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Preliminary communication

A binuclear nickel–azobenzene complex

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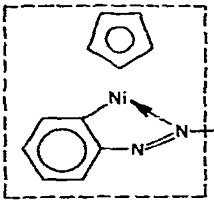
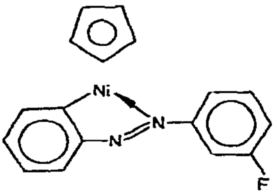
Transition metals have been reported as incorporated in complexes in which one[1-3] or two[4,5] azobenzene molecules are bonded to one atom of the metal. The formation of a complex in which two metal atoms are bonded with one azobenzene is described below.

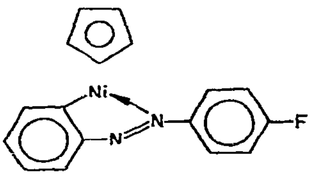
Whilst studying the electron effects of the 2-(cyclopentadienylnickel)phenylazo group in cyclopentadienyl[2-(phenylazo)phenyl]nickel (I) we have synthesised complexes (II) and (III) from nickelocene, 2-chloro-3′-fluoroazobenzene, and 2-chloro-4′-fluoroazobenzene, respectively★:



(I)



(II)



(III)

Through the use of this method it is possible to obtain complexes (II) and (III) completely free from the normal isomeric contaminants[6].

The ^{19}F chemical shifts of (II) and (III), dissolved in tetrahydrofuran, are (in ppm from fluorobenzene): $\delta_{m\text{-F}} = -0.53 \pm 0.05$, $\delta_{p\text{-F}} = +0.35 \pm 0.05$. The Taft equations[7] give σ_I and σ_R equal to +0.16 and −0.03, respectively, for the 2-(cyclopentadienylnickel)phenylazo group. For the phenylazo group, these parameters are[7]: $\sigma_I = +0.19$ and $\sigma_R = +0.08$.

If a chlorine substituent is present in the *ortho*-position with respect to the phenylazo group of the azobenzene, then unlike unsubstituted azobenzene, 2-chloroazobenzene will react with nickelocene★★ to give complex (I) very readily[6]. The electronic effects of the

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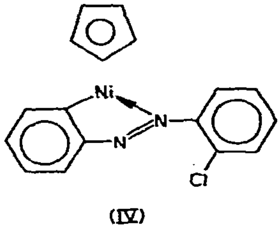
★The syntheses of (II), (III), and (IV) are similar to the synthesis of (I) from nickelocene and 2-chloroazobenzene[6].

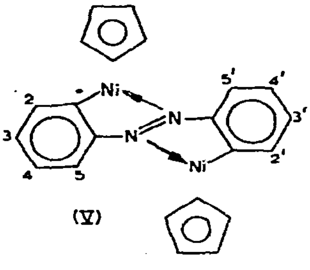
★★2-Chloro- and 2,2-dichloroazobenzenes react with nickelocene even at room temperature. After two weeks, the yields of (I) and (IV) were ca. 20 and 39%, respectively.

2-(cyclopentadienylnickel)phenylazo group hardly differ from those of the 2-phenylazo group and for this reason it may be anticipated that nickelocene will react with complex (IV) in the same way as with 2-chloroazobenzene.

The binuclear complex (V) results from such a reaction.



(IV)



(V)

In a typical experiment*, nickelocene (0.63 g, 3.3 mmole) was refluxed with (IV) (0.38 g, 1.1 mmole) in 18 ml *p*-xylene for one hour. The mixture was filtered hot, cooled down to room temperature, and the resulting crystals separated, and washed in hexane. The yield was 21%. Since complex (IV) is formed from nickelocene and 2,2-dichloroazobenzene, complex (V) may be obtained directly from these reactants through the use of a large excess of nickelocene. In this case, however, the yield was found to be somewhat lower (12%).

Complex (V) is a shining dark-blue crystalline compound which does not melt up to 350° and is sparingly soluble in organic solvents. The resulting solutions are extremely unstable in air. [Anal.: Found: C, 61.57; H, 4.08; N, 6.67; Ni, 26.92. $C_{22}H_{18}N_2Ni_2$, calcd.: C, 61.76; H, 4.24; N, 6.54; Ni, 27.44%. UV (λ_{max} in THF (log ϵ)): 264 (4.72), 388 (4.19), 720 (4.11), 780 (4.50)].

The PMR spectrum (of a saturated solution of complex (V) in CS_2, 100 Mc, Varian HA-100D, using TMS as a standard) contains a singlet corresponding to the protons of the two cyclopentadienyls (δ 5.49 ppm), and signals for the protons of the two equivalent phenyl nuclei (ABMX spectrum at 6.6 to 7.9 ppm), the integral intensity ratio being close to that expected theoretically, *i.e.* 5/4. The ABMX spectrum coincides with the spectrum of the respective structural fragment of complex (I)[8]: $\delta(H_2) = \delta\ (H_2') = 7.55$ ppm; $\delta\ (H_5) = \delta\ (H_5') = 7.80$ ppm, the symmetric well-resolved multiplet of H_3 and H_3', H_4 and H_4' being centred at 6.83 ppm, $J_{3,4} \approx J_{2,3} \approx J_{4,5} \approx 7.6$ Hz; $J_{3,5} \approx J_{2,4} \approx 2$ Hz.

The molecular weight of complex (V) was 428 (mass spectra), being identical to that expected theoretically. Consequently, the data reported here agree with the structure proposed, with the azo group coordinated to the nickel through the nitrogen lone pair electrons.

The authors are grateful to I.F. Leshchova for providing the ^{19}F spectra and for valuable discussions.

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

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