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A NEW σ-BONDED ARYL–COBALT(III) COMPLEX

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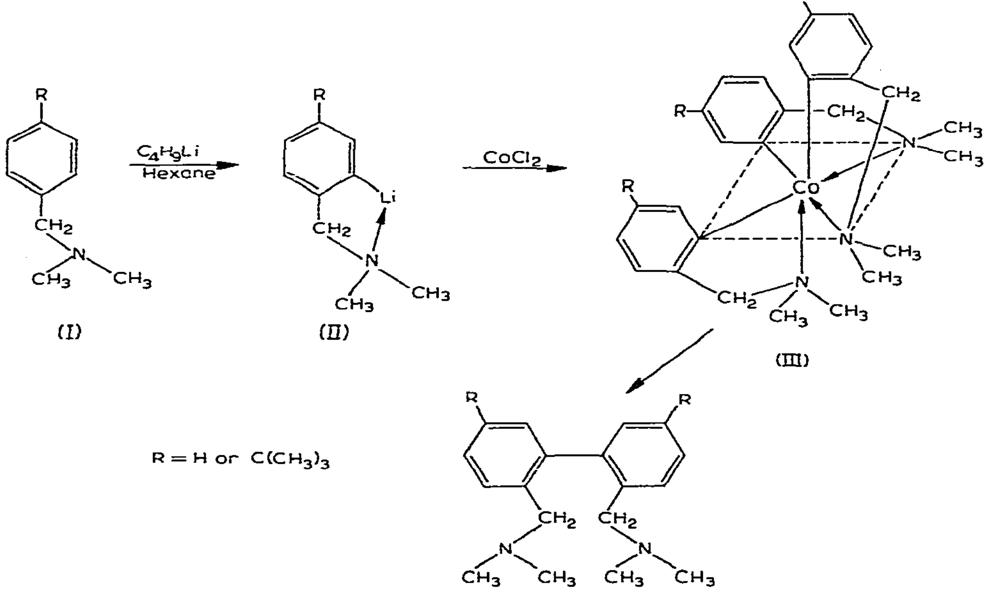
The first stable σ-bonded aryl complexes of cobalt were described by Chatt and Shaw[1]. These had the structure $Ar_2Co(PPhEt_2)_2$, in which there was stabilization by π-bonding phosphine donors, and had the greatest stability when the aryl group bonded to cobalt carried bulky *ortho* substituents. Other carbon–cobalt σ-bonded complexes of Aetioporphyrin I. The compounds described in the two latter examples cyclopentadienyl[3] groups. Schrauzer and Kohnle[4] have prepared some cobalt complexes containing both dimethylglyoxime and σ-bonded aryl groups as ligands and more recently Johnson and co-workers[5] have described some aryl–cobalt(III) complexes of Aetioporphyrin I. The compounds described in the two latter examples both contain four nitrogen–cobalt links in a chelating structure and this must be the reason for their stability.



(I) (II) (III) (IV)

We have now prepared a novel cobalt complex III (scheme 1) in which stability

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is helped by nitrogen and which contains three aryl groups σ-bonded to cobalt. The *N,N*-dimethylbenzylamine derivative (I) [R = H or $C(CH_3)_3$] reacted with n-butyllithium in refluxing hexane to give the *o*-lithioamine (II). This then reacted with anhydrous cobalt chloride in ether/hexane to give the red crystalline complex (III) (best yield obtained, 45%) together with the biphenyl derivative (IV). The *o*-metalation of *N,N*-dimethylbenzylamine has previously been reported by Jones and co-workers[6]. They carried out the reaction in ether at room temperature. When we prepared the *o*-lithioamine in this way and reacted it with anhydrous cobalt chloride the same results were obtained. We also prepared the *o*-lithioamine (II) by halogen–metal interchange of *o*-bromo-*N,N*-dimethylbenzylamine[7] with n-butyllithium and this again gave the complex (III) (R = H) on reaction with anhydrous cobalt chloride.

The structure of (III) was assigned as follows. Because of its high insolubility the unsubstituted complex (III) (R = H) was difficult to purify. It was only slightly soluble in methylene chloride and tetrahydrofuran, and almost insoluble in all other organic solvents (including acetone, benzene, ethanol and dimethylformamide). The elemental analysis was unsatisfactory in that it gave a small chlorine figure (Cl, 1.6). The insolubility also precluded NMR and molecular weight measurements. Attempts to purify (III) by chromatography on neutral alumina or silicic acid brought about its decomposition. The presence of a bond between cobalt and the carbon of the benzene ring *ortho* to the $CH_2N(CH_3)_2$ group was established in the following way. The complex (III) (R = H) was treated with lithium aluminium deuteride in tetrahydrofuran. After decomposition of the reaction mixture with deuterium oxide a quantitative yield of monodeutero-*N,N*-dimethylbenzylamine was obtained. VPC analysis of this showed it to have the same retention time as an authentic sample of non-deuterated amine. Mass spectrometric analysis of the product showed the following deuterium content: 85% d_1, 8% d_2 species, and also that this single deuterium was in the benzene ring.

Because of the insolubility of (III) (R = H) the complex (III) [R = $C(CH_3)_3$] was prepared in the hope that the tert-butyl group would increase its solubility. This turned out to be so, the resultant complex being quite soluble in methylene chloride, fairly soluble in benzene and ether, but still almost insoluble in ethanol. The elemental analysis for the substituted complex was satisfactory and the molecular weight, as measured by the freezing-point depression of a benzene solution, was 623, agreeing well with the calculated value of 630. Lithium aluminium deuteride reduction of (III)

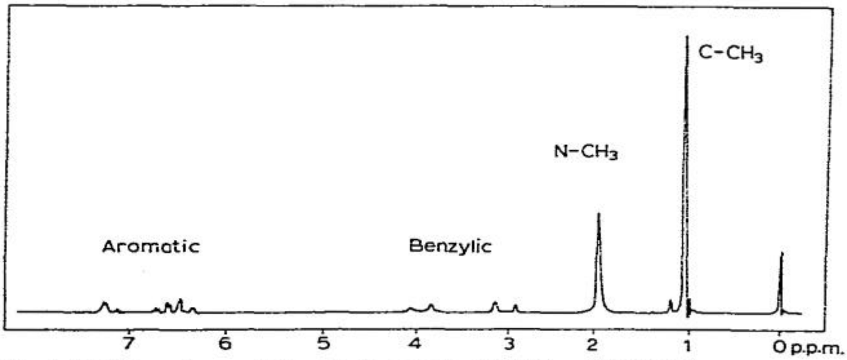

Fig. 1. NMR spectrum of the cobalt complex (III) [R = $C(CH_3)_3$].

[R = $C(CH_3)_3$] gave *p*-tert-butyl-*N*,*N*-dimethylbenzylamine which was shown by mass spectrometry to have the deuterium content: 97.5% d_1 species. This high deuterium content indicates that all three amines are joined to cobalt through a covalent carbon–metal bond. The NMR spectrum of this product integrated for three aromatic protons.

The NMR spectrum of the complex (III) [R = $C(CH_3)_3$] taken in deuterochloroform at 35° is shown in Fig. 1. The spectrum is consistent with the structure (III). We think that (III) is probably the *cis* isomer of an octahedral complex because the benzylic protons appear as two doublets at 3.0 and 3.9 ppm. The two protons in each pair of benzylic protons are non-equivalent but the three pairs are equivalent. If (III) was the *trans* isomer then a more complicated pattern for the benzylic protons would be expected. The aromatic protons appear as a multiplet centred at 6.5 ppm and a slightly split singlet at 7.2 ppm. In the free amine (I) [R = $C(CH_3)_3$] the aromatic protons appear as a singlet at 7.1 ppm. The *N*-methyl protons appear as a singlet at 2.0 ppm. When the spectrum was taken at lower temperatures it was found that this peak is still evident at 10° but collapses at −10°. At −30° the *N*-methyl signal reappears as a doublet at 1.3 and 2.6 ppm. This shows that the *N*-methyl groups are non-equivalent and hence that the nitrogen is coordinated to the metal in the complex.

The magnetic susceptibility of the complex (III) [R = $C(CH_3)_3$] has been measured with a Gouy balance and it was found that there is only a small residual magnetic moment for cobalt. This indicates that the complex contains spin-paired Co(III). Comparison with other strong-field cobalt(III) complexes[8] suggests that the corrected susceptibility should lie in the region of 100 to 200×10^{-6} cgs units per gram-ion of cobalt. This agrees with our figure of 150×10^{-6} cgs units. The magnetic susceptibility of the unsubstituted complex (III) (R = H) was also measured and was consistent with the complex containing cobalt(III). The fact that the substituted complex gives a sharp signal pattern in its NMR spectrum is also an indication that it is diamagnetic and so contains cobalt(III).

The complex is stable when kept at room temperature in air but when heated to 120° or allowed to remain in solution, especially acetone, it decomposes to give the crystalline biphenyl derivative (IV). This biphenyl derivative (IV) [R = $C(CH_3)_3$] had a satisfactory elemental analysis and its NMR spectrum was consistent with the assigned structure. The mass spectrum showed the correct molecular ion peak at 380 *m/e* and the base peak at 290 *m/e* is best assigned to the ion of a phenanthrene derivative arising by the loss of two $N(CH_3)_2$ groups and two hydrogen atoms.

A notable feature of the complex is its unreactivity. Attempts were made to react it with phosphines, carbon monoxide, acetylacetone and ethylene diamine but there was no reaction at room temperature and on heating only decomposition of the complex was brought about. Its stability is probably due to the effect of the three chelating groups with three nitrogen atoms coordinating to the central cobalt. The formation of the complex involves the oxidation of Co(II) to Co(III) which seems unusual under the reaction conditions used (reaction with an organolithium compound in a nitrogen atmosphere). The complex (III) [R = $C(CH_3)_3$] was also obtained in small yield (5%) when the *o*-lithioamine (II) [R = $C(CH_3)_3$] was reacted with $Cl_2Co(PPh_3)_2$. It was thought that a compound similar to that of Chatt and Shaw[1], $Ar_2Co(PPh_3)_2$, would be formed in this reaction but only the complex (III) [R = $C(CH_3)_3$] and triphenylphosphine were isolated. Of some relevance to our work is the paper by Bähr and Zohm[9] in which they report a chromium complex containing three molecules of *N,N*-diethylbenzylamine bonded to a chromium atom in a similar manner to our cobalt complex.

EXPERIMENTAL

Hexane, ether and tetrahydrofuran were distilled from lithium aluminium hydride just before use. NMR spectra were recorded on a Varian Associates A-60 instrument using tetramethylsilane as an internal standard. Analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and by Dr. S. M. Nagy of this department. Cobalt was determined by atomic absorption spectrophotometry by the Schwarzkopf Microanalytical Laboratory.

N,N-Dimethylbenzylamine

This was commercial material, purified by distillation, b.p. 57–58° (9 mm).

p-tert-Butyl-N,N-dimethylbenzylamine

A mixture of *p*-tert-butyl benzoic acid (20 g, 0.11 mole), thionyl chloride (24 g, 0.20 mole) and benzene (80 ml) was refluxed for 4 h. The clear solution was concentrated to remove excess thionyl chloride and benzene. The residual liquid acid chloride was dissolved in benzene (20 ml) and added dropwise to a stirred solution of anhydrous dimethylamine (36 g, 0.8 mole) in benzene (80 ml) cooled in an ice-bath. The mixture was stirred overnight at room temperature. Water (100 ml) was added and the mixture stirred, allowed to settle, the benzene layer removed and the aqueous layer extracted twice with ether. The combined benzene and ether extracts were washed with brine, dried ($MgSO_4$) and concentrated to give a white solid which was crystallized from ether/hexane to give 20 g (81%) of *p*-tert-butyl-*N,N*-dimethylbenzamide, m.p. 87°. This amide (19.5 g, 0.095 mole) was dissolved in ether (150 ml) and added dropwise over 30 min to a stirred suspension of lithium aluminium hydride (5 g, 0.13 mole) in ether (50 ml) cooled in an ice-bath. The mixture was then stirred under reflux for 3 h, cooled in an ice-bath, and decomposed by addition of water (5 ml), then 15% sodium hydroxide and then water (15 ml). The mixture was stirred for 2 h, filtered under suction, the precipitate washed with ether and the filtrates evaporated. The residue was dissolved in 10% hydrochloric acid and the acid solution extracted with ether and then made alkaline by adding cold 15% sodium hydroxide. The alkaline mixture was then extracted with ether, the extract dried (K_2CO_3), concentrated, and distilled giving 12.5 g (69%) of *p*-tert-butyl-*N,N*-dimethylbenzylamine, b.p. 109° (10 mm), n_D^{26} 1.4952, homogeneous to gas chromatography (silicone rubber, 130°). (Found: C, 81.3; H, 11.1; N, 7.5. $C_{13}H_{21}N$ calcd.: C, 81.7; H, 11.0; N, 7.3%.)

Reaction of o-lithio-N,N-dimethylbenzylamine with cobalt chloride

A mixture of *N,N*-dimethylbenzylamine (10.13 g, 0.075 mole), n-butyllithium (Foote Mineral Company) in hexane (56 ml containing 0.09 mole) and hexane (90 ml) was refluxed with stirring in a nitrogen atmosphere for 16 h. To the resulting suspension of the *o*-lithioamine was added anhydrous ether (250 ml). The stirred mixture was cooled in an ice-salt bath and then anhydrous cobalt chloride[10] (9.75 g, 0.075

mole) added under a fast stream of nitrogen. The mixture quickly went dark green and after 30 min a dark red tinge developed. After stirring for 12 h at room temperature the mixture was cooled to 0°, treated with water (50 ml) and extracted with methylene chloride (6 × 300 ml portions). The bright red extract was dried ($MgSO_4$), concentrated to 100 ml, ether (100 ml) added and the red cobalt complex (III) (R = H) was filtered off, (5.25 g, 45 % yield), m.p. 160–161° dec. The infrared spectrum (KBr pellet) reveals major absorptions at 3020, 1575, 1470, 1448, 1005, 850, and 750 cm^{-1}. (Found: C, 69.8; H, 7.7; Cl, 1.6; N, 9.0. $C_{27}H_{36}N_3Co$ calcd.: C, 70.3; H, 7.8; N, 9.1 %.)

Reduction of the cobalt complex (III) (R = H) with lithium aluminium deuteride

To a stirred mixture of the complex (0.075 g) and tetrahydrofuran (50 ml) was added lithium aluminium deuteride (0.1 g). After stirring for 30 min at 25° the red colour of the complex had disappeared. The mixture was stirred for a further $1\frac{1}{2}$ h and then decomposed by adding deuterium oxide (1 ml). The mixture was made acid with dilute hydrochloric acid and the tetrahydrofuran removed by evaporation under reduced pressure. After making alkaline with sodium carbonate the mixture was extracted with ether, the ether extracts dried ($MgSO_4$) and evaporated to give *N,N*-dimethylbenzylamine-d_1 (0.046 g), homogeneous to gas chromatography and with the same retention time as an authentic sample of non-deuterated *N,N*-dimethylbenzylamine. Mass spectrometric analysis showed that the product contained 85 % d_1, 8 % d_2 species.

Reaction of o-lithio-p-tert-butyl-N,N-dimethylbenzylamine with cobalt chloride

A mixture of *p*-tert-butyl-*N,N*-dimethylbenzylamine (5 g, 0.026 mole), n-butyllithium in hexane (16.5 ml containing 0.026 mole) and hexane (60 ml) was refluxed with stirring in a nitrogen atmosphere for 16 h. To the resulting suspension of the *o*-lithioamine was added anhydrous ether (120 ml). The stirred mixture was cooled to −30° and then anhydrous cobalt chloride (3.4 g, 0.026 mole) added under a fast stream of nitrogen. The mixture, which went green, was stirred for 15 min at −30° and then for 2 h at 0°. It was then cooled to −30° and water (50 ml) was added over five min. After allowing the mixture to reach 10° the ether layer was separated and the aqueous portion extracted twice with ether. The combined ether extracts were washed with water, dried (K_2CO_3) and concentrated to 10 ml. The resultant red oil was triturated at 0° with petroleum ether (b.p. 30–50°) and red crystals were quickly formed. After 20 min the red crystalline cobalt complex (III) [$R = C(CH_3)_3$] was filtered off and washed with petroleum ether. The yield was 1.81 g (33 %), m.p. 126–127° dec. The infrared spectrum (KBr pellet) reveals major absorptions at 2950, 1580, 1465, 1000, and 850 cm^{-1}; ultraviolet spectrum [$m\mu(\varepsilon)$]: λ_{max} in CCl_4 258 (13070) and 490 (303), λ_{max} in $CHCl_3$ 245 (15770), 382 (568) and 490 (570).

A sample was recrystallised twice for analysis by dissolving it in a little benzene at 25°, adding petroleum ether (b.p. 30–50°) and concentrating on the rotary evaporator until crystals began to appear. Crystallisation was completed by letting the mixture stand at 0° for one hour. (Found: C, 74.5; H, 9.8; Cl, 0.0; Co, 9.7; N, 6.7. $C_{39}H_{60}CoN_3$ calcd.: C, 74.4; H, 9.5; Co, 9.4; N, 6.7 %.)

The mother liquor from the complex above gave, on standing, a pink solid, which on crystallisation from hot acetone gave 2,2′-bis(*N,N*-dimethylaminomethyl)-4,4′-di-tert-butylbiphenyl, (IV) [$R = C(CH_3)_3$] (0.3 g, 6 %), m.p. 123°. (Found: C, 81.9; H, 10.7; N, 7.4. $C_{26}H_{40}N_2$ calcd.: C, 82.1; H, 10.5; N, 7.4%.)

The sublimation of the cobalt complex (III) [$R = C(CH_3)_3$] was attempted (0.01 mm). The complex decomposed at its m.p. (126°) and the biphenyl derivative (IV) [$R = C(CH_3)_3$] sublimed.

Reduction of the cobalt complex (III) [$R = C(CH_3)_3$] with lithium aluminium deuteride

This was carried out in a similar manner to the unsubstituted complex (III) (R = H) except that in this case the solvent was ether and the reaction time was 15 min. Mass spectrometric, gas chromatographic and infrared analysis of the product (quantitative yield) showed it to be *p*-tert-butyl-*N*,*N*-dimethylbenzylamine-d_1, containing 97.5% d_1 species.

Dichlorobis(triphenylphosphine)cobalt(II)

This was prepared from anhydrous cobalt chloride and triphenylphosphine according to the method of Chatt and Shaw[1], yield 85%, m.p. 244–245°, (lit.[1] m.p. 247–251°).

Reaction of o-lithio-p-tert-butyl-N,N-dimethylbenzylamine with dichlorobis(triphenylphosphine)cobalt(II)

A mixture of *p*-tert-butyl-*N*,*N*-dimethylbenzylamine (7.9 g, 0.041 mole), n-butyllithium in hexane (26 ml containing 0.041 mole) and hexane (25 ml) was refluxed with stirring in a nitrogen atmosphere for 16 h. The resultant lithium compound was then reacted with dichlorobis(triphenylphosphine)cobalt(II) (9 g, 0.014 mole) in ether in a similar manner to the reaction with anhydrous cobalt chloride described above. After the reaction was complete (2 h) the mixture was treated with water and extracted with ether as before. This gave a red oil which on triturating with cold petroleum ether gave 4.6 g (64%) of triphenylphosphine as a crystalline white solid (after filtering and washing with petroleum ether), identified by m.p., mixture m.p. and infrared spectrum comparison with authentic triphenylphosphine. The red mother liquor was cooled to −5° and the red crystalline complex (III) [$R = C(CH_3)_3$] obtained (0.42 g, 5%), identical in m.p. and infrared spectrum with that previously obtained.

SUMMARY

The reaction of the *o*-lithio-*N*,*N*-dimethylbenzylamine derivative (II) [R = H or $C(CH_3)_3$] with anhydrous cobalt chloride yielded the complex (III), which contains three carbon–cobalt σ-bonds. Evidence for this structure, based on lithium aluminium deuteride reduction of the complex, and on NMR, molecular weight and magnetic susceptibility measurements is presented.

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