

Polycyanovinyl, Dicyanomethylenecarbene, and Dicyanomethylene Derivatives of Metal Carbonyls

Sir:

Known transition metal complexes of cyanocarbons¹ can be classified into one of the following three types: (1) oxidative addition products involving reactions of tetracyanoethylene, dicyanoacetylene, and similar unsaturated cyanocarbon systems with transition metal derivatives such as [(C₅H₅)₃P]₂Ir(CO)Cl, in which the metal atom is in a relatively low oxidation state;²

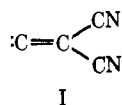
of the extremely nucleophilic⁷ anion⁸ [C₅H₅Fe(CO)₂]⁻. However, substitution of cyano groups for the vinyl hydrogens in vinylic halides enhances greatly the reactivity of the carbon-halogen bond such that the polycyanovinyl halides (NC)₂C=CHCl,⁹ (NC)₂C=C(CN)Cl,¹⁰ and (NC)₂C=CCl₂¹¹ react easily with metal carbonyl anions of even moderate nucleophilicity⁷ such as Mn(CO)₅⁻ and C₅H₅M(CO)₃⁻ (M = Mo and W). These reactions make a wide range of polycyanovinyl transition metal derivatives of structural types II (X = H, Cl, and CN) and III (X = H

Table I. Some Polycyanovinyl Derivatives of Transition Metals

Compound ^a	Color	Mp, °C	Yield, ^b %	Infrared spectra ^c	
				ν(CN)	ν(CO)
A. 2,2-Dicyanovinyl Derivatives					
(NC) ₂ C=CHMo(CO) ₃ C ₅ H ₅	Yellow	Dec 127	37	2233 (m), 2226 (m)	2055 (s), 1971 (vs)
(NC) ₂ C=CHW(CO) ₃ C ₅ H ₅	Yellow	170-171	31	2235 (s), 2227 (s)	2053 (s), 1957 (vs)
(NC) ₂ C=CHMn(CO) ₅	White	Dec 155	36	2243 (m), 2233 (m)	2140 (s), 2050 (s)
(NC) ₂ C=CHFe(CO) ₂ C ₅ H ₅	Yellow	115-116	32	2234 (s), 2223 (s)	2053 (s), 2002 (s)
B. Tricyanovinyl Derivatives					
(NC) ₂ C=C(CN)Mo(CO) ₃ C ₅ H ₅	Yellow-brown	133 dec	37	2231 (m), 2209 (w), 2190 (w)	2068 (w), 1983 (vs)
(NC) ₂ C=C(CN)W(CO) ₃ C ₅ H ₅	Orange	Dec 125	9	2206 (s), 2187 (s)	2027 (s), 1956 (s)
(NC) ₂ C=C(CN)Mn(CO) ₅	Pale yellow	141-142 dec	84	2238 (m), 2197 (w)	2149 (w), 2064 (vs)
C. 1-Chloro-2,2-dicyanovinyl Derivatives					
(NC) ₂ C=C(Cl)Mo(CO) ₃ C ₅ H ₅	Yellow	134-136 dec	89	2227 (m)	2063 (s), 1981 (vs)
(NC) ₂ C=C(Cl)W(CO) ₃ C ₅ H ₅	Yellow	Dec ~132	91	2225 (m)	2056 (s), 1965 (vs)
(NC) ₂ C=C(Cl)Mn(CO) ₅	Yellow	133-135 dec	42	2229 (m)	2143 (s), 2056 (vs) 1990 (s)

^a All of these compounds gave correct analyses for four elements. ^b These yields were obtained by reaction of the sodium salt of the metal carbonyl anion with the polycyanovinyl chloride in tetrahydrofuran at -78° followed by stirring for several hours at room temperature. ^c CH₂Cl₂ solution.

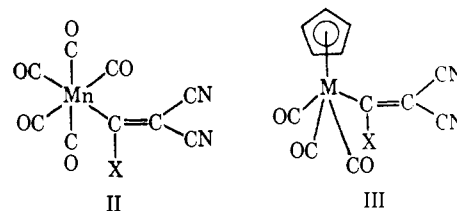
(2) metal π complexes of tetracyanoethylene such as C₂(CN)₂Cr(CO)₅;³ (3) metal carbonyl tricyanomethanide derivatives such as C₅H₅Fe(CO)₂C(CN)₃.⁴ This communication describes the synthesis of the following three new types of metal carbonyl cyanocarbon derivatives: (1) compounds with a transition metal σ-bonded to an unsaturated cyanocarbon system; (2) transition metal derivatives of the novel carbene dicyanomethylenecarbene (I); (3) a dicyanomethylene metal carbonyl



derivative. The dicyanomethylenecarbene ligand I is of particular interest in being derived from carbon monoxide by replacement of the oxygen atom with a dicyanomethylene group. Previous work⁵ has suggested an electronic similarity between the oxygen atom and the dicyanomethylene group.

Vinylic halides normally are unreactive toward metal carbonyl anions.⁶ Thus vinyl chloride does not react with most metal carbonyl anions and reacts only to a very limited extent (~2%) with the sodium salt

Cl, and CN; M = Mo and W) readily available for the first time. The properties of the compounds of this type which have been prepared are summarized in Table I.



The reactions of the dichloride (NC)₂C=CCl₂¹¹ with the less nucleophilic metal carbonyl anions Mn(CO)₅⁻ and C₅H₅M(CO)₃⁻ (M = Mo and W) resulted in the replacement of only one chlorine atom with the transition metal carbonyl group to give the compounds (NC)₂C=C(Cl)Mn(CO)₅ (II, X = Cl) and (NC)₂C=C(Cl)M(CO)₃C₅H₅ (III, X = Cl; M = Mo, and W) (Table I). However, the reaction of (NC)₂C=CCl₂ with the sodium salt of the extremely nucleophilic⁷ anion C₅H₅Fe(CO)₂⁻ in tetrahydrofuran solution was more complex. Extensive coupling to

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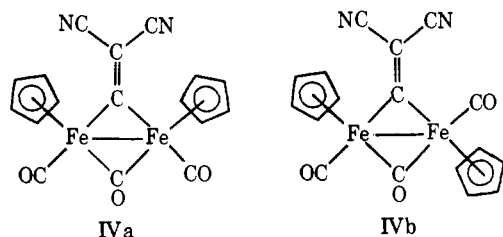
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form $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ was observed. However, two isomeric compounds of composition¹² $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{C}=\text{C}(\text{CN})_2]$ were also isolated although in very low yield. These could be separated by repeated chromatography on an alumina column using as solvents various mixtures of hexane and dichloromethane. The less strongly adsorbed isomer of $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{C}=\text{C}(\text{CN})_2]$, isolated in up to 0.5% yield, was a red-violet apparently air-stable solid, dec pt $\sim 255^\circ$, which exhibited in its infrared spectrum (CH_2Cl_2 solution) a single $\nu(\text{CN})$ frequency at 2214 cm^{-1} (m), a single terminal metal $\nu(\text{CO})$ frequency at 1987 cm^{-1} (vs), and a single bridging metal $\nu(\text{CO})$ frequency at 1827 cm^{-1} (s). The more strongly adsorbed isomer of $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{C}=\text{C}(\text{CN})_2]$, isolated in up to 2.7% yield, was a red-orange apparently air-stable solid, dec pt $\sim 260^\circ$, subliming unchanged at 150° (0.05 mm), which exhibited in its infrared spectrum (CH_2Cl_2 solution) a single $\nu(\text{CN})$ frequency at 2217 cm^{-1} (m), terminal metal $\nu(\text{CO})$ frequencies at 2031 (vs) and 1991 cm^{-1} (s), and a single bridging metal $\nu(\text{CO})$ frequency at 1828 cm^{-1} (s). The infrared spectra of both $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{C}=\text{C}(\text{CN})_2]$ isomers also exhibited a strong band at 1480 cm^{-1} (KBr pellet) assigned to the $\nu(\text{C}=\text{C})$ frequency of the complexed dicyanomethylenecarbene ligand. This assignment is supported by the failure to find a comparable band in the infrared spectrum of either $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ or $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{C}(\text{CN})_2$ (see below). The proton nmr spectrum of each $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{C}=\text{C}(\text{CN})_2]$ isomer exhibits a single sharp C_5H_5 resonance around τ 4.97 indicating that in each isomer both cyclopentadienyl rings, and hence the groups surrounding each iron atom, are equivalent.

On the basis of their infrared and proton nmr spectra, we formulate the two $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{C}=\text{C}(\text{CN})_2]$ isomers as IVa and IVb both containing a



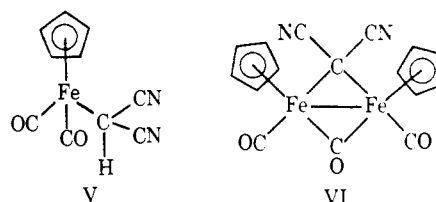
bridging dicyanomethylenecarbene ligand and differing only in cis or trans stereochemistry of the nonbridging groups (carbonyl and cyclopentadienyl) bonded to each iron atom. Similar cis-trans isomerism in $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ has been established.¹³ The less strongly adsorbed red-violet isomer of $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{C}=\text{C}(\text{CN})_2]$ is assigned the trans configuration IVb, since it exhibits only one terminal metal $\nu(\text{CO})$ frequency similar to the trans isomer of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$.¹³ The following observations in the infrared spectra of the $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{C}=\text{C}(\text{CN})_2]$ isomers suggest that the dicyanomethylenecarbene ligand is a stronger π acceptor than even the very strong π acceptor carbon monoxide: (1) the higher value of the bridging $\nu(\text{CO})$

(12) These compounds were characterized by correct analyses for at least four elements. In addition, the bimetallic derivatives were characterized by correct molecular weight determinations in benzene solution.

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frequency in each $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{C}=\text{C}(\text{CN})_2]$ isomer ($1827 \pm 1\text{ cm}^{-1}$) than that of the bridging $\nu(\text{CO})$ frequency in $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ (1794 cm^{-1});¹⁴ (2) the very low value (1480 cm^{-1}) of the $\nu(\text{C}=\text{C})$ frequency in the dicyanomethylenecarbene ligand suggesting a very large amount of electron donation from the iron atom into the antibonding orbitals of this carbon-carbon double bond. We are currently investigating the preparations of metal complexes with terminal dicyanomethylenecarbene ligands in order to define in further detail the chemical and spectroscopic properties of metal complexes of this unusually strong π acceptor.

In a further attempt to prepare related compounds, the reaction of dibromomalononitrile¹⁵ with $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ in tetrahydrofuran solution was investigated. In addition to $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Br}$ and $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$, the following cyanocarbon cyclopentadienyliron carbonyl derivatives were isolated in low yield after chromatography on an alumina column: (1) yellow $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}(\text{CN})_2\text{H}$ (V), mp $150.5\text{--}151.5^\circ$, obtained



in 2.5% yield from the reaction of dibromomalononitrile with $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and also from the reaction of monobromomalononitrile with $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ (this compound was identified by proton nmr resonances in CDCl_3 solution at τ 4.92 and 7.73 of relative intensities 5:1); (2) brown $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{C}(\text{CN})_2$ (VI), dec pt $\sim 245^\circ$, obtained in 0.6% yield from the reaction of dibromomalononitrile with $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and characterized by its elemental analyses, molecular weight determination, infrared spectrum, and proton nmr spectrum. The infrared spectrum of $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{C}(\text{CN})_2$ (CH_2Cl_2 solution) exhibited a single $\nu(\text{CN})$ frequency at 2190 cm^{-1} (m), two terminal metal $\nu(\text{CO})$ frequencies at 2026 (s) and 1987 cm^{-1} (s), and a single bridging metal $\nu(\text{CO})$ frequency at 1831 cm^{-1} (s). The infrared spectrum of $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{C}(\text{CN})_2$ (VI), unlike that of either $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3[\text{C}=\text{C}(\text{CN})_2]$ isomer IVa and IVb, did not exhibit a $\nu(\text{C}=\text{C})$ band around 1480 cm^{-1} (KBr pellet). The proton nmr spectrum of $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{C}(\text{CN})_2$ exhibited a single C_5H_5 resonance at τ 5.02. All of these observations are consistent with the formulation of $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{C}(\text{CN})_2$ as VI, the first known dicyanomethylene transition metal complex. Further work on these and related transition metal cyanocarbon complexes is currently in progress.

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