

Preliminary communication

Insertion of tetracyanoethylene into transition metal-carbon σ -bonds

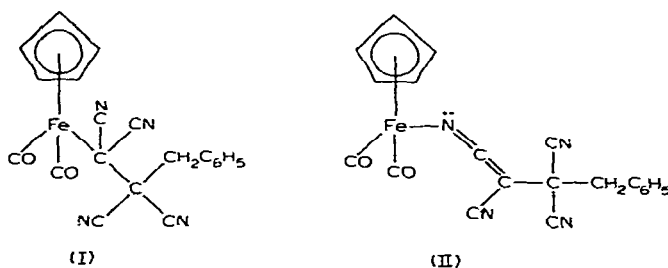
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Studies on sulfur dioxide insertion of transition-metal alkyl carbonyl complexes revealed that accumulation of negative charge at the metal promotes the rate of these reactions¹. Such an increase in rate is readily explicable on the assumption that SO_2 functions as an electrophile toward the metal. To elucidate further this type of behavior we have investigated reactions of a known electrophilic reagent, tetracyanoethylene, with several alkyls of π -cyclopentadienylchromiumnitrosyl, ironcarbonyl, and molybdenum-carbonyl.

Although insertion of tetracyanoethylene into an iridium-hydrogen bond has been observed in a recent study², the literature contains no reports of complexes derived from addition of M-R moieties to $(\text{NC})_2\text{C}=\text{C}(\text{CN})_2$. We find that the reaction between equimolar amounts of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$ and $(\text{NC})_2\text{C}=\text{C}(\text{CN})_2$ in dichloromethane at 25° for 9 h yields two products which are readily separable by alumina chromatography and can be purified by crystallization. Chemical analyses and molecular weight measurements indicate formulae consistent with $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{C}_6\text{N}_4)\text{CH}_2\text{C}_6\text{H}_5$ for both complexes.



The yellow isomer, obtained in 12% yield, exhibits the following salient features. In the IR spectrum, there are strong carbonyl stretching absorptions at 2062 and 2017 cm^{-1} and a weak-intensity CN stretching band at 2217 cm^{-1} ; the ^1H NMR spectrum consists of signals at τ 2.30(C_6H_5), 4.44(C_5H_5), and 6.15(CH_2). These data support structure (I), which is derived from 1,2-insertion of $(\text{NC})_2\text{C}=\text{C}(\text{CN})_2$ into the $\text{Fe}-\text{CH}_2\text{C}_6\text{H}_5$ bond.

The IR spectrum of the red isomer, which was isolated in *ca.* 42% yield, shows the CO stretching bands at 2073 and 2034 cm^{-1} , a CN stretch at 2206 cm^{-1} , and a strong absorption at 2151 cm^{-1} . In the 1350–1200 cm^{-1} region, there is a strong band at 1296 cm^{-1} . The last two absorptions have been assigned to the asymmetric and symmetric N=C=C stretches; bands of similar intensity and frequency have been observed for dicyano-ketenimine³ and for a number of complexes containing M–N=C=C(CN)₂ bonds^{4, 5}. From this evidence, corroborated by the ¹H NMR data - τ 2.41(C₆H₅), 4.68(C₅H₅), and 6.56(CH₂) - we propose structure(II) for the red complex.

Both isomers are stable with respect to interconversion in dichloromethane at 25°, thus demonstrating that their formation from C₅H₅Fe(CO)₂CH₂C₆H₅ and (NC)₂C=C(CN)₂ almost certainly involves two different reaction paths.

Similarly, other alkyl complexes - C₅H₅Fe(CO)₂R (R = CH₃ and C₂H₅), C₅H₅Fe(CO)[P(C₆H₅)₃]CH₂C₆H₅, C₅H₅Cr(NO)₂CH₂C₆H₅, and C₅H₅Mo(CO)₂[P(C₆H₅)₃]CH₃ - afford analogous isomeric insertion products when allowed to react with tetracyanoethylene under comparable conditions.

The foregoing reactions represent a rare example of insertion of an olefin into transition metal-alkyl bonds which proceeds at ambient temperatures and results in stable, readily isolable products. Considerable interest and significance attach to such processes because of their proposed occurrence in the polymerization of olefins by Ziegler-Natta and other transition metal catalysts⁶. Many features of the reactions described herein render them well suited for a detailed study in the framework of a broader investigation of such olefin insertions.

We are continuing to examine the systematics and the scope of these tetracyanoethylene and other related reactions and will report full details later.

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