

## Preliminary communication

### The interaction of nickelocene with benzal anilines

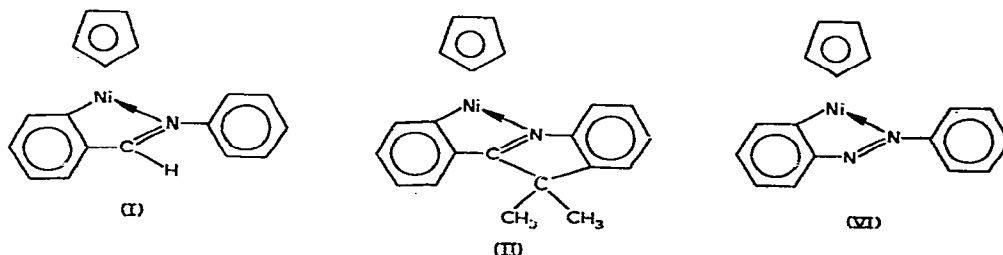
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Molnar and Orchin appear to be the first who investigated the problem of how the metal is bonded to the azo group in 2-(phenylazo)phenyl complexes of the transition metals\*. They compared the IR spectra of benzalanilines with those of the corresponding palladium complexes and of phenylnitron\*\*, and came to the conclusion that benzalaniline was probably coordinated to the palladium atom through the nitrogen lone pair rather than through the  $\pi$ -electrons of the azomethyne<sup>1</sup>. Molnar and Orchin presumed that the same coordination occurred in other complexes of azobenzene<sup>2</sup>.

In this communication new evidence is reported which helps to clarify the role played by the nitrogen lone pair in the coordination of benzal anilines to a metal. We have synthesised\*\*\* cyclopentadienyl [2-(*N*-phenylformimidoyl)phenyl] nickel (I) and cyclopentadienyl-2-[2'-(3',3'-dimethylindolenyl)phenyl] nickel (II) from nickelocene (III), 2-bromobenzalaniline (IV) and 2-phenyl-3,3-dimethylindolenine (V), respectively.



In a typical experiment, 1.18 g of (III) and 1.30 g of (IV), dissolved in 25 ml benzene, were stirred and refluxed for 1.5 h. The mixture was filtered, the solvent removed in vacuo, and the residue recrystallised from 30 ml hexane to give 0.40 g (26%) of dark-red crystals, m.p. 106–108° (dec.). [Anal.: Found: C, 71.59; H, 5.17; N, 4.79. C<sub>18</sub>H<sub>15</sub>NNi, calcd.: C, 71.06; H, 4.61; N, 4.95%. IV( $\lambda_{\max}$  in isooctane (log  $\epsilon$ )): 245 (sh) (4.57), 286

\*For 2-(phenylazo)phenyl complexes see ref. 2 and references quoted in that paper.

\*\*Phenylnitron = Ph-CH=N(Ph)  $\rightarrow$  O.

\*\*\*All syntheses were carried out in an argon atmosphere. Absolute solvents, distilled in an argon atmosphere, were used throughout.

(4.44), 398 (3.70)]. Complex (II) was obtained by refluxing a solution of 1.94 g of (III) and 2.79 g of (IV) in 25 ml mesitylene for 2.5 h; chromatographic separation (alumina, benzene/hexane 1/2) followed by recrystallisation from hexane yielded 1.6 g (44%) of dark-red crystals, m.p. 200–201°. [Anal.: Found: C, 73.18; H, 5.73; N, 4.06.  $C_{21}H_{19}NNi$ , calcd.: C, 73.32; H, 5.53; N, 4.07%. UV ( $\lambda_{max}$  in isooctane (log  $\epsilon$ ): 232 (4.33), 259 (4.41), 283 (4.23), 310 (4.14), 402 (3.37), 538 (3.62), 573 (3.61)].

The PMR spectrum of compound (I) displays two singlets at 5.1 and 7.68 ppm, the intensities ratio being 5/1. These have been assigned to the cyclopentadienyl ring protons and to the  $-CH=N-$  methyne proton, respectively. The aromatic protons give a complex multiplet centred at 7.2 ppm, the integral intensity indicating the participation of nine protons. The signal of the methyne of the complex (7.68 ppm) is close to that for the methyne of benzalaniline (8.27 ppm), thus providing strong evidence in favour of the coordination of the azomethyne to the nickel atom through the nitrogen lone pair. If the  $\pi$ -electrons of azomethyne had been involved in the coordination process the azomethyne proton would have produced a signal shifted by ca. 2 ppm upfield<sup>3</sup>.

The PMR spectrum of complex (II) contains a singlet at 1.5 ppm (six equivalent protons of two methyls), a singlet at 5.38 ppm (the cyclopentadienyl ring protons), and a complex multiplet lying at the aromatic domain and corresponding to eight protons.

The mass spectra of complexes (I) and (II) have also been studied. At higher mass numbers, each compound gives two peaks,  $m/e$  303 and 305 (I), 343 and 345 (II) respectively, the intensity ratio being 2.58/1 and 2.62/1. This agrees with the natural abundance of the two most widespread isotopes of nickel. Hence, complexes (I) and (II) contain one nickel atom each. The molecular weights found coincide precisely with those calculated.

The fact that complex (II) is more stable than (I) may be explained by assuming that either the coordinated indolenine possesses the planar conformation<sup>★</sup> or the  $C=N$  double bond is less reactive in indolenine (V) than it is in benzalaniline<sup>★★</sup>, whether these ligands be free or coordinated.

The presence of unchanged indolenine in the complex (II) has been verified by the reaction with trifluoroacetic acid which produces the initial indolenine (V) in a yield of 90%.

In summary, therefore, the azo group in cyclopentadienyl-[2[(phenylazo)-phenyl]nickel (VI) is also capable of coordination to nickel through the lone pair of the nitrogen atom furthest from the phenyl containing the Ni-C  $\sigma$ -bond.

## REFERENCES

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★The dimethylmethylene bridge stabilises the planar conformation in 2-phenyl-3,3-dimethylindolenine<sup>4, 5</sup>.

★★Unlike benzalaniline, 2-phenyl-3,3-dimethylindolenine is not hydrolyzed even when refluxed in concentrated aqueous acids<sup>5</sup>.