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Preliminary communication

Azobenzene complexes of dicyclopentadienyltitanium and dicyclopentadienylvanadium

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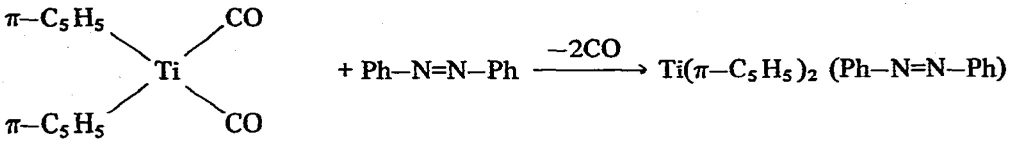
SUMMARY

Reactions of azobenzene with dicarbonyldicyclopentadienyltitanium(II), $Ti(\pi\text{-}C_5H_5)_2(CO)_2$, and dicyclopentadienylvanadium(II), $V(\pi\text{-}C_5H_5)_2$, have yielded the corresponding dicyclopentadienylmetal–azobenzene complexes.

The reactions of transition metal complexes with azo compounds and cleavage of N–N bonds by organometallic reagents are of interest in connection with the problems of dinitrogen coordination and atmospheric N_2 fixation[1]. It has been suggested that the –N=N– function in azo compounds should be capable of forming olefin-like π bonds to transition metals[2].

The very few known azobenzene (Az) complexes such as $Mo(\pi\text{-}C_5H_5)_2(Az)$[3], $Ni(PR_3)_2(Az)$[4] and Ni(t-BuNC)$_2$ (Az)[5], appear to contain the azobenzene as a side-bonded, olefin-type ligand. This was definitely proved, in the case of Ni(t-BuNC)$_2$(Az), by X-ray structure determination[6]. The importance of transition metal organic π complexes in homogeneous catalysis, coupled with the probability that coordination of the simple azo compound diimide (HN=NH) plays a significant role in the nitrogen fixation process, has prompted us to report the synthesis and properties of the $Ti(\pi\text{-}C_5H_5)_2(Az)$ and $V(\pi\text{-}C_5H_5)_2(Az)$ complexes.

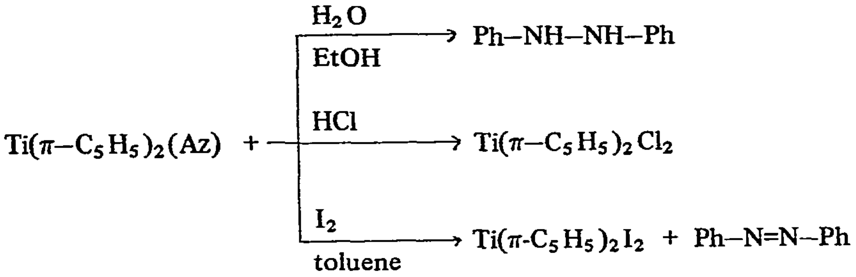
Dicarbonyldicyclopentadienyltitanium(II), $Ti(\pi\text{-}C_5H_5)_2(CO)_2$[7], (I), reacts during two days at room temperature with azobenzene as represented in Eqn. (1), to give black-maroon crystals of (II) (ca. 80%). The product is thermally stable, soluble in aromatic hydrocarbons, and easily hydrolysable. The elemental analysis and mol.wt. determination in benzene (found 375, calcd. 360) indicated a mononuclear titanium complex. This was characterised by its IR and NMR spectra; τ (C_6D_6) 2.6–3.5 ppm (10 H, m, Ph) and 4.24 ppm (10 H, s, C_5H_5).



(1)

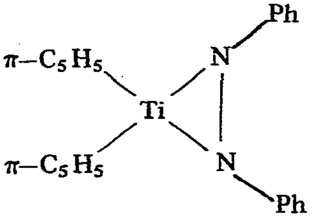
(I) (II)

In order to provide some insight into the nature of (II) the reactions shown in Eqn. (2) were studied. All the products of these reactions were obtained in high yield (ca. 80%).

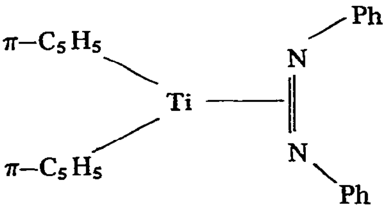


(2)

Bonding in the azobenzenetitanium complex (II) can be considered in terms of two limiting situations: a σ-bonded three-membered ring, (A), or a system, (B), in which the nitrogen atoms remain essentially sp^2 hybridised, and the π^* low-energy orbital allows back-bonding from titanium.

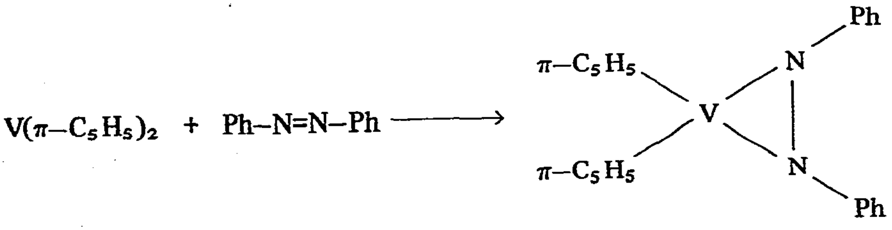


(A)



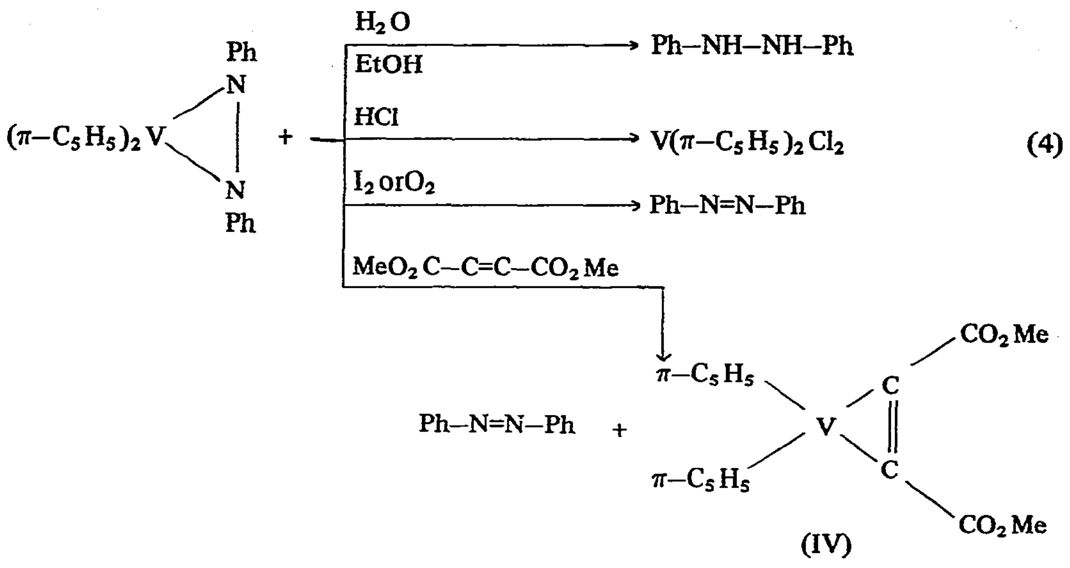
(B)

Our results do not enable us to distinguish definitely between these two limiting descriptions. On the other hand, the fact that hydrolysis of (II) gives hydrazobenzene leads us to suggest (A) as the most likely formulation so that Eqn. (1) can be regarded as an oxidative addition to (I)[8]. Vanadocene, $V(\pi\text{-}C_5H_5)_2$[9], reacts during one day with azobenzene in toluene at room temperature to give black-maroon crystals of (III) (ca. 80%).



(3)

(III)



(4)

Elemental analysis, mol-wt. determination in benzene (found 350, calcd. 363) and magnetic moment at 292 K (μ_{eff} 1.77 BM) indicated a mononuclear vanadium–azobenzene complex. (III) is thermally stable, soluble in aromatic hydrocarbons, and enters readily into several oxidative, hydrolytic and displacement reactions (Eqn. 4). All the products indicated in Eqn (4) are obtained in high hield (ca. 80%)

Reactions (2) and (4) were primarily carried out in order to exclude *ortho*-metalated structures for (II) and (III).

The similarity, from chemical bonding considerations, of (III) to the stoichiometrically analogous $V(\pi\text{-}C_5H_5)_2$ ($MeO_2C–C≡C–CO_2Me$) (IV)[10], is evident.. Moreover, treatment of (III) with $MeO_2C–C≡C–CO_2Me$ gave quantitatively (IV) and azobenzene. In this context it seems of interest to compare the $d\pi$-acceptor properties of an –N=N– linkage in, *e.g.*, azobenzene[5] with those of an olefin or acetylene. The two limiting bonding schemes discussed for (II) can also be used for the azobenzene-vanadium complex (III).

The azobenzene complexes (II) and (III) may provide model intermediates for the reduction of nitrogen–nitrogen multiple bonds catalysed by titanium(II) and vanadium(II) complexes[11].

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