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Transition-Metal Cyanocarbon Derivatives. 6. Reactions of (1-Chloro-2,2-dicyanovinyl)metal Derivatives with Tris(dialkylamino)phosphines and Related Reagents: A Novel Dialkylamino Transfer from Phosphorus to Carbon[1,2]

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Ultraviolet irradiations of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ (Pf-Pf = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) with the aminophosphines $[(CH_3)_2N]_3P$, $[(CH_3)_2N]_2PC_6H_5$, $(C_6H_5)_2PCH_2CH_2P[N(CH_3)_2]_2$, tris(piperidino)phosphine, and tris(morpholino)phosphine in tetrahydrofuran solution result in transfer of a dialkylamino group from phosphorus to carbon to give the corresponding yellow η^2-dicyanoketenimmonium-*C,C* derivatives $[R_2N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)$ (R = CH_3 or $R_2 = (CH_2)_5$ or $O(CH_2)_4$). The corresponding diethylamino derivative $[(C_2H_5)_2N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)$ is obtained by ultraviolet irradiation of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ with diethylamine. However, similar ultraviolet irradiation of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ with dimethylamine, pyrrolidine, piperidine, and morpholine result instead in the formation of the corresponding dialkylcarbamoyl derivatives $(NC)_2C{=}C(NHR_2)Mn(CO)_2(CONR_2)(Pf\text{-}Pf)$ (R = CH_3 or $R_2 = (CH_2)_4$, $(CH_2)_5$, or $O(CH_2)_4$). Reactions of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with the aminophosphines $[(CH_2)_2N]_3P$, $[(CH_3)_2N]_2PC_6H_5$, $(C_6H_5)_2PCH_2CH_2P[N(CH_3)_2]_2$, and tris(piperidino)phosphine in boiling tetrahydrofuran give the corresponding yellow η^2-dicyanoketenimmonium-*C,C* derivatives $[R_2N{=}C{=}C(CN)_2]Mo(CO)_2C_5H_5$. Ultraviolet irradiation of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ with pyrazole gives a mixture of the yellow-brown η^2-dicyanoketenimmonium-*C,N* derivative $[(NC)_2C{=}C{=}N_2C_3H_3]Mn(CO)_2(Pf\text{-}Pf)$ and the purple monocarbonyl $(NC)_2C{=}C(N_2C_3H_3)Mn(CO)(Pf\text{-}Pf)_2$. A similar ultraviolet irradiation of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3[P(OC_2H_5)_3]_2$ with pyrazole gives a mixture of the yellow dicyanoketenimmonium derivatives $[(NC)_2C{=}C{=}CN_2C_3H_3]Mn(CO)_2[P(OC_2H_5)_3]_2$ and $[(NC)_2C{=}C{=}CN_2C_3H_3]Mn(CO)[P(OC_2H_5)_3]_3$. The spectroscopic properties of these new complexes are presented and discussed.

Introduction

The previous paper of this series[1] describes the photochemical reactions of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ (Pf-Pf = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) with trialkyl phosphites $(RO)_3P$. Such reactions result in a Michaelis–Arbusov elimination of alkyl chloride, RCl, to give the dialkyl(2,2-dicyanovinyl)phosphonato derivatives $(NC)_2C{=}CP(O)(OR)_2Mn(CO)L(Pf\text{-}Pf)$ (R = CH_3 and C_2H_5, L = $(RO)_3P$; R = $(CH_3)_2CH$, L = CO). These results suggested similar photochemical reactions of $(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ with the closely related tris(dialkylamino)phosphines, $(R_2N)_3P$ (R = CH_3 or $R_2 = (CH_2)_5$ or $O(CH_2)_4$). These reactions have been found to follow a completely different pattern leading to transfer of the dialkylamino group from the phosphorus atom to a vinylic carbon atom to give the corresponding dicyanoketenimmonium derivatives $[R_2N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)$. Related dicyanoketenimmonium derivatives $[R_2N{=}C{=}C(CN)_2]Mo(CO)_2C_5H_5$ had previously[4] been obtained by treatment of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with secondary amines. We have now found that the same molybdenum complexes $[R_2N{=}C{=}C(CN)_2]Mo(CO)_2C_5H_5$ can also be obtained by a thermal reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with the corresponding tris(dialkylamino)phosphines, $(R_2N)_3P$.

This paper describes the details of our studies on the reactions of the (1-chloro-2,2-dicyanovinyl)metal complexes $(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ and $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with tris(dialkylamino)phosphines and related aminophosphines. Some reactions of the (1-chloro-2,2-dicyanovinyl)manganese derivatives with secondary amines are also described. In some cases such reactions do not form dicyanoketenimmonium derivatives but instead the novel dialkylcarbamoyl derivatives $(NC)_2C{=}C(NHR_2)Mn(CO)_2(CONnR_2)L_2$.

Experimental Section

Microanalyses (Table I) were performed by Atlantic Microanalytical Laboratory, Atlanta, Ga. Melting and decomposition points (Table I) were determined in capillaries and are uncorrected. The general procedures used to obtain infrared (Table II), proton NMR (Tables III and IV), and carbon-13 NMR (Tables V and VI) spectra are described in detail in the previous paper of this series.[1]

All reactions were carried out under nitrogen. Ultraviolet irradiations were performed by placing a Westinghouse H44-4GS 100-W mercury spot lamp ~20 cm from the Pyrex glass reaction vessel. Alumina (80–200 mesh) for chromatography was used as received from Fisher Scientific Co. Tetrahydrofuran was redistilled over $LiAlH_4$ under nitrogen.

The ligand $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (abbreviated as Pf-Pf) was prepared by a standard published procedure.[5] The aminophosphines $[(CH_3)_2N]_3P$,[6] $[(CH_3)_2N]_2PC_6H_5$,[7] $(C_6H_5)_2PCH_2CH_2P[N(CH_3)_2]_2$,[8] tris(piperidino)phosphine,[9] and tris(morpholino)phosphine[10] were prepared by the cited published procedures. The 1-chloro-2,2-dicyanovinyl derivatives *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3L_2$ (L = $(C_2H_5O)_3P$ or $L_2 = (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$[11] and $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$)[12] were prepared by the cited published procedures.

Reactions of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ with Aminophosphines (Table VII). A mixture of the indicated quantities of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$, aminophosphine, and tetrahydrofuran was exposed to ultraviolet irradiation for the indicated period of time (Table VII). Solvent was then removed at 25 °C (25 mm). A concentrated dichloromethane solution of the residue was chromatographed on an alumina column. The major yellow band of product was eluted with mixtures of dichloromethane and hexane. Evaporation of the eluate at 25 °C (25 mm) followed by crystallization from mixtures of dichloromethane and hexane gave yellow crystals of the $[R_2N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)$ derivatives in the indicated yields (Table I). In some cases (Table I) the products contained dichloromethane of crystallization which was not removed by drying at 25 °C (0.1 mm).

Reactions of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with Aminophosphines (Table VII). A mixture of the indicated quantities of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$, aminophosphine, and tetrahydrofuran was boiled under reflux for the indicated period of time (Table VII). Solvent was then removed from the reaction mixture at 25 °C (25 mm). The brown residue was extracted with dichloromethane. The combined dichloromethane extracts were filtered through Celite 545. Chromatography of the concentrated filtrate on an alumina column gave a major yellow band which was eluted with a mixture of dichloromethane and hexane. Evaporation of the filtrate at 25 °C (25 mm) followed by crystallization from a mixture of dichloromethane and hexane gave yellow crystals of the $[R_2N{=}C{=}C(CN)_2]Mo(CO)_2C_5H_5$ derivatives in the indicated yield (Table VII).

Ultraviolet Irradiations of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ with Saturated Aliphatic and Heterocyclic Secondary Amines. A mixture of 1–2 mmol of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$, 4–8 mmol of the secondary amine, and 40 mL of tetrahydrofuran was exposed to

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Table I. New (Cyanocarbon)manganese Carbonyl Derivatives Described in this Paper

compd[a]	color	mp, °C	yield,[b] %		% C	% H	% N	% Cl	mol wt
A. Compounds of the Type $[R_2N{=}C{=}C(CN)_2]Mn(CO)_2L_2$									
$[Me_2N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)\cdot CH_2Cl_2$	yellow	196–205 dec	37 P	calcd	58.8	4.5	5.9	9.9	714
				found	58.0	4.5	5.8	10.2	720
$[Et_2N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)\cdot CH_2Cl_2$	yellow	211–215 dec	43	calcd	60.0	4.6	5.7	9.6	739
				found	60.0	4.6	5.7	9.5	726
$[C_5H_{10}N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)\cdot CH_2Cl_2$	yellow	>210 dec	23 P	calcd	60.5	4.8	5.6	9.4	
				found	60.5	4.8	5.6	9.3	
$[OC_4H_8N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)$	yellow	209–214 dec	65 P	calcd	64.4	4.8	6.3	0.0	
				found	64.5	4.8	6.3	0.0	
$[(NC)_2C{=}C{=}N_2C_3H_3]Mn(CO)_2(Pf\text{-}Pf)$	yellow-brown	128–130 dec	24	calcd	64.4	4.1	8.6	0.0	
				found	64.1	4.2	8.3	0.0	
$[(NC)_2C{=}C{=}N_2C_3H_3]Mn(CO)_2[P(OEt)_3]_2$	yellow	102–103	24	calcd	43.0	5.6	9.6	0.0	
				found	43.2	5.7	9.6	0.0	
$[(NC)_2C{=}C{=}N_2C_3H_3]Mn(CO)[P(OEt)_3]_3$	yellow-brown	127–128	6	calcd	43.1	6.6	7.7	0.0	
				found	43.6	6.7	7.7	0.0	
$(NC)_2C{=}C(N_2C_3H_3)Mn(CO)(Pf\text{-}Pf)_2$	purple	147–150 dec	18	calcd	70.5	5.0	5.5	0.0	
				found	70.1	5.2	5.2	0.0	
B. Compounds of the Type $(NC)_2C{=}C(NHR_2)Mn(CO)_2(CONR_2)L_2$									
$(NC)_2C{=}C(NHMe_2)Mn(CO)_2(CONMe_2)(Pf\text{-}Pf)$	light yellow	172–174	49	calcd	63.2	5.3	8.0	0.0	702
				found	63.2	5.5	8.2	0.0	620
$(NC)_2C{=}C(NHC_4H_8)Mn(CO)_2(CONC_4H_8)(Pf\text{-}Pf)$	yellow	179–184 dec	60	calcd	65.3	5.4	7.4	0.0	
				found	64.1	5.6	7.3	0.0	
$(NC)_2C{=}C(NHC_5H_{10})Mn(CO)_2(CONC_5H_{10})(Pf\text{-}Pf)\cdot CH_2Cl_2$	yellow	161 dec	48	calcd	60.9	5.4	6.5	8.2	
				found	61.2	5.8	6.5	8.1	
$(NC)_2C{=}C(NHC_4H_8O)Mn(CO)_2(CONC_4H_8O)(Pf\text{-}Pf)\cdot CH_2Cl_2$	yellow	135–138	29	calcd	59.0	5.0	6.5	8.3	855
				found	58.0	5.3	6.7	8.6	823
$(NC)_2C{=}C(NHC_5H_{10})Mn(CO)_2(CONC_5H_{10})[P(OEt)_3]_2$	white	137–139 dec	32	calcd	48.6	7.1	7.8	0.0	
				found	48.8	7.6	8.0	0.0	

[a] Me = methyl, Et = ethyl, C_4H_8N = pyrrolidino, $C_5H_{10}N$ = piperidino, OC_4H_8N = morpholino, $C_3H_3N_2$ = pyrazolyl, Pf-Pf = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. [b] These yields were obtained using the procedure described in the Experimental Section. The yields followed by P were obtained using the tris(dialkylamino)phosphine (Table VII); the other yields were obtained by using the secondary amine.

Table II. Infrared Spectra of the (Cyanocarbon)manganese Derivatives Described in this Paper

compd[a]	infrared spectrum, cm^{-1}				
	$\nu(C{\equiv}N)$[b]	$\nu(CO)$[b,c]	$\nu(C{=}N)$[c]	$\nu(C{=}C)$[c]	$\nu(N{-}H)$[c]
$[Me_2N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)\cdot CH_2Cl_2$	2200 m, 2193 m	1950 s, 1866 s	1576 m	1431 m	
$[Et_2N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)\cdot CH_2Cl_2$	2203 m, 2195 m	1951 s, 1871 s	1541 m	1432 m	
$[C_5H_{10}N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)\cdot CH_2Cl_2$	2205 m	1942 s, 1863 s	1566 m	1434 m	
$[OC_4H_8N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)$	2209 m, 2199 m	1956 s, 1874 s	1537 m	1431 m	
$[C_3H_3N_2{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)$	2229 m, 2217 m	1951 s, 1882 s	1518 m	1483 m	
$(NC)_2C{=}C(N_2C_3H_3)Mn(CO)(Pf\text{-}Pf)_2$	2219 m, 2202 m	1831 s		1430 s	
$[C_3H_3N_2{=}C{=}C(CN)_2]Mn(CO)_2[P(OEt)_3]_2$	2215 m, 2201 m	1957 s, 1887 s	1530 s	1497 m	
$[C_3H_3N_2{=}C{=}C(CN)_2]Mn(CO)[P(OEt)_3]_3$	2230 m, 2208 m	1863 vs	1519 w	1466 s	
$(NC)_2C{=}C(NHMe_2)Mn(CO)_2(CONMe_2)(Pf\text{-}Pf)$	2166 m	1911 vs, 1832 vs, 1541 m		1421 m	3394 w
$(NC)_2C{=}C(NHC_4H_8)Mn(CO)_2(CONC_4H_8)(Pf\text{-}Pf)\cdot CH_2Cl_2$	2163 m	1916 vs, 1833 vs, 1530 m		1410 m	3370 w
$(NC)_2C{=}C(NHC_5H_{10})Mn(CO)_2(CONC_5H_{10})(Pf\text{-}Pf)\cdot CH_2Cl_2$	2169 m	1912 vs, 1830 vs, 1530 m		1414 m	3371 w
$(NC)_2C{=}C(NHC_4H_8O)Mn(CO)_2(CONC_4H_8O)(Pf\text{-}Pf)\cdot CH_2Cl_2$	2172 m	1920 vs, 1840 vs, 1532 m		1425 m	3365 w
$(NC)_2C{=}C(NHC_5H_{10})Mn(CO)_2(CONC_5H_{10})[P(OEt)_3]_2$	2173 m	1928 vs, 1846 vs, 1548 m		1419 s	3392 m

[a] See Table I for a list of abbreviations used in formulas. [b] The $\nu(C{\equiv}N)$ and the $\nu(CO)$ frequencies (except for the dialkylcarboxamido $\nu(CO)$) were measured in CH_2Cl_2 solutions. [c] The dialkylcarbamoyl $\nu(CO)$, $\nu(C{=}N)$, $\nu(C{=}C)$, and $\nu(N{-}H)$ frequencies were measured in KBr pellets.

ultraviolet irradiation for 3–4 h. Solvent was then removed at 25 °C (25 mm). Chromatography of a concentrated dichloromethane solution of the yellow residue on an alumina column followed by elution of the major yellow band with a mixture of dichloromethane and hexane gave the indicated yield (Table I) of the corresponding $(NC)_2C{=}C(NHR_2)Mn(CO)_2(CONR_2)(Pf\text{-}Pf)$ or, in the case of diethylamine, $[(C_2H_5)_2N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)$ derivative. The analytical samples were obtained by crystallizations from mixtures of dichloromethane and hexane or pentane at −20 °C.

Ultraviolet Irradiation of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3[P(OC_2H_5)_3]_2$ with Piperidine. A mixture of 1.16 g (2.0 mmol) of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3[P(OC_2H_5)_3]_2$, 0.8 mL (0.68 g, 8.0 mmol) of piperidine, and 40 mL of dichloromethane was exposed to ultraviolet irradiation for 3 h. Solvent was removed from the resulting light orange solution at 25 °C (25 mm). A concentrated dichloromethane solution of the residue was chromatographed on an alumina column. The major yellow band was eluted with mixtures of dichloromethane and hexane. Evaporation of the eluate followed by crystallization from a mixture of dichloromethane and hexane at −20 °C gave 0.42 g (30% yield) of light yellow crystalline $(NC)_2C{=}C(NHC_5H_{10})Mn(CO)_2(CONC_5H_{10})[P(OC_2H_5)_3]_2$.

Ultraviolet Irradiation of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ with Pyrazole. A mixture of 0.95 g (1.5 mmol) of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$, 0.54 g (8.0 mmol) of pyrazole, and 40 mL of dichloromethane was exposed to ultraviolet irradiation for 5 h. Solvent was then removed from the residue at 25 °C (25 mm). A concentrated dichloromethane solution of the residue was chromatographed on an alumina column. The first band (yellow) was eluted with a 23:7 mixture of dichloromethane and hexane. Evaporation of the eluate at 25 °C (25 mm) followed by crystallization of the residue from a

Table III. Proton NMR Spectra of the $[R_2N=C=C(CN)_2]Mn(CO)_nL_{4-n}$ Derivatives

	proton NMR spectrum,[b] τ		
compd[a]	C_6H_5[c]	NR_2	other
$[Me_2N=C=C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)\cdot CH_2Cl_2$	2.53 br	CH_3: 6.28 s, 6.82 s	CH_2Cl_2: 4.65 s
$[Et_2N=C=C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)\cdot CH_2Cl_2$	2.58 br, 2.90 br	CH_2: ~6.4 br CH_3: 8.58 t (7), 9.26 t (7)	CH_2Cl_2: 4.65 s
$[C_5H_{10}N=C=C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)\cdot CH_2Cl_2$	2.38 br	CH_2: ~6.8 vbr, ~8.0 vbr	CH_2Cl_2: 4.65 s
$[OC_4H_8N=C=C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)$	2.62 s, br	CH_2: 5.97 br, 6.15 br, 6.50 br	
$[(NC)_2C=C=N_2C_3H_3]Mn(CO)_2(Pf\text{-}Pf)$	2.35 br	*d*	
$(NC)_2C=C(N_2C_3H_3)Mn(CO)(Pf\text{-}Pf)_2$	~2.8	*d*	
$[(NC)_2C=C=N_2C_3H_3]Mn(CO)_2[P(OEt)_3]_2$		$N_2C_3H_3$: 1.75 d (2), 2.58 d (2), 3.67 br	CH_2: 5.98 m CH_3: 8.75 t (7)
$[(NC)_2C=C=N_2C_3H_3]Mn(CO)[P(OEt)_3]_3$		$N_2C_3H_3$: 1.79 br, 2.58 br, 3.70 br	CH_2: 5.98 m CH_3: 8.75 m

[a] See Table I for a list of abbreviations used in formulas. [b] s = singlet, d = doublet, t = triplet, br = broad, vbr = very broad, m = multiplet; coupling constants in hertz are given in parentheses. [c] The CH_2 resonances of the $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ could not be unambiguously identified. [d] These pyrazolyl resonances were hidden by the very large phenyl resonance.

Table IV. Proton NMR Spectra of the $(NC)_2C=C(NHR_2)Mn(CO)_2(CONR_2)L_2$ Derivatives

	proton NMR spectrum,[b] τ			
compd[a]	Pf-Pf or $P(OEt)_3$	NHR_2[c]	$CONR_2$	CH_2Cl_2
$(NC)_2C=C(NHMe_2)Mn(CO)_2(CONMe_2)(Pf\text{-}Pf)$	C_6H_5: 2.54 br CH_2: ~7.6 br	CH_3: 6.42 s	CH_3: 7.70 s	
$(NC)_2C=C(NHC_4H_8)Mn(CO)_2(CONC_4H_8)(Pf\text{-}Pf)\cdot CH_2Cl_2$	C_6H_5: 2.5 br CH_2: ~7.4 br	CH_2: ~6.0 br, ~8.1 br	CH_2: ~7.2, ~8.4 br	4.65 s
$(NC)_2C=C(NHC_5H_{10})Mn(CO)_2(CONC_5H_{10})(Pf\text{-}Pf)\cdot CH_2Cl_2$	C_6H_5: 2.5 br	CH_2: ~5.9 br, ~8.2 br	CH_2: ~7.5 br, ~8.5 br	4.65 s
$(NC)_2C=C(NHC_4H_8O)Mn(CO)_2(CONC_4H_8O)(Pf\text{-}Pf)\cdot CH_2Cl_2$	C_6H_5: 2.5 br CH_2: ~7.4 br	CH_2: ~5.9 br, ~6.5 br	CH_2: ~6.2 br, ~7.6 br	4.65 s
$(NC)_2C=C(NHC_5H_{10})Mn(CO)_2(CONC_5H_{10})[P(OEt)_3]_2$	CH_2: 6.01 m CH_3: 8.70 t (7)	CH_2: ~6.7 br, ~8.2 br	CH_2: ~6.8 br, ~8.4 br	

[a] See Table I for a list of abbreviations used in formulas. [b] s = singlet, t = triplet, m = multiplet, br = broad; coupling constants in hertz are given in parentheses. [c] The N–H protons could not be unambiguously observed presumably owing to broadening from the nitrogen quadrupole.

Table V. Carbon-13 NMR Spectra of the $[R_2N=C=C(CN)_2]Mn(CO)_nL_{4-n}$ Derivatives

	carbon-13 NMR spectrum,[b] δ				
compd[a]	CO[c]	Pf-Pf[d]	CN	NR_2[e]	other[f]
$[Me_2N=C=C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)\cdot CH_2Cl_2$		C_6H_5: 128–133 m CH_2: 28.3 br	119.4	CH_3: 45.9, 45.0	CH_2Cl_2: 53.3
$[Et_2N=C=C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)\cdot CH_2Cl_2$	230.9	C_6H_5: 127–134 m CH_2: 28.5 t (20), 27.4 t (24)	119.4	CH_2: 51.1, 50.2 CH_3: 13.4	CH_2Cl_2: 53.3
$[C_5H_{10}N=C=C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)\cdot CH_2Cl_2$	233.2 224.0	C_6H_5: 128–139 m CH_2: ~28.0 br	119.4	α-CH_2: 57.1, 56.2 β-CH_2: 26.3 γ-CH_2: 23.9	CH_2Cl_2: 53.3
$[OC_4H_8N=C=C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)$	~231 br	C_6H_5: 128–139 m CH_2: 27.4 br	119.2	α-CH_2: 55.8, 54.9 β-CH_2: 66.6	
$[(NC)_2C=C=N_2C_3H_3]Mn(CO)_2(Pf\text{-}Pf)$		C_6H_5: 129–133 m CH_2: 25.7 m	117.6 114.0	$N_2C_3H_3$: 143.0, 125.4, 109.0	C=C: ~73
$[(NC)_2C=C=N_2C_3H_3]Mn(CO)_2[P(OEt)_3]_2$			117.0 114.3	$N_2C_3H_3$: 144.7, 126.2, 110.2	C=C: 73.7 CH_2: 60.8 CH_3: 16.2

[a] See Table I for a list of abbreviations used in formulas. [b] t = triplet, m = multiplet, br = broad; unlabeled resonances were apparent singlets; coupling constants in hertz are given in parentheses. [c] The metal carbonyl CO resonances were either very weak or not observed at all apparently because of quadrupole broadening by the manganese. [d] The individual carbon resonances of the phenyl groups were not assigned because of the complexity of the system. [e] Positions of CH_2 groups in heterocyclic systems are given relative to the nitrogen atom. [f] Olefinic carbon atoms directly bonded to manganese were not observed apparently because of quadrupole broadening.

mixture of dichloromethane and hexane at −20 °C gave 0.20 g (20% yield) of yellow-brown crystalline $[(NC)_2C=C=N_2C_3H_3]Mn(CO)_2(Pf\text{-}Pf)$. The second band (purple) was eluted with pure dichloromethane. Evaporation of the eluate at 25 °C (25 mm) followed by crystallization of the residue from a mixture of dichloromethane and hexane at −20 °C gave 0.20 g (26% yield based on Pf-Pf) of purple crystalline $(NC)_2C=C(N_2C_3H_3)Mn(CO)(Pf\text{-}Pf)_2$.

Ultraviolet Irradiation of *fac*-$(NC)_2C=C(Cl)Mn(CO)_3[P(OC_2H_5)_3]_2$ with Pyrazole. A mixture of 1.16 g (2.0 mmol) of $(NC)_2C=C(Cl)Mn(CO)_3[P(OC_2H_5)_3]_2$, 0.27 g (4.0 mmol) of pyrazole, and 40 mL of dichloromethane was exposed to ultraviolet irradiation for 3 h. Solvent was removed from the dark red-brown reaction mixture at 25 °C (25 mm). A concentrated dichloromethane solution of the residue was chromatographed on an alumina column. The initial yellow band was eluted with a 1:1 mixture of dichloromethane and hexane. Evaporation of this eluate at 25 °C (25 mm) followed by crystallization of the residue from a mixture of dichloromethane and hexane at −20 °C gave 0.28 g (24% yield) of yellow $[(NC)_2C=C=N_2C_3H_3]Mn(CO)_2[P(OC_2H_5)_3]_2$. After removal of this yellow band, intermediate yellow and purple bands were eluted with 4:1 mixtures of dichloromethane and hexane. Evaporation of these eluates gave negligible quantities of products which were discarded. The next band (orange–brown) was eluted with pure dichloromethane. The eluate was evaporated at 25 °C (25 mm). The residue was rechromatographed under similar conditions. The final product was recrystallized from a mixture of dichloromethane and hexane at −20 °C to give 0.08 g (5.5% yield) of orange-brown $[(NC)_2C=C=N_2C_3H_3]Mn(CO)[P(OC_2H_5)_3]_3$.

Phosphorus-31 NMR Spectra. The following phosphorus-31 NMR spectra were taken in CH_2Cl_2 solutions and recorded at 40.3 MHz

Table VI. Carbon-13 NMR Spectra of the $(NC)_2C{=}C(NHR_2)Mn(CO)_2(CONR_2)L_2$ Derivatives

	carbon-13 NMR spectrum,[b] δ				
compd[a]	L	C=C	CN	NHR_2[c]	$CONR_2$
$(NC)_2C{=}C(NHMe_2)Mn(CO)_2(CONMe_2)$(Pf-Pf)	C_6H_5: 127–136 m CH_2: 26.6 t (20)	78.3	122.7	CH_3: 48.3	CH_3: 39.0 CO: 173.8 d (8)
$(NC)_2C{=}C(NHC_4H_8)Mn(CO)_2(CONC_4H_8)$(Pf-Pf)	C_6H_5: 127–137 m CH_2: 26.7 m, br	77.0	123.6	α-CH_2: 57.3 br β-CH_2: 26.2	α-CH_2: 47.4 β-CH_2: 25.3 CO: 169.5 d (9)
$(NC)_2C{=}C(NHC_4H_8O)Mn(CO)_2(CONC_4H_8O)$(Pf-Pf)	C_6H_5: 128–137 m CH_2: 26.7 m, br	80.3	122.1	α-CH_2: 67.8 β-CH_2: 56.7	α-CH_2: 66.2 β-CH_2: 47.3 CO: 175.3 d (9)
$(NC)_2C{=}C(NHC_5H_{10})Mn(CO)_2(CONC_5H_{10})[P(OEt)_3]_2$	CH_2: 60.0 CH_3: 16.5	78.9	122.7	α-CH_2: 57.5 β-CH_2: 26.9 γ-CH_2: 24.8	α-CH_2: 49.3 β-CH_2: 25.8 γ-CH_2: 24.8 CO: 177.4
$(CO)_4Mn(CONHC_2H_5)(NH_2C_2H_5)$[d]				CH_2: 45.3 CH_3: 19.0	CH_2: 35.8 CH_3: 15.4 CO: 187.2

[a] See Table I for a list of abbreviations used in formulas. [b] d = doublet, t = triplet, m = multiplet; unlabeled resonances were apparent singlets; coupling constants in hertz are given in parentheses. [c] Positions of CH_2 groups in heterocyclic systems are given relative to the nitrogen atom. [d] This complex was prepared according to R. J. Angelici and D. L. Denton, *Inorg. Chim. Acta,* **2**, 3 (1968).

Table VII. Reactions of (1-Chloro-2,2-dicyanovinyl)metal Derivatives with Aminophosphines

(1-chloro-2,2-dicyanovinyl)metal derivative (g, mmol)	aminophosphine[a] (g, mmol)	solvent (mL)	*T*, °C	time, h	product (% isolated yield[b])
$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) (1.28, 2.0)	$(Me_2N)_3P$ (0.96, 6.0)	THF (70)	25	4 (UV)	$[Me_2N{=}C{=}C(CN)_2]Mn(CO)_2$(Pf-Pf) (58)
$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) (0.64, 1.0)	$(Me_2N)_2PPh$ (1.5, 7.9)	THF (40)	25	3.5 (UV)	$[Me_2N{=}C{=}C(CN)_2]Mn(CO)_2$(Pf-Pf) (47)
$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) (0.64, 1.0)	$Ph_2PCH_2CH_2P(NMe_2)_2$ (0.33, 1.0)	THF (30)	25	3 (UV)	$[Me_2N{=}C{=}C(CN)_2]Mn(CO)_2$(Pf-Pf) (31)
$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) (1.28, 2.0)	$(C_5H_{10}N)_3P$ (1.94, 6.86)	THF (80)	25	2.5 (UV)	$[C_5H_{10}N{=}C{=}C(CN)_2]Mn(CO)_2$(Pf-Pf) (53)
$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) (1.28, 2.0)	$(OC_4H_8N)_3P$ (1.13, 4.0)	THF (70)	25	3.5 (UV)	$[OC_4H_8N{=}C{=}C(CN)_2]Mn(CO)_2$(Pf-Pf) (65)
$(NC)_2C{=}C(Cl)Mo(CO)_3Cp$ (0.71, 2.0)	$(Me_2N)_3P$ (0.32, 2.0)	THF (30)	65	3	$[Me_2N{=}C{=}C(CN)_2]Mo(CO)_2Cp$ (16)
$(NC)_2C{=}C(Cl)Mo(CO)_3Cp$ (0.71, 2.0)	$(Me_2N)_2PPh$ (0.5, 2.6)	THF (40)	65	5	$[Me_2N{=}C{=}C(CN)_2]Mo(CO)_2Cp$ (14)
$(NC)_2C{=}C(Cl)Mo(CO)_3Cp$ (0.71, 2.0)	$Ph_2PCH_2CH_2P(NMe_2)_2$ (0.33, 1.0)	THF (30)	65	24	$[Me_2N{=}C{=}C(CN)_2]Mo(CO)_2Cp$ (10)
$(NC)_2C{=}C(Cl)Mo(CO)_3Cp$ (0.71, 2.0)	$(C_5H_{10}N)_3P$ (0.97, 3.4)	THF (40)	65	6	$[C_5H_{10}N{=}C{=}C(CN)_2]Mo(CO)_2Cp$ (15)

[a] See Table I for a list of abbreviations used in formulas. [b] The indicated yields of product were obtained by using the procedures described in the Experimental Section.

on a Jeolco PFT-100 spectrometer operating in the pulsed Fourier transform mode with proton noise decoupling and a deuterium lock. Phosphorus-31 chemical shifts are reported relative to 85% phosphoric acid with positive numbers indicating upfield chemical shifts.

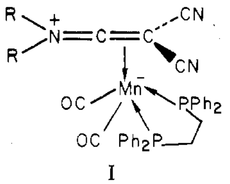
A. **$[OC_4H_8N{=}C{=}C(CN)_2]Mn(CO)_2$(Pf-Pf)** gave a broad resonance at δ −86.1.

B. **$(NC)_2C{=}C[NH(CH_3)_2]Mn(CO)_2[CON(CH_3)_2]$(Pf-Pf)** gave broad resonances at δ −92.3 and −69.0.

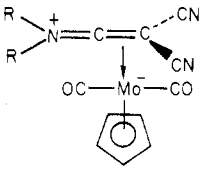
C. **$(NC)_2C{=}C[NHC_5H_{10}]Mn(CO)_2(CONC_5H_{10})[P(OC_2H_5)_3]_2$** gave a broad resonance at δ −168.2.

Results

Photolyses of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with the aminophosphines $[(CH_3)_2N]_3P$, $[(CH_3)_2N]_2PC_6H_5$, $(C_6H_5)_2PCH_2CH_2P[N(CH_3)_2]_2$, $(C_5H_{10}N)_3P$, and $(OC_4H_8N)_3P$ all give products of the type $[R_2N{=}C{=}C(CN)_2]Mn(CO)_2$(Pf-Pf) in which the dialkylamino group of the aminophosphine has migrated from phosphorus to a vinylic carbon (Table VII). The proton (Table III) and carbon-13 (Table V) NMR spectra of these $[R_2N{=}C{=}C(CN)_2]Mn(CO)_2$(Pf-Pf) derivatives indicate nonequivalence of the two R groups in the R_2N unit but equivalence of the two CN groups in the $C(CN)_2$ unit. These complexes are therefore formulated as the η^2-dicyanoketenimmonium-*C,C* derivatives, I (R = CH_3 or R_2 = $(CH_2)_5$ or $O(CH_2)_4$), in which the carbon–carbon double bond rather than the carbon–nitrogen double bond is bonded to the metal atom. They are therefore closely related to previously reported dicyanoketenimmonium[4] and tetraalkylketenimmonium[13] derivatives whose structures have been assigned on the basis of similar arguments based on NMR spectra.



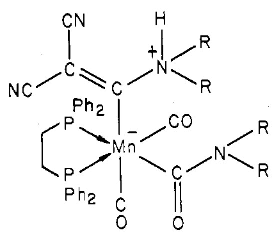
I



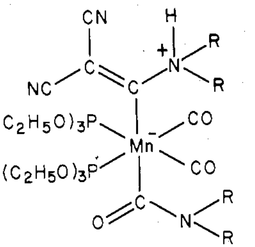
II

The previously reported[4] dicyanoketenimmonium derivatives $[R_2N{=}C{=}C(CN)_2]Mo(CO)_2C_5H_5$ (II: R = CH_3 or R_2 = $(CH_2)_5$) have been obtained in mediocre yields by reactions of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with the corresponding secondary amines at room temperature in the absence of ultraviolet irradiation. We have now found that these same complexes II can be prepared by reactions of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ with the aminophosphines $[(CH_3)_2N]_3P$, $[(CH_3)_2N]_2PC_6H_5$, $(C_6H_5)_2PCH_2CH_2P[N(CH_3)_2]_2$, and $(C_5H_{10}N)_3P$ in boiling tetrahydrofuran. Ultraviolet irradiation was not necessary for these reactions.

The previously reported[4] synthesis of the (dicyanoketenimmonio)molybdenum derivatives $[R_2N{=}C{=}C(CN)_2]Mo(CO)_2C_5H_5$ (II) from $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ and secondary amines led us to investigate reactions of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with secondary amines. Diethylamine was the only saturated aliphatic or heterocyclic amine tried which was found to react with *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) upon ultraviolet irradiation to give the dicyanoketenimmonium derivative $[R_2N{=}C{=}C(CN)_2]Mn(CO)_2$(Pf-Pf) (I: R = C_2H_5). The less hindered saturated secondary amines dimethylamine, pyrrolidine, piperidine, and morpholine all react with $(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) in the presence of ultraviolet irradiation to give 2:1 adducts



III

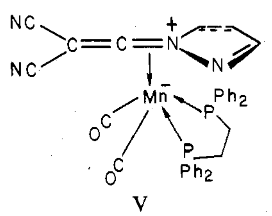


IV

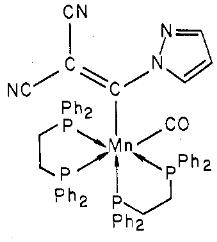
formulated as the dialkylcarbamoyl derivatives $(NC)_2C{=}C(NHR_2)Mn(CO)_2(CONR_2)(Pf\text{-}Pf)$ (III: R = CH_3 or R_2 = $(CH_2)_4$, $(CH_2)_5$, or $O(CH_2)_4$). Important features in the infrared spectra of these complexes (Table II) in support of structure III include the single ν(N–H) frequency in the range 3370–3394 cm^{-1} and the ν(CO) frequency at 1530–1548 cm^{-1} assigned to the dialkylcarbamoyl ($CONR_2$) carbonyl group.[14] The carbamoyl carbonyl carbon in the complexes $(NC)_2C{=}C(NHR_2)Mn(CO)_2(CONR_2)(Pf\text{-}Pf)$ (III) exhibits a proton-decoupled carbon-13 resonance in the range δ 169–174 which appears as a doublet (J = 8–9 Hz) apparently from coupling with one of the phosphorus atoms of the di(tertiary phosphine) (Table VI). This significant coupling of the dialkylcarbamoyl carbonyl carbon with one of the ligand phosphorus atoms suggests that the carbamoyl group is trans to a ligand phosphorus atom. The phosphorus-31 NMR spectrum of the dimethylamino derivative $(NC)_2C{=}C[NH(CH_3)_2]Mn(CO)_2[CON(CH_3)_2](Pf\text{-}Pf)$ (III: R = CH_3) indicates that the two ligand phosphorus atoms are highly nonequivalent. The stereochemistry indicated in structure III for the $(NC)_2C{=}C[NHR_2]Mn(CO)_2(CONR_2)(Pf\text{-}Pf)$ derivatives is consistent with all of these spectroscopic observations.

Ultraviolet irradiation of the triethyl phosphite complex *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3[P(OC_2H_5)_3]_2$ with piperidine was found to give a dialkylcarbamoyl derivative $(NC)_2C{=}C(NHC_5H_{10})Mn(CO)_2(CONC_5H_{10})[P(OC_2H_5)_3]_2$ which appears to be closely related to the dialkylcarbamoyl derivatives III. The phosphorus-31 NMR spectrum of this triethyl phosphite complex exhibits only a single, albeit somewhat broad, triethyl phosphite resonance suggesting that both ligands are equivalent in accord with structure IV (R_2 = $(CH_2)_5$).

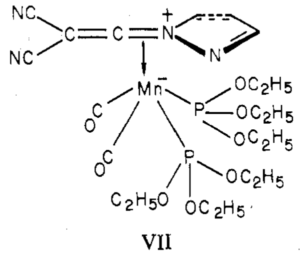
Ultraviolet irradiation of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ with the "secondary aromatic" amine pyrazole was found to give an orange and a purple product. The orange product has the stoichiometry $[(NC)_2C{=}C{=}N_2C_3H_3]Mn(CO)_2(Pf\text{-}Pf)$ and thus appears to be a dicyanoketenimmonium derivative similar to the complexes I obtained from *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ and the aminophosphines. However, the carbon-13 NMR spectrum of the complex $[(NC)_2C{=}C{=}N_2C_3H_3]Mn(CO)_2(Pf\text{-}Pf)$ (Table V) indicates nonequivalence of the two cyano groups. This suggests the η^2-dicyanoketenimmonium-*C,N* structure V since in the isomeric η^2-dicyanoketenimmonium-*C,C* structure the allene-like geometry of the ketenimmonium ligand places the unsymmetrical planar pyrazole ring in the plane of symmetry thereby retaining the equivalence of the two cyano groups despite the asymmetry of the pyrazole ring. Further support of the η^2-dicyanoketenimmonium-*C,N* structure V for the pyrazole complex $[(NC)_2C{=}C{=}N_2C_3H_3]Mn(CO)_2(Pf\text{-}Pf)$ is indicated by the ability to observe one olefinic carbon-13 resonance thereby suggesting that one of the olefinic carbon atoms is not directly bonded to the quadrupolar manganese atom. In the η^2-dicyanoketenimmonium-*C,C* derivatives, I, neither olefinic carbon can be observed in the carbon-13 NMR spectrum because of quadrupolar broadening of the manganese atom to which both olefinic carbons are directly bonded.



V



VI



VII

The purple product obtained by the ultraviolet irradiation of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ with pyrazole is a monocarbonyl of stoichiometry $(NC)_2C{=}C(N_2C_3H_3)Mn(CO)(Pf\text{-}Pf)_2$. If the di(tertiary phosphines) in this complex function as the usual bidentate ligands, then the 1-pyrazolyl-2,2-dicyanovinyl structure VI is suggested for this complex where the 1-pyrazolyl-2,2-dicyanovinyl group, effectively a substituted σ-vinyl group, functions as a one-electron donor. The formation of $(NC)_2C{=}C(N_2C_3H_3)Mn(CO)(Pf\text{-}Pf)_2$ from a photochemical reaction of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ in the absence of excess di(tertiary phosphine) suggests a certain mobility of the di(tertiary phosphines) under photolysis.

The ultraviolet irradiation of the triethyl phosphite complex *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3[P(OC_2H_5)_3]_2$ with pyrazole was found to give a yellow dicarbonyl $[(NC)_2C{=}C{=}N_2C_3H_3]Mn(CO)_2[P(OC_2H_5)_3]_2$ indicated by its carbon-13 NMR spectrum (Table V) to have nonequivalent cyano groups. It is therefore formulated as the dicyanoketenimmonium-*C,N* derivative VII similar to the di(tertiary phosphine) complex V discussed above. A minor product obtained from the ultraviolet irradiation of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3[P(OC_2H_5)_3]_2$ with pyrazole is the monocarbonyldicyanoketenimmonium derivative $[(NC)_2C{=}C{=}N_2C_3H_3]Mn(CO)[P(OC_2H_5)_3]_3$ containing three triethyl phosphite ligands. The formation of this latter complex like that of $[(NC)_2C{=}CN_2C_3H_3]Mn(CO)(Pf\text{-}Pf)_2$ discussed above indicates the mobility of L ligands in *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3L_2$ upon ultraviolet irradiation.

Discussion

An interesting observation from this work is the difference in the apparent pathways of the photochemical reactions of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ with the secondary amines R_2NH and with the tris(dialkylamino)phosphines $(R_2N)_3P$ when R = CH_3 or R_2 = $(CH_2)_5$ or $O(CH_2)_4$. This suggests that the photochemical reactions of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ with $(R_2N)_3P$ do not involve the corresponding secondary amine R_2NH as an intermediate.

The photochemical reactions of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ with the secondary amines R_2NH (R = CH_3 or R_2 = $(CH_2)_5$ or $O(CH_2)_4$) to give the dialkylcarbamoyl derivatives can be represented by eq 1. These reactions thus

$$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf) + 3R_2NH \rightarrow (NC)_2C{=}C(NHR_2)Mn(CO)_2(CONR_2)(Pf\text{-}Pf) + [R_2NH_2]Cl \quad (1)$$

do not involve loss of any carbonyl groups. The photochemical reactions of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ with the tris(dialkylamino)phosphines can be represented by eq 2.

$$\mathrm{(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf) + (R_2N)_3P \rightarrow [R_2N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf) + (R_2N)_2PCl + CO} \quad (2)$$

These reactions thus involve loss of one of the three carbonyl groups. In some cases (e.g., diethylamine and pyrazole) the photochemical reactions of *fac*-$\mathrm{(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)}$ with secondary amines also involve CO loss according to eq 3. Whether the photochemical reaction of a secondary amine with $\mathrm{(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)}$ proceeds according to eq 1 or eq 3 depends upon the reactivity of a metal carbonyl group toward addition of the secondary amine to form a dialkylcarbamoyl group as compared with the ease of photochemical elimination of a metal carbonyl group as carbon monoxide. Relatively small and highly basic secondary amines such as the saturated amines dimethylamine ($\mathrm{p}K_\mathrm{a} = 10.732$), pyrrolidine ($\mathrm{p}K_\mathrm{a} = 11.123$), and morpholine ($\mathrm{p}K_\mathrm{a} = 8.33$) will add to a metal carbonyl group to form the corresponding dialkylcarbamoyl group according to eq 1 faster than a metal carbonyl group can be photochemically eliminated according to eq 3. On the other hand, more bulky amines such as diethylamine ($\mathrm{p}K_\mathrm{a} = 10.489$) or less basic amines such as pyrazole ($\mathrm{p}K_\mathrm{a} = 2.53$) will react so slowly with a metal carbonyl group to form the corresponding dialkylcarbamoyl group (eq 1) that photochemical elimination of a carbonyl group (eq 3) will occur preferentially.

$$\mathrm{(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf) + 2R_2NH \rightarrow [R_2N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf) + [R_2NH_2]Cl + CO} \quad (3)$$

Another point of interest is the site of bonding of the dicyanoketenimmonium ligand to the metal system. The cyano groups in this ligand have vacant π^* orbitals which can participate in back-bonding with filled metal d orbitals. In the absence of any π^* orbitals in the $\mathrm{R_2N}$ group these vacant π^* orbitals of the cyano groups will act as a "magnet" to draw the metal atom to the $\mathrm{C(CN)_2}$ side of the dicyanoketenimmonium ligand thereby leading to η^2-*C,C* bonding (i.e., structure I). Such is the case with the dicyanoketenimmonium ligands $\mathrm{R_2N{=}C{=}C(CN)_2}$ derived from the saturated amines dimethylamine, diethylamine, pyrrolidine, piperidine, and morpholine (i.e., $\mathrm{R = CH_3}$ or $\mathrm{C_2H_5}$ or $\mathrm{R_2 = (CH_2)_4}$, $\mathrm{(CH_2)_5}$, or $\mathrm{O(CH_2)_4}$, respectively) which contain no vacant π^* orbitals. However, in the case of the ligand $\mathrm{C_3H_3N_2{=}C{=}C(CN)_2}$ derived from pyrazole, the $\mathrm{C_3H_3N_2}$ unit as well as the cyano groups has vacant π^* orbitals to participate in back-bonding with filled metal orbitals. Apparently, the vacant π^* orbitals in the pyrazole ring are stronger "magnets" than those in the cyano groups so that in the $\mathrm{C_3H_3N_2{=}C{=}C(CN)_2}$ ligand the metal is preferentially drawn toward the pyrazole end of the molecule thereby leading to η^2-*C,N* bonding (i.e., structure V).

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Registry No. $\mathrm{[Me_2N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)}$, 68129-70-4; $\mathrm{[Et_2N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)}$, 68129-71-5; $\mathrm{[C_5H_{10}N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)}$, 68129-72-6; $\mathrm{[OC_4H_8N{=}C{=}C(CN)_2]Mn(CO)_2(Pf\text{-}Pf)}$, 68129-73-7; $\mathrm{[(NC)_2C{=}C{=}N_2C_3H_3]Mn(CO)_2(Pf\text{-}Pf)}$, 68170-94-5; $\mathrm{[(NC)_2C{=}C{=}N_2C_3H_3]Mn(CO)_2[P(OEt)_3]_2}$, 68170-93-4; $\mathrm{[(NC)_2C{=}C{=}N_2C_3H_3]Mn(CO)[P(OEt)_3]_3}$, 68200-47-5; $\mathrm{(NC)_2C{=}C(N_2C_3H_3)Mn(CO)(Pf\text{-}Pf)_2}$, 68129-74-8; $\mathrm{(NC)_2C{=}C(NHMe_2)Mn(CO)_2(CONMe_2)(Pf\text{-}Pf)}$, 68138-97-6; $\mathrm{(NC)_2C{=}C(NHC_4H_8)Mn(CO)_2(CONC_4H_8)(Pf\text{-}Pf)}$, 68129-75-9; $\mathrm{(NC)_2C{=}C(NHC_5H_{10})Mn(CO)_2(CONC_5H_{10})(Pf\text{-}Pf)}$, 68129-76-0; $\mathrm{(NC)_2C{=}C(NHC_4H_8O)Mn(CO)_2(CONC_4H_8O)(Pf\text{-}Pf)}$, 68129-77-1; $\mathrm{(NC)_2C{=}C(NHC_5H_{10})Mn(CO)_2(CONC_5H_{10})[P(OEt)_3]_2}$, 68129-78-2; $\mathrm{[Me_2N{=}C{=}C(CN)_2]Mo(CO)_2Cp}$, 54083-47-5; $\mathrm{[C_5H_{10}N{=}C{=}C(CN)_2]Mo(CO)_2Cp}$, 54083-48-6; $\mathrm{(CO)_4Mn(CONHC_2H_5)(NH_2C_2H_5)}$, 68170-57-0; *fac*-$\mathrm{(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)}$, 66705-73-5; $\mathrm{(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5}$, 36312-92-2; *fac*-$\mathrm{(NC)_2C{=}C(Cl)Mn(CO)_3[P(OC_2H_5)_3]_2}$, 66705-72-4; $\mathrm{(Me_2N)_3P}$, 1608-26-0; $\mathrm{(Me_2N)_2PPh}$, 6143-71-1; $\mathrm{Ph_2PCH_2CH_2P(NMe_2)_2}$, 36892-72-5; $\mathrm{(C_5H_{10}N)_3P}$, 13954-38-6; $\mathrm{(OC_4H_8N)_3P}$, 5815-61-2; piperidine, 110-89-4; pyrazole, 288-13-1; dimethylamine, 124-40-3; pyrrolidine, 123-75-1; morpholine, 110-91-8.

References and Notes

(1) For part 5 of this series see: R. B. King and S. P. Diefenbach, *Inorg. Chem.*, preceding paper in this issue.
(2) Portions of this work were presented at the 173rd National Meeting of the American Chemical Society, New Orleans, La., March 1977; paper INOR 121 in abstracts.
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