*-Pd(*m*-tolyl)(Br)(PEt_2Ph)$_2$, 117308-41-5; *trans*-PdPhCl(PEt_3)$_2$, 15697-59-3; *trans*-PdMe(*p*-tolyl)(PEt_2Ph)$_2$, 117308-42-6; *trans*-PdMe(*p*-ClC_6H_4)(PEt_2Ph)$_2$, 117339-85-2; *trans*-PdMe(*p*-FC_6H_4)(PEt_2Ph)$_2$, 117308-43-7; *trans*-PdMe(*p*-$CF_3C_6H_4$)(PEt_2Ph)$_2$, 117308-44-8; *trans*-PdPh(Br)(PMe_2Ph), 117308-45-9; *cis*-PdMePh($PMePh_2$)$_2$, 117308-46-0; PhI, 591-50-4; MeMgI, 917-64-6; *trans*-Pd(*m*-tolyl)I(PEt_2Ph)$_2$, 104114-87-6; *m*-MeC_6H_4I, 625-95-6; CD_3I, 865-50-9; toluene, 108-88-3; biphenyl, 92-52-4; *m*-tolyl iodide, 625-95-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; *p*-chlorotoluene, 106-43-4; *p*-fluorotoluene, 352-32-9.

Isometallocenes. 2.[1] (Aminoarene)(tetramethylcyclobutadiene)cobalt(I) Hexafluorophosphates

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A range of both ring and nitrogen-substituted aromatic amines have been shown to give the title complexes in good yield when treated with tricarbonyl(tetramethylcyclobutadiene)cobalt(I) hexafluorophosphate and trimethylamine *N*-oxide. Various bases deprotonate the complexes with NH groups, but the resultant neutral complexes proved too unstable for full characterization. Iodomethane converts these neutral intermediates to the (*N*,*N*-dialkylamino)arene complexes.

Introduction

In part 1[1] we reported the formation of a range of (arene)(tetramethylcyclobutadiene)cobalt(I) salts by reaction of dicarbonyliodo(tetramethylcyclobutadiene)cobalt, $C_4Me_4Co(CO)_2I$, with arenes in the presence of aluminum chloride. Although this route is applicable to a wide range of arenes, the yields are only moderate. Moreover, the iodo complex is obtained from the tricarbonyl salt 1, making it desirable to seek a direct route from the latter. This was indeed found in its reaction with arene plus trimethylamine *N*-oxide. Two examples of its use were described:[1] anisole giving comparable yields by both methods (the yield of 20% reported[1] using Me_3NO has subsequently been improved to 38%), whereas the benzene complex was

(1) Cook, M. R.; Härter, P.; Pauson, P. L.; Śraga, J. *J. Chem. Soc., Dalton Trans* **1987**, 2757.

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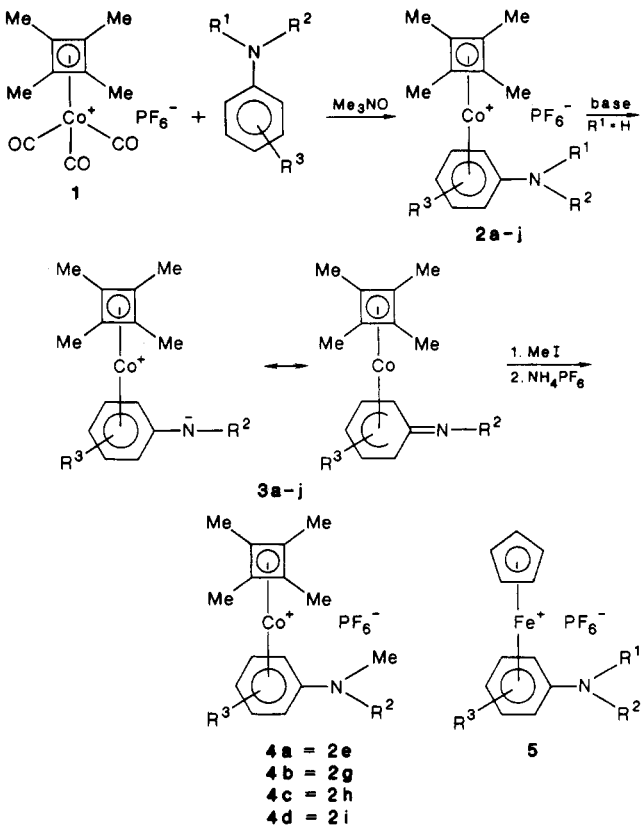
Table I

complex	yield[a] (%)	decompn temp (°C)	formula	anal. found C	found H	found N	anal. calcd C	calcd H	calcd N
2a	64	231–240	$C_{14}H_{19}CoF_6NP$[b]						
2b	78	242–252	$C_{15}H_{21}CoF_6NP$	42.9	4.9	3.3	43.0	5.0	3.3
2c	70	248–258	$C_{15}H_{21}CoF_6NP$	42.9	4.8	3.3	43.0	5.0	3.3
2d	68[c]	227–237	$C_{15}H_{21}CoF_6NP$	42.8	5.1	3.3	43.0	5.0	3.3
2e	64	206–216	$C_{15}H_{21}CoF_6NP$	43.0	5.3	3.3	43.0	5.0	3.3
2f	21	196–201	$C_{18}H_{27}CoF_6NP$	46.65	5.7	3.1	46.85	5.9	3.0
2g	56, 64,[d] 69[e]	219–224[f]	$C_{16}H_{23}CoF_6NP$	44.3	5.4	3.2	44.35	5.35	3.2
2h	54, 17[g]	249–251[f]	$C_{17}H_{25}CoF_6NP$	45.6	5.8	3.2	45.65	5.6	3.1
	97[h]	129–13[f]		45.8	5.8	3.0			
2i	95[i]	175–178	$C_{19}H_{29}CoF_6NP$	47.6	6.1	2.85	48.0	6.15	2.95
2j	46	187–189[f]	$C_{18}H_{27}CoF_6NP$	46.45	6.0	3.0	46.85	5.9	3.0

[a] By direct preparation from **1** unless otherwise specified. [b] See Ref 1. [c] Using 4.40 g (40 mmol) of *p*-toluidine dissolved in isooctane (10 mL). [d] From **2a**. [e] From **2e**. [f] Melting point. [g] From **2d** using 1 mol of *t*-BuOK—see Experimental Section. [h] From **2d** in presence of CH_3I with excess *t*-BuOK—see Experimental Section. [i] From **2f**.

only obtained in low yield from the tricarbonyl salt **1**. The suspicion that the latter is only suitable for arenes with strongly electron-donating substituents is fully borne out by our subsequent experience. Even hexamethylbenzene gives only poor yields by this method. However, we now show that it is well suited to the preparation of arene complexes bearing the strongly electron-donating amino substituents. We also describe the deprotonation/alkylation of the resulting aminoarene complexes.



4a = **2e**
4b = **2g**
4c = **2h**
4d = **2i**

a, $R^1 = R^2 = R^3 = H$; **b**, $R^1 = R^2 = H$, $R^3 = 2\text{-}CH_3$; **c**, $R^1 = R^2 = H$, $R^3 = 3\text{-}CH_3$; **d**, $R^1 = R^2 = H$, $R^3 = 4\text{-}CH_3$; **e**, $R^1 = R^3 = H$; $R^2 = CH_3$; **f**, $R^1 = R^3 = H$, $R^2 = C(CH_3)_3$; **g**, $R^1 = R^2 = CH_3$, $R^3 = H$; **h**, $R^1 = R^2 = CH_3$, $R^3 = 4\text{-}CH_3$; **i**, $R^1 = CH_3$, $R^2 = C(CH_3)_3$, $R^3 = H$; **j**, $R^1 = R^2 = CH_2CH_3$, $R^3 = H$

Discussion

Nine simple primary, secondary, and tertiary arylamines have been converted to their (tetramethylcyclobutadiene)cobalt(I) hexafluorophosphate complexes (**2a–h**) by the trimethylamine *N*-oxide method[1] in good yield (Table I). That for aniline (64%) compares with only 25% by the aluminum chloride method.[1] Complexes of primary and secondary amines can be deprotonated by strong bases (NaH, KO-*t*-Bu, etc.) to give neutral red complexes soluble in nonpolar organic solvents. These are relatively unstable, and we have failed to isolate them in pure form. However, there can be little doubt that they have the expected structures **3** since alkylation with iodomethane either directly or after isolation of the crude neutral species yields the tertiary amine complexes **4**. A mass spectrum of the deprotonated complex **2d** was consistent with formulation of the product as **3d**. Similar transformations have been described in the cyclopentadienyliron series **5**.[2] As in that series, only the tertiary amine complexes are isolated following deprotonation/alkylation of primary amine complexes. Although the secondary amine complexes (e.g. **2e**) must be intermediates, they were not detected, reaction with a deficiency of alkylating agent giving a mixture of tertiary and unreacted primary amine complexes. It is not known whether this is the result of greater acidity of the secondary amine complexes, leading to rapid proton exchange (e.g. **4a** + **3a** ⇌ **2a** + **3e**) or to much more rapid alkylation of the *N*-alkyl than the N–H complexes **3**. The directly prepared secondary amine complexes **2e,f** were alkylated to the tertiary amine complexes **2g,i** as expected.

Experimental Section

All experiments were carried out under nitrogen.

Reactions of Tricarbonyl(tetramethylcyclobutadiene)-cobalt(I) Hexafluorophosphate (1) with Arylamines. Under a rapid stream of dinitrogen, complex **1** (1.19 g, 3 mmol), trimethylamine *N*-oxide dihydrate (1.00 g, 9 mmol), and the appropriate arylamine (15 mL) were heated to 80 °C with stirring for 0.5–1 h. After the solution was cooled to 25 °C, ammonium hexafluorophosphate (0.98 g, 6 mmol) in water (15 mL) was added and the mixture stirred for 1 h. The precipitated product was filtered off, washed with water and ether, dissolved in acetone, and recovered by evaporation of the filtered solution. Further purification was by reprecipitation from acetone solution with ether, or, if necessary, by column chromatography on neutral alumina (cf. ref 1). The pale yellow products are listed in table I and their ^1H NMR spectra in Table II; IR spectra are given below.

Deprotonation and Alkylation Reactions. Both ether and benzene were found to be convenient inert solvents for the following reactions, although deprotonation proceeds very slowly, presumably because of the low solubility of the salts **2** in such media. Completion of this step is evident from the disappearance of these salts as they are transformed to the neutral imino complexes **3** which form orange-red solutions.

(2) Helling, J. F.; Hendrickson, W. A. *J. Organomet. Chem.* **1979**, *168*, 97.

Table II. ^{1}H NMR Spectra [δ in $(CD_3)_2CO$ (ppm)] Obtained Using a Bruker WP 250 MHz Spectrometer with Tetramethylsilane as Internal Standard

complex	aryl-H	NH[a]	CH_3N	$CH_3C_6H_4NR^1R^2$	$(CH_3)_4C_4$	other
2a	5.9–6.4	3.1–3.9	...	...	1.60	
2b	6.25 (2H, m), 6.00 (2 H, m)	3.20–3.55	...	2.23	1.53	
2c	6.95 (d, H-4), 6.85 (d, H-6), 6.24 (t, H-5), 5.82 (s, H-2)	3.3–3.7	...	2.31	1.54	
2d	6.14 (d, H-3,5), 5.89 (d, H-2, 6)	3.0–3.4	...	2.29	1.54	
2e	6.30 (2 H, m), 6.00 (3 H, m)	3.0–3.4	2.91	...	1.58	
2f	6.19 (2 H, m), 5.91 (3 H, m)	3.49	...	...	1.47	1.32 [$C(CH_3)_3$]
2g	6.19 (2 H, dd, H-3,5) 5.86 (1 H, t, H-4), 5.77 (2 H, d, H-2, 6)	...	3.11	...	1.56	
2h	5.97 (d, H-3,5), 5.70 (d, H-2,6)	...	3.08	2.23	1.50	
2i	6.26 (2 H, m), 6.02 (3 H, m)	...	2.98	...	1.57	1.39 [$C(CH_3)_3$]
2j	6.18 (2 H, dd, H-3,5), 5.83 (1 H, t, H-4), 5.71 (2 H, d, H-2, 6)	...	...	...	1.53	3.40 (q) [NCH_2], 1.23 (t) [CH_2CH_3]

[a] Plus H_2O from solvent.

(a) Dimethylanilne Complex 2g from the Aniline Complex 2a. The salt **2a** (405 mg, 1 mmol), sodium hydride (2 g, 83 mmol), and ether (30 mL) were stirred for 18 h. Iodomethane (2 mL) was then added and stirring continued for 1 h. Ammonium hexafluorophosphate (1.63 g, 10 mmol) in water was added dropwise (*caution*: vigorous H_2 evolution) and stirring continued for 1 h. The mixture was then poured into ether (100 mL) and the precipitated product collected by filtration and taken up in chloroform. The filtered chloroform solution was evaporated in vacuo and the residue purified by precipitation from acetone solution by addition of ether; yield 279 mg (64%).

(b) Dimethylaniline Complex 2g from the Methylaniline Complex 2e. The salt **2c** (420 mg, 1 mmol) and sodium hydride (2 g, 83 mmol) were used following an identical procedure to case a; yield 300 mg (69%).

(c) Deprotonation of (η^4-Tetramethylcyclobutadiene)(η^6-*p*-toluidine)cobalt(I) Hexafluorophosphate (2d). Using Schlenk-type glassware throughout, a suspension of the salt **2d** (0.42 g, 1 mmol) and potassium *tert*-butoxide (0.168 g, 1.5 mmol) in benzene (20 mL) was refluxed for 18 h. Solids A were removed by filtration, and the filtrate was evaporated under reduced pressure, leaving a residue that was extracted with dichloromethane. Addition of ether to this extract at −10 °C precipitated an orange-yellow solid (98 mg) believed to be the neutral complex **3d**. The mass spectrum showed a relatively weak parent ion (m/z 273.0914; calcd for $C_{15}H_{20}CoN$, m/z 273.0928). The strongest fragment ions corresponded to $CH_3C_6H_4NH_2$ (found, m/z 107.0729; calcd for C_7H_9N, m/z 107.0735) and $CH_3C_6H_4NH$ (found, m/z 106.0636; calcd for C_7H_8N, m/z 106.0657). From the above solids A, unreacted starting material **2d** (0.13 g, 31%) was recovered by extraction with acetone and precipitation with ether.

(d) Dimethyl-*p*-toluidine Complex 2h from the *p*-Toluidine Complex (2d). The salt **2d** (610 mg, 1.45 mmol) and potassium *tert*-butoxide (163 mg, 1.45 mmol) were heated in refluxing benzene (25 mL) for 18 h. The mixture was cooled and filtered and the residue washed with benzene. Iodomethane (2 mL) was added to the combined benzene solutions and the mixture stirred for 1 h. Ammonium hexafluorophosphate (980 mg, 6 mmol) in water (50 mL) was then added and stirring continued for 1 h. The precipitate was filtered off, washed with water and ether, taken up in acetone, and refiltered and the solvent removed. The residue was chromatographed on neutral alumina using acetone/dichloromethane (1:4) as eluant. This separated the product **2h** (112 mg, 17%) from the slower moving starting material **2d** (59 mg, 10%). The product **2h** so obtained was the high-melting form.

The reaction was repeated with the salt **2d** (420 mg, 1 mmol), but in the presence of iodomethane (0.2 mL, 3.2 mmol) and using excess of the base (340 mg, 3 mmol). Stirring this mixture in benzene (25 mL) for 18 h at room temperature gave directly a precipitate which, after dissolution in chloroform, filtration, evaporation redissolution in acetone, and precipitation with ether, gave yellow crystals (434 mg, 97%) of the low melting form of complex **2h**. Despite the large difference in melting points the IR and ^{1}H NMR spectra of the two products were indistinguishable.

(e) *N*-*tert*-Butyl-*N*-methylaniline Complex 2i. The *N*-*tert*-butylaniline complex **2f** (461 mg, 1 mmol) was added to a stirred suspension of sodium hydride (2 g, 83 mmol) in ether (50 mL) and the mixture stirred at 25 °C for 18 h. Iodomethane (2 mL) was added and stirring continued for 2 h. Ammonium hexafluorophosphate (1.63 g, 10 mmol) in water was then added dropwise (*caution*: H_2) and the mixture stirred for a further 2 h and then poured into ether (150 mL). The precipitated product **2i** was collected, taken up in acetone, and reprecipitated by addition of ether to the filtered solution: yield 450 mg (95%).

Acknowledgment. M.R.C. thanks the SERC for a research studentship.

Registry No. 1, 86664-08-6; **2a**, 115680-32-5; **2b**, 117095-21-3; **2c**, 117095-23-5; **2d**, 117095-25-7; **2e**, 117095-27-9; **2f**, 117095-29-1; **2g**, 117095-31-5; **2h**, 117095-33-7; **2i**, 117095-35-9; **2j**, 117095-37-1; **3d**, 117095-38-2; aniline, 62-53-3; *o*-toluidine, 95-53-4; *m*-toluidine, 108-44-1; *p*-toluidine, 106-49-0; methylaniline, 100-61-8; *N*-*tert*-butylaniline, 937-33-7; dimethylaniline, 121-69-7; dimethyl-*p*-toluidine, 99-97-8; *N*-*tert*-butyl-*N*-methylaniline, 70974-88-8; *N*,*N*-diethylaniline, 91-66-7; iodomethane, 74-88-4.

Supplementary Material Available: A list of IR peaks (in KCl) of all new compounds (**2a–j**) (2 pages). Ordering information is given on any current masthead page.