usually, as in crystalline CaODA·$6H_2O$, water molecules are included to satisfy the preferred coordination number of eight for $Ca^{2+}$.

The vibrational spectra of this material cannot unambiguously be interpreted at present to help elucidate its structure, except in one respect. The absence of a 1660-$cm^{-1}$ Raman line rules out the formation of hydrogen bonded dimers between COOH groups of neighboring HODA ligands.[41] Because $Ca(HODA)_2$ very likely provides an illustration of $Ca^{2+}$ binding to both neutral carboxyl and ether oxygen atoms, we are about to carry out the single-crystal X-ray determination of its expectedly interesting structure.[42]

**Acknowledgments.** The authors acknowledge the experimental assistance of M. Becker and K. Littlepage.

[41] Acid dimers are known to display the Raman-active carboxyl stretching vibration at *ca.* 1660 $cm^{-1}$ [N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 258] as we found for solid $H_2ODA$, for example.

[42] NOTE ADDED IN PROOF: We are grateful to Drs. S. H. Whitlow and G. Davey of the Department of Environment, Ottawa, Canada, for communicating to us their X-ray structure data for oxydiacetic acid prior to publication and for permitting us to mention them here. They have determined the acid skeletal conformation to be gauche–gauche in the solid state, in complete accord with the preceding spectral interpretation. During the course of our work, we observed C–C stretching bands only at 890 (vs) and 876 $cm^{-1}$ (m) for this material (the latter probably due to vibrational coupling in the solid phase). Unlike the spectrum of aqueous $H_2ODA$, peaks located near the assigned frequency for the trans–trans acid conformer, *ca.* 940 $cm^{-1}$, were conspicuously absent (*cf.* Table VI and the section on $Ca^{2+}$–$H_2ODA$ complexation).

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# Transition Metal Cyanocarbon Derivatives. I. Polycyanovinyl, Dicyanovinylidene, and Dicyanomethylene Derivatives of Metal Carbonyls from Cyanocarbon Halides and Metal Carbonyl Anions[1,2]

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**Abstract:** Reactions of the sodium salts $NaM(CO)_3C_5H_5$ (M = Mo and W), $NaMn(CO)_5$, and $NaFe(CO)_2C_5H_5$ with the 2,2-dicyanovinyl chlorides $(NC)_2C{=}C(X)Cl$ (X = H, CN, and Cl) in tetrahydrofuran solution give the corresponding polycyanovinyl transition metal derivatives $(NC)_2C{=}C(X)M(CO)_3C_5H_5$ (X = H, CN, and Cl; M = Mo and W), $(NC)_2C{=}C(X)Mn(CO)_5$ (X = H, CN, and Cl), and $(NC)_2C{=}CHFe(CO)_2C_5H_5$ in fair to good yields. Reaction of $NaFe(CO)_2C_5H_5$ with $(NC)_2C{=}CCl_2$ in tetrahydrofuran solution gives low to very low yields of the cis and trans isomers of $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$, which are the first known transition metal complexes of the dicyanovinylidene (dicyanomethylenecarbene) ligand. Reaction of $NaFe(CO)_2C_5H_5$ with $(NC)_2CBr_2$ in tetrahydrofuran solution gives low yields of $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$ containing a bridging dicyanomethylene group and of $(NC)_2CHFe(CO)_2C_5H_5$, the first dicyanomethyl transition metal derivative. The infrared and proton nmr spectra of these new compounds are discussed.

Within the last few years the reactions of metal carbonyl anions with various halogen compounds have been used to prepare a variety of unusual transition metal organometallic compounds.[4] This paper reports the extension of reactions of this type to the synthesis of novel cyanocarbon derivatives of transition metals by reactions of metal carbonyl anions with various cyanocarbon halides, particularly polycyanovinyl chlorides. New cyanocarbon derivatives described in this paper include not only a wide range of polycyanovinyl derivatives of molybdenum, tungsten, manganese, and iron but also the first known compounds with dicyanovinylidene (dicyanomethylenecarbene[5]) ligands bonded to transition metals.

## Experimental Section

Microanalyses were performed by Meade Microanalytical Laboratory, Amherst, Mass., and by Mr. M. L. Kshatriya and Mr. W Swanson of the Microanalytical Laboratory at the University of Georgia. Infrared spectra (Table I) were taken in dichloromethane solutions or potassium bromide pellets and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Proton nmr spectra were taken in $CDCl_3$ solutions and recorded on a Varian HA-100 spectrometer at 100 MHz. Melting points were taken in capillaries and are uncorrected.

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of organometallic compounds, (c) filling evacuated vessels containing organometallic compounds. Alumina for chromatography (80–200 mesh) was used as received from Matheson Coleman and Bell.

**Materials:** Malononitrile and tetracyanoethylene were purchased from Kay-Fries Chemicals, Inc., New York, N. Y. Malononitrile was converted to 2,2-dicyanovinyl chloride ($(NC)_2C{=}CHCl$)[6] and this to 1,1-dichloro-2,2-dicyanoethylene[7] ($(NC)_2C{=}CCl_2$) by the cited published procedures. Tetracyanoethylene was converted to

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[1] For a preliminary communication of this work, see R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **94**, 1784 (1972).

[2] Portions of this work were presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept. 1971, Abstract INOR 160.

[3] Postdoctoral research associate, 1969–1973.

[4] R. B. King, *Accounts Chem. Res.*, **3**, 417 (1970).

[5] The name "dicyanovinylidene," for the carbene ligand $:C{=}C(CN)_2$, seems preferable to the longer name "dicyanomethylenecarbene," used in the preliminary communication (ref 1).

[6] K. Friedrich, *Angew. Chem., Int. Ed. Engl.*, **6**, 959 (1967).

[7] A. D. Josey, C. L. Dickinson, K. C. Dewhirst, and B. C. McKusick, *J. Org. Chem.*, **32**, 1941 (1967).

**Table I.** Infrared Spectra of the New Cyanocarbon Derivatives Prepared in This Work

| Compound | Infrared spectrum,[a] cm$^{-1}$ | | | |
|---|---|---|---|---|
| | $\nu$(CH)[b] | $\nu$(CN)[c] | $\nu$(CO)[c] | $\nu$(C=C)[b] |
| $(NC)_2C{=}CHCl$[d] | 3070 (m) | 2248 (m) | | 1569 (s) |
| $(NC)_2C{=}CHMo(CO)_3C_5H_5$ | 3132 (w), 3114 (w) | 2233 (m), 2226 (m) | 2055 (s), 1971 (vs) | 1474 (m) |
| $(NC)_2C{=}CHW(CO)_3C_5H_5$ | 3132 (w), 3108 (m) | 2235 (m), 2227 (m) | 2053 (s), 1957 (vs) | 1469 (m) |
| $(NC)_2C{=}CHMn(CO)_5$ | 2985 (m) | 2243 (m), 2233 (m) | 2140 (s), 2050 (vs) | 1485 (m) |
| $(NC)_2C{=}CHFe(CO)_2C_5H_5$ | 3132 (w), 3111 (m) | 2234 (m), 2223 (m) | 2053 (s), 2002 (s) | 1452 (m) |
| $(NC)_2C{=}C(CN)Cl$ | | 2244 (m), 2238 (m) | | 1565 (s) |
| $(NC)_2C{=}C(CN)Mo(CO)_3C_5H_5$ | 3100 (m) | 2231 (m), 2209 (w), 2190 (w) | 2068 (s), 1983 (vs) | 1472 (m) |
| $(NC)_2C{=}C(CN)W(CO)_3C_5H_5$ | 3100 (w) | 2228 (m), 2194 (m) | 2057 (s), 1971 (vs) | 1469 (m) |
| $(NC)_2C{=}C(CN)Mn(CO)_5$ | | 2238 (m), 2197 (w) | 2149 (s), 2064 (vs) | 1480 (m) |
| $(NC)_2C{=}CCl_2$ | | 2245 (m) | | 1541 (m) |
| $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ | 3110 (w) | 2226 (m) | 2064 (s), 1981 (vs) | 1450 (m) |
| $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ | 3110 (w) | 2225 (m) | 2056 (s), 1961 (vs) | 1452 (m) |
| $(NC)_2C{=}C(Cl)Mn(CO)_5$ | | 2230 (m) | 2143 (s), 2055 (vs), 1990 (s) | |
| *trans*-$[C_5H_5Fe(CO)_2]_2$ | | | 1954 (s), 1781 (s)[e] | |
| *cis*-$[C_5H_5Fe(CO)_2]_2$ | | | 1998 (s), 1954 (m) 1810 (m),[e] 1777 (s)[e] | |
| *trans*-$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ | 3100 (w) | 2214 (m) | 1987 (s), 1827 (s)[e] | 1481 (m) |
| *cis*-$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ | 3100 (w) | 2216 (m) | 2030 (vs), 1989 (m), 1825 (s)[e] | 1480 (m) |
| $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$ | 3108 (w) | 2190 (m) | 2026 (s), 1987 (s), 1831 (s)[e] | |
| $(NC)_2CHFe(CO)_2C_5H_5$ | 3120 (m), 2954 (m) | 2230 (m) | 2050 (s), 1997 (s) | |
| $(NC)_2CHBr$ | 2968 (m) | 2264 (w) | | |

[a] These infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated against the 1601-cm$^{-1}$ band of polystyrene film. [b] These frequencies were obtained from spectra taken in KBr pellets. [c] These frequencies were obtained from spectra taken in $CH_2Cl_2$ solution. [d] These frequencies were obtained from spectra taken in a 3:1 v/v $CS_2$–$C_6D_5CD_3$ mixture using data reported by J. G. Bullitt, F. A. Cotton, and T. J. Marks, *Inorg. Chem.*, **11**, 671 (1972). [e] Bridging $\nu$(CO) frequency.

tricyanovinyl chloride ($(NC)_2C{=}C(CN)Cl$) by the published procedure.[8] Bromination of malononitrile was used to prepare the halides $(NC)_2CBr_2$[9] and $(NC)_2CHBr$.[10]

The metal carbonyls $CH_3C_5H_4Mn(CO)_3$ (Ethyl Corp., New York, N. Y.), $M(CO)_6$ (M = Mo and W; Pressure Chemical Corp., Pittsburgh, Pa.), and $Fe(CO)_5$ (GAF Corp., New York, N. Y.) were commercial products. The $CH_3C_5H_4Mn(CO)_3$ was converted to $Mn_2(CO)_{10}$ and $Fe(CO)_5$ was converted to $[C_5H_5Fe(CO)_2]_2$ by the published procedures.[11,12] Reactions of the metal hexacarbonyls $M(CO)_6$ (M = Mo and W) with sodium cyclopentadienide in boiling tetrahydrofuran for ~12 hr gave the sodium salts $NaM(CO)_3C_5H_5$ (M = Mo and W).[13,14] Reduction of the bimetallic derivatives $Mn_2(CO)_{10}$ and $[C_5H_5Fe(CO)_2]_2$ with dilute sodium amalgam in tetrahydrofuran gave the sodium salts $NaMn(CO)_5$[15] and $NaFe(CO)_2C_5H_5$.[13,14]

**Preparations of the Polycyanovinyl Metal Carbonyl Derivatives.** A tetrahydrofuran solution of the sodium salt of the corresponding metal carbonyl anion was treated at −78° with a stoichiometric amount of the polycyanovinyl chloride dissolved in tetrahydrofuran. The reaction mixture was allowed to warm to room temperature and stirred at room temperature for at least 1.5 hr. Solvent was then removed from the reaction mixture at 25° (35 mm). The residue was extracted with dichloromethane. Product was generally isolated from the filtered dichloromethane extract by chromatography on alumina in dichloromethane solution followed by crystallization from mixtures of dichloromethane and hexane.

In some cases, chromatography of these reaction mixtures led to highly colored still unidentified metal complexes as decomposition products in addition to the desired polycyanovinyl transition metal derivatives. Thus chromatography of the mixture obtained from the reaction between $NaMo(CO)_3C_5H_5$ and 2,2-dicyanovinyl chloride gave not only the 2,2-dicyanovinylmolybdenum derivative $(NC)_2C{=}CHMo(CO)_3C_5H_5$ but also a more strongly adsorbed deep blue product of variable stoichiometry exhibiting a $\nu$(CN) frequency at 2222 (m) cm$^{-1}$ and $\nu$(CO) frequencies at 1991 (s), 1951 (s), 1916 (s), and 1878 (s) cm$^{-1}$. Chromatography of the tricyanovinyltungsten derivative $(NC)_2C{=}C(CN)W(CO)_3C_5H_5$ gave magenta and blue decomposition products on Florisil and an orange decomposition product on alumina. The tricyanovinylmanganese derivative $(NC)_2C{=}C(CN)Mn(CO)_5$ decomposed completely upon attempted chromatography on alumina. In such cases (indicated below) chromatography was omitted.

The following polycyanovinyl metal carbonyl derivatives were prepared by this general method.

A. $(NC)_2C{=}CHMo(CO)_3C_5H_5$: yellow, dec 127°; subl 100° (0.1 mm); 37% yield; proton nmr $\tau$ 4.36 ($C_5H_5$) and −0.24 (=CH). *Anal.* Calcd for $C_{12}H_6MoN_2O_3$: C, 44.7; H, 1.8; N, 8.7; O, 14.9. Found: C, 44.0; H, 2.0; N, 8.9; O, 15.1.

B. $(NC)_2C{=}CHW(CO)_3C_5H_5$: yellow mp 170–171°; subl 105° (0.1 mm); 31% yield; proton nmr $\tau$ 4.26 ($C_5H_5$) and −0.15 (=CH). *Anal.* Calcd for $C_{12}H_6N_2O_3W$: C, 35.1; H, 1.5; N, 6.8; O, 11.7. Found: C, 34.8; H, 1.5; N, 6.8; O, 11.9.

C. $(NC)_2C{=}CHMn(CO)_5$: white, dec >155°; subl 100° (0.1 mm); 36% yield; proton nmr $\tau$ +0.24 (=CH). *Anal.* Calcd for $C_9HMnN_2O_5$: C, 39.7; H, 0.4; N, 10.3; O, 29.4. Found: C, 40.3; H, 0.8; N, 10.3; O, 30.2.

D. $(NC)_2C{=}CHFe(CO)_2C_5H_5$: yellow, mp 115–116°; subl 100° (0.1 mm); 32% yield; proton nmr $\tau$ 4.92 ($C_5H_5$) and −0.27 (=CH). *Anal.* Calcd for $C_{11}H_6FeN_2O_2$: C, 51.9; H, 2.4; N, 11.0; O, 12.6. Found: C, 51.4; H, 2.8; N, 10.9; O, 13.4.

E. $(NC)_2C{=}C(CN)Mo(CO)_3C_5H_5$: yellow, mp 133° dec; subl 105° (0.1 mm) with dec, 37% yield; proton nmr $\tau$ 4.28 ($C_2H_5$). *Anal.* Calcd for $C_{13}H_5MoN_3O_3$: C, 44.8; H, 1.4; N, 12.1; O, 13.8. Found: C, 44.6; H, 1.6; N, 12.9; O, 13.6.

F. $(NC)_2C{=}C(CN)W(CO)_3C_5H_5$: yellow, dec >167°; subl 130° (0.1 mm); 23% yield after chromatography on Florisil; proton nmr $\tau$ 4.15 ($C_5H_5$). *Anal.* Calcd for $C_{13}H_5N_3O_3W$: C, 35.8; H, 1.2; N, 9.7; O, 11.0. Found: C, 36.1; H, 1.3; N, 9.5; O, 10.0.

G. $(NC)_2C{=}C(CN)Mn(CO)_5$: pale yellow, mp 141–142°; subl 105° (0.1 mm) dec; 84% yield avoiding chromatography.

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*Anal.* Calcd for $C_{10}MnN_3O_5$: C, 40.4; H, 0.0; N, 14.1; O, 26.9. Found: C, 40.4; H, 0.2; N, 14.1; O, 26.9.

H. $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$: yellow, dec >120°; 95% yield avoiding chromatography; proton nmr $\tau$ 4.28 ($C_5H_5$). *Anal.* Calcd for $C_{12}H_5ClMoN_2O_3$: C, 40.4; H, 1.4; N, 7.8; O, 13.5; Cl, 9.8. Found: C, 41.0; H, 2.0; N, 7.6; O, 15.5; Cl, 9.9.

I. $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$: yellow, dec >170°; 91% yield avoiding chromatography; proton nmr $\tau$ 4.16 ($C_5H_5$). *Anal.* Calcd for $C_{12}H_5ClN_2O_3W$: C, 32.4; H, 1.1; N, 6.3; O, 10.8; Cl, 8.0. Found: C, 31.8; H, 1.2; N, 6.0; O, 10.4; Cl, 7.4.

J. $(NC)_2C{=}C(Cl)Mn(CO)_5$: yellow, mp 133–135°; subl 80° (0.2 mm); 43% yield avoiding chromatography. *Anal.* Calcd for $C_9ClMnN_2O_5$: C, 35.2; H, 0.0; N, 9.1; O, 26.1; Cl, 11.4; Mn, 18.0. Found: C, 34.1; H, 0.4; N, 8.2; O, 25.8; Cl, 11.9; Mn, 19.5.

**Isolation of the Two Isomers of $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$.** A solution of 60 mmol of $NaFe(CO)_2C_5H_5$ in 150 ml of tetrahydrofuran was treated with 4.0 g (27 mmol) of 1,1-dichloro-2,2-dicyanoethylene at 0°. The reaction mixture was then stirred for 1 hr at room temperature. Solvent was then removed from the reaction mixture at 25° (35 mm). The residue was extracted with 250 ml of dichloromethane in several portions. The filtered dichloromethane extracts were concentrated to ~50 ml and then chromatographed on a 2.5 × 30-cm alumina column prepared in hexane. Development of the chromatogram with mixtures of dichloromethane and hexane gave the following bands in the indicated order: (1) red-brown containing $[C_5H_5Fe(CO)_2]_2$, (2) yellow-brown containing a small amount of unidentified material, (3) red-orange containing the two isomers of $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$. These bands were eluted with mixtures of dichloromethane and hexane. The product from evaporation of the eluate from the red-orange band was chromatographed a second time on alumina in order to separate the two isomers of $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$. In the second chromatogram a pink band of the trans isomer appeared followed by an orange band of the cis isomer. Each band was eluted with 3:7 dichloromethane–hexane. Each product was purified further by recrystallization from a mixture of dichloromethane and hexane. In this manner 0.03 g (0.3% yield) of red-violet *trans*-$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$, dec ~255°, proton nmr $\tau$ 5.00 ($C_5H_5$), and 0.3 g (2.7% yield) of red-orange *cis*-$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$, dec ~260°, proton nmr $\tau$ 4.97 ($C_5H_5$), were obtained. These compounds could be sublimed at 150° (0.1 mm) with extensive decomposition.

*Anal.* Calcd for $C_{17}H_{10}Fe_2N_2O_3$: C, 50.8; H, 2.5; Fe, 27.9; N, 7.0; O, 11.9; mol wt, 402. Found on trans isomer (red-violet): C, 50.3; H, 3.1; Fe, 27.7; N, 6.6; O, 12.1; mol wt, 404 (osmometer in benzene). Found on cis isomer (red-orange): C, 51.7; H, 3.0; Fe, 27.6; N, 6.8; O, 11.9; mol wt, 405 (osmometer in benzene).

**Attempted Reactions of *cis*-$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$.** The following reactions were attempted with the more abundant cis isomer (red-orange) of $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$.

A. **Iodine.** Reaction of 0.132 g (0.33 mmol) of *cis*-$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ with 0.088 g (0.35 mmol) of $I_2$ in either boiling dichloromethane or boiling chloroform for 2 hr resulted only in recovery of unchanged *cis*-$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ identified by its infrared spectrum. Some unchanged *cis*-$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ was even recovered when the reaction with iodine was carried out in boiling toluene for 5 hr. This last reaction also gave an unidentified brown-black solid insoluble in dichloromethane and toluene but soluble in acetone.

B. **Bromine.** Reaction of 0.03 g of *cis*-$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ with excess bromine in chloroform at room temperature gave a dark brown precipitate and a light brown solution which exhibited no bridging $\nu$(CO) bands but terminal $\nu$(CO) bands at ~2050 and ~2000 $cm^{-1}$ in its infrared spectrum.

C. **Triphenylphosphine.** Reaction of 0.05 g (0.124 mmol) of *cis*-$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ with 0.03 g (0.115 mmol) of triphenylphosphine in boiling benzene gave only a mixture of the cis and trans isomers of $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ which were separated by chromatography on alumina and identified by their infrared spectra. A similar reaction of *cis*-$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ with triphenylphosphine in boiling toluene gave some infrared evidence of triphenylphosphine substitution but the product could not be separated because of the very small quantities available.

**Reaction of $NaFe(CO)_2C_5H_5$ with Dibromomalononitrile.** A solution of 30 mmol of $NaFe(CO)_2C_5H_5$ in ~150 ml of tetrahydrofuran was treated at 0° with 3.3 g (15 mmol) of dibromomalononitrile. The reaction mixture was stirred for about 1 hr while warming to room temperature. Solvent was removed at 25° (35 mm). The residue was extracted with ~200 ml of dichloromethane in three portions. The filtered dichloromethane extracts were concentrated at 25° (35 mm) to a volume of ~50 ml and then chromatographed on a 2.5 × 30-cm alumina column prepared in hexane. The following three bands appeared in the indicated order: (1) a yellow band of unidentified material, (2) a red-brown band of $[C_5H_5Fe(CO)_2]_2$, (3) a red-brown band containing the cyanocarbon derivatives of interest. These bands were eluted with mixtures of dichloromethane and hexane. The product from evaporation of the eluate from the third band was chromatographed again on a 2.5 × 30-cm alumina column. Development of this chromatogram with a mixture of dichloromethane and hexane gave the following bands in the order listed: (1) a yellow band of unidentified material, (2) a red-brown band of $[C_5H_5Fe(CO)_2]_2$, (3) an orange band of unidentified material but free of cyanocarbon groups as indicated by the absence of $\nu$(CN) frequencies in its infrared spectrum, (4) a yellow band containing $(NC)_2CHFe(CO)_2C_5H_5$, (5) a pale red band containing $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$. These bands were eluted with mixtures of dichloromethane and hexane. The products from evaporation of the eluates from the last two bands were crystallized from mixtures of dichloromethane and hexane to give 0.18 g (2.5% yield) of yellow $(NC)_2CHFe(CO)_2C_5H_5$, mp 151–152° dec, proton nmr $\tau$ 4.92 ($C_5H_5$) and 7.73 (CH), and 0.037 g (0.6% yield) of brown $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$, dec >245°, proton nmr $\tau$ 5.02 ($C_5H_5$).

*Anal.* Calcd for $(NC)_2CHFe(CO)_2C_5H_5$ (*i.e.*, $C_{10}H_6FeN_2O_2$): C, 49.6; H, 2.5; N, 11.6. Found: C, 49.6; H, 2.5; N, 11.7. Calcd for $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$ (*i.e.*, $C_{16}H_{10}Fe_2N_2O_3$): C, 49.2; H, 2.6; Fe, 28.7; N, 7.2; mol wt, 390. Found: C, 49.3; H, 3.3; Fe, 28.4; N, 7.1; mol wt, 394 (osmometer in benzene).

**Reaction of $NaFe(CO)_2C_5H_5$ with Bromomalononitrile.** A solution of 40 mmol of $NaFe(CO)_2C_5H_5$ in ~150 ml of tetrahydrofuran was treated at 0° with 5.4 g (37 mmol) of bromomalononitrile (proton nmr $\tau$ 4.96). The reaction mixture was stirred for about 1 hr while warming to room temperature. Solvent was removed at 25° (35 mm). The residue was extracted with ~200 ml of dichloromethane in three portions. The filtered dichloromethane extracts were concentrated at 25° (35 mm) to a volume of ~50 ml and then chromatographed on a 2.5 × 30-cm alumina column prepared in hexane. The following three bands appeared in the indicated order: (1) a yellow band of unidentified material, (2) a red-brown band which gave about 5 g (~70% yield) of $[C_5H_5Fe(CO)_2]_2$, (3) an orange-red band. The product from this last band was rechromatographed. This time the following four bands appeared in the indicated order: (1) a yellow band containing a trace of unidentified material; (2) a red band containing some more $[C_5H_5Fe(CO)_2]_2$; (3) a red band from which 0.03 g of a red-brown solid, apparently $C_5H_5Fe(CO)_2Br$ from its infrared spectrum, was isolated; (4) a yellow band from which 0.15 g (1.5% yield) of the dicyanomethyl derivative $(NC)_2CHFe(CO)_2C_5H_5$, mp 151–152°, was isolated. The infrared and nmr spectra of $(NC)_2CHFe(CO)_2C_5H_5$ prepared from reactions of $NaFe(CO)_2C_5H_5$ with either bromomalononitrile or dibromomalononitrile were identical.

**Ultraviolet Irradiation of $[C_5H_5Fe(CO)_2]_2$ with Tetracyanoethylene Oxides.** A mixture of 1.0 g (2.82 mmol) of $[C_5H_5Fe(CO)_2]_2$, 1.0 g (6.94 mmol) of tetracyanoethylene oxide,[16] and 50 ml of tetrahydrofuran was exposed 2 hr to the ultraviolet irradiation from a Westinghouse H44-4GS 100-W mercury spot lamp placed ~5 cm from the glass reaction vessel. The reaction mixture was then boiled under reflux for 10 hr. The resulting reaction mixture was filtered hot. Solvent was removed from the filtrate at 25° (35 mm). The residue was extracted with ~50 ml of dichloromethane. The filtered dichloromethane extract was chromatographed on a 2.5 × 30-cm alumina column prepared in hexane. After elution of a preliminary light band with 4:1 dichloromethane–hexane the major yellow band was eluted with a 1:20 to 1:10 mixture of tetrahydrofuran and dichloromethane. Evaporation of this eluate at 25° (35 mm) followed by crystallization from a mixture of dichloromethane and hexane and washing with hexane gave 0.08 g (7% yield) of yellow crystalline $C_5H_5Fe(CO)_2CN$, mp 113° (lit.[17] mp 120° dec), infrared spectrum ($CH_2Cl_2$ solution): $\nu$(CN) at 2125 (m) $cm^{-1}$, $\nu$(CO) at 2063 (s), and 2019 (s) $cm^{-1}$ (lit.[17] 2125 (vs), 2060 (vs), and 2020 (vs) in $CHCl_3$ solution).

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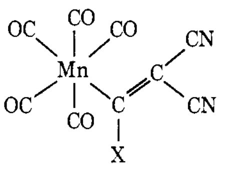
(16) W. J. Linn, *Org. Syn.*, **49**, 103 (1969).

(17) F. A. Cotton, T. S. Piper, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

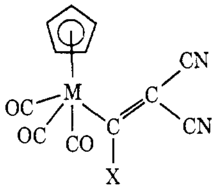
*Anal.* Calcd for $C_8H_5FeNO_2$: C, 47.3; H, 2.5; N, 6.9. Found: C, 46.2; H, 2.5; N, 7.0.

## Discussion

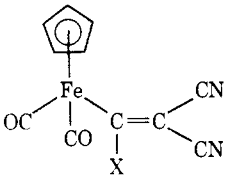
**A. Polycyanovinyl Derivatives.** Vinylic halides are normally unreactive toward metal carbonyl anions.[4] Thus vinyl chloride does not react with most metal carbonyl anions and reacts only to a very limited extent (~2%) with the sodium salt of the extremely nucleophilic[18] anion[19] $[C_5H_5Fe(CO)_2]^-$. However, substitution of cyano groups for the vinyl hydrogens in vinylic halides increases greatly the reactivity of the carbon–halogen bond such that the polycyanovinyl halides $(NC)_2C{=}CHCl$, $(NC)_2C{=}C(CN)Cl$, and $(NC)_2C{=}CCl_2$ react easily with metal carbonyl anions of even moderate nucleophilicity[18] such as $Mn(CO)_5^-$ and $C_5H_5M(CO)_3^-$ (M = Mo and W) to give a wide range of polycyanovinyl derivatives of structural types I (X = H, Cl, and CN), II (X = H, Cl, and CN; M = Mo and W), and III (X = H). In the reactions of polycyanovinyl halides with metal carbonyl anions the following points of interest were observed. (1) The dichloride $(NC)_2C{=}CCl_2$ reacted with the moderately nucleophilic anions $Mn(CO)_5^-$ and $C_5H_5M(CO)_3^-$ (M = Mo and W) with replacement of only one of the two chlorine atoms by the metal carbonyl group. (2) The very nucleophilic anion $C_5H_5Fe(CO)_2^-$ failed to give isolable polycyanovinyl derivatives with the halides $(NC)_2C{=}CCl_2$ and $(NC)_2C{=}C(CN)Cl$ presumably because of side reactions arising from its high reactivity.



I



II



III

The high reactivity of the 2,2-dicyanovinyl halides $(NC)_2C{=}CHCl$, $(NC)_2C{=}C(CN)Cl$, and $(NC)_2C{=}CCl_2$ toward metal carbonyl anions as well as other nucleophiles relates to the electronic similarity[20] between an oxygen atom and a dicyanomethylene group which makes these 2,2-dicyanovinyl chlorides analogs of the very reactive acyl chlorides.

The polycyanovinyl derivatives of types I, II and III prepared in this work were relatively air-stable solids with colors and infrared ν(CO) frequencies similar to those of the corresponding alkyl and perfluoroalkyl derivatives. Most of them could be sublimed under vacuum (~0.1 mm) at temperatures in the range 80–130° with some decomposition. The instability of these compounds upon such vacuum sublimation prevented satisfactory mass spectra from being obtained. Instead trivial decomposition products such as $(C_5H_5)_2Fe$ for the iron compound $(NC)_2C{=}CHFe(CO)_2C_5H_5$, $Mn_2(CO)_{10}$ for the manganese compound $(NC)_2C{=}CHMn(CO)_5$, and $W(CO)_6$ for the tungsten compound $(NC)_2C{=}CHW(CO)_3C_5H_5$ were observed in attempts to obtain their mass spectra. The polycyanovinyl metal carbonyl derivatives could be crystallized from mixtures of either dichloromethane or tetrahydrofuran with hexane. Many of the polycyanovinyl metal carbonyl derivatives were also purified by chromatography on alumina or Florisil. However, in some cases this led to complete decomposition. In other cases chromatography led to highly colored metal carbonyl derivatives of unknown types which are still under investigation.

The infrared spectra (Table I) of the polycyanovinyl derivatives of types I, II, and III besides exhibiting the expected metal carbonyl ν(CO) frequencies exhibited ν(CN) and ν(C=C) frequencies from the polycyanovinyl group. The ν(C=C) frequencies in these polycyanovinyl–metal carbonyl complexes appeared in the range 1450–1490 $cm^{-1}$ which was about 90–100 $cm^{-1}$ lower than the ν(C=C) frequencies in the corresponding polycyanovinyl halides. This relatively large decrease in the ν(C=C) frequency of a polycyanovinyl group upon bonding directly to a transition metal can be attributed to a reduction of the order of the carbon–carbon "double" bond in the polycyanovinyl group by partial donations of electrons from filled transition metal d orbitals into antibonding orbitals of the carbon–carbon double bond. The strong electron-withdrawing effects of multiple cyano substitution would be expected to make polycyanovinyl ligands strong π acceptors in accord not only with this large decrease in the ν(C=C) frequency in the polycyanovinyl transition metal complexes but also with the relatively high ν(CO) frequencies compared with those of many other metal carbonyl derivatives of the same types.

The reduction in the ν(C=C) frequency from the polycyanovinyl halides to the corresponding metal carbonyl derivatives decreased in the order $RFe(CO)_2C_5H_5$ (III) (largest reduction) > $RM(CO)_3C_5H_5$ (II; M = Mo and W) > $RMn(CO)_5$ (I) (smallest reduction) in accord with the greater competition for the metal electron density offered by the very strongly π-accepting carbonyl groups relative to the less strongly π-accepting cyclopentadienyl ring.

The electron density from the transition metal d orbitals can be transmitted not only into the antibonding orbitals of the carbon–carbon double bond but also into the antibonding orbitals of the carbon–nitrogen triple bond of the cyano substituents in the polycyanovinyl groups. Thus the ν(CN) frequencies at 2238–2248 $cm^{-1}$ in the polycyanovinyl halides decreased by 15–20 $cm^{-1}$ to 2225–2243 $cm^{-1}$ in the corresponding metal carbonyl complexes in accord with the expected effects of some donation of electron density from the filled metal d orbitals into the antibonding orbitals of the carbon–nitrogen triple bonds of these cyano groups. This reduction in the ν(CN) frequency of the polycyanovinyl group upon bonding to a metal carbonyl group was least for the $Mn(CO)_5$ derivatives relative to the $C_5H_5Fe(CO)_2$ and $C_5H_5M(CO)_3$ (M = Mo and W) deriv-

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(18) R. E. Dessy, R. L. Pohl, and R. B. King, *J. Amer. Chem. Soc.*, **88**, 5121 (1966).

(19) M. L. H. Green, M. Ishaq, and T. Mole, *Z. Naturforsch. B*, **20**, 598 (1965).

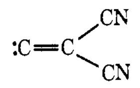
(20) H. Köhler, B. Eichler, and R. Salewski, *Z. Anorg. Allg. Chem.*, **379**, 183 (1970); K. Wallenfels, *Chimia*, **20**, 303 (1966).

atives as was found for the corresponding decrease in the $\nu$(C=C) frequency discussed above. The tricyanovinyl transition metal derivatives (I and II; X = CN) exhibited not only a $\nu$(CN) frequency in the range 2233 ± 5 $cm^{-1}$ like the other polycyanovinyl transition metal derivatives but also a second $\nu$(CN) frequency at 2194 ± 4 $cm^{-1}$ which may be assigned to the 1-cyano group bonded to the same carbon atom as the transition metal since this $\nu$(CN) frequency is not found in the other polycyanovinyl derivatives (I, II, and III; X = H and Cl) which do not have such a cyano group. The reduction by about 45 $cm^{-1}$ of the $\nu$(CN) frequency of this 1-cyano group from tricyanovinyl chloride to the tricyanovinyl transition metal derivatives indicates a larger effect of the metal atom on this cyano group than the reduction of only 15–20 $cm^{-1}$ on the $\nu$(CN) frequency of the 2-cyano groups caused by the metal atom. This is in accord with the closer proximity of the 1-cyano group than the 2-cyano group to the metal atom.

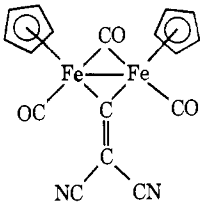
The proton nmr spectra of the polycyanovinyl derivatives of the cyclopentadienylmetal carbonyls (II and III) exhibited the expected singlet resonances from the five equivalent cyclopentadienyl protons. In addition, the 2,2-dicyanovinyl derivatives (I, II, and III; X = H) exhibited a singlet resonance around $\tau$ 0 arising from the single olefinic proton of the 2,2-dicyanovinyl group. This resonance was not only unusually low for an olefinic proton (which generally occurs around $\tau$ 4) but appreciably lower than the olefinic proton resonance in 2,2-dicyanovinyl chloride $(NC)_2C{=}CHCl$, which appeared at $\tau$ +2.19. This indicates strong deshielding of the 2,2-dicyanovinyl proton when this group is bonded to a transition metal. This deshielding effect was noticeably less for the $Mn(CO)_5$ derivative $(NC)_2C{=}CHMn(CO)_5$ (I; X = H) than for the cyclopentadienylmetal carbonyl derivatives $(NC)_2C{=}CHM(CO)_3C_5H_5$ (II; M = Mo and W) and $(NC)_2C{=}CHFe(CO)_2C_5H_5$ (III; X = H) suggesting that it may relate to the tendency of the transition metal group to donate electrons from filled metal d orbitals into suitable antibonding orbitals in the 2,2-dicyanovinyl group.

**B. Dicyanovinylidene Derivatives.** The analogy between the oxygen atom and the dicyanomethylene group[20] makes the dicyanovinylidene ligand (IV) analogous to carbon monoxide. This suggests the existence of a series of metal dicyanovinylidene complexes analogous to the well-known metal carbonyls.[21] A difficulty in the preparation of an extensive series of metal dicyanovinylidene complexes is the present unavailability of the free ligand dicyanovinylidene (IV) as a reagent for reactions with appropriate transition metal compounds.

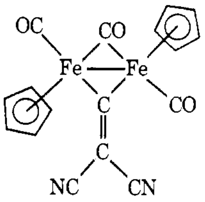
In the absence of free dicyanovinylidene (IV) as a reagent for the preparation of its metal complexes, an alternative route to such metal complexes appeared to be the dehalogenation of 1,1-dichloro-2,2-dicyanoethylene, $(NC)_2C{=}CCl_2$ (*i.e.*, dicyanovinylidene chloride), in the presence of an appropriate transition metal derivative. Since metal carbonyl anions have reducing properties, their reactions with the halide $(NC)_2C{=}CCl_2$ represented a possible route to dicyanovinylidene transition metal complexes.



IV



Va



Vb

The reactions of the metal carbonyl anions $Mn(CO)_5^-$ and $C_5H_5M(CO)_3^-$ (M = Mo and W) with $(NC)_2C{=}CCl_2$ gave the derivatives $(NC)_2C{=}C(Cl)Mn(CO)_5$ (I; X = Cl) and $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (II; X = Cl, M = Mo and W) as discussed above. However, the reaction of the very nucleophilic metal carbonyl anion $C_5H_5Fe(CO)_2^-$ with $(NC)_2C{=}CCl_2$ resulted in the desired dehalogenation reaction to give low to very low yields of two isomers of a dicyanovinylidene complex $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$. These isomers could be separated from each other and from other reaction products, such as $[C_5H_5Fe(CO)_2]_2$, by careful and repeated chromatography on alumina.

The proton nmr spectrum of each of the two $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ isomers exhibited only one singlet resonance around $\tau$ 5.0 indicating that both cyclopentadienyl rings, and hence both iron atoms, must be equivalent. The single dicyanovinylidene ligand thus must bridge the two iron atoms. Therefore, the compounds $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ are closely related to the well-known[17,21–23] $[C_5H_5Fe(CO)_2]_2$ but with a bridging dicyanovinylidene ligand replacing a bridging carbonyl group. Two isomers of $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ (Va and Vb) are possible which correspond to the cis and trans isomers, respectively, of $[C_5H_5Fe(CO)_2]_2$. The less strongly adsorbed and much rarer red-violet isomer of $(C_5H_5)_2Fe(CO)_3[C{=}C(CN)_2]$ is assigned the trans configuration Vb, since it exhibits only one terminal metal $\nu$(CO) frequency similar to the trans isomer of $[C_5H_5Fe(CO)_2]_2$.[23] The more strongly adsorbed red-orange isomer of $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ is then assigned the cis configuration Va since it exhibits two terminal metal $\nu$(CO) frequencies similar to the cis isomer of $[C_5H_5Fe(CO)_2]_2$.[23] The bridging dicyanovinylidene ligand in either isomer of $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ exhibits a $\nu$(CN) frequency at 2215 ± 1 $cm^{-1}$ and a $\nu$(C=C) frequency at 1480 $cm^{-1}$. Both of these frequencies are appreciably below those in similar metal-free cyano olefins such as $(NC)_2C{=}CHCl$ suggesting strong electron donation from iron d orbitals into antibonding orbitals of both the carbon–carbon multiple bond and the carbon–nitrogen multiple bonds in the dicyanovinylidene ligand as was found for the polycyanovinyl transition metal derivatives discussed above.

The unusually high $\pi$-acceptor properties of the carbonyl group in metal carbonyls make of interest an estimation of the $\pi$-acceptor properties of the dicyanovinylidene ligand IV from the spectroscopic properties of the two isomers of $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$. The $\nu$(CO) frequencies of each of the two isomers of

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(21) For a summary of many aspects of metal carbonyl chemistry, see R. B. King, "Transition Metal Organometallic Chemistry: An Introduction," Academic Press, New York, N. Y., 1969.

(22) O. S. Mills, *Acta Crystallogr.*, 11, 620 (1958).

(23) R. F. Bryan, P. T. Greene, D. S. Field, and M. J. Newlands, *Chem. Commun.*, 1477 (1969); J. G. Bullitt, F. A. Cotton, and T. J. Marks, *Inorg. Chem.*, 11, 671 (1972).

$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ were higher by about 30 $cm^{-1}$ than the corresponding $\nu(CO)$ frequencies of the corresponding isomer of $[C_5H_5Fe(CO)_2]_2$ (Table I). This indicates that less electron density is available in the iron d orbitals for donation into the $\pi^*$ antibonding orbitals of the carbonyl ligands in the dicyanovinylidene complexes $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ than in the corresponding carbonyl complexes $[C_5H_5Fe(CO)_2]_2$. The dicyanovinylidene ligand therefore has a higher tendency than the carbonyl ligand to remove electrons from a transition metal. This leads to the conclusion that the dicyanovinylidene ligand is a stronger $\pi$ acceptor than even the very strong $\pi$ acceptor carbon monoxide. This is consistent with the stronger electron-withdrawing characteristics of the dicyanomethylene moiety relative to the oxygen atom which cause other interesting chemical effects such as the very high acidity[24] of cyanocarbon acids relative to the corresponding oxyacids where dicyanomethylene moieties are replaced by oxygen atoms.

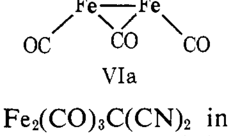
Some preliminary investigations on the chemical reactions of the less rare cis isomer of $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ were made in order to ascertain the effects on the chemical properties when a bridging carbonyl group is changed to a bridging dicyanovinylidene group. The carbonyl analog $[C_5H_5Fe(CO)_2]_2$ is reported to react at or near room temperature with the halogens bromine[25] and iodine[26] to undergo cleavage of the iron–iron bond giving the corresponding halides $C_5H_5Fe(CO)_2X$ (X = Br or I). However, the dicyanovinylidene derivative *cis*-$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ was inert to iodine in boiling chloroform and only slowly destroyed by iodine in boiling toluene. The reaction of *cis*-$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ with bromine in chloroform at room temperature (which is much more reactive than iodine) gave a complex mixture clearly containing no bridging $\nu(CO)$ groups. This suggests that bromine can cleave the iron–iron bond in *cis*-$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$. The reaction of *cis*-$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ with triphenylphosphine in boiling toluene was sluggish and resulted in the recovery of much unchanged $(C_5H_5)_2Fe(CO)_3[C{=}C(CN)_2]$ as well as conversion to a different iron carbonyl derivative which could not be purified and characterized because of the small quantities available. However, no product from this reaction was green in contrast to the reaction of the carbonyl analog $[C_5H_5Fe(CO)_2]_2$ with triphenylphosphine in boiling benzene or toluene[27] which gives the green substitution product $(C_5H_5)_2Fe_2(CO)_3P(C_6H_5)_3$. The small quantities of either isomer of $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ available because of the maximum yield of 3% from its preparation prevented the detailed characterization of the products obtained from its reactions with bromine and with triphenylphosphine.

The isolation of pure cis and trans isomers of the dicyanovinylidene complex $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ (Va and Vb) by chromatography at room temperature in contrast to the cis and trans isomers of $[C_5H_5Fe(CO)_2]_2$ which interconvert at room temperature[23] indicates that substitution of one bridging carbonyl group with a bridging dicyanovinylidene ligand retards appreciably the cis–trans interconversion in this type of system. A cis–trans interconversion in $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ requires a nonbridged isomer of the type $C_5H_5Fe(CO)[C{=}C(CN)_2]X$ (X = $Fe(CO)_2C_5H_5$) as an intermediate. Such a nonbridged intermediate with the extremely strong $\pi$-acceptor terminal dicyanovinylidene ligand (see above) in competition with the strong $\pi$-acceptor carbonyl groups may be so unfavorable that the cis–trans interconversion in $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ cannot readily take place. The difficulty in obtaining compounds of the type $C_5H_5Fe(CO)[C{=}C(CN)_2]X$ with a terminal dicyanovinylidene ligand is also indicated by the lack of reaction of $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ with iodine to give an iodide $C_5H_5Fe(CO)[C{=}C(CN)_2]I$ under conditions where $[C_5H_5Fe(CO)_2]_2$ forms the iodide $C_5H_5Fe(CO)_2I$.[26]

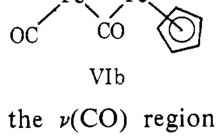
**C. Dicyanomethylene Derivatives.** The preparation of the two isomers of $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ (Va and Vb) with a dicyanovinylidene ligand bridging two iron atoms makes of interest the synthesis of compounds with other cyanocarbene ligands bridging two iron atoms. One of the simplest such cyanocarbene ligands is the dicyanomethylene ligand. The synthesis of a compound of the stoichiometry $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$ was investigated in order to compare its properties with those of the dicyanovinylidene derivatives $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$. For this synthesis, the reaction of $NaFe(CO)_2C_5H_5$ with dibromomalononitrile, $(NC)_2CBr_2$, was used in analogy to the synthesis of the two isomers of $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ from $NaFe(CO)_2C_5H_5$ and $(CN)_2C{=}CCl_2$ as discussed above.

The synthesis of $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$ from $NaFe(CO)_2C_5H_5$ and $(NC)_2CBr_2$ suffers from the halogenating tendencies of $(NC)_2CBr_2$ because of the relatively positive bromine atoms. Indeed, the predominant cyclopentadienyliron carbonyl derivatives obtained from the reaction between $NaFe(CO)_2C_5H_5$ and $(NC)_2CBr_2$ were the coupling product $[C_5H_5Fe(CO)_2]_2$ and the bromide $C_5H_5Fe(CO)_2Br$. However, by careful chromatography of the reaction mixture a trace (~0.6% yield) of the desired $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$ could be obtained.

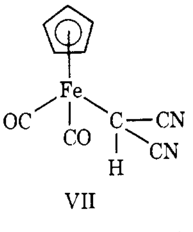
The spectroscopic properties of $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$ were in accord with formulation as the cis isomer VIa (although the presence of the trans isomer VIb as an impurity cannot be rigorously excluded). The proton nmr spectrum of $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$ exhibited only one cyclopentadienyl resonance indicating that both cyclopentadienyl rings, and hence both iron atoms, are equivalent. This indicates that the dicyanomethylene ligand must act as a bridge between the two iron atoms. The infrared spectrum of $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$ in the $\nu(CO)$ region exhibited both terminal and bridging carbonyl frequencies almost



VIa



VIb



VII

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[24] W. J. Middleton, E. L. Little, D. D. Coffman, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, 80, 2795 (1958).

[25] B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 3030 (1956).

[26] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 2, 38 (1956).

[27] R. J. Haines and A. L. du Preez, *Inorg. Chem.*, 8, 1459 (1969).

identical with those of the corresponding dicyanovinylidene complex $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$. This not only confirms the structural similarities of these two complexes but also indicates that the dicyanomethylene ligand has similar strong $\pi$-acceptor properties as the dicyanovinylidene ligand and appreciably stronger $\pi$-acceptor properties than carbon monoxide. The infrared spectrum of $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$ exhibited no frequency in the 1480-cm$^{-1}$ region of the $\nu(C{=}C)$ frequency of the dicyanovinylidene derivative $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ (V) in accord with the absence of a carbon–carbon double bond in $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$.

A second product from the reaction of $(NC)_2CBr_2$ with $NaFe(CO)_2C_5H_5$ was the dicyanomethyl derivative $(NC)_2CHFe(CO)_2C_5H_5$ (VII). The same compound was obtained in likewise low yield from $(NC)_2CHBr$ and $NaFe(CO)_2C_5H_5$. The formulation $(NC)_2CHFe(CO)_2C_5H_5$ (VII) is supported particularly by its proton nmr spectrum which exhibited singlet resonances of relative intensities 5:1 arising from the five $\pi$-cyclopentadienyl protons and the single proton of the dicyanomethyl group, respectively. The formation of $(NC)_2CHFe(CO)_2C_5H_5$ (VII) from $(NC)_2CBr_2$ and $NaFe(CO)_2C_5H_5$ is somewhat anomalous and may involve as the first step the bromination of the tetrahydrofuran solvent with $(NC)_2CBr_2$ to give $(NC)_2CHBr$.

The extremely low yield of the dicyanomethylene derivative $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$ from $(NC)_2CBr_2$ and $NaFe(CO)_2C_5H_5$ prompted some attempts to devise improved preparations of this compound in order to make it available in quantities sufficient for a study of its chemistry. One possible source of a dicyanomethylene group is tetracyanoethylene oxide[28] which undergoes facile fragmentation into carbonyl cyanide and a reactive dicyanomethylene fragment. However, ultraviolet irradiation of $[C_5H_5Fe(CO)_2]_2$ with tetracyanoethylene oxide led to formation of the known[13] cyanide $C_5H_5Fe(CO)_2CN$ rather than to conversion to a dicyanomethyleneiron derivative such as $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$.

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[28] W. J. Linn, O. W. Webster, and R. E. Benson, *J. Amer. Chem. Soc.*, 87, 3651 (1965).

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# Transition Metal Cyanocarbon Derivatives. II. Formation of Metal Complexes with Terminal Dicyanovinylidene Ligands from Reactions of 1-Chloro-2,2-dicyanovinylmolybdenum and -tungsten Derivatives with Trivalent Phosphorus and Related Ligands[1-3]

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**Abstract:** Reaction of $(NC)_2C{=}CHMo(CO)_3C_5H_5$ with triphenylphosphine in boiling benzene proceeds in the normal manner to give yellow $C_5H_5Mo(CO)_2P(C_6H_5)_3CH{=}C(CN)_2$. However, the reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with triphenylphosphine under similar conditions results in the complete substitution of the three carbonyl ligands with two triphenylphosphine ligands to give the red-orange complex $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ containing a terminal dicyanovinylidene (*i.e.*, dicyanomethylenecarbene) ligand. The reaction of the tungsten compound $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ with triphenylphosphine in boiling xylene gives not only the carbonyl-free dicyanovinylidene complex $C_5H_5W[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ but also the cyanocarbon-free complex $C_5H_5W(CO)_2P(C_6H_5)_3Cl$. Similar dicyanovinylidene complexes of molybdenum and tungsten of the general type $C_5H_5ML_2[C{=}C(CN)_2]Cl$ ($M$ = Mo; $L$ = $(C_6H_5)_3As$, $(C_6H_5)_3Sb$, $(CH_3)_2PC_6H_5$, $(CH_3O)_3P$, $(C_2H_5O)_3P$, and $(C_6H_5O)_3P$; $M$ = W; $L$ = $(C_6H_5)_3As$, $(CH_3O)_3P$, and $(C_2H_5O)_3P$) have been prepared by analogous methods. Reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with the saturated di(tertiary phosphine) $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (abbreviated as Pf-Pf) gives either the orange-red monoligate monometallic derivative $C_5H_5Mo(\text{Pf-Pf})_2[C{=}C(CN)_2]Cl$ or the brown biligate monometallic derivative $C_5H_5Mo(\text{Pf-Pf})[C{=}C(CN)_2]Cl$ depending upon the reaction conditions. Reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with the cis olefinic di(tertiary phosphine) *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ gives deep green $C_5H_5Mo(\text{diphos})[C{=}C(CN)_2]Cl$. Reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with the tri(tertiary phosphine) $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ gives the yellow cation $[C_5H_5Mo(\text{triphos})C{=}C(CN)_2]^+$ containing a terminal dicyanovinylidene ligand in the absence of halogen; this cation is most conveniently isolated as its hexafluorophosphate salt. The shift of a chlorine atom from a vinylic carbon atom to the metal atom which leads to the formation of these dicyanovinylidene complexes is discussed.

The first paper of this series[1] described the dehalogenation of $(NC)_2C{=}CCl_2$ with the very nucleophilic metal carbonyl anion[4] $NaFe(CO)_2C_5H_5$ to give the complexes $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ containing

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[1] For part I of this series, see R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **95**, 1811 (1973).

[2] For a preliminary communication of some of this work, see R. B. King and M. S. Saran, *J. Chem. Soc., Chem. Commun.*, 1053 (1972).

[3] Portions of this work were presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972.

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