

INSERTION REACTIONS OF 2-(ARYLAZO)ARYLTRICARBONYLCOBALT *

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Summary

In contrast to *o*-metallated azobenzene-palladium complexes, 2-(phenylazo)-phenyltricarbonylcobalt is shown to undergo insertion of styrene, methyl acrylate, acrylonitrile and dimethyl fumarate as well as certain alkynes. New tricarbonylcobalt complexes derived from azotoluene, azoanisole and *N*-*t*-butylbenzaldimine and a new route to the azobenzene-derived complex are described.

Introduction

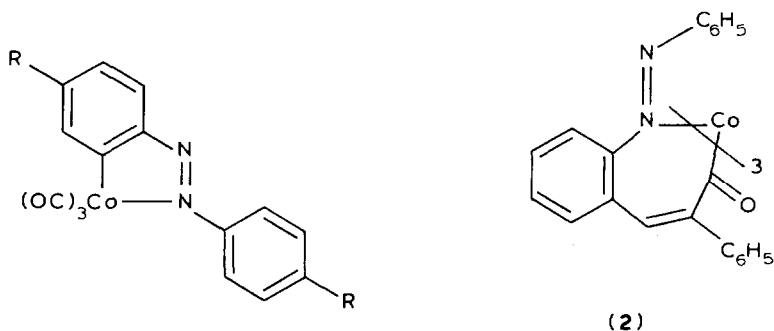
In a recent paper [1] we showed inter al. that in contrast to other *o*-metallated palladium complexes, those derived from azoarenes are resistant to insertion reactions. Since 2-(phenylazo)phenyltricarbonylcobalt (**1a**) was known [2] to insert hexafluorobutyne we have examined whether complexes of this type possess more general reactivity allowing insertion of other alkynes and of alkenes.

Results and discussion

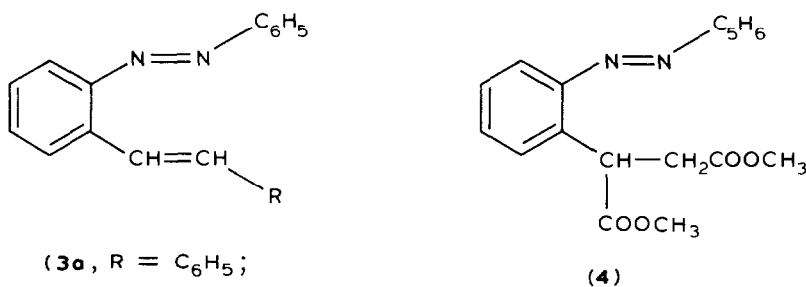
In addition to the unsubstituted complex **1a** we have prepared the dimethyl (**1b**) and dimethoxy derivative (**1c**) from the available palladium compounds [1] with sodio-tetracarbonylcobalt by the known method [2]. In addition we have shown that reaction of 2-(chloromercuri)azobenzene with octacarbonyldicobalt affords an alternative route to complex **1a**.

In contrast to reaction with hexafluoro-2-butyne reaction of complex **1a** with dimethyl acetylenedicarboxylate failed to yield isolable insertion products under comparable conditions. Although some decomposition occurred, part of the complex **1a** was recovered even after 60 h reaction time. A complex reaction occurred when this cobalt chelate **1a** was treated with phenylacetylene. In addition to free

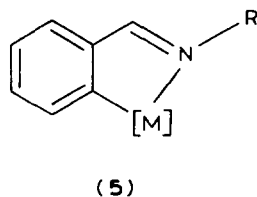
* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday.



- (1a, R = H;
 1b, R = CH₃;
 1c, R = OCH₃)



- (3a, R = C₆H₅;
 3b, R = COOCH₃;
 3c, R = CN)



azobenzene and unreacted azobenzene complex **1a** we identified the well-known phenylacetylenehexacarbonyldicobalt (11%). The major product however was a deep blue compound; C, H and N analysis suggested the composition C₆₃H₄₅CoN₆O₃ possibly corresponding to a formulation of the type **2**. Unfortunately attempts to analyse it for cobalt gave extremely low values and its poor crystallinity prevented fuller identification. The substituted complexes **1b**, **1c** did not give analogous compounds yielding only phenylacetylene hexacarbonyldicobalt.

Insertion of alkenes proved more general. Reaction with styrene yielded the insertion product **3a**, a compound only tentatively identified as a trace product from the palladium-azobenzene chelate [1]. An analogous insertion product was obtained from complex **1b**. Methyl acrylate and acrylonitrile inserted into the azobenzene

complex **1a** to give respectively the products **3b** and **3c**. Thus the reactivity of the 2-phenylazophenylcobalt complex **1a** is substantially greater than that of palladium complexes with this ligand [1] and closely similar to that of e.g. (2-dimethylaminomethyl)phenylpalladium derivatives.

Even dimethyl fumarate reacts with the cobalt complex **1a** giving, albeit in low yield, the reduced adduct **4** but alkenes lacking electron-withdrawing groups (1-heptene, cyclooctene and norbornene) gave no insertion products or at most traces.

Since the oximino palladium complex (dimer of **5**; M = PdCl; R = OH) had also failed to undergo insertion reactions we attempted its conversion to a cobalt complex (**5**, M = Co(CO)₃; R = OH) but this reaction failed, whereas the imino-cobalt complex (**5**, M = Co(CO)₃; R = Bu^t) was readily produced in fair yield by treating the corresponding palladium complex (dimer of **5**, M = PdCl; R = Bu^t) with sodiotetracarbonylcobalt as in the azoarene series.

Experimental

2-(Phenylazo)phenyltricarbonylcobalt (**1a**)

This was obtained from bis-[2-(phenylazo)phenylchloropalladium] (2 g, 3.2 mmol) and sodiotetracarbonylcobalt (1.26 g, 6.5 mmol) by the literature method [2,3] as deep red crystals (from light petroleum at -78°C), m.p. 60–62.5°C; yield: 1.13 g (55%) [Lit. [2,3]: yield 59%, 26%; m.p. 64–64.5°C] Anal. Found: C, 55.85; H, 2.9; N, 8.9. C₁₅H₉CoN₂O₃ calc: C, 55.6; H, 2.8; N, 8.6%.

Alternatively, octacarbonyldicobalt (1 g, 2.9 mmol) was added under argon to a suspension of 2-chloromercuriazobenzene [4] (1.25 g, 3 mmol) in dry tetrahydrofuran (50 ml). The mixture was stirred at room temperature for 2 h and then evaporated under reduced pressure. The residue was extracted with dry hexane, the extract concentrated and chromatographed on alumina (12 × 2.5 cm). Hexane first eluted bis(tetracarbonylcobalt)mercury, orange crystals, m.p. 80–81°C [Lit. [5]: 81–82°C]. Anal. Found: C, 17.75. C₈Co₂HgO₈ calc: C, 17.7%. Hexane then eluted the azobenzencobalt complex **1a** (0.3 g, 32%). Anal. Found: C, 55.4; H, 2.75; N, 8.7%.

5-Methyl-2-(4-methylphenylazo)phenyltricarbonylcobalt (**1b**)

A mixture of bis{[5-methyl-2-(4-methylphenylazo)phenyl]-chloropalladium} (1 g, 1.42 mmol) and sodiotetracarbonylcobalt (0.55 g, 2.85 mmol) in tetrahydrofuran (30 ml) was stirred at room temperature for 1 h. The solvent was removed at 0°C under reduced pressure and the residue extracted with light petroleum (b.p. 40–60°C) (6 × 20 ml). The combined extracts were filtered under nitrogen through a bed of Florisil (ca. 3 cm) to remove fine black suspended particles, then concentrated and cooled to -78°C, to give deep red crystals of the product **1b** (0.52 g, 52%). Anal. Found: C, 57.5; H, 3.7; N, 7.9. C₁₇H₁₃CoN₂O₃ calc: C, 58.0; H, 3.7; N, 7.95%.

5-Methoxy-2-(4-methoxyphenylazo)phenyltricarbonylcobalt (**1c**)

This was obtained (0.45 g, 45%) by the method described for the preceding compound from bis-[5-methoxy-2-(4-methoxyphenylazo)phenylchloropalladium] (1 g, 1.3 mmol) and sodiotetracarbonylcobalt (0.5 g, 2.6 mmol) in tetrahydrofuran (30 ml). Anal. Found: C, 53.7; H, 3.5; N, 7.7. C₁₇H₁₃CoN₂O₅ calc: C, 53.1; H, 3.4; N, 7.3%.

2-(N-t-butyliminomethylene)phenyltricarbonylcobalt (5, M = Co(CO)₃; R = Bu')

This was obtained by the same method as the two preceding compounds from bis-[2-(N-t-butyliminomethylene)phenylchloropalladium] (2.0 g, 3.31 mmol) and sodiotetracarbonylcobalt (1.41 g, 7.28 mmol) in tetrahydrofuran (80 ml) as yellow crystals (from light-petroleum at -70°C), m.p. $78-80^{\circ}\text{C}$. Yield: 650 mg (32%). ¹H NMR (CDCl₃): δ 8.37 (s, 1H, -CH=N), 7.05–7.96 (m, 4H, ring H) and 1.51 ppm (s, 9H, CH₃). IR (film): 2050, 1985, 1960 cm⁻¹ (CO). Anal. Found: C, 53.2; H, 4.7; N, 4.5. C₁₄H₁₄CoNO₃ calc: C, 55.45; H, 4.7; N, 4.6%.

Reaction of phenylacetylene with complex 1a

Under nitrogen phenylacetylene (0.17 g, 1.67 mmol) was added to the complex **1a** (0.5 g, 1.54 mmol) in benzene (20 ml) and the mixture stirred for 12 h. The solution was then concentrated and chromatographed on alumina. Light petroleum (b.p. $40-60^{\circ}\text{C}$) eluted azobenzene (60 mg) followed by unreacted complex (**1a** (60 mg). Dichloromethane/light petroleum then eluted hexacarbonyl(phenylacetylene)dib-cobalt, identified by IR comparison with an authentic sample. [Anal. Found: C, 43.1; H, 1.5. C₁₄H₆Co₂O₆ calc: C, 43.3; H, 1.6%], and finally a deep blue compound (0.12 g) showing no metal carbonyl stretching bands in the IR. It crystallised from dichloromethane/light petroleum. Anal. Found: C, 76.0; H, 4.7; N, 8.5. C₆₃H₄₅CoN₆O₃ calc: C, 76.2; H, 4.6; N, 8.5%.

Reactions of styrene with complex 1a

To a solution of the azobenzene-cobalt complex **1a** (0.5 g, 1.54 mmol) in benzene (20 ml) styrene (0.8 g, 7.7 mmol) was added and the mixture was stirred under reflux at 80°C until all the starting complex had been consumed (TLC) (~ 15 h). After evaporation under reduced pressure, the residue was extracted with light petroleum (b.p. $40-60^{\circ}\text{C}$) and filtered. The solid residue was not identified. The filtrate was concentrated and chromatographed on alumina. Light petroleum (b.p. $30-40^{\circ}\text{C}$) eluted azobenzene (23 mg) followed by *trans*-2-styrylazobenzene (**3a**) (0.125 g, 29%), orange crystals, [6] m.p. $124-125^{\circ}\text{C}$. ¹H NMR (CDCl₃): δ 8.22 (d, 1H, *J* 16.5 Hz, -CH=), 7.24–8.0 (m, 14H, ring H), 7.21 ppm (d, 1H, -CH=). MS: *m/z* 284.1314 (C₂₀H₁₆N₂ calc: 284.1313), 207.0921 (base peak; C₁₄H₁₁N₂: 207.0922), 178.0786 (C₁₄H₁₀: 178.0782), 77.0416 (C₆H₅: 77.0391). Anal. Found: C, 83.9; H, 5.6; N, 9.5. C₂₀H₁₆N₂ calc: C, 84.5; H, 5.7; N, 9.85%.

This was followed by a trace of a compound shown by mass spectrometry to be C₂₈H₂₄N₂ [*m/z* 388.1919; calc: 388.1939].

Reaction of styrene with complex 1b

Reaction of this complex (0.3 g, 0.86 mmol) and styrene (0.45 g, 4.3 mmol) in benzene (15 ml) (~ 9 h) was conducted like the preceding reaction. Following 4,4'-dimethylazobenzene (~ 15 mg) light petroleum/dichloromethane (3/2) eluted *trans,trans*-4,4'-dimethyl-2-styrylazobenzene (65 mg, 24%), orange crystals, m.p. $117-119^{\circ}\text{C}$. ¹H NMR (CDCl₃): δ 8.21 (d, 1H, *J* 16.5 Hz, -CH=), 7.15–7.94 (m, 12H, ring H); 7.18 (d, 1H, -CH=), 7.15–7.94 (m, 12H, ring H); 7.18 (d, 1H, -CH=) and 2.44 ppm (s, 6H, CH₃). Anal. Found: C, 84.6; H, 6.4; N, 8.9. C₂₂H₂₀N₂ calc: C, 84.6; H, 6.5; N, 9.0%.

Reaction of methyl acrylate with complex 1a

A mixture of the complex **1a** (0.5 g, 1.54 mmol) and methyl acrylate (1.32 g, 15.4 mmol) was stirred in benzene (20 ml) at 70 °C for 3 h. The solution was concentrated and chromatographed on silica gel (60–120 mesh). Chloroform eluted the product **3b** (130 mg, 31%), red crystals, m.p. 48–50 °C. ¹H NMR (CDCl₃): 8.80 (d, 1H, *J* 17 Hz, $-\text{CH}=\text{CHC}\begin{smallmatrix} \diagup \\ \text{O} \end{smallmatrix}$), 7.39–8.10 (m, 9H, ring H), 6.56 (d, 1H, $=\text{CHC}\begin{smallmatrix} \diagup \\ \text{O} \end{smallmatrix}$) and 3.85 ppm (s, 3H, CH₃). Anal. Found: C, 72.6; H, 5.4; N, 10.5. C₁₆H₁₄N₂O₂ calc: C, 72.15; H, 5.3; N, 10.5%.

Reaction of acrylonitrile with complex 1a

The complex **1a** (0.5 g, 1.54 mmol) and acrylonitrile (0.41 g, 7.7 mmol) were stirred in benzene (20 ml) at 80 °C for 3 h, then worked up as in the preceding experiment. Light petroleum/chloroform (3/2) eluted azobenzene (~10 mg); chloroform then eluted the product **3c** (100 mg, 28%), red crystals, m.p. 70–72 °C. ¹H NMR (CDCl₃): δ 8.48 (d, 1H, *J* 17 Hz, $\text{CH}=\text{CHCN}$) 7.42–8.04 (m, 9H, ring H), 5.99 ppm (d, 1H, $=\text{CH-CN}$). Anal. Found: C, 77.6; H, 4.9; N, 18.2. C₁₅H₁₁N₃ calc: C, 77.1; H, 4.8; N, 18.0%.

Reaction of dimethyl fumarate with complex 1a

The complex **1a** (2 g, 6.16 mmol), dimethyl fumarate (2.66 g, 18.5 mmol) and benzene (100 ml) were stirred for 24 h at 80 °C and the products worked up as in the preceding insertion reactions. Benzene eluted azobenzene (80 mg) and benzene/ether (4/1) then eluted the product **4** (140 mg, 7%) as a red oil. ¹H NMR (CDCl₃): δ 7.20–7.98 (m, 9H, ring H), 4.94 (dd, 1H, *J* 8.5, *J* 6.5 Hz, CHCH_2) 3.65 (s, 3H, CH₃), 3.60 (s, 3H, CH₃), 3.37 (dd, 1H, *J* 17.5, *J* 8.5 Hz) and 2.71 ppm (dd, 1H, *J* 17.5, *J* 6.5 Hz). MS *m/z* 326.1252 (C₁₈H₁₈N₂O₄ calc: 326.1266); 295.1091 (C₁₇H₁₅N₂O₃: 295.1083); 267.1095 (base peak, *M* – COOCH₃, C₁₆H₁₅N₂O₂: 267.1133); 253.0991 (C₁₅H₁₃N₂O₂: 253.0977); 207.0910 (C₁₄H₁₁N₂: 207.0922). Anal. Found: C, 66.6; H, 5.6; N, 9.2. C₁₈H₁₈N₂O₄ calc: C, 66.2; H, 5.6; N, 8.6%.

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