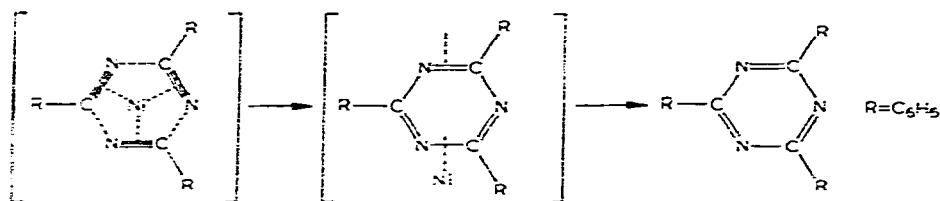


Trimerization of benzonitrile to *sym*-triazine on degassed Raney Nickel surfaces

Alkyl and aryl cyanides form a large number of complexes when added to a nickel halide^{1,2} or generally any metal halide³. The Lewis base character of the alkyl/aryl cyanides can arise either by donation of the π -electrons of the $C\equiv N$ triple bond or the "lone pair" localized on the nitrogen. X-ray^{4,5} and infrared^{6,7} studies suggest that in all³ complexes isolated thus far, bonding is of the latter type. When these alkyl cyanide complexes are heated, linear conjugated polymers of the type $[-CR=N-]_n$ are formed^{8,9}.

When an excess of freshly distilled benzonitrile was refluxed under dry nitrogen with degassed Raney Nickel¹⁰, a yellow, nickel-containing complex separated out. The empirical formula corresponded approximately to $(C_6H_5CN)_3Ni$, but all attempts to obtain it analytically pure failed. Recrystallization of this composition from glacial acetic acid yielded triphenyltriazine. No triphenyltriazine was isolated in the absence of Raney Nickel.

Zerovalent nickel is known to be a very effective catalyst for the cyclomerization of acetylene^{11,12} and diolefins¹³. Cyclomerization of acetylene and diolefins to six-, eight- and twelve-member rings can be best understood¹¹⁻¹³ if one assumes π or π -allyl complex formation around the template nickel. π -Complex formation places a higher p -contribution on the carbon atoms of acetylene which facilitates the re-hybridization $sp \rightarrow sp^2$. The π -bonded acetylene assumes thereby the reactivity of a biradical which tri- or tetramerizes depending upon the stereochemistry and the ligands present in this complex. A similar cyclomerization mechanism operates in all probability in the trimerization of benzonitrile:



It is of interest to note that apparently the only other transition metal complex which cyclomerized benzonitrile to triphenyltriazine is $Fe(CO)_5$ ¹⁴ which interestingly enough also cyclomerized acetylene to benzene and cyclooctatetraene¹⁵. This suggests, as in the case of Raney Nickel, π -complex formation with the $C\equiv N$ triple bond rather than coordination to nitrogen as observed for the group VI transition metal carbonyls¹⁶. The current experiments seem to indicate for the first time that cyclo-oligomerization using Ni^0 may not be limited to triple bonds and conjugated double bonds containing *solely* carbon.

Experimental

Raney Nickel was prepared according to the procedure of Monzingo *et al.*¹⁷. Two teaspoons full (about 6 g) of Raney Nickel were dried in nitrogen under 0.1 mm Hg vacuum until all ethyl alcohol was removed. Without admission of air, 100 ml of

dry (freshly distilled from P_2O_5) benzonitrile was added and the reaction mixture was refluxed for two days. The Raney Nickel was filtered and the filtrates were concentrated *in vacuo*, yielding 2.5 g of a yellow residue decomposing at about 265–270°. A maximum conversion of 9.0 g to the yellow complex was achieved after 10 days refluxing. (Found: Ni, 9.0–11.2. $C_{21}H_{15}N_3Ni$ calcd.: N, 15.95 %.)

This yellow residue was recrystallized from glacial acetic acid yielding long needles of triphenyltriazine, m.p. 228–230°. (Found: C, 81.80; H, 4.85; N, 13.62. $C_{21}H_{15}N_3$ calcd.: C, 81.53; H, 4.89; N, 13.58 %.) The infrared spectrum of this specimen was identical with that of triphenyltriazine and the sample did not depress the melting point of triphenyltriazine upon admixture.

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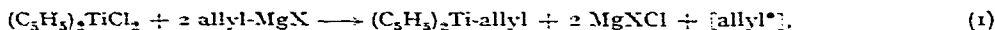
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PRELIMINARY NOTES

A novel synthesis of allyldicyclopentadienyltitanium(III) complexes

Allyldicyclopentadienyltitanium(III)^{1,2} and some methylallyl and dimethylallyl homologues² have previously been prepared by reaction of 1 mole of dicyclopentadienyltitanium(IV) dichloride with 2 moles of the (methyl)allyl Grignard reagent in ether or tetrahydrofuran solution:



where allyl = C_3H_5 , C_4H_7 or C_5H_9 ; and X = Cl or Br.

The extremely air-sensitive compounds $(C_5H_5)_2Ti\text{-allyl}$ are monomeric; they have one unpaired electron per molecule. Evidence has been presented, indicating that

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