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References and Notes

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Transition Metal Cyanocarbon Derivatives. III. Novel Chelates and Dicyanoketeneimmonium Derivatives from Hydrolyses, Alcoholyses, and Aminolyses of 1-Chloro-2,2-dicyanovinyl and Tricyanovinyl Derivatives of Molybdenum and Tungsten[1,2]

R. B. KING* and MOHAN SINGH SARAN[3]

Hydrolyses of $(NC)_2C{=}C(CN)M(CO)_3C_5H_5$ (M = Mo and W) in the presence of alumina or triethylamine give orange $C_3(CN)_2NH_2M(CO)_2C_5H_5$ (M = Mo and W). Similar hydrolyses of $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (M = Mo and W) give red $C_3H(CN)(OH)NHM(CO)_2C_5H_5$ (M = Mo and W). The NH and OH but not the CH hydrogens in these two types of complexes can be deuterated with D_2O in tetrahydrofuran at room temperature. Alcoholyses of $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (M = Mo and W) in the presence of sodium hydroxide or sodium alkoxide give the red esters $C_3(CO_2R)(CN)(OR)NHM(CO)_2C_5H_5$ (M = Mo or W, R = CH_3 or C_2H_5). Aminolyses of $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (M = Mo and W) with the secondary amines $(CH_3)_2NH$ and piperidine give the bright yellow dicyanoketeneimmonium derivatives $[R_2NCC(CN)_2]M(CO)_2C_5H_5$ (M = Mo or W; R = CH_3 or 2R = $-(CH_2)_5-$). Infrared, proton, and carbon-13 nmr spectroscopies have been used to elucidate the structures of these new types of complexes. A reaction scheme for the formation of $C_3H(CN)(OH)NHM(CO)_2C_5H_5$ and $C_3(CO_2R)(CN)(OR)NHM(CO)_2C_5H_5$ derivatives from $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ through terminal dicyanovinylidene intermediates of the type $RM(CO)_2[C{=}C(CN)_2](C_5H_5)$ (R = H or CO_2R) is proposed and discussed.

Introduction

The first paper of this series[4] described the preparation of an extensive series of polycyanovinyl transition metal derivatives by the nucleophilic displacement of chloride in polycyanovinyl chlorides with metal carbonyl anions. An example of a reaction of this type was the formation of the tricyanovinyltungsten derivative $(NC)_2C{=}C(CN)W(CO)_3C_5H_5$ (I, M = W) from tricyanovinyl chloride and $NaW(CO)_3C_5H_5$. This tricyanovinyltungsten derivative could be isolated as a yellow crystalline solid by chromatography of the reaction

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

Compd[a]	Infrared spectrum, cm^{-1}			
	ν(CH), ν(NH), ν(OH)[b]	ν(C≡N)[c]	ν(CO)[c]	ν(C=C), ν(C=N)[c]
C$_3$(CN)$_2$NH$_2$Mo(CO)$_2$Cp	3414 m, 3311 m, 3257 w, 3215 m, 3195 m, 3116 w	2209 m, 2190 m	2032 vs, 1966 vs	1653 s, 1603 s
C$_3$(CN)$_2$ND$_2$Mo(CO)$_2$Cp	3110 w, 2564 m, 2434 m, 2393 m	2209 m, 2193 m	2030 vs, 1966 vs	1635 s
C$_3$(CN)$_2$NH$_2$W(CO)$_2$Cp	3420 m, 3329 m, 3269 w, 3232 m, 3119 w, 3111 w	2207 m, 2187 m	2028 vs, 1957 vs	1638 s, 1597 s
C$_3$(CN)$_2$ND$_2$W(CO)$_2$Cp	3104 w, 2565 m, 2430 m, 2390 m	2210 s, 2194 m	2031 vs, 1958 vs	1616 s
C$_3$(CN)$_2$NH$_2$W(CO)(PPh$_3$)Cp	3432 m, 3343 m, 3214 w, 3108 vw, 3057 w	2192 s, 2169 m	1931 vs	1630 s, 1592 s
C$_3$H(CN)(OH)NHMo(CO)$_2$Cp	3393 m, 3310 m, 3220 m, 3190 m, 3110 w, 2950 vvw	2212 s	1975 vs, 1891 vs	1620 s, 1540 m
C$_3$H(CN)(OD)NDMo(CO)$_2$Cp	3100 w, 2955 w, 2549 m, 2388 m	2210 s	1972 vs, 1888 vs	1565 vs
C$_3$H(CN)(OH)NHW(CO)$_2$Cp	3387 m, 3310 m, 3221 m, 3178 vw, 3107 w	2210 m	1964 s, 1882 s	1617 s, 1526 m
C$_3$(CO$_2$Me)(CN)(OMe)NHMo(CO)$_2$Cp	3268 s, 3116 w, 3006 w, 2991 w, 2950 w	2224 s	1976 vs, 1902 vs, 1700 s[d]	1570 s
C$_3$(CO$_2$Et)(CN)(OEt)NHMo(CO)$_2$Cp	3305 s, 3114 vw, 2986 w, 2970 vw, 2935 vw, 2905 vw, 2871 vw	2222 s	1979 vs, 1900 vs, 1693 s[d]	1570 s
C$_3$(CO$_2$Me)(CN)(OMe)NHW(CO)$_2$Cp	3255 s, 3117 w, 3106 w, 2989 w, 2946 w	2223 s	1968 vs, 1888 vs, 1701 s[d]	1552 s
C$_3$(CO$_2$Et)(CN)(OEt)NHW(CO)$_2$Cp	3303 s, 3114 vw, 2988 w, 2970 vw, 2938 vw, 2903 vw, 2871 vw	2224 s	1966 vs, 1887 vs, 1696 vs[d]	1546 s
[Me$_2$NCC(CN)$_2$]Mo(CO)$_2$Cp	3116 w, 3110 w, 2945 w	2213 s	1992 vs, 1919 vs	1590 s
[(CH$_2$)$_5$NCC(CN)$_2$]Mo(CO)$_2$Cp	3105 w, 3005 vw, 2964 w, 2949 m, 2935 w, 2926 w, 2865 m	2218 s	1991 vs, 1916 vs	1573 s
[Me$_2$NCC(CN)$_2$]W(CO)$_2$Cp	3123 w, 3112 w, 3103 w, 2982 vvw, 2939 w	2213 s	1982 vs, 1905 vs	1582 s
[(CH$_2$)$_5$NCC(CN)$_2$]W(CO)$_2$Cp	3104 w, 3000 vvw, 2970 vw, 2952 m, 2932 w, 2860 w	2213 s	1980 vs, 1903 vs	1566 s

[a] Me = methyl, Et = ethyl, Cp = cyclopentadienyl, (CH$_2$)$_5$N = piperidino. [b] KBr pellets. [c] CH$_2$Cl$_2$ solutions. [d] Ester ν(CO).

mixture on Florisil followed by crystallization from mixtures of dichloromethane and hexane. However, if alumina rather than Florisil were used for this chromatography, the yellow tricyanovinyl derivative I (M = W) could not be isolated. Instead a different orange tungsten complex was obtained.[5] Analytical and spectroscopic data indicated this orange tungsten complex to have the stoichiometry C$_3$(CN)$_2$NH$_2$-W(CO)$_2$C$_5$H$_5$ formed by hydrolysis of the tricyanovinyl-tungsten derivative I (M = W) according to

$$(NC)_2C=C(CN)W(CO)_3C_5H_5 + H_2O \rightarrow C_3(CN)_2NH_2W(CO)_2C_5H_5 + CO_2$$
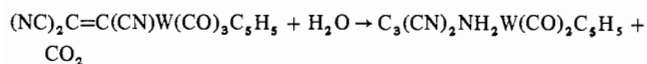
In this reaction one of the cyano groups of the tricyanovinyl derivative becomes a primary amine apparently through hydrolysis followed by reduction by one of the three carbonyl groups.

This observation suggested that reactions of polycyanovinyl transition metal derivatives with protonic reagents such as water, alcohols, or secondary amines might result in the conversion of the polycyanovinyl ligand through destruction of one or more of the cyano groups to give other novel ligands of interest in coordination chemistry. Present indications suggest that reactions of polycyanovinyl transition metal derivatives with such protonic reagents can be extremely complex. This paper describes some reactions of the poly-cyanovinylmolybdenum and tungsten derivatives (NC)$_2$C=C(CN)M(CO)$_3$C$_5$H$_5$ (I, M = Mo and W) and (NC)$_2$C=C(Cl)M(CO)$_3$C$_5$H$_5$ (II, M = Mo and W) with water, alcohols, and secondary amines under basic conditions. Such reactions have yielded as tractable products some unusual chelates characterized by infrared, proton, and carbon-13 nmr spectroscopy as well as the first known dicyanoketene-

immonium transition metal complexes (III, M = Mo or W, R$_2$N = dimethylamino or *N*-piperidino).
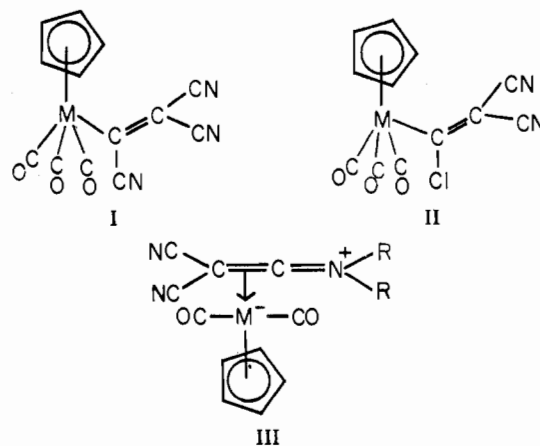
Experimental Section

Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Ga., Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., and the microanalytical laboratory at the University of Georgia. Molecular weights were determined by Schwarzkopf using vapor pressure osmometry in 2-butanone. 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. Each spectrum was calibrated against the 1601-cm^{-1} band of polystyrene film. Proton nmr spectra were taken in CDCl$_3$ or (CD$_3$)$_2$CO solutions and recorded on a Varian HA-100 spectrometer at 100 MHz. Carbon-13 nmr spectra (Table II) were taken in the indicated solvents using a Jeolco PFT-100 spectrometer operating at 25.0336 MHz in

Table II. Carbon-13 Nmr Spectra of the New Cyanocarbon Derivatives Prepared in This Work

Compd	Solvent	Carbon-13 nmr spectrum, δ^a				
		CO	CN	C_5H_5	Other olefinic	Alkyl
$(NC)_2C=C(Cl)Mo(CO)_3Cp$	$(CD_3)_2CO$	234.2, 227.8	116.2, 112.3	98.3	217.3, 100.7	
$(NC)_2C=C(Cl)W(CO)_3Cp$	$(CD_3)_2CO$	222.5, 217.7	116.4, 113.3	97.1	195.7, 101.6	
$C_3(CN)_2NH_2Mo(CO)_2Cp$	$(CD_3)_2CO$	224.3 s	120.2 s, 116.3 s	95.0 d	213.6 s, 188.7 s, 65.2 s	
$C_3(CN)_2NH_2W(CO)_2Cp$	$(CD_3)_2CO$	214.1	121.1, 118.6	93.8	201.0, 177.3, 60.0	
$C_3H(CN)(OH)NHMo(CO)_2Cp$	$(CD_3)_2CO$	249.2 s	115.6 s	94.3 d	247.1 d, 178.0 s, 101.2 s	
$C_3(CO_2Me)(CN)(OMe)NHMo(CO)_2Cp$	$(CD_3)_2CO$	247.5, 168.6	114.1	94.1	233.6, 176.1, 102.1	CH_3: 56.0, 51.9
$C_3(CO_2Et)(CN)(OEt)NHMo(CO)_2Cp$	$(CD_3)_2CO$	247.7, 168.3	114.0	94.1	233.5, 175.8, 102.5	CH_3: 14.8, 14.4 CH_2: 64.7, 64.1
$[Me_2NCC(CN)_2]Mo(CO)_2Cp$	$(CD_3)_2CO$	233.3	120.0	95.4	224.4	CH_3: 47.6, 46.0
$[(CH_2)_5NCC(CN)_2]Mo(CO)_2Cp$	$CDCl_3$	231.1 s	119.6 s	94.4 d	219.6 s	$(CH_2)_5$: 57.6 t, 56.3 t, 26.9 t, 23.8 t
$[(CH_2)_5NCC(CN)_2]W(CO)_2Cp$	$CDCl_3$	220.8	120.2	93.0	208.9	$(CH_2)_5$: 58.9, 55.9, 27.1, 24.0

^{a} Key: s, singlet; d, doublet; t, triplet. Multiplicities were determined by off-resonance proton decoupling.

the Fourier transform mode with proton decoupling and a deuterium lock.[7] A pulse angle of ~45° and pulse intervals of 3-4 sec were used. Carbon-13 nmr chemical shifts (δ) are reported in ppm downfield from internal tetramethylsilane. The carbon-13 nmr data on polycyanovinyl derivatives in a previous paper[8] were quoted as ppm *above* internal carbon disulfide and can be converted to the present scale by the relationship $\delta(Me_4Si) = 192.8 - \delta(CS_2)$. 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 filtered solutions of organometallic compounds, and (c) filling evacuated vessels containing organometallic compounds. Alumina (chromatographic grade F-20) and Florisil for chromatography were used as received from Alcoa Chemicals and Fisher Scientific, respectively. Tetrahydrofuran was redistilled under nitrogen over sodium benzophenone ketyl but dichloromethane was used as received.

The polycyanovinyl–transition metal derivatives were prepared as described in the first paper of this series.

Hydrolysis of $(NC)_2C=C(CN)W(CO)_3C_5H_5$ on Alumina. A mixture of 1.0 g (2.3 mmol) of $(NC)_2C=C(CN)W(CO)_3C_5H_5$, 20 g of chromatography grade alumina, and 100 ml of unredistilled reagent grade dichloromethane was stirred at room temperature for 6 hr. Infrared spectra of the reaction mixture at that time indicated that all of the $(NC)_2C=C(CN)W(CO)_3C_5H_5$ had reacted. The reaction mixture was filtered and the alumina washed with 50 ml of additional dichloromethane followed by 50 ml of acetone in three portions. Removal of solvents from the combined filtrate and washings followed by crystallization from a mixture of dichloromethane and hexane gave 0.2 g (21% yield) of orange $C_3(CN)_2NH_2W(CO)_2C_5H_5$, dec pt >159°.

Essentially the same results were obtained by allowing equimolar amounts of $NaW(CO)_3C_5H_5$ and tricyanovinyl chloride to react in tetrahydrofuran followed by chromatography of the resulting mixture on an alumina column without isolation of $(NC)_2C=C(CN)W(CO)_3C_5H_5$. The orange band from the resulting chromatogram upon elution with tetrahydrofuran gave orange crystalline $C_3(CN)_2NH_2W(CO)_2C_5H_5$ in ~15% yield based on $W(CO)_6$.

Anal. Calcd for $C_{12}H_7N_3O_2W$: C, 35.2; H, 1.7; N, 10.3; O, 7.8; mol wt 409. Found: C, 35.4; H, 1.8; N, 10.2; O, 7.7; mol wt 452. Proton nmr spectrum: NH_2 resonance at τ 1.2 (broad; width at half-height ~20 Hz) and C_5H_5 resonance at τ 4.00 (sharp singlet) in $CDCl_3$ solution.

Hydrolyses of $(NC)_2C=C(CN)M(CO)_3C_5H_5$ (M = Mo or W) in the Presence of Triethylamine. A mixture of 0.694 g (2.0 mmol) of $(NC)_2C=C(CN)Mo(CO)_3C_5H_5$, 1.0 ml (0.73 g, 7.2 mmol) of triethylamine, and 70 ml of dichloromethane was stirred for 17 hr at room temperature. The reaction mixture was then concentrated to ~20 ml and chromatographed on a 2 × 45 cm Florisil column. After elution of weak yellow and light pink bands with mixtures of dichloromethane and hexane (these bands did not contain significant quantities of tractable products), the major yellow-orange band was eluted with 3:1 dichloromethane–hexane. Evaporation of the eluate followed by crystallization from a mixture of dichloromethane and hexane gave 0.16 g (25% yield) of orange $C_3(CN)_2NH_2Mo(CO)_2C_5H_5$, dec pt >145°.

Repetition of this reaction on the same scale using the same procedure except for saturating the dichloromethane with water before

use gave 0.06 g (9.3% yield) of $C_3(CN)_2NH_2Mo(CO)_2C_5H_5$.

Anal. Calcd for $C_{12}H_7MoN_3O_2$: C, 44.9; H, 2.2; N, 13.1; mol wt 321. Found: C, 44.6; H, 2.2; N, 13.1; mol wt 291. Proton nmr spectrum: broad NH_2 resonances (widths at half height ~20 Hz) at τ 0.82 and 1.24 of equal relative intensities and C_5H_5 resonance at τ 4.14 (sharp singlet) in $(CD_3)_2CO$ solution.

Similar treatment of 1.0 g (2.3 mmol) of $(NC)_2C=C(CN)W(CO)_3C_5H_5$ with 1.0 ml (0.73 g, 7.2 mmol) of triethylamine in 75 ml of dichloromethane (not saturated with water) at room temperature for 42 hr gave 0.63 g (67% yield) of $C_3(CN)_2NH_2W(CO)_2C_5H_5$ identified by comparison of its infrared and proton nmr spectra with those of the product obtained by the alumina-catalyzed hydrolysis of $(NC)_2C=C(CN)W(CO)_3C_5H_5$ as described above.

Deuteration of $C_3(CN)_2NH_2M(CO)_2C_5H_5$ (M = Mo or W). The $C_3(CN)_2NH_2M(CO)_2C_5H_5$ derivative (0.15–0.2 g) was stirred at room temperature for several hours with 1 ml of D_2O and 25 ml of anhydrous tetrahydrofuran. Volatile materials were removed under vacuum. The treatment with D_2O and anhydrous tetrahydrofuran was repeated similarly a total of two times for the tungsten derivative and four times for the molybdenum derivative. The orange solid was then crystallized from a mixture of dichloromethane and hexane to give the corresponding $C_3(CN)_2ND_2M(CO)_2C_5H_5$ derivative in 85–90% yield.

The proton nmr spectrum of the $C_3(CN)_2ND_2M(CO)_2C_5H_5$ derivatives (M = Mo or W) did not exhibit the broad resonances around τ 1 assigned to the NH_2 protons in the $C_3(CN)_2NH_2M(CO)_2C_5H_5$ derivatives. Infrared spectra (Table I) also confirmed that complete deuteration had taken place.

The $C_3(CN)_2ND_2M(CO)_2C_5H_5$ derivatives could not be purified by chromatography under normal conditions, since hydrogen exchange back to $C_3(CN)_2NH_2M(CO)_2C_5H_5$ occurred.

Anal. Calcd for $C_{12}H_5D_2MoN_3O_2$: C, 44.6; N, 13.0. Found: C, 45.2; N, 13.2. Calcd for $C_{12}H_5D_2N_3O_2W$: C, 35.1; N, 10.2. Found: C, 35.8; N, 10.3.

Reaction of $C_3(CN)_2NH_2W(CO)_2C_5H_5$ with Triphenylphosphine. A mixture of 0.18 g (0.44 mmol) of $C_3(CN)_2NH_2W(CO)_2C_5H_5$, 0.5 g (1.91 mmol) of triphenylphosphine, and 50 ml of methylcyclohexane was boiled under reflux for 16 hr. After cooling to room temperature, the yellow crystals were filtered, washed with hexane, and dried. Crystallization from a mixture of dichloromethane and hexane gave 0.23 g (81% yield) of yellow $C_3(CN)_2NH_2W(CO)[P(C_6H_5)_3](C_5H_5)$, dec pt >208°.

Anal. Calcd for $C_{29}H_{22}N_3OPW$: C, 54.2; H, 3.4; N, 6.5; O, 2.5. Found: C, 53.4; H, 3.5; N, 6.3; O, 2.7. Proton nmr spectrum ($CDCl_3$ solution): NH_2 resonance too weak to be unequivocally observed, phenyl resonances at τ 2.6 (complex multiplet) and 2.8 (complex multiplet) of approximate relative intensities 4:1, respectively, and C_5H_5 resonance at τ 4.62 (sharp singlet).

Reaction of $(NC)_2C=C(CN)Mo(CO)_3C_5H_5$ with Triphenylphosphine. A mixture of 0.17 g (0.49 mmol) of $(NC)_2C=C(CN)Mo(CO)_3C_5H_5$, 3.0 g (11.4 mmol) of triphenylphosphine, and 60 ml of benzene was boiled under reflux for 21 hr. Solvent was then removed at 35° (35 mm). A solution of the residue in 50 ml of dichloromethane was chromatographed on a 2 × 35 cm Florisil column. The major orange band was eluted with 19:1 dichloromethane–tetrahydrofuran and the eluate evaporated at 25° (35 mm). Crystallization of the residue from a mixture of dichloromethane and

hexane gave 0.08 g (28% yield) of brown $(NC)_2C=C(CN)Mo(CO)_2[P(C_6H_5)_3](C_5H_5)$.

Anal. Calcd. for $C_{30}H_{20}MoN_3O_2P$: C, 62.0; H, 3.5; N, 7.2; O, 5.5. Found: C, 61.0; H, 3.6; N, 7.4; O, 5.6.

Reaction of $(NC)_2C=C(CN)W(CO)_3C_5H_5$ with Triphenylphosphine. A mixture of 0.435 g (1 mmol) of $(NC)_2C=C(CN)W(CO)_3C_5H_5$, 0.6 g (2.29 mmol) of triphenylphosphine, and 60 ml of toluene was boiled under reflux for 18 hr. After cooling to room temperature, the reaction mixture was poured onto a 2×35 cm Florisil column prepared in hexane. After elution with mixtures of hexane and dichloromethane to remove impurities, a yellow band containing unreacted $(NC)_2C=C(CN)W(CO)_3C_5H_5$ was eluted with pure dichloromethane. The following orange-red band of product was then eluted with 9:1 dichloromethane–tetrahydrofuran. Evaporation of this eluate followed by crystallization from a mixture of dichloromethane and hexane gave 0.21 g (31% yield) of orange $(NC)_2C=C(CN)W(CO)_2[P(C_6H_5)_3](C_5H_5)$.

Anal. Calcd for $C_{30}H_{20}N_3O_2PW$: C, 53.8; H, 3.0; N, 6.3; O, 4.8. Found: C, 53.2; H, 3.1; N, 6.2; O, 5.1.

Hydrolyses of $(NC)_2C=C(Cl)M(CO)_3C_5H_5$ (M = Mo and W) on Alumina. A solution of 1–2 g of $(NC)_2C=C(Cl)M(CO)_3C_5H_5$ (M = Mo and W) in 25–80 ml of dichloromethane was stirred with 20–25 g of alumina for 10–15 min. The resulting slurry was chromatographed on a 2×45 cm alumina column. The chromatogram was developed first with mixtures of dichloromethane and hexane and finally with pure dichloromethane. This process led to the formation of an orange band of the corresponding $C_3H(CN)(OH)NHM(CO)_2C_5H_5$ derivative. This orange band was eluted with mixtures of dichloromethane and tetrahydrofuran. Solvent was removed from these eluates at $\sim25°$ (35 mm). The residue was crystallized from a mixture of dichloromethane and hexane to give the pure $C_3H(CN)(OH)NHM(CO)_2C_5H_5$ derivative.

This method was used to prepare the following compounds.

A. $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$: red-orange, dec pt >150°, mp 215–216° (preheated bath); 20% yield; proton nmr in $(CD_3)_2CO$ shows $=CH$ resonance at τ –1.71 (singlet), NH resonance at τ 2.46 (broad, width at half-height ~10 Hz), C_5H_5 resonance at τ 4.50 (singlet), OH resonance not unequivocally observed. *Anal.* Calcd for $C_{11}H_8MoN_2O_3$: C, 42.3; H, 2.6; N, 9.0; O, 15.4; mol wt 312. Found: C, 42.4; H, 2.6; N, 9.1; O, 15.6; mol wt 337.

B. $C_3H(CN)(OH)NHW(CO)_2C_5H_5$: red, dec pt >160°, mp 240–241° (preheated bath); 26% yield; proton nmr in $(CD_3)_2CO$ shows $=CH$ resonance at τ –1.87 (singlet), NH resonance at τ 2.49 (broad, width at half-height ~12 Hz), C_5H_5 resonance at τ 4.36, OH resonance not unequivocally observed. *Anal.* Calcd for $C_{11}H_8N_2O_3W$: C, 33.0; H, 2.0; N, 7.0; O, 12.0. Found: C, 32.5; H, 2.1; N, 7.2; O, 12.0.

Hydrolysis of $(NC)_2C=C(Cl)Mo(CO)_3C_5H_5$ in the Presence of Triethylamine. A mixture of 1.0 g (2.8 mmol) of $(NC)_2C=C(Cl)Mo(CO)_3C_5H_5$, 2.0 ml (1.46 g, 14.4 mmol) of triethylamine, 0.5 ml (0.5 g, 28 mmol) of water, and 100 ml of dichloromethane was stirred at room temperature for 16 hr. The resulting mixture was chromatographed on a 2×45 cm Florisil column. Traces of a reddish compound were first eluted with 3:1 dichloromethane–hexane. The major orange-red band of product was then eluted with pure dichloromethane. Evaporation of the eluate and addition of hexane gave 0.2 g (23% yield) of red-orange $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$ identified by its infrared and proton nmr spectra.

Decreasing the amount of water in this hydrolysis reduced the yield of $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$. Thus if water was not added to the reaction mixture but the dichloromethane merely saturated with water before use, the yield of $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$ fell to 16%. Use of reagent grade solvents without addition of any water reduced the yield of $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$ further to 3%.

Deuteration Studies on $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$. (a) The molybdenum compound $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$ (0.2 g) was stirred for 1 hr with 1 ml of D_2O and 25 ml of anhydrous tetrahydrofuran. Volatile materials were then removed under vacuum. The treatment with D_2O and anhydrous tetrahydrofuran was repeated a total of three times. Crystallization of the orange solid from a mixture of dichloromethane and hexane gave 0.1 g (50% recovery) of $C_3H(CN)(OD)NDMo(CO)_2C_5H_5$. Integration of the greatly attenuated NH proton resonance in this product relative to the $=CH$ and C_5H_5 resonances indicated that this product was about 70% deuterated. Deuteration of the NH and OH groups was also con-

firmed by its infrared spectrum (Table I).

Anal. Calcd for $C_{11}H_6D_2MoN_2O_3$: C, 42.1; N, 8.9. Found: C, 42.8; N, 8.8.

Prolonged treatment (~16 hr) of $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$ with a mixture of D_2O and tetrahydrofuran at room temperature led to complete decomposition.

(b) A mixture of 1.0 g (2.8 mmol) of $(NC)_2C=C(Cl)Mo(CO)_3C_5H_5$, 2.0 ml (1.46 g, 4.4 mmol) of triethylamine, 0.5 ml of D_2O, and 70 ml of dichloromethane was stirred for 20 hr at room temperature. The triethylamine and dichloromethane used for this experiment were dried by previous distillations over sodium hydroxide and P_4O_{10}, respectively. The reaction mixture was chromatographed on a 2×45 cm Florisil column. The orange band of product was eluted with dichloromethane. Evaporation of the eluate followed by crystallization from a mixture of dichloromethane and hexane gave 0.15 g (17% yield) of red-orange $C_3D(CN)(OH)NHMo(CO)_2C_5H_5$. The product was shown to be at least 90% deuterated by integration of the extremely weak resonance at τ –1.7 from the residual methine protons. However, proton nmr and infrared spectroscopy indicated no deuteration of the NH and OH groups.

Alcoholyses of $(NC)_2C=C(Cl)M(CO)_3C_5H_5$ (M = Mo and W) in the Presence of Sodium Hydroxide. A solution of 0.1–0.3 g of sodium hydroxide in 50 ml of methanol or ethanol was treated with 1.0–1.5 g of $(NC)_2C=C(Cl)M(CO)_3C_5H_5$ (M = Mo and W). The reaction mixture became red-orange immediately. After 5–10 minutes solvent was removed under vacuum. A dichloromethane solution of the residue was chromatographed on a 2×35 cm Florisil column. The major red-orange band was eluted with 1:1 tetrahydrofuran–dichloromethane. Evaporation of the eluate at $\sim25°$ (35 mm) followed by crystallization from a mixture of dichloromethane and hexane gave the red $C_3(CO_2R)(CN)(OR)NHM(CO)_2C_5H_5$ derivative (M = Mo or W, R = CH_3 or C_2H_5).

This method was used to prepare the following compounds.

A. $C_3(CO_2CH_3)(CN)(OCH_3)NHMo(CO)_2C_5H_5$: red, dec pt >145°, mp 203–206° (preheated bath); 60% yield; proton nmr in $(CD_3)_2CO$ shows NH resonance at τ 1.0 (broad, barely observable), C_5H_5 resonance at τ 4.58 (singlet), and methyl resonances at τ 5.97 and 6.18 (singlets). *Anal.* Calcd for $C_{14}H_{12}MoN_2O_5$: C, 43.8; H, 3.1; N, 7.3; O, 20.8; mol wt 384. Found: C, 43.7; H, 3.1; N, 7.5; O, 21.3; mol wt 371.

B. $C_3(CO_2C_2H_5)(CN)(OC_2H_5)NHMo(CO)_2C_5H_5$: red, mp 169–171°; 29% yield after repeating the chromatography three times to remove a persistent impurity; proton nmr in $(CD_3)_2CO$ shows NH resonance at τ 1.0 (broad, barely observable), C_5H_5 resonance at τ 4.59 (singlet), ethyl CH_2 resonances at τ 5.65 and 5.72 (overlapping quartets, $J = \sim7$ Hz), and ethyl CH_3 resonances at τ 8.65 and 8.68 (overlapping triplets, $J = \sim7$ Hz). *Anal.* Calcd for $C_{16}H_{16}MoN_2O_5$: C, 46.6; H, 3.9; N, 6.8; O, 19.4; mol wt 412. Found: C, 46.6; H, 3.9; N, 4.0; O, 18.4; mol wt 370.

C. $C_3(CO_2CH_3)(CN)(OCH_3)NHW(CO)_2C_5H_5$: red, dec pt >157°, mp 211–213° (preheated bath); 51% yield; proton nmr in $(CD_3)_2CO$ shows NH resonance at τ 0.7 (broad, barely observable), C_5H_5 resonance at τ 4.47 (singlet), and methyl resonances at τ 5.96 and 6.19 (singlets). *Anal.* Calcd for $C_{14}H_{12}N_2O_5W$: C, 35.6; H, 2.6; N, 5.9; O, 16.9. Found: C, 35.8; H, 2.5; N, 6.1; O, 17.2.

D. $C_3(CO_2C_2H_5)(CN)(OC_2H_5)NHW(CO)_2C_5H_5$: red, mp 187–189°; 8% yield; proton nmr in $(CD_3)_2CO$ shows NH resonance at τ 0.8 (broad, barely observable), C_5H_5 resonance at τ 4.47 (singlet), ethyl CH_2 resonances at τ 5.60 and 5.70 (overlapping quartets, $J = 7$ Hz), and ethyl CH_3 resonances at τ 8.64 and 8.67 (overlapping triplets, $J = 7$ Hz). *Anal.* Calcd for $C_{16}H_{16}N_2O_5W$: C, 38.4; H, 3.2; N, 5.6. Found: C, 38.3; H, 3.5; N, 5.8.

Reactions of the molybdenum derivative $(NC)_2C=C(Cl)Mo(CO)_3C_5H_5$ with alcohols in the presence of the corresponding sodium alkoxide rather than sodium hydroxide gave a 62% yield of the methyl derivative $C_3(CO_2CH_3)(CN)(OCH_3)NHMo(CO)_2C_5H_5$ but only a 5% yield of the corresponding ethyl derivative $C_3(CO_2C_2H_5)(CN)(OC_2H_5)NHMo(CO)_2C_5H_5$ using similar procedures for isolation of the products.

Reaction of $C_3(CO_2CH_3)(CN)(OCH_3)NHMo(CO)_2C_5H_5$ with D_2O in anhydrous tetrahydrofuran for a total of 12 hr similar to the procedure described above for the conversion of $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$ to $C_3H(CN)(OD)NDMo(CO)_2C_5H_5$ did not result in deuteration as shown by the infrared spectrum of the red crystalline product.

Reaction of $(NC)_2C=C(CN)Mo(CO)_3C_5H_5$ with Methanolic

Sodium Hydroxide. A mixture of 1.0 g (2.9 mmol) of $(NC)_2C=C(CN)Mo(CO)_3C_5H_5$, 0.2 g (50 mmol) of sodium hydroxide, and 50 ml of methanol was stirred at room temperature for 2 hr. Solvent was then removed from the reaction mixture at ~25° (35 mm). The residue was extracted with 50 ml of dichloromethane. The dichloromethane extracts were filtered. The filtrate was concentrated to 10 ml and then chromatographed on a 2 × 45 cm Florisil column in hexane solution. The first band (pink) was eluted with 1:1 dichloromethane–hexane. A small amount of $[C_5H_5Mo(CO)_3]_2$ was isolated from this eluate. The second band (yellow) was eluted with 19:1 dichloromethane–tetrahydrofuran. Evaporation of this eluate followed by crystallization from a mixture of dichloromethane and hexane gave 0.08 g (10% yield) of yellow $C_5H_5Mo(CO)_3CN$, dec pt >155°, mp 170–172° (preheated bath); infrared spectrum in CH_2Cl_2 shows $\nu(CN)$ at 2130 (w) cm^{-1}; $\nu(CO)$ at 2068 (s) and 1990 (vs) cm^{-1}; proton nmr in $CDCl_3$ shows $\tau(C_5H_5)$ 4.39. *Anal.* Calcd for $C_9H_5MoNO_3$: C, 39.9; H, 1.9; N, 5.2; O, 17.7. Found: C, 39.6; H, 2.0; N, 5.4; O, 17.7.

Reaction of $(NC)_2C=C(CN)W(CO)_3C_5H_5$ with Methanolic Sodium Hydroxide. A mixture of 1.0 g (2.3 mmol) of $(NC)_2C=C(CN)W(CO)_3C_5H_5$, 0.1 g (25 mmol) of sodium hydroxide, and 75 ml of methanol was stirred for 40 min at room temperature. Methanol was then removed at 25° (35 mm). The residue was extracted with dichloromethane. The filtered dichloromethane extracts were concentrated to ~10 ml and then chromatographed on a 2 × 45 cm Florisil column prepared in hexane. Elution of the first band (yellow) with hexane followed by evaporation of the eluate and low-temperature crystallization of the residue gave 0.09 g (11% yield) of CH_3-$W(CO)_3C_5H_5$ identified by its infrared and proton nmr spectrum. The second band (pink) after elution with 1:1 dichloromethane–hexane gave 0.025 g (3.3% yield) of $[C_5H_5W(CO)_3]_2$ identified by its infrared spectrum. The third band (yellow) after elution with 1:9 tetrahydrofuran–dichloromethane and evaporation of the eluate gave a mixture of unreacted $(NC)_2C=C(CN)W(CO)_3C_5H_5$ and C_5H_5-$W(CO)_3CN$. This mixture was chromatographed on a second 2 × 45 cm Florisil column. Elution of the first band (yellow) with pure dichloromethane gave 0.01 g (1% recovery) of unchanged $(NC)_2$-$C=C(CN)W(CO)_3C_5H_5$. Elution of the second band (bright yellow) with 1:9 tetrahydrofuran–dichloromethane gave 0.18 g (22% yield) of yellow $C_5H_5W(CO)_3CN$ identified by comparison of its infrared spectrum in the $\nu(CN)$ and $\nu(CO)$ regions with that reported[9] in the literature.

Reactions of $(NC)_2C=C(Cl)M(CO)_3C_5H_5$ (M = Mo and W) with Dimethylamine. Gaseous dimethylamine was bubbled for ~15 min into a solution of 1.4–2.0 g of the $(NC)_2C=C(Cl)M(CO)_3C_5H_5$ derivative (M = Mo or W) in 75–80 ml of dichloromethane. Volatile materials were then removed from the red-brown reaction mixture at 25° (35 mm). A solution of the residue in ~15 ml of dichloromethane was chromatographed on a 2 × 45 cm Florisil column. A yellow band appeared followed by a larger red band. The yellow band was eluted with 3:2 dichloromethane–hexane. Evaporation of the eluate followed by crystallization from a mixture of dichloromethane and hexane gave the bright yellow crystalline $[(CH_3)_2NCC(CN)_2]M(CO)_2C_5H_5$ derivative. The more strongly adsorbed red band could be eluted with mixtures of dichloromethane and tetrahydrofuran or with acetone. The complexity of the infrared and proton nmr spectra of the red product suggested that it was a complex mixture; it therefore was not investigated further.

The following $[(CH_3)_2NCC(CN)_2]M(CO)_2C_5H_5$ derivatives were prepared by this method.

A. $[(CH_3)_2NCC(CN)_2]Mo(CO)_2C_5H_5$: bright yellow, mp 169–170°; 4.2% yield; proton nmr in $CDCl_3$ shows C_5H_5 resonance at τ 4.57 (singlet) and CH_3 resonances at τ 6.31 and 6.32 (two very closely spaced singlets of equal relative intensities). *Anal.* Calcd for $C_{13}H_{11}MoN_3O_2$: C, 46.3; H, 3.3; N, 12.4; O, 9.5; mol wt 337. Found: C, 46.4; H, 3.3; N, 12.3; O, 9.4; mol wt 339.

B. $[(CH_3)_2NCC(CN)_2]W(CO)_2C_5H_5$: bright yellow, mp 153–154°; 1.2% yield; proton nmr in $CDCl_3$ shows C_5H_5 resonance at τ 4.47 (singlet) and methyl resonances at τ 6.29 and 6.37 (singlets of equal relative intensities). *Anal.* Calcd for $C_{13}H_{11}N_3O_2W$: C, 36.7; H, 2.6; N, 9.9; O, 7.5. Found: C, 37.3; H, 2.7; N, 9.7; O, 8.1.

Reactions of $(NC)_2C=C(Cl)M(CO)_3C_5H_5$ (M = Mo and W) with Piperidine. A mixture of 3 mmol of the $(NC)_2C=C(Cl)M$-$(CO)_3C_5H_5$ derivative (1.06 g for M = Mo, 1.33 g for M = W), 0.6 ml (0.51 g, 6 mmol) of piperidine, and 80–100 ml of dichloromethane was stirred at room temperature for 15–22 hr. The mixture was

concentrated to 15–20 ml at 25° (35 mm) and then chromatographed on a 2 × 45 cm Florisil column. The first band (weak yellow) was eluted with a mixture of dichloromethane and hexane. This contained a negligible quantity of product and was discarded. The second band (bright yellow—much larger than the first band) was eluted with a mixture of dichloromethane and hexane (~1:1). Evaporation of this eluate followed by crystallization from a mixture of dichloromethane and hexane gave the bright yellow $[(CH_2)_5NCC(CN)_2]M(CO)_2C_5H_5$ derivative. A large red-orange band remained on the column. This could be eluted with mixtures of dichloromethane and tetrahydrofuran or with pure acetone, but infrared and proton nmr spectra suggested that this band was a complex mixture. It was therefore not investigated further.

This method was used to prepare the following compounds.

A. $[(CH_2)_5NCC(CN)_2]Mo(CO)_2C_5H_5$: bright yellow, mp 159–161°; 28% yield; proton nmr in $CDCl_3$ shows C_5H_5 resonance at τ 4.58 (singlet) and CH_2 resonances at τ 5.96 (for 2 CH_2 groups) and 8.17 (for 3 CH_2 groups). *Anal.* Calcd for $C_{16}H_{15}MoN_3O_2$: C, 50.9; H, 4.0; N, 11.1; O, 8.5; mol wt 377. Found: C, 51.4; H, 4.1; N, 11.3; O, 7.9; mol wt 407.

B. $[(CH_2)_5NCC(CN)_2]W(CO)_2C_5H_5$: bright yellow, mp 136–137°; 24% yield; proton nmr in $CDCl_3$ shows C_5H_5 resonance at τ 4.40 (singlet) and CH_2 resonances at τ 5.93 (for 2 CH_2 groups) and 8.20 (for 3 CH_2 groups). *Anal.* Calcd for $C_{16}H_{15}N_3O_2W$: C, 41.3; H, 3.2; N, 9.0; O, 6.9. Found: C, 42.2; H, 3.3; N, 8.8; O, 6.9.

Results

The stoichiometry $C_3(CN)_2NH_2W(CO)_2C_5H_5$ for the orange product obtained by chromatography of $(NC)_2C=C(CN)W(CO)_3C_5H_5$ (I, M = W) on alumina indicates that a hydrolysis has taken place. Attempts to effect a similar hydrolysis of the molybdenum analog $(NC)_2C=C(CN)$-$Mo(CO)_3C_5H_5$ (I, M = Mo) on alumina failed to give a tractable product although there was some evidence by infrared spectroscopy for the analogous $C_3(CN)_2NH_2Mo(CO)_2C_5H_5$ in the product. However, both tricyanovinyl derivatives $(NC)_2C=C(CN)M(CO)_3C_5H_5$ (I) can be converted to the corresponding $C_3(CN)_2NH_2M(CO)_2C_5H_5$ derivatives by reaction with triethylamine in dichloromethane solution. Normal reagent grade chemicals apparently contain enough water for this reaction to take place since addition of water to the reaction mixture was not necessary and even deleterious in the case of the molybdenum compound.

Spectroscopic studies demonstrate that both "extra" hydrogen atoms in the $C_3(CN)_2NH_2M(CO)_2C_5H_5$ are bonded to nitrogen. Thus the only resonances in the nmr spectra besides the sharp singlet cyclopentadienyl resonances in both the molybdenum and tungsten derivatives are one or two broad resonances around τ 1. These can be assigned to hydrogens bonded to nitrogen on the basis of their breadth, which can arise by coupling with the quadrupolar ^{14}N nucleus. Furthermore, off-resonance proton decoupling of the carbon-13 nmr spectrum of the molybdenum derivative $C_3(CN)_2N$-$H_2Mo(CO)_2C_5H_5$ (Table II) indicates that the only carbons directly bonded to hydrogen are the five equivalent cyclopentadienyl ring carbons.

The amino hydrogens in both $C_3(CN)_2NH_2M(CO)_2C_5H_5$ derivatives (M = Mo or W) can be deuterated by repeated stirring with deuterium oxide in tetrahydrofuran solution. The completeness of the conversion to the corresponding C_3-$(CN)_2ND_2M(CO)_2C_5H_5$ derivatives can be shown by the disappearance of the broad proton resonance(s) around τ 1 assigned to the amino protons and by the shifts of all of the infrared bands in the 3150–3450-cm^{-1} range to the 2570–2390-cm^{-1} range (Table I). Deuteration of the C_3-$(CN)_2NH_2M(CO)_2C_5H_5$ derivatives also resulted in the collapse of two strong infrared bands in the 1660–1590-cm^{-1} range to a single band at an intermediate value. An attempt to prepare the deuterated derivative $C_3(CN)_2ND_2Mo(C$-$O)_2C_5H_5$ by reaction of $(NC)_2C=C(CN)Mo(CO)_3C_5H_5$ with anhydrous triethylamine in anhydrous dichloromethane in the

presence of deuterium oxide gave only the proton derivative $C_3(CN)_2NH_2Mo(CO)_2C_5H_5$ apparently owing to reprotonation during the product isolation procedure, probably the chromatography step.

Assignment of structures to the $C_3(CN)_2NH_2M(CO)_2C_5H_5$ derivatives is very difficult in the absence of X-ray crystallographic information. The observed diamagnetism requires the neutral $C_3(CN)_2NH_2$ ligand to act as a net three-electron donor.[10] The presence of two nonequivalent cyano groups in the $C_3(CN)_2NH_2$ ligand is shown by the two $\nu(C\equiv N)$ frequencies around 2200 cm^{-1} (Table I) and by two carbon-13 resonances (Table II) in the range δ 121–115 typical for organic cyano (nitrile) groups.[11] These observations combined with the need to avoid structures with linear sp-hybridized carbons or nitrogens in chelate rings are consistent with structure IV for the $C_3(CN)_2NH_2M(CO)_2C_5H_5$ derivatives in which the $C_3(CN)_2NH_2$ ligand is bonded to the molybdenum atom both through a metal–carbon bond similar to the metal–carbon bond in the polycyanovinyl derivatives (*i.e.*, a one-electron donor) and through a metal–carbene bond similar to the metal–carbene bond in aminocarbene complexes of the type $RC(NR'_2)Cr(CO)_5$.[12] However, more unusual structures

IV   V
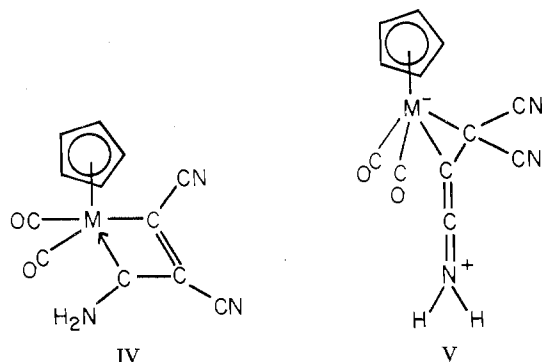
such as V cannot be rigorously excluded until X-ray crystallography data become available.

The infrared spectra of the $C_3(CN)_2NH_2M(CO)_2C_5H_5$ derivatives (Table I) can be interpreted on the basis of structure IV. However, the interpretation of the infrared spectra of the deuterated derivatives is easier since deuteration separates certain bands of similar frequencies in the proton derivatives. In the $C_3(CN)_2ND_2M(CO)_2C_5H_5$ derivatives the band at 3110–3100 cm^{-1} can be assigned to the $\nu(CH)$ of the cyclopentadienyl ring, the bands at 2565–2564, 2434–2430, and 2393–2390 cm^{-1} to $\nu(ND)$ of the ND_2 group with the lower band split by solid-state effects or Fermi resonance, the two bands around 2200 cm^{-1} to the $\nu(C\equiv N)$ of the two different cyano groups, the two bands in the range 2035–1957 cm^{-1} to the $\nu(CO)$ of the two metal carbonyl groups, and the single strong band in the range 1635–1610 cm^{-1} to the $\nu(C=C)$ in the chelate ring. The presence of two bands in the 1653–1597-cm^{-1} region of the proton derivatives $C_3(CN)_2NH_2M(CO)_2C_5H_5$ rather than a single band as found in the deuterated derivatives can arise from the NH deformation of the primary amine which is normally found in this region.[13]

The preparation of the unusual $C_3(CN)_2NH_2M(CO)_2C_5H_5$ derivatives by the alumina-catalyzed hydrolysis of the tricyanovinyl derivatives $(NC)_2C=C(CN)M(CO)_3C_5H_5$ (I, M = Mo or W) suggested an investigation of the alumina-catalyzed hydrolysis of other polycyanovinyl–transition metal derivatives. In this connection, alumina treatment of the 1-chloro-2,2-dicyanovinyl derivatives $(NC)_2C=C(Cl)M(CO)_3C_5H_5$ (II, M = Mo or W) gave red products of the type $C_3H(CN)(OH)NHM(CO)_2C_5H_5$. The molybdenum derivative $(NC)_2C=C(Cl)Mo(CO)_3C_5H_5$ (II, M = Mo) was also converted to $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$ with

triethylamine in dichloromethane, similar to the conversion of $(NC)_2C=C(CN)M(CO)_3C_5H_5$ to $C_3(CN)_2NH_2M(CO)_2C_5H_5$ as discussed above.

The proton nmr spectra of the $C_3H(CN)(OH)NHM(CO)_2C_5H_5$ (M = Mo or W) derivatives exhibit, besides the sharp singlet cyclopentadienyl resonance, a sharp resonance at a very low chemical shift of τ −1.8 corresponding to one proton and a broad resonance at τ 2.5. The assignment of the sharp resonance at τ −1.8 to a proton bonded to carbon is confirmed by the off-resonance proton decoupling of the carbon-13 nmr spectrum of the molybdenum derivative $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$, which indicates that the carbon with a chemical shift of δ 247.1 as well as the cyclopentadienyl ring carbons at δ 94.3 are each bonded to single protons. The proton exhibiting the sharp resonance at τ −1.71 in $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$ is thus bonded to the carbon exhibiting the resonance at δ 247.1 in the carbon-13 nmr spectrum (Table II). These low chemical shift values for both protons and carbon-13 are similar to those of the methine group in the 2,2-dicyanovinyl derivative $(NC)_2C=CH-Mo(CO)_3C_5H_5$ where the proton[4] and carbon-13[8] chemical shifts of the =CH of the 2,2-dicyanovinyl group are τ −0.24 and δ 206.3, respectively, except that the effect in $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$ is even more extreme. The broad proton nmr resonances around τ 2.5 in the $C_3H(CN)(OH)NHM(CO)_2C_5H_5$ derivatives can be assigned to the NH proton. However, since the OH proton cannot be unambiguously found in the proton nmr spectrum, this broad τ 2.5 resonance could also be an NH_2 group or the average value for exchanging OH and NH protons. The breadth and low height of this τ 2.5 resonance made its integration unreliable.

The labilities of the protons in $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$ were explored by deuteration studies. Treatment of $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$ with D_2O in tetrahydrofuran results in deuteration of the NH and OH hydrogens but not of the CH hydrogen to give $C_3H(CN)(OD)NDMo(CO)_2C_5H_5$. This deuteration pattern was established by a shift of the infrared frequencies in the 3400–3150-cm^{-1} region to single bands at 2549 and 2388 cm^{-1} as well as disappearance of the broad τ 2.46 but retention of the sharp τ −1.71 proton resonance. Reaction of $(NC)_2C=C(Cl)Mo(CO)_3C_5H_5$ (II, M = Mo) with D_2O in the presence of triethylamine followed by isolation of the product under normal conditions gives $C_3D(CN)(OH)NHMo(CO)_2C_5H_5$. This pattern of deuteration was established by disappearance of the τ −1.71 but retention of the broad τ 2.46 proton resonance and the absence of significant shifts of the infrared frequencies in the 2900–3400-cm^{-1} region. These deuteration studies indicate that the NH and OH hydrogens but not the CH hydrogen in the $C_3H(CN)(OH)NH$ ligand of $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$ undergo rapid exchange but that all three hydrogens of this ligand arise from the water used in the hydrolysis. The isolation of $C_3D(CN)(OH)NHMo(CO)_2C_5H_5$ rather than $C_3D(CN)(OD)NDMo(CO)_2C_5H_5$ from the reaction of $(NC)_2C=C(Cl)Mo(CO)_3C_5H_5$ with D_2O can arise from conversion of the labile deuterons of the ND and OD groups back to protons by exchange with traces of H_2O during the product isolation steps.

The available data on the $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$ (M = Mo or W) complexes suggest structure VI for this complex. The alternative structure VII proposed earlier[1] now appears improbable because of the low nmr chemical shifts of both the methinyl proton of the $C_3H(CN)(OH)NH$ ligand and the carbon atom to which it is bonded. These low nmr chemical shifts suggest that the methinyl group in the $C_3H(CN)(OH)NH$ ligand has *all* of the following three features: (a) direct bonding to the metal atom; (b) sp^2 hybridization of the methinyl carbon atom; (c) bonding to another

carbon atom (probably also sp^2) bearing a cyano group.

VI   VII

VIII   IX
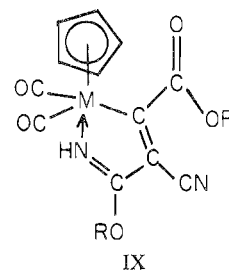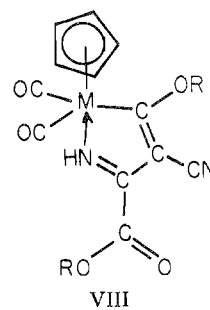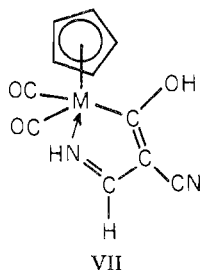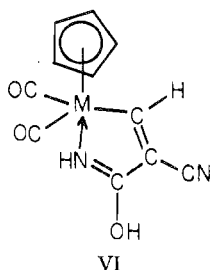
The isolation of unusual products from the hydrolyses of $(NC)_2C$=$C(CN)M(CO)_3C_5H_5$ (I, M = Mo or W) and $(NC)_2C$=$C(Cl)M(CO)_3C_5H_5$ (II, M = Mo or W) under basic conditions suggested reactions of these polycyanovinyl derivatives with other protonic derivatives in the presence of bases. Reactions of the 1-chloro-2,2-dicyanovinyl derivatives $(NC)_2C$=$C(Cl)M(CO)_3C_5H_5$ (II, M = Mo or W) with methanol or ethanol in the presence of sodium hydroxide or the corresponding sodium alkoxide proceed almost instantly at room temperature to give the red derivatives $C_3(CO_2R)$-$(CN)(OR)NHM(CO)_2C_5H_5$ (M = Mo or W, R = CH_3 or C_2H_5). The yields and reaction rates in these base-catalyzed alcoholyses decrease as the length and size of the alkyl chain on the alcohol is increased. Thus, the yields of the methyl derivatives are 50–60%; the yields of the ethyl derivatives are below 30%; only trace quantities of the isopropyl derivative (M = Mo) are obtained and identified by comparison of its infrared spectrum in the 2200–1500-cm^{-1} region with those of the characterized derivatives; and the reaction fails with potassium *tert*-butoxide in *tert*-butyl alcohol. Reactions of the tricyanovinyl derivatives $(NC)_2C$=$C(CN)M(CO)_3C_5H_5$ (I, M = Mo or W) with methanolic sodium hydroxide were complex and gave large amounts of product insoluble in dichloromethane (unlike the $C_3(CO_2R)(CN)(OR)NHM$-$(CO)_2C_5H_5$ derivatives which are very soluble in dichloromethane) which appeared from infrared spectroscopy to be a complex mixture. Chromatography of the dichloromethane-soluble fractions from the reactions of $(NC)_2C$=$C(CN)M(CO)_3C_5H_5$ with methanolic sodium hydroxide gave some $[C_5H_5M(CO)_3]_2$ from rupture of the metal–cyanocarbon bond as well as some $C_5H_5M(CO)_3CN$, apparently through a shift of a cyano group from carbon to the metal. In addition, some $CH_3W(CO)_3C_5H_5$, of obscure origin, was isolated from the reaction of $(NC)_2C$=$C(CN)W(CO)_3C_5H_5$ with methanolic sodium hydroxide. The molybdenum analog CH_3-$Mo(CO)_3C_5H_5$ was not isolated from the corresponding reaction of $(NC)_2C$=$C(CN)Mo(CO)_3C_5H_5$ (I, M = Mo) with methanolic sodium hydroxide presumably because it is less stable than the tungsten derivative[14] and thus cannot survive the reaction conditions.

The NH group in the $C_3(CO_2R)(CN)(OR)NHM$-$(CO)_2C_5H_5$ derivatives exhibits the expected broad proton resonance, this time around τ 1. The proton nmr spectra of all four $C_3(CO_2R)(CN)(OR)NHM(CO)_2C_5H_5$ derivatives exhibit two sets of resonances from the R group (*i.e.*, methyl or ethyl) of equal relative intensities indicating the expected nonequivalence of these two alkyl groups. The ester functionality in the $C_3(CO_2R)(CN)(OR)NHM(CO)_2C_5H_5$ derivatives is indicated by its infrared ν(C=O) frequency in the range 1693–1701 cm^{-1} (Table I) and a carbon-13 resonance around δ 168 (Table II) in the two molybdenum derivatives of this type. The single cyano group in the $C_3(CO_2R)$-$(CN)(OR)NHM(CO)_2C_5H_5$ derivatives is indicated by the single ν(C≡N) frequency in the range 2222–2224 cm^{-1} and a carbon-13 nmr resonance at δ 114 in the two molybdenum derivatives of this type. The chemical shifts of the carbon-13 resonances (Table II) of the chelate ring carbons in the

$C_3(CO_2R)(CN)(OR)NHMo(CO)_2C_5H_5$ derivatives (δ 234, 176, and 102) are similar to those of the chelate ring carbons in $C_3H(CN)(OH)NHMo(CO)_2C_5H_5$ (δ 247, 178, and 101) except for the modest expected shift from δ 234 to δ 247 of the metal-bonded carbon which bears an alkoxycarbonyl group in the former complexes and a hydrogen atom in the latter complexes. This suggests that the general structure of the chelate rings is the same in the two series of complexes. The similarity of the chelate rings in the complexes $C_3(CO_2R)$-$(CN)(OR)NHMo(CO)_2C_5H_5$ and $C_3H(CN)(OH)NH$-$Mo(CO)_2C_5H_5$ demonstrated by carbon-13 nmr spectroscopy suggests structure IX rather than structure VIII for the former series of complexes, since the only difference in the chelate rings of VI, the probable structure of the $C_3H(CN)(OH)$-$NHM(CO)_2C_5H_5$ complexes, and of IX likely to have any significant effect on the carbon-13 chemical shifts of the chelate ring carbons is the group on the carbon atom directly bonded to the metal.

The formation of the ester derivatives IX upon the base-catalyzed alcoholysis of the 1-chloro-2,2-dicyanovinyl derivatives $(NC)_2C$=$C(Cl)M(CO)_3C_5H_5$ (II, M = Mo or W) suggested that aminolysis of these derivatives with secondary amines might give amide derivatives. Reactions of $(NC)_2C$=$C(Cl)M(CO)_3C_5H_5$ (II, M = Mo or W) with the secondary amines dimethylamine and piperidine gave a complex mixture which upon chromatography separated into a red band and a less strongly adsorbed bright yellow band. Examination of the products from elution of the red bands by infrared and proton nmr spectroscopy suggested that they were complex mixtures possibly containing amide derivatives analogous to the esters IX. However, the irreproducibility of the spectra in different preparations as well as the observation of several cyclopentadienyl nmr resonances of varying relative intensities prevented us from investigating the red substances in detail. The yellow bands, on the other hand, upon elution followed by crystallization gave bright yellow solids of the stoichiometry $[R_2NCC(CN)_2]M(CO)_2C_5H_5$ (R = methyl or R_2N = piperidino, M = Mo or W). The yields of these yellow complexes are low in the cases of the dimethylamine derivatives presumably because of the difficulty in getting the gaseous dimethylamine to react well in this system. The yields of the piperidino derivatives $[C_5H_{10}NCC(CN)_2]M(CO)_2C_5H_5$ (M = Mo or W) are considerably better, but most of the product from the reactions of $(NC)_2C$=$C(Cl)M(CO)_3C_5H_5$ (II, M = Mo or W) with these secondary amines appears to be the complex mixture of red compounds mentioned above.

The spectroscopic properties of the $[R_2NCC(CN)_2]M$-$(CO)_2C_5H_5$ derivatives support their formulations as dicyanoketeneimmonium derivatives. The proton nmr spectra of the dimethylamino derivatives $[(CH_3)_2NCC(CN)_2]M$-$(CO)_2C_5H_5$ (M = Mo or W) indicate that the two methyl groups are nonequivalent. Furthermore, the carbon-13 nmr spectra (Table II) of the piperidino derivatives $[C_5H_{10}NCC(CN)_2]M(CO)_2C_5H_5$ (M = Mo or W) indicate nonequivalence of the two NCH_2 carbons of the piperidine rings (the two resonances in the range δ 55–60 in each compound) showing that the two sides of the piperidino rings

in both compounds are different. The carbon-13 nmr spectra of the [R2NCC(CN)2]M(CO)2C5H5 derivatives exhibit a single sharp resonance around δ 120 for both cyano groups indicating their equivalence. All of these nmr data indicate that, in the keteneimmonium ligand of the [R2NCC-(CN)2]M(CO)2C5H5 derivatives, the substituents bonded to the terminal carbon of the keteneimmonium ligand (*i.e.*, the cyano groups) are equivalent but the substituents bonded to the terminal nitrogen of the keteneimmonium ligand (*i.e.*, the R groups) are nonequivalent. These conditions are only fulfilled if the carbon–carbon double bond of the dicyano-keteneimmonium ligand is bonded to the metal atom as in III. If the complexes [R2NCC(CN)2]M(CO)2C5H5 have the alternative structure X with the dicyanoketeneimmonium ligand bonded to the metal through the carbon–nitrogen double bond, then the substituents on the terminal dicyanoketene-immonium carbon would be nonequivalent and the substituents on the dicyanoketeneimmonium nitrogen would be equivalent in contradiction to the actual nmr observations. Similar logic has recently been used to deduce the structures of several tetraalkylketeneimmonium complexes (*e.g.*, XI and XII) obtained from α-chloroenamines and metal carbonyl anions.[15] In the [R2NCC(CN)2]M(CO)2C5H5 complexes discussed in this paper, the strong infrared band at 1590–1566 cm^{-1} can be assigned to the uncomplexed carbon–nitrogen double bond of the dicyanoketeneimmonium ligand in structure III.

X   XI

XII
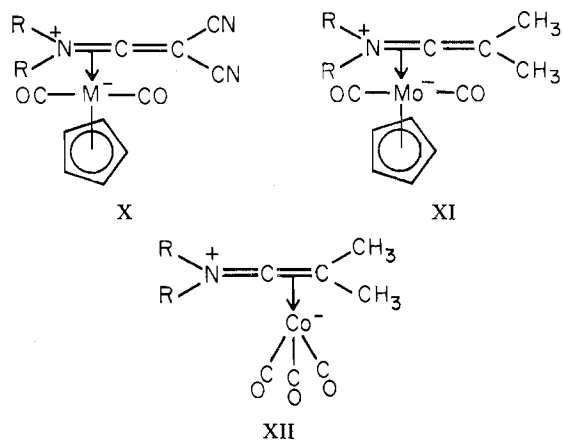
The carbon-13 nmr spectra of the dicyanoketeneimmonium complexes III exhibited only one olefinic carbon resonance which appeared in the range δ 205–225. The missing carbon-13 resonance is probably that of the center carbon atom, which could be broadened beyond recognition because of strong coupling through a cylindrically dissymmetric double bond to the adjacent nitrogen atom, which has a quadrupole moment.

Discussion

Scheme I presents a general picture which rationalizes the structures of the unusual chelates formed by hydrolysis and alcoholysis of the 1-chloro-2,2-dicyanovinyl derivatives (NC)2C=C(Cl)M(CO)3C5H5 (II, M = Mo or W). The strong electron-withdrawing characteristics of the poly-cyanovinyl group in derivatives such as II (**1-1** in Scheme I) make the central metal relatively electropositive as in a metal carbonyl cation. The carbonyl groups in (NC)2C=C(Cl)-M(CO)3C5H5 should thus be susceptible to nucleophilic attack like the carbonyl groups in cationic derivatives.[16] Such an attack by hydroxide or alkoxides would give an adduct of structure **1-2** (Scheme I) with a carboxy or alkoxycarbonyl group directly bonded to the metal atom.[16]

The pathway for further reaction of the anionic intermediate **1-2** will depend upon whether the reaction is an alcoholysis (*i.e.*, R = CH3 or C2H5) or a hydrolysis (R = H). In the case of alcoholysis, the next step can be loss of a chloride from the 1-chloro-2,2-dicyanovinyl group to give a neutral terminal

Scheme I. A Possible Scheme for the Hydrolysis and Alcoholysis of the 1-Chloro-2,2-Dicyanovinyl Derivatives II^a
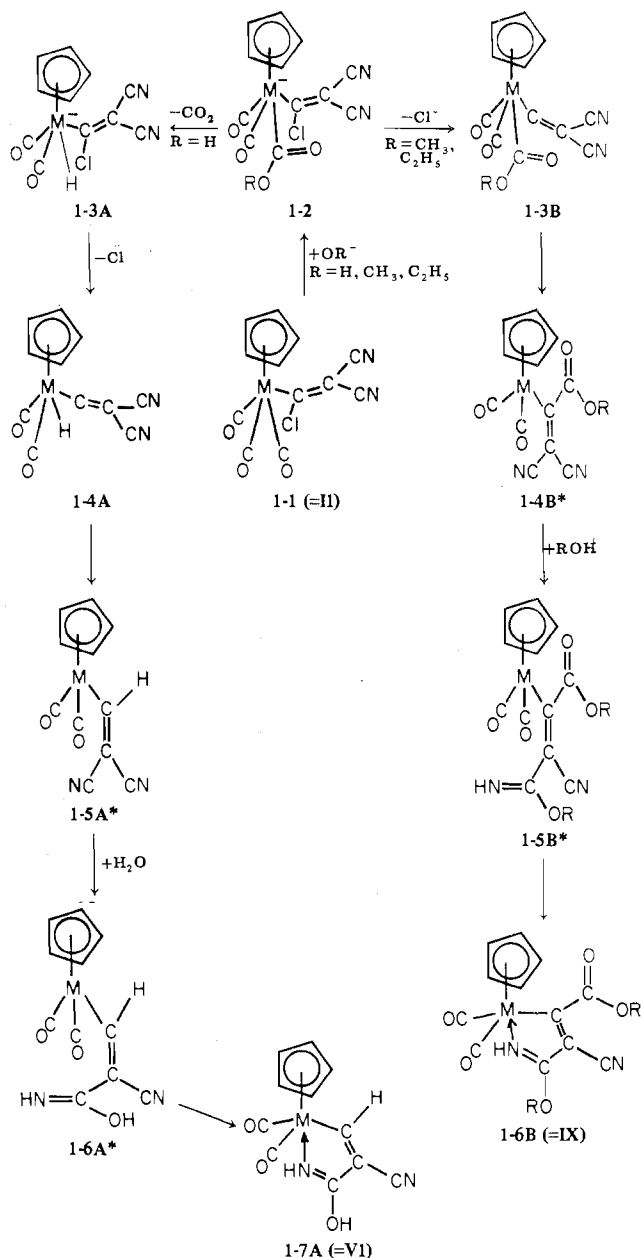
^{a} Intermediates in which the metal has two electrons less than the rare gas electronic configuration are designated with an asterisk.

dicyanovinylidene complex **1-3B** which may be regarded as a dicyanomethylene analog[17] of an alkyl RMo(CO)3C5H5.[14] Our previous work has established the existence of terminal dicyanovinylidene complexes of a type similar to **1-3B** but stabilized by the substitution of the two carbonyl groups with tertiary phosphine or phosphite ligands and containing chloride rather than the alkoxycarbonyl group.[2,18] The metal-bonded alkoxycarbonyl group in **1-3B** can migrate to the very electron-deficient carbene carbon of the terminal dicyano-vinylidene ligand to give the 1-alkoxycarbonyl-2,2-dicyanovinyl derivative **1-4B**. In **1-4B** the central metal atom is electron deficient since its electron configuration is two short of that of the next rare gas. This electron deficiency can be removed if the metal finds an available additional two-electron donor ligand.[10] If such a ligand is located at a site within the molecule where it could bond to the metal to form a new chelate ring, the chelate effect can make the resulting complex readily formed and relatively stable. However, in **1-4B** no

appropriate group exists to provide such intramolecular chelation to remove the electron deficiency since the rigidity of the linear sp hybridization of the carbon atoms in the two 2-cyano groups prevents them from bending back to coordinate with the metal. However, addition of alcohol to the carbon–nitrogen triple bond of a cyano group to give an imine **(1-5B)** converts the linear sp carbon of a 1-cyano group into a trigonal sp² carbon which can then bend back to form a chelate by coordination of the resulting imino group to the metal to form **1-6B**, which is the demonstrated structure (IX) of the alcoholysis products discussed above.

In the hydrolysis of the 1-chloro-2,2-dicyanovinyl derivative II **(1-1** in Scheme I) the hydroxide adduct **1-2** (R = H) has a carboxyl group directly bonded to the central metal atom. Such metal-bonded carboxyl groups are known[19] to undergo facile decarboxylation to form a metal–hydrogen bond. Decarboxylation of **1-2** gives the anionic derivative **1-3A**. This can then undergo chloride loss to form the neutral terminal dicyanovinylidene complex **1-4A**, the dicyanomethylene analog[17] of the hydride HM(CO)₃C₅H₅.[14] The further conversion of **1-4A** to the observed product **1-7A** exactly parallels the conversion of **1-3B** to **1-6B** discussed above.

Scheme I depends upon the conversion of a 1-chloro-2,2-dicyanovinyl group to a terminal dicyanovinylidene ligand by loss of chloride. A process of this type occurs in the reaction of $(NC)_2C=C(Cl)M(CO)_3C_5H_5$ (II, M = Mo or W) with triphenylphosphine under mild conditions to give the terminal dicyanovinylidene derivatives $C_5H_5M[P(C_6H_5)_3]_2[C=C-(CN)_2]Cl$.[2,18] However, the reactions of the tricyanovinyl derivatives $(NC)_2C=C(CN)M(CO)_3C_5H_5$ (I, M = Mo or W) with triphenylphosphine under even more vigorous conditions do not result in the conversion of the tricyanovinyl group to terminal dicyanovinylidene and cyanide but instead in the simple substitution of one carbonyl group with triphenylphosphine to give the dicarbonyls $(NC)_2C=C(CN)M-(CO)_2[P(C_6H_5)_3](C_5H_5)$ (M = Mo or W). For this reason the hydrolysis of the tricyanovinyl derivatives $(NC)_2C=C-(CN)M(CO)_3C_5H_5$ (I, M = Mo or W) can only follow Scheme I as far as an intermediate XIII corresponding to **1-3A**. Conversion of XIII to a product of structure IV can occur through intramolecular hydrometalation of XIII to give XIV
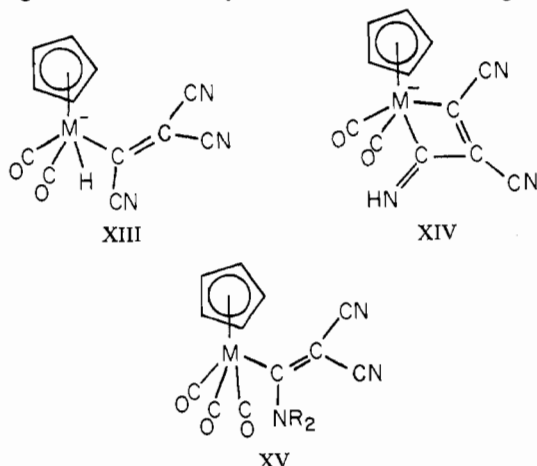
followed by reorganization of the bonding and protonation.

The scheme for the reactions of $(NC)_2C=C(Cl)M-(CO)_3C_5H_5$ (I, M = Mo or W) with secondary amines to give the dicyanoketeneimmonium derivatives III can be considerably less complex. Simple nucleophilic substitution of the chlorine in II with the secondary amine can give the 1-dialkyl-amino-2,2-dicyanovinyl derivatives $(NC)_2C=C(NR_2)M-(CO)_3C_5H_5$ (XV, M = Mo or W) which can then undergo decarbonylation with the necessary reorganization of the $R_2NCC(CN)_2$ ligand to give the observed dicyanoketene-

immonium complexes III. Exactly analogous processes have been observed in the reactions of the α-chloroenamines $(CH_3)_2C=C(NR_2)Cl$ (R = methyl or NR₂ = piperidino) with NaMo(CO)₃C₅H₅ to give XI,[15] except that the ketene-immonium ligand in the final product is bonded to the metal through the carbon–nitrogen rather than the carbon–carbon double bond.

References and Notes

(1) (a) Portions of this work were presented at the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974; see Abstracts, No. INOR 240. (b) This work was also discussed at the U.S.–Japan Seminar on Prospects in Organotransition Metal Chemistry, Honolulu, Hawaii, May 1974. See R. B. King in "Organo-transition-Metal Chemistry," Y. Ishii and M. Tsutsui, Ed., Plenum Press, New York, N.Y., 1975, pp 37–47.
(2) Part II: R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **95**, 1817 (1973).
(3) Postdoctoral research associate.
(4) R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **95**, 1811 (1973).
(5) The preliminary communication⁶ on polycyanovinyl–transition metal derivatives was written before the reactivity of $(NC)_2C=C(CN)-W(CO)_3C_5H_5$ toward alumina was recognized. Furthermore, at that time (1971–1972) alumina was the adsorbent routinely used for chromatography of most transition metal organometallic derivatives. For these reasons the orange "$(NC)_2C=C(CN)W(CO)_3C_5H_5$" reported in the preliminary communication⁶ is actually the compound now recognized to be $C_3(CN)_2NH_2W(CO)_2C_5H_5$ and discussed in this paper. The full paper⁴ describes the correct yellow $(NC)_2C=C(CN)W(CO)_3C_5H_5$ and its conversion to an orange compound on alumina. However, even then (1973) we did not understand the nature of the orange $C_3(CN)_2N-H_2W(CO)_2C_5H_5$ and so could not then discuss the reaction of $(NC)_2C=C(CN)W(CO)_3C_5H_5$ on alumina now described in this paper.
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