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 π-acceptor properties as the dicyanovinylidene ligand and appreciably stronger π-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 π-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 $(C_5H_5)_2Fe_2(CO)_3C(CN)_2$.

Acknowledgment. We are indebted to the Office of Naval Research for partial support of this research.

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

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 $C_5H_5Mo(Pf\text{-}Pf)_2[C{=}C(CN)_2]Cl$ or the brown biligate monometallic derivative $C_5H_5Mo(Pf\text{-}Pf)[C{=}C(CN)_2]Cl$ 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 $C_5H_5Mo(diphos)[C{=}C(CN)_2]Cl$. 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 $[C_5H_5Mo(triphos)C{=}C(CN)_2]^+$ 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).

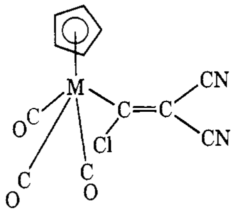
(2) For a preliminary communication of some of this work, see R. B. King and M. S. Saran, *J. Chem. Soc., Chem. Commun.*, 1053 (1972).

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

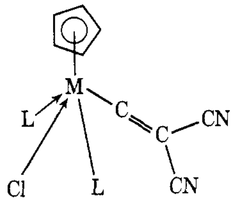
(4) Postdoctoral research associate, 1969–1973.

a bridging dicyanovinylidene (*i.e.*, dicyanomethylenecarbene[5]) ligand. The reaction of $(NC)_2C{=}CCl_2$ with the less nucleophilic[4] metal carbonyl anions $NaM(CO)_3C_5H_5$ (M = Mo and W) was found to proceed only as far as the monosubstituted 1-chloro-2,2-dicyanovinyl derivatives $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (I, M = Mo and W). The high reactivity of polycyanovinyl halides toward metal carbonyl anions[1,6] suggested that the chlorine atom in the derivatives $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (I, M = Mo and W) might retain some significant reactivity toward certain nucleophiles.

These considerations led to an investigation of the reactions of the molybdenum compound $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ (I, M = Mo) with various nucleophiles. In this connection, the reaction of this molybdenum compound with triphenylphosphine under relatively mild conditions led to a stable orange crystalline solid of stoichiometry $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(C_5H_5)$. The complete displacement of carbonyl groups in an alkyl of the type $RMo(CO)_3C_5H_5$ by triphenylphosphine under mild conditions was entirely unexpected since alkyls of the type $RMo(CO)_3C_5H_5$ usually react with triphenylphosphine and related trivalent phosphorus ligands to form either the acyls $RCOMo(CO)_2[P(C_6H_5)_3](C_5H_5)$ without carbonyl loss or the alkyls $RMo(CO)_2[P(C_6H_5)_3](C_5H_5)$ with loss of only one of the three carbonyl groups.[7,8] A further unusual feature of the reaction between $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ and triphenylphosphine to give $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(C_5H_5)$ is the replacement of three carbonyl groups with only two triphenylphosphine ligands despite the fact that both the carbonyl group and the triphenylphosphine ligand always act as two electron donors[9] in transition metal systems. These considerations suggested a more detailed investigation of the triphenylphosphine derivative $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(C_5H_5)$ and related compounds prepared from other trivalent phosphorus, arsenic, or antimony ligands and using the tungsten compound I (M = W) as well as the molybdenum compound.



I



II

This work led to an extensive accumulation of experimental evidence supporting formulation of $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(C_5H_5)$ as the complex II (M = Mo; L = $P(C_6H_5)_3$) containing the first example of a terminal dicyanovinylidene ligand. The dicyanovinylidene ligand is of particular intrest because of its relationship to the familiar carbonyl[10] ligand by replacement of an oxygen atom with a dicyanomethylene group. Previous work[11] on other types of systems indicates a close similarity between otherwise analogous compounds in which an oxygen atom is replaced by a dicyanomethylene group.

This paper presents the details of our studies on terminal dicyanovinylidene complexes of the type II.

Experimental Section

Microanalyses were performed by Meade Microanalytical Laboratory, Amherst, Mass., and by the Microanalytical Laboratory of the University of Georgia under the direction of Mr. W. Swanson. Infrared spectra (Table I) were taken in dichloromethane solutions or in potassium bromide pellets and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics Proton nmr spectra (Table I) were taken in the indicated solvents ($CDCl_3$ in most cases) and recorded on a Varian HA-100 spectrometer at 100 MHz using tetramethylsilane as an internal standard. Phosphorus-31 nmr spectra were taken in dichloromethane solution and recorded on a Varian HA-100 spectrometer at 40.5 MHz using 85% phosphoric acid as an external standard. 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. The preparations of $(NC)_2C{=}C(H)Mo(CO)_3C_5H_5$ and $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (M = Mo and W) are described in the first paper of this series. The ligands $(C_6H_5)_3E$ (E = P, As, and Sb), $(RO)_3P$ (R = CH_3, C_2H_5, and C_6H_5), and $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (abbreviated as Pf-Pf) were commercial products. The ligands *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$[12] (abbreviated as *c*Pf=Pf), $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ (abbreviated as Pf-Pf-Pf),[13] and dimethylphenylphosphine[14] were prepared by the cited published procedures.

Reaction of $(NC)_2C{=}C(H)Mo(CO)_3C_5H_5$ with Triphenylphosphine. A mixture of 1.1 g (3.42 mmol) of $(NC)_2C{=}CHMo(CO)_3C_5H_5$, 2.7 g (10.3 mmol) of triphenylphosphine, and 50 ml of benzene was boiled under reflux for 15 hr. The reaction mixture was filtered hot. Evaporation of the filtrate gave 1.3 g (69% yield) of brown $C_5H_5Mo(CO)_2P(C_6H_5)_3CH{=}C(CN)_2$. A dichloromethane solution of this crude product was chromatographed on an alumina column prepared in hexane. The yellow band of product was eluted with dichloromethane. Further purification by crystallization from a mixture of dichloromethane and hexane gave 0.61 g (32% yield) of yellow $C_5H_5Mo(CO)_2P(C_6H_5)_3CH{=}C(CN)_2$, mp 179–181° dec.

Anal. Calcd for $C_{29}H_{21}MoN_2O_2P$: C, 62.6; H, 3.8; N, 5.0; O, 5.8. Found: C, 61.6; H, 3.8; N, 5.1; O, 5.2.

Reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with Triphenylphosphine. A mixture of 0.6 g (1.68 mmol) of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$, 1.5 g (5.73 mmol) of triphenylphosphine, and 50 ml of dichloromethane was boiled under reflux for 203 hr. Aliquots were periodically removed from the reaction mixture and their infrared spectra examined in the ν(CN) and ν(CO) regions in attempts to detect any intermediates in the formation of $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ from $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ and triphenylphosphine. After the reaction had proceeded a relatively short time (*e.g.*, 1.5 hr) a new ν(CO) frequency began to appear at 1903 cm^{-1} which tentatively can be assigned to the lower ν(CO) frequency of $C_5H_5Mo(CO)_2P(C_6H_5)_3CCl{=}C(CN)_2$. However, before the intensity of this 1903-cm^{-1} band became appreciable relative to the ν(CO) frequencies at 2061 and 1978 cm^{-1} from the $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ starting material (*e.g.*, after 19.5 hr reaction time), a new ν(CN) frequency at 2198 cm^{-1} began to appear which may be assigned to $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$. At longer times (142 hr) the ν(CO) frequencies of the $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ starting material had essentially disappeared but a pair of ν(CO) frequencies at 1983 and 1903 cm^{-1} assignable to a C_5H_5-

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(5) The name "dicyanovinylidene" for the carbene ligand $:C{=}C(CN)_2$ seems preferable to the longer name "dicyanomethylenecarbene" used in the preliminary communications (ref 2 and 6).

(6) R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **94**, 1784 (1972).

(7) K. W. Barnett and P. M. Treichel, *Inorg. Chem.*, **6**, 294 (1967).

(8) P. J. Craig and M. Green, *J. Chem. Soc. A*, 1978 (1968).

(9) R. B. King, *Advan. Chem. Ser.*, **No. 62**, 203 (1967).

(10) R. B. King, "Transition-Metal Organometallic Chemistry: An Introduction," Academic Press, New York, N. Y., 1969.

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

(12) A. M. Aguiar and D. Daigle, *J. Amer. Chem. Soc.*, **86**, 2299 (1964).

(13) R. B. King and P. N. Kapoor, *ibid.*, **93**, 4158 (1971).

(14) K. Bowden and E. A. Braude, *J. Chem. Soc.*, 1068 (1952).

Table I. Spectroscopic Properties of Dicyanovinylidene Derivatives and Other New Compounds Described in This Paper

Compound[a]	Ir spectrum,[b] cm^{-1} ν(CN)	Proton nmr spectrum,[c] τ			
		Solvent	C_5H_5	C_6H_5	Other
$CpMo(CO)_2(PPh_3)[CH{=}C(CN)_2]$	2233 (m), 2221 (m), 2210 (m)[g]	CH_2Cl_2	*d*	2.52 s, 2.6 br	=CH −0.60 s
$CpMo(PPh_3)_2[C{=}C(CN)_2]Cl$	2192 (m)	$CDCl_3$	A(75%) 4.91 t (2.2) B(25%) 5.16 t (2.2)	2.33 br, 2.59 s	
$CpMo(PPh_3)_2[C{=}C(CN)_2]Cl\cdot C_6H_6$		$CDCl_3$	4.91 t (2)	~2.3 br, 2.57 s	C_6H_6 2.67 s
$CpMo(PPh_3)_2[C{=}C(CN)_2]Cl\cdot CH_3C_6H_5$		$CDCl_3$	4.90 t (2)	~2.3 br, 2.57 s, 2.80 s,[e] 2.84 s[e]	CH_3 7.67 s
$CpMo(AsPh_3)_2[C{=}C(CN)_2]Cl$	2198 (m)	$CDCl_3$	4.75 s	2.45 m, 2.55 m	
$CpMo(SbPh_3)_2[C{=}C(CN)_2]Cl$	2198 (m)	$CDCl_3$	A(90%) 4.60 s B(10%) 4.82 s	~2.45 m, ~2.65 m	
$CpMo(PMe_2Ph)_2[C{=}C(CN)_2]Cl$	2197 (m)	$CDCl_3$	5.07	2.27, 2.55	CH_3 8.00 dd (9, 4)
$CpMo[P(OMe)_3]_2[C{=}C(CN)_2]Cl$	2199 (m)	$CDCl_3$	4.47 t (2)		CH_3 6.11 t (5)
$CpMo[P(OEt)_3]_2[C{=}C(CN)_2]Cl$		$CDCl_3$	4.52 t (2)		CH_3 8.65 t (7) CH_2 5.80 qt (7, 4)
$CpMo[P(OPh)_3]_2[C{=}C(CN)_2]Cl$	2201 (m)	$CDCl_3$	4.88 t (2)	2.75 s	
$CpMo(Pf\text{-}Pf)_2[C{=}C(CN)_2]Cl$	2194 (m)	$CDCl_3$	5.19 t (2)	2.63 s, 2.74 s	CH_2 7.71 br, 7.94 t (4)
$CpMo(Pf\text{-}Pf)[C{=}C(CN)_2]Cl$	2195 (m)	$CDCl_3$	5.26	2.59 br	CH_2[f]
$CpMo(cPf{=}Pf)[C{=}C(CN)_2]Cl$	2199 (m)	$CDCl_3$	4.99 d (3)	2.53 m	=CH 2.24 dd (17, 9)
$\{CpMo(Pf\text{-}Pf\text{-}Pf)[C{=}C(CN)_2]\}Cl$	2203 (m)	$CDCl_3$	4.46	2.48, 2.72	CH_2 ~7.3 br
$\{CpMo(Pf\text{-}Pf\text{-}Pf)[C{=}C(CN)_2]\}[PF_6]$	2203 (m)	$(CD_3)_2CO$	4.42	~2.35, ~2.45, ~2.8 m	CH_2 6.6–7.3 br
$CpW(PPh_3)_2[C{=}C(CN)_2]Cl$	2191 (m)	$CDCl_3$	A(75%) 4.88 t (2) B(25%) 5.12 t (2)	2.36 br, 2.57 s	
$CpW(AsPh_3)_2[C{=}C(CN)_2]Cl$		$CDCl_3$	4.75 s	2.43, 2.55	
$CpW[P(OMe)_3]_2[C{=}C(CN)_2]Cl$		$CDCl_3$	4.47 t (2)		CH_3 6.10 t (5)
$CpW[P(OEt)_3]_2[C{=}C(CN)_2]Cl$		$CDCl_3$	4.51 t (2)		CH_3 8.65 t (6) CH_2 5.81 qt (6, 3)

[a] The following abbreviations are used: Cp = π-cyclopentadienyl, Me = methyl, Et = ethyl, Ph = phenyl, Pf-Pf = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, *c*Pf=Pf = *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$. [b] These infrared spectra were taken in CH_2Cl_2 solution and recorded on a Perkin-Elmer 621 spectrometer with grating optics. Each spectrum was calibrated against the 1601-cm^{-1} band of polystyrene film. [c] These proton nmr spectra were taken in the indicated solvents and recorded on a Varian HA-100 spectrometer. The following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets, qt = quartet of triplets. Coupling constants in Hz are given in parentheses. [d] The resonance of the CH_2Cl_2 solvent masked this cyclopentadienyl resonance. [e] These resonances are assigned to the phenyl protons of the toluene of solvation. [f] This methylene resonance could not be clearly observed. [g] The ν(CO) frequencies in this compound were observed at 1981 (s) and 1904 (vs) cm^{-1}.

$Mo(CO)_2P(C_6H_5)_3CCl{=}C(CN)_2$ intermediate could be observed as well as a ν(CO) frequency at $\sim$1815 cm^{-1} which might arise from a monocarbonyl derivative such as $C_5H_5Mo(CO)[P(C_6H_5)_3]_2CCl{=}C(CN)_2$.

After completion of the reaction period of 203 hr solvent was removed from the filtered reaction mixture at 25° (35 mm). The residue was crystallized from a mixture of hexane and dichloromethane to give 1.3 g (97% yield) of red-orange $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$. The analytical sample (mp 162–164° dec, molar conductance 1.1 ohm^{-1} cm^2/mol in CH_3NO_2) was purified further by chromatography on Florisil in a mixture of dichloromethane and hexane.

Anal. Calcd for $C_{45}H_{35}ClMoN_2P_2$: C, 67.8; H, 4.4; N, 3.5; Cl, 4.5; Mo, 12.0; P, 7.8; mol wt, 797. Found: C, 67.3; H, 4.4; N, 3.6; Cl, 5.1; Mo, 12.4; P, 8.1; mol wt, 767.

The reaction time for the preparation of $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ could be reduced drastically by carrying out the reaction between $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ and triphenylphosphine in heptane solution. In this case, a mixture of 0.6 g (1.68 mmol) of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$, 1.6 g (6.1 mmol) of triphenylphosphine, and 50 ml of *n*-heptane was boiled under reflux for 10 hr. The brown precipitate was filtered hot and washed with 50 ml of cold hexane. A solution of this product in 50 ml of dichloromethane was chromatographed on a 2.5 × 30-cm Florisil column. The orange-red band was eluted with dichloromethane. After evaporation of the eluate, the residue was recrystallized from a mixture of dichloromethane and hexane to give 1.2 g (90% yield) of red-orange $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$, mp 162–167° dec.

Similar reactions of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with triphenylphosphine in the aromatic hydrocarbons benzene and toluene gave 1:1 solvates of $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ with the aromatic hydrocarbon.

A. **Benzene Solvate.** Orange, mp 181–182°. *Anal.* Calcd for $C_{51}H_{41}ClMoN_2P_2$: C, 70.0; H, 4.7; N, 3.2. Found: C, 68.7; H, 4.6; N, 3.4.

B. **Toluene Solvate.** Orange, mp 181–182°. *Anal.* Calcd for $C_{52}H_{43}ClMoN_2P_2$: C, 70.3; H, 4.9; Cl, 3.9; Mo, 10.8; N, 3.1; P, 7.0; mol wt, 889. Found: C, 70.0; H, 4.9; Cl, 4.2; Mo, 9.3; N, 3.1; P, 6.3; mol wt, 927 (osmometer in benzene).

Reaction of $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ with Triphenylphosphine. A mixture of 0.45 g (1.0 mmol) of $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$, 0.8 g (3.0 mmol) of triphenylphosphine, and 50 ml of xylene was boiled under reflux for 11 hr. The reaction mixture was then cooled to room temperature and filtered. The brown residue was washed with $\sim$40 ml of dichloromethane. Solvent was removed from the combined dichloromethane washings and xylene filtrate. The residue was dissolved in a minimum of dichloromethane and chromatographed on a 2.5 × 30-cm Florisil column prepared in hexane. The first yellow-orange band was eluted with a 3:2 mixture of dichloromethane and hexane. Evaporation of the filtered eluate followed by crystallization from a mixture of dichloromethane and hexane gave 0.015 g (1.9% yield) of light yellow crystalline $C_5H_5W(CO)_2P(C_6H_5)_3Cl$, mp 195–197° (lit.[15] mp 194°), ν(CO) in CH_2Cl_2: 1959 (s), 1863 (s) cm^{-1} (lit.[15] ν(CO) in $CHCl_3$: 1965 (vs), 1872 (vs) cm^{-1}).

Anal. Calcd for $C_{25}H_{20}ClO_2PW$: C, 49.8; H, 3.3; N, 0.0. Found: C, 49.5; H, 3.5; N, 0.3.

After removal of the $C_5H_5W(CO)_2P(C_6H_5)_3Cl$ a red-orange band remained on the chromatography column. This band was eluted with a 1:19 mixture of tetrahydrofuran and dichloromethane. Evaporation of the eluate followed by crystallization of the residue from a mixture of dichloromethane and hexane gave 0.3 g (35% yield) of yellow-orange $C_5H_5W[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$, mp 166–168°, molar conductance 1.5 ohm^{-1} cm^2/mol in CH_3NO_2.

Anal. Calcd for $C_{45}H_{35}ClN_2P_2W$: C, 61.1; H, 4.0; Cl, 4.0; N, 3.2. Found: C, 61.1; H, 4.3; Cl, 3.0; N, 3.1.

General Procedure for the Reactions of $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (I, M = Mo and W) with Monodentate Ligands. A mixture of $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (I; M = Mo, 0.6 g, 1.68 mmol; M = W, 0.45 g, 1.0 mmol), the monodentate ligand, and 50 ml of the solvent (benzene for M = Mo, generally xylene for M = W) was boiled under reflux for periods of 3–43 hr. In the case of the ligands $(C_6H_5)_3E$ (E = As or Sb) 3 equiv of ligand were used for each equivalent of metal complex. In the cases of the phosphites a slight excess (1.0–1.5 ml) of the ligand was used relative to the metal complex. The absence of ν(CO) frequencies in the infrared spectrum of an aliquot of the reaction mixture could be used to determine whether the reaction had gone to completion.

After the reaction period was over, solvent was removed from the reaction mixture at $\sim$25° (35 mm) (for M = Mo) or 25° (0.1 mm) (for M = W). A dichloromethane solution of the residue was chromatographed on a 2.5 × 30-cm Florisil column prepared in hexane. The orange band of the product was eluted with dichloromethane containing a little tetrahydrofuran if necessary to speed up the rate of elution. Solvent was removed from the eluate at $\sim$25° (35 mm). The chromatography was repeated for the preparations of $C_5H_5Mo[Sb(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ and $C_5H_5Mo[P(OR)_3]_2[C{=}C(CN)_2]Cl$ (R = C_2H_5 and C_6H_5). The product from chromatography was recrystallized from a mixture of dichloromethane and hexane and then washed with hexane to give the pure $C_5H_5ML_2[C{=}C(CN)_2]Cl$ derivative. This final crystallization was omitted for the triethyl phosphite derivatives because they gave oils when such crystallizations were attempted.

The reactions of the tungsten compound $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ with triphenyl phosphite and triphenylarsine in boiling xylene failed to give any tractable products when carried out as described above. However, the compound $C_5H_5W[As(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ could be prepared from $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ and triphenylarsine in boiling toluene solution using the general procedure given above.

The following $C_5H_5ML_2[C{=}C(CN)_2]Cl$ derivatives were prepared by this method.

A. $C_5H_5Mo[As(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$: orange-brown, mp 130–132° dec, 76% yield, molar conductance 2.5 ohm^{-1} cm^2/mol in CH_3NO_2. *Anal.* Calcd for $C_{45}H_{35}As_2ClMoN_2$: C, 61.1; H, 4.0; N, 3.2. Found: C, 61.2; H, 4.2; N, 3.3.

B. $C_5H_5Mo[Sb(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$: red-brown, mp 120° dec, 34% yield, molar conductance 0.9 ohm^{-1} cm^2/mol in CH_3NO_2. *Anal.* Calcd for $C_{45}H_{35}ClMoN_2Sb_2$: C, 55.3; H, 3.6; N, 2.9. Found: C, 54.4; H, 3.8; N, 3.0.

C. $C_5H_5Mo[P(OCH_3)_3]_2[C{=}C(CN)_2]Cl$: orange-yellow, mp 135–136° dec, 61% yield, molar conductance 0.7 ohm^{-1} cm^2/mol in CH_3NO_2. *Anal.* Calcd for $C_{15}H_{23}ClMoN_2O_6P_2$: C, 34.6; H, 4.4; N, 5.4; O, 18.4. Found: C, 33.6; H, 4.5; N, 5.7; O, 19.0.

D. $C_5H_5Mo[P(OC_2H_5)_3]_2[C{=}C(CN)_2]Cl$: yellow, mp 86–87°, 49% yield. *Anal.* Calcd for $C_{21}H_{35}ClMoN_2O_6P_2$: C, 41.7; H, 5.8; N, 4.6. Found: C, 42.0; H, 5.8; N, 4.7.

E. $C_5H_5Mo[P(OC_6H_5)_3]_2[C{=}C(CN)_2]Cl$: orange-yellow, mp 123–124° dec, 67% yield, molar conductance 0.5 ohm^{-1} cm^2/mol in CH_3NO_2. *Anal.* Calcd for $C_{45}H_{35}ClMoN_2O_6P_2$: C, 60.6; H, 4.0; N, 3.1; O, 10.8. Found: C, 60.6; H, 3.9; N, 3.3; O, 12.2.

F. $C_5H_5W[As(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$: orange-yellow, dec >131°, 10% yield. *Anal.* Calcd for $C_{45}H_{35}As_2ClN_2W$: C, 55.5; H, 3.6; N, 2.9. Found: C, 55.6; H, 4.1; N, 2.8.

G. $C_5H_5W[P(OCH_3)_3]_2[C{=}C(CN)_2]Cl$: yellow, dec >149°, 26% yield, molar conductance 0.5 ohm^{-1} cm^2/mol in CH_3NO_2. *Anal.* Calcd for $C_{15}H_{23}ClN_2O_6P_2W$: C, 29.6; H, 3.8; N, 4.6. Found: C, 29.2; H, 4.3; N, 4.3.

H. $C_5H_5W[P(OC_2H_5)_3]_2[C{=}C(CN)_2]Cl$: yellow, 17% yield. *Anal.* Calcd for $C_{21}H_{35}ClN_2O_6P_2W$: C, 36.4; H, 5.1; N, 4.0; O, 13.9. Found: C, 36.0; H, 5.1; N, 4.0; O, 13.4.

Reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with Dimethylphenylphosphine. A mixture of 1.78 g (5.0 mmol) of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$, 1.5 ml (2.1 g, 15.2 mmol) of dimethylphenylphosphine, and 75 ml of benzene was boiled under reflux for 3 hr. The infrared spectrum of the reaction mixture indicated that the reaction was complete after 30 min. The reaction mixture was chromatographed on a 2.5 × 30-cm Florisil column prepared in hexane. The initial orange-red band was eluted with a 1:1 mixture of dichloromethane and hexane. Evaporation of this eluate (25° (35 mm)) followed by crystallization from a mixture of dichloromethane and hexane gave 0.35 g (18% yield) of red-orange $C_5H_5Mo(CO)_2[P(CH_3)_2C_6H_5]Cl$, mp 118–119°, ν(CO) in CH_2Cl_2: 1966 (s), 1872 (s) cm^{-1}.

Anal. Calcd for $C_{15}H_{16}ClMoO_2P$: C, 45.2; H, 4.1; Cl, 9.1. Found: C, 47.0; H, 4.2; Cl, 9.2.

The proton nmr spectrum of this sample of $C_5H_5Mo(CO)_2[P(CH_3)_2C_6H_5]Cl$ in $CDCl_3$ solution exhibited phenyl resonances at τ 2.4–2.7 (broad, complex multiplet), a cyclopentadienyl resonance at τ 4.63 (singlet), and overlapping methyl resonances at τ 8.14 (doublet, J = 9.5 Hz) and τ 8.16 (doublet, J = 9 Hz).

After removal of the orange-red band of $C_5H_5Mo(CO)_2[P(CH_3)_2C_6H_5]Cl$ from the chromatogram, the column was eluted with pure dichloromethane which removed the next yellow band.

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[15] P. M. Treichel, K. W. Barnett, and R. L. Shubkin, *J. Organometal. Chem.*, 7, 449 (1967).

Evaporation of this eluate at $\sim$25° (35 mm) followed by crystallization from a mixture of dichloromethane and hexane and washing with hexane gave 0.3 g (11% yield) of orange-yellow $C_5H_5Mo[P(CH_3)_2C_6H_5]_2[C{=}C(CN)_2]Cl$, mp 181–183°, molar conductance 0.4 ohm^{-1} cm^2/mol in CH_3NO_2. The analytical sample was purified by rechromatography followed by another recrystallization from a mixture of dichloromethane and hexane.

Anal. Calcd for $C_{25}H_{27}ClMoN_2P_2$: C, 54.6; H, 5.0; N, 5.1; Cl, 7.0. Found: C, 54.4; H, 5.0; N, 4.8; Cl, 6.9.

The reaction between $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ and dimethylphenylphosphine was also carried out in tetrahydrofuran rather than benzene. In this case, the cyanocarbon-free derivative $C_5H_5Mo(CO)_2[P(CH_3)_2C_6H_5]Cl$ was the major product. Only a trace of the dicyanomethylenecarbene complex $C_5H_5Mo[P(CH_3)_2C_6H_5]_2[C{=}C(CN)_2]Cl$ was isolated

Reactions of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with Di(tertiary phosphines). A. $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. A mixture of 1.2 g (3.37 mmol) of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$, 2.8 g (7.04 mmol) of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, and 50 ml of tetrahydrofuran was boiled under reflux for 16 hr. Solvent was then removed at 25° (35 mm). A concentrated dichloromethane solution of the residue was chromatographed on a 2.5 × 30-cm Florisil column prepared in hexane. The orange-red band was eluted with dichloromethane containing $\sim$2% tetrahydrofuran. The eluate was evaporated and the product purified by repetition of the chromatography. After washing the purified product with hot hexane 1.8 g (50% yield) of red-orange $C_5H_5Mo(Pf\text{-}Pf)_2[C{=}C(CN)_2]Cl$, mp 123–124°, molar conductance 2.3 ohm^{-1} cm^2/mol in CH_3NO_2, was obtained.

Anal. Calcd for $C_{61}H_{53}ClMoN_2P_4$: C, 68.5; H, 5.0; N, 2.6. Found: C, 67.8; H, 5.2; N, 2.5.

A mixture of 0.6 g (1.68 mmol) of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$, 0.66 g (1.66 mmol) of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, and 50 ml of benzene was boiled under reflux for 12 hr. The reaction mixture was filtered hot. The brown precipitate was washed with 30 ml of hot benzene and dried to give 0.68 g (60% yield) of crude $C_5H_5Mo(Pf\text{-}Pf)[C{=}C(CN)_2]Cl$. Additional less pure product was obtained by evaporation of the benzene filtrate. The analytical sample, mp 199–202° dec, was purified by dissolving the crude product in a 1:1 mixture of tetrahydrofuran and chloroform and reprecipitating with hexane.

Anal. Calcd for $C_{35}H_{29}ClMoN_2P_4$: C, 62.7; H, 4.4; N, 4.2. Found: C, 61.9; H, 4.5; N, 4.2.

B. *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$. A mixture of 1.2 g (3.37 mmol) of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$, 2.6 g (6.57 mmol) of *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$, and 50 ml of tetrahydrofuran was boiled under reflux for 16 hr. Solvent was then removed at $\sim$25° (35 mm). A concentrated dichloromethane solution of the residue was chromatographed on a 2.5 × 30-cm Florisil column prepared in hexane. A small yellow band was first eluted with a mixture of dichloromethane and hexane. This contained a negligible amount of material and so was discarded. The major purple band was eluted with dichloromethane containing about $\sim$2% of tetrahydrofuran. This eluate was evaporated to dryness at $\sim$25° (35 mm). The residue was recrystallized from a mixture of dichloromethane and hexane to give 1.53 g (68% yield) of deep green crystalline $C_5H_5Mo(cPf{=}Pf)[C{=}C(CN)_2]Cl$, mp 252–254° in a preheated bath, molar conductance 4.9 ohm^{-1} cm^2/mol in CH_3NO_2.

Anal. Calcd for $C_{35}H_{27}ClMoN_2P_4$: C, 62.8; H, 4.1; N, 4.2; Cl, 5.4; Mo, 14.4; mol wt 669. Found: C, 62.5; H, 4.2; N, 3.8; Cl, 5.8; Mo, 13.9; mol wt 690 ($CHCl_3$).

Reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with the Tri(tertiary phosphine) $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$. A mixture of 0.6 g (1.68 mmol) of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$, 0.94 g (1.76 mmol) of $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$, and 50 ml of octane was boiled under reflux for 23 hr. After cooling to room temperature, the precipitate was filtered, washed with hexane, and dried to give 1.2 g of a yellow-brown solid. Recrystallization of this solid from a mixture of chloroform and tetrahydrofuran followed by washing with two 10-ml portions of hexane gave 0.83 g (61% yield) of yellow crystalline $[C_5H_5Mo(Pf\text{-}Pf\text{-}Pf)[C{=}C(CN)_2]]Cl$, dec 220–222°, molar conductance 68 ohm^{-1} cm^2/mol in CH_3NO_2.

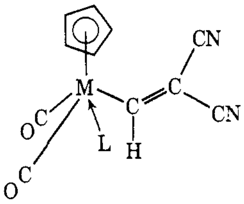
Anal. Calcd for $C_{43}H_{38}ClMoN_2P_3$: C, 63.9; H, 4.7; N, 3.5. Found: C, 63.7; H, 4.9; N, 3.5.

A solution of 0.25 g (0.31 mmol) of $[C_5H_5Mo(Pf\text{-}Pf\text{-}Pf)[C{=}C(CN)_2]]Cl$ in 20 ml of ethanol was treated with 0.5 g (3.06 mmol) of NH_4PF_6 in 25 ml of ethanol. Concentration of the reaction mixture at $\sim$25° (35 mm) gave yellow crystals which were filtered and dried. This product was purified by crystallization from a mixture of acetone and ethanol followed by washing with both ethanol and hexane to give 0.24 g (85% yield) of yellow-orange $[C_5H_5Mo(Pf\text{-}Pf\text{-}Pf)[C{=}C(CN)_2]][PF_6]$, dec 275°, molar conductance 79 ohm^{-1} cm^2/mol in CH_3NO_2.

Anal. Calcd for $C_{43}H_{38}F_6MoN_2P_4$: C, 56.3; H, 4.2; F, 12.4; N, 3.1; Cl, 0.0. Found: C, 56.2; H, 4.5; F, 12.1; N, 3.0; Cl, 0.0

Discussion

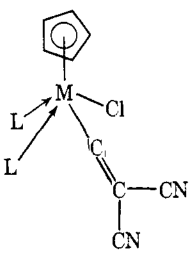
The reaction of the 2,2-dicyanovinylmolybdenum derivative $(NC)_2C{=}C(H)Mo(CO)_3C_5H_5$ (III; M = Mo; L = CO) with triphenylphosphine proceeded in a usual manner for an $RMo(CO)_3C_5H_5$ derivative with replacement of one carbonyl group with the tertiary phosphine to give yellow $(NC)_2C{=}C(H)Mo(CO)_2P(C_6H_5)_3(C_5H_5)$ (III, M = Mo; L = $(C_6H_5)_3P$). The infrared spectrum of this product exhibited the two terminal ν(CO) frequencies expected for an $RMo(CO)_2L(C_5H_5)$ derivative. The proton nmr spectrum of this product exhibited not only the usual phenyl and cyclopentadienyl resonances but also a very low field resonance at τ −0.60 arising from the single olefinic proton of the 2,2-dicyanovinyl group. This resonance appeared to be a singlet suggesting that coupling of the triphenylphosphine phosphorus atom in III (M = Mo; L = $(C_6H_5)_3P$) with the 2,2-dicyanovinyl proton was negligible. The downfield shift of the 2,2-dicyanovinyl proton resonance in $(NC)_2C{=}CHMo(CO)_2P(C_6H_5)_3(C_5H_5)$ at τ −0.60 from the corresponding resonance in $(NC)_2C{=}CHMo(CO)_3C_5H_5$ at τ 0.24 indicates that the increase in electron density on the metal atom upon replacement of a carbonyl group with the weaker π-acceptor triphenylphosphine deshields the 2,2-dicyanovinyl proton. This is consistent with the previous observation[1] that the 2,2-dicyanovinyl proton in $(NC)_2C{=}CHMn(CO)_5$ (τ +0.24) exhibits an appreciably higher nmr chemical shift than the 2,2-dicyanovinyl protons in $(NC)_2C{=}CHM(CO)_3C_5H_5$ (M = Mo and W) or $(NC)_2C{=}CHFe(CO)_2C_5H_5$ where some of the carbonyl groups are replaced by the π-cyclopentadienyl ring, a weaker π acceptor.



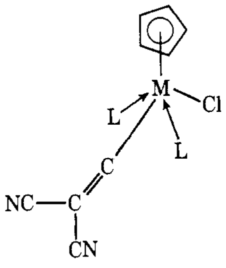
III

Replacement of the 2,2-dicyanovinyl hydrogen in compounds of the type $(NC)_2C{=}CHMo(CO)_3C_5H_5$ (III, M = Mo; L = CO) with chlorine to give the 1-chloro-2,2-dicyanovinyl derivatives $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ (I, M = Mo) changes dramatically the course of the reaction of the complex with triphenylphosphine. The reaction between the 1-chloro-2,2-dicyanovinyl derivative $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ and triphenylphosphine results in complete displacement of all carbonyl groups to give an orange carbonyl-free product of stoichiometry $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(C_5H_5)$. The replacement of three carbonyl ligands by two triphenylphosphine ligands in this reaction is unusual since both ligands are two-electron donors. Conversion of the $(NC)_2C{=}C(Cl)$ group from a one-electron donor to a three-electron donor is necessary to preserve the 18-electron configuration of the complex in going from $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ (I, M = Mo) to $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(C_5H_5)$.

The proton nmr spectrum of $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(C_5H_5)$ provides strong evidence concerning the structure of this complex. The presence of aryl and π-cyclopentadienyl resonances in the expected positions and of the expected relative intensities (6:1) indicates the complex to be diamagnetic and confirms the stoichiometry indicated by the elemental analyses. The complexity of the π-cyclopentadienyl resonance in $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(C_5H_5)$, which consisted of two 1:2:1 triplets of approximate 3:1 relative intensities centered at τ 4.91 and 5.16, respectively, suggests that $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(C_5H_5)$ consists of a mixture of two isomers. Isomerism leading to similar nmr effects has been shown to be possible for numerous $C_5H_5MA_2BC$ compounds[16] such as $C_5H_5Mo(CO)_2[P(NMe_2)_3]I$[17] and $C_5H_5Mo(NO)[P(OC_6H_5)_3]I_2$.[18] Similar isomerism is not possible for a $C_5H_5MA_2B$ compound. This indirect demonstration of the formulation of $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(C_5H_5)$ as a $C_5H_5MA_2BC$ compound rather than a $C_5H_5MA_2B$ compound indicates that the $(NC)_2C{=}CCl$ moiety occupies two not necessarily adjacent coordination positions rather than only one coordination position of the molybdenum. This is possible if $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(C_5H_5)$ is formulated as a mixture of the $C_5H_5MA_2BC$ isomers IVa and IVb ($M = Mo$; $L = (C_6H_5)_3P$) containing the first example of a terminal dicyanovinylidene ligand. In structures IVa and IVb the central molybdenum atom has the favored 18-electron rare gas configuration whereas in an alternative formulation of $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(C_5H_5)$ as a $C_5H_5MA_2B$ complex in which the 1-chloro-2,2-dicyanovinyl group is retained, the central molybdenum atom has only a 16-electron configuration.



IVa



IVb

The reaction between $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ and triphenylphosphine was carried out in boiling dichloromethane (37°) in an attempt to detect and isolate a dicarbonyl intermediate $(NC)_2C{=}C(Cl)Mo(CO)_2P(C_6H_5)_3(C_5H_5)$ under these mild reaction conditions. Infrared ν(CO) frequencies were observed at 1983 and 1903 cm^{-1} which could be assigned to $(NC)_2C{=}C(Cl)Mo(CO)_2P(C_6H_5)_3(C_5H_5)$ analogous to $(NC)_2C{=}CHMo(CO)_2P(C_6H_5)_3(C_5H_5)$ discussed above. However, the infrared spectrum of this reaction mixture at various times (Experimental Section) indicated that this $(NC)_2C{=}C(Cl)Mo(CO)_2P(C_6H_5)_3(C_5H_5)$ reacted with triphenylphosphine to form $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ (IV, $M = Mo$; $L = (C_6H_5)_3P$) in appreciable quantities while appreciable concentrations of unreacted $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ remained in the reaction mixture. No attempt was made to isolate a pure sample of $(NC)_2C{=}C(Cl)Mo(CO)_2P(C_6H_5)_3(C_5H_5)$ from this reaction mixture because of anticipated difficulties in separating it from the large quantities of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ and/or $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ accompanying it at all reaction times investigated.

The reactions between $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ (I, $M = Mo$) and triphenylphosphine in the aromatic hydrocarbons benzene and toluene gave orange arene adducts of the stoichiometry $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl \cdot$arene. The presence of the aromatic hydrocarbon was clearly indicated from the proton nmr spectra of these adducts. The toluene in the toluene complex of this type could not be removed by drying at 78° (0.5 mm). The well-known[19] tendency for polycyano olefins such as tetracyanoethylene to form stable charge-transfer complexes with aromatic hydrocarbons suggested that these compounds could be similar charge-transfer complexes involving the unsaturation of the terminal dicyanovinylidene ligand. However, the following observations appear to exclude unambiguously formulation of the adducts $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl \cdot$arene as charge-transfer complexes. (1) The similarities in colors of the adducts $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl \cdot$arene to the arene-free $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$. (2) The failure of the stronger π-donor hexamethylbenzene to form a similar $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl \cdot$arene complex upon reaction with arene-free $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$. (3) The failure of other $C_5H_5ML_2[C{=}C(CN)_2]Cl$ derivatives to form similar arene complexes. These $C_5H_5Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl \cdot$arene complexes therefore appear to be exceptionally stable clathrate derivatives.

The reaction of the tungsten compound $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ (I, $M = W$) with triphenylphosphine was somewhat more sluggish than the corresponding reaction of its molybdenum analog in accord with the greater stability of tungsten–carbon bonds relative to corresponding molybdenum–carbon bonds.[20] Thus the reaction of $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ with triphenylphosphine in boiling benzene for 72 hr resulted in recovery of some unchanged $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$. However, the reaction of $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ with triphenylphosphine in boiling xylene gave the carbonyl-free $C_5H_5W[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ (IV; $M = W$). This tungsten compound exhibited two triplet cyclopentadienyl proton nmr resonances like its molybdenum analog again indicating the presence of diagonal and lateral isomers of types IVa and IVb.

A second product from the reaction of $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ (I; $M = W$) with triphenylphosphine is the known[15] cyanocarbon-free derivative $C_5H_5W(CO)_2P(C_6H_5)_3Cl$ obtained in much lower yield than $C_5H_5W[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$. The formation of $C_5H_5W(CO)_2P(C_6H_5)_3Cl$ from $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ and triphenylphosphine can arise by migration of the chlorine from the vinylic carbon atom to the tungsten atom followed by loss of the dicyanovinylidene ligand.

The reactions of $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (I; $M = Mo$ and W) with triphenylphosphine under fairly

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(16) J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **92**, 5852 (1970).

(17) R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

(18) R. B. King, *ibid.*, **6**, 30 (1967).

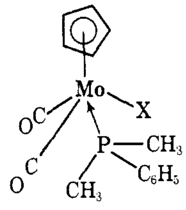
(19) L. R. Melby in "The Chemistry of the Cyano Group," Z. Rappoport, Ed., Interscience, London, 1970, pp 639–670.

(20) R. B. King, *Inorg. Nucl. Chem. Lett.*, **5**, 905 (1969).

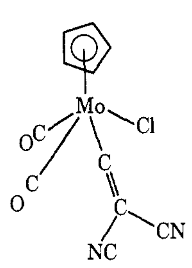
mild conditions thus result in the conversion of the 1-chloro-2,2-dicyanovinyl group to a coordinated chloride and to a coordinated dicyanovinylidene ligand through a novel migration of the chlorine from the vinylic carbon atom to the molybdenum atom. Such reactions of the molybdenum compound $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ (I; M = Mo) with ligands containing trivalent phosphorus and its heavier congeners to give dicyanovinylidene complexes of the type $C_5H_5MoL_2[C{=}C(CN)_2]Cl$ (IV; M = Mo) appear to be fairly general since analogous compounds of the ligands $(C_6H_5)_3E$ (E = As and Sb), $(CH_3)_2PC_6H_5$, and $(RO)_3P$ (R = CH_3, C_2H_5, and C_6H_5) have been prepared. Of these compounds, only the triphenylstibine derivative $C_5H_5Mo[Sb(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ shows two cyclopentadienyl proton nmr resonances indicative of the presence of both the diagonal isomer IVa and the lateral isomer IVb. The nmr spectra of all of the other $C_5H_5MoL_2[C{=}C(CN)_2]Cl$ derivatives prepared in this work exhibit only one cyclopentadienyl resonance indicating the presence of only one of the two isomers IVa and IVb in the product. The cyclopentadienyl resonances in the compounds of the type $C_5H_5Mo(PR_3)_2[C{=}C(CN)_2]Cl$ (IV) were 1:2:1 triplets ($J \approx 2$ Hz) because of spin–spin coupling of the cyclopentadienyl protons with the two approximately equivalent spin $^1/_2$ phosphorus atoms.

The range of tungsten complexes of monodentate ligands of the type $C_5H_5WL_2(C{=}C(CN)_2]Cl$ which could be prepared was somewhat more limited because of the higher temperatures necessary for the reactions of $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ (I; M = W) with the ligands. These higher reaction temperatures led to complete decomposition in some of the systems. Thus, reactions of $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ with triphenylarsine and with triphenyl phosphite in boiling xylene both led to complete decomposition rather than formation of the corresponding $C_5H_5WL_2[C{=}C(CN)_2]Cl$ derivative. However, the triphenylarsine derivative $C_5H_5W[As(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ was obtained when the reaction between $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ (I; M = W) and triphenylarsine was carried out in boiling toluene.

The reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ (I; M = Mo) with the very basic dimethylphenylphosphine, $(CH_3)_2PC_6H_5$, gave not only the dicyanovinylidene complex $C_5H_5Mo[P(CH_3)_2C_6H_5]_2[C{=}C(CN)_2]Cl$ (IV; M = Mo, L = $(CH_3)_2PC_6H_5$) but also the cyanocarbon-free complex $C_5H_5Mo(CO)_2[P(CH_3)_2C_6H_5]Cl$ analogous to the reaction of $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ (I; M = W) with triphenylphosphine discussed above. The proton nmr spectrum of the $C_5H_5Mo(CO)_2[P(CH_3)_2C_6H_5]Cl$ exhibited only a single cyclopentadienyl resonance indicating it to be a single isomer.[16] This isomer was identified as the lateral ("cis") isomer V (X = Cl) by the two overlapping doublet methyl resonances in the proton nmr spectrum similar to the methyl proton nmr resonances found by Faller and Anderson[16] for the lateral isomer of the analogous iodide $C_5H_5Mo(CO)_2[P(CH_3)_2C_6H_5]I$ (V; X = I).

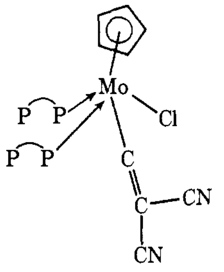


V

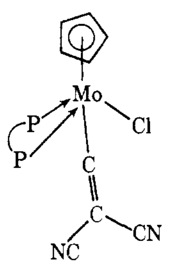


VI

Some reactions of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ (I; M = Mo) with di(tertiary phosphines) were investigated. The saturated di(tertiary phosphine) $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (abbreviated as Pf-Pf) can act as either a monoligate monometallic ligand or a biligate monometallic ligand[21,22] in its reactions with $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ depending upon the reaction conditions including the mole ratios of the reactants. The ^{31}P nmr spectrum of the red-orange monoligate monometallic derivative $C_5H_5Mo(Pf\text{-}Pf)_2[C{=}C(CN)_2]Cl$ (structure of type VII) exhibits two resonances of approximately equal relative intensities at −41.9 and +12.6 ppm relative to external 85% H_3PO_4 indicating the presence of equal numbers of coordinated and uncoordinated trivalent phosphorus atoms required by a structure of the type VII. However, the ^{31}P nmr spectrum of the brown biligate monometallic derivative $C_5H_5Mo(Pf\text{-}Pf)[C{=}C(CN)_2]Cl$ (structure of type VIII) exhibited only a single resonance at −42.2 ppm relative to external ~85% H_3PO_4 indicating the presence of only coordinated phosphorus atoms.



VII



VIII

The cis olefinic di(tertiary phosphine), *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (abbreviated as *c*Pf=Pf), reacted with $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ to give a dark green product $C_5H_5Mo(c\text{Pf}{=}\text{Pf})[C{=}C(CN)_2]Cl$ formulated as a biligate monometallic derivative of type VIII. The doublet (J = 3 Hz) cyclopentadienyl proton resonance in $C_5H_5Mo(c\text{Pf}{=}\text{Pf})[C{=}C(CN)_2]Cl$ indicates significant coupling of the protons in the cyclopentadienyl ring with only one phosphorus atom in the *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ ligand. However, in a complex of structure VIII the two phosphorus atoms of the chelating di(tertiary phosphine) are nonequivalent since one is diagonal to a dicyanovinylidene ligand and the other diagonal to a chlorine atom. Therefore, it is not unreasonable for only one of the phosphorus atoms in a compound of structure VIII to couple appreciably with the cyclopentadienyl protons.

The reaction of the potentially chelating tri(tertiary phosphine) $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ (abbreviated as Pf-Pf-Pf) with $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ in boiling octane results in displacement not only of the three carbonyl groups but also of the chlorine to give the $[C_5H_5Mo(Pf\text{-}Pf\text{-}Pf)C{=}C(CN)_2]^+$ cation (IX). The initially formed chloride salt can be converted to the corresponding hexafluorophosphate salt by metathesis. The proton nmr spectrum and elemental analyses of

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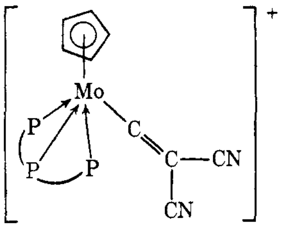
(21) R. B. King, *J. Coord. Chem.*, 1, 67 (1971).

(22) R. B. King and A. Efraty, *Inorg. Chem.*, 8, 2374 (1969).

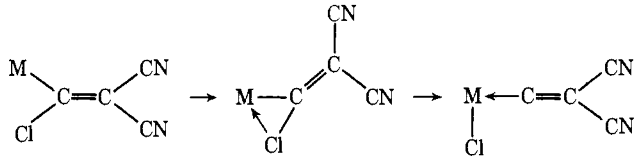


IX

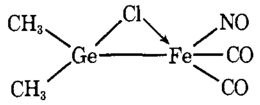
$[C_5H_5Mo(Pf\text{-}Pf\text{-}Pf)C{=}C(CN)_2][PF_6]$ clearly indicate the presence of a cyclopentadienyl ring and the chelating tri(tertiary phosphine) ligand but the absence of chlorine. The cation $[C_5H_5Mo(Pf\text{-}Pf\text{-}Pf)C{=}C(CN)_2]^+$ (IX) exemplifies a terminal dicyanovinylidene ligand in the absence of coordinated chloride and provides additional evidence for the presence of dicyanovinylidene ligands rather than 1-chloro-2,2-dicyanovinyl groups in the compounds of stoichiometry $(NC)_2C{=}CCl\text{-}MoL_2C_5H_5$ discussed in this paper.

The infrared spectrum[1] of the bridging dicyanovinylidene ligand in the complexes *cis-* and *trans-*$(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ exhibits a single ν(CN) frequency at 2215 ± 1 cm^{-1} and a single ν(C=C) frequency at 1481 ± 1 cm^{-1}. The infrared spectrum of the terminal dicyanovinylidene ligand in the complexes $C_5H_5ML_2[C{=}C(CN)_2]Cl$ (M = Mo and W, L = tertiary phosphines, phosphites, arsines, and stibines) described in this paper exhibits a single ν(CN) frequency in the range 2199 ± 4 cm.$^{-1}$ The infrared ν(C=C) frequencies in these $C_5H_5ML_2[C{=}C(CN)_2]Cl$ complexes could not be unambiguously located because of interference from absorptions in the 1400–1500-cm^{-1} regions from the $(C_6H_5)_3E$ (E = P, As, or Sb) or $(RO)_3P$ (R = CH_3, C_2H_5, or C_6H_5) ligand also present in these complexes. However, careful comparison of the infrared spectra of the free ligands and those of their $C_5H_5MoL_2[C{=}C(CN)_2]Cl$ complexes always indicated the presence of much stronger absorptions at 1410–1425 cm^{-1} in the complexes than in the free ligands. This extra absorption around 1420 cm^{-1} is therefore assigned tentatively to the ν(C=C) frequency in the terminal dicyanovinylidene complexes $C_5H_5ML_2[C{=}C(CN)_2]Cl$. A comparison of the 2215 and 1481-cm^{-1} positions of the ν(CN) and ν(C=C) frequencies, respectively, in the bridging dicyanovinylidene complexes $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ with the lower 2199 and 1420-cm^{-1} positions of the corresponding frequencies in the terminal dicyanovinylidene complexes $C_5H_5ML_2[C{=}C(CN)_2]Cl$ indicates that there is more retrodative bonding from the filled transition metal d orbitals into the antibonding orbitals of the dicyanovinylidene ligand in the terminal dicyanovinylidene complexes $C_5H_5ML_2[C{=}C(CN)_2]Cl$ than in the bridging dicyanovinylidene complexes $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$. This is in sharp disagreement with the numerous observations of lower ν(CO) frequencies for bridging carbonyls than for terminal carbonyls. However, the other ligands in the compounds $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ and $C_5H_5ML_2[C{=}C(CN)_2]Cl$ are very different. Comparisons between the ν(CN) and ν(C=C) frequencies in these two classes of dicyanovinylidene complexes may be similar to a comparison of the ν(CO) frequencies of 1748 and 1645 cm^{-1} in the dianion[23] $[C_5H_5V(CO)_3]^{2-}$ with the bridging ν(CO) frequency of 1780 cm^{-1} in $[C_5H_5Fe(CO)_2]_2$ where other effects (*i.e.*, different retrodative bonding tendencies of the other ligands and/or the charge on the system) override the difference between bridging and terminal carbonyl or dicyanovinylidene groups. Certainly the complete substitution of the very strong π-acceptor carbon monoxide with the weaker trivalent phosphorus π-acceptors in going from $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ to $C_5H_5ML_2[C{=}C(CN)_2]Cl$ (M = Mo or W; L = trivalent phosphorus ligand) would be expected to increase the electron density on the metal atom available for retrodative bonding in the latter molybdenum or tungsten complexes relative to the former iron complexes.

The reactions of the compounds $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (I) with the trivalent phosphorus and related ligands to give the complexes $C_5H_5ML_2[C{=}C(CN)_2]Cl$ (II) involve the conversion of a 1-chloro-2,2-dicyanovinyl group to a coordinated dicyanovinylidene and chloride possibly *via* a chlorine shift according to the following sequence



The intermediate with a chlorine bridge between carbon and the transition metal is similar to recently reported organogermanium transition metal derivatives[24] (*e.g.* $(CH_3)_2GeClFe(CO)_2NO$, (X)) with a chlorine bridge between germanium and a transition metal. This chlorine shift process involves ultimate rupture of a carbon–chlorine bond and thus may be regarded as an intramolecular addition reaction. Factors influencing the ease of oxidative addition reactions[25] should have a similar influence on the ease of conversion of a 1-chloro-2,2-dicyanovinyl group to a coordinated dicyanovinylidene and chloride. Oxidative addition reactions are facilitated by an increase in the electron density on the central transition metal atom such as would occur by replacement of the strongly π-accepting carbonyl groups with less strongly π-accepting trivalent phosphorus ligands. A relatively electron-rich metal atom may also be necessary for the formation of stable complexes containing terminal dicyanovinylidene ligands since the spectroscopic properties[1] of the $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ isomers suggest that the dicyanovinylidene ligand is even a stronger π acceptor than carbon monoxide because of the stronger electron withdrawing tendencies of the dicyanomethylene group relative to an oxygen atom. For these reasons, the replacement of carbonyl groups by tertiary phosphines or similar ligands may be necessary before chemistry of the type discussed in this paper can be observed.



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(23) R. D. Fischer, *Chem. Ber.*, **93**, 165 (1960).

(24) M. D. Curtis and R. C. Job, *J. Amer. Chem. Soc.*, **94**, 2153 (1972).

(25) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).