reochemically.

Previously reported diphosphorus zwitterions include **3**, **4**, and **5**. Compound **1**, however, has two distinctive features: (i) it is acyclic and (ii) it involves a carbon rather than a nitrogen atom between the tetra- and hexacoordinate phosphorus centers.

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Registry No. **1**, 68036-86-2; $F_4PCH_2PF_4$, 57080-69-0; Me_3SiNMe_2, 2083-91-2.

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Transition-Metal Cyanocarbon Derivatives. 5. Reactions of (1-Chloro-2,2-dicyanovinyl)manganese Derivatives with Trialkyl Phosphites: A Novel Variant of the Michaelis–Arbusov Reaction Leading to [(2,2-Dicyanovinyl)phosphonato]metal Complexes[1,2]

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Ultraviolet irradiations of the (1-chloro-2,2-dicyanovinyl)manganese derivative $(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ (Pf-Pf $= (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) with the trialkyl phosphites $(RO)_3P$ ($R = CH_3$, C_2H_5, $(CH_3)_2CH$) in tetrahydrofuran solutions result in Michaelis–Arbusov reactions to give the (2,2-dicyanovinyl)phosphonato derivatives $(NC)_2C{=}CP(O)(OR)_2Mn(CO)(Pf\text{-}Pf)[P(OR)_3]$ ($R = CH_3$, C_2H_5) and $(NC)_2C{=}CP(O)(OR)_2Mn(CO)_2(Pf\text{-}Pf)$ ($R = (CH_3)_2CH$). The closely related compounds $(NC)_2C{=}CP(O)(OR)_2Mn(CO)_2(Pf\text{-}Pf)$ ($R = CH_3$ and C_2H_5) can be prepared by ultraviolet irradiation of $(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)$ with $LiP(O)(OR)_2$ ($R = CH_3$ and C_2H_5) in tetrahydrofuran solution. Ultraviolet irradiations of the dicarbonyls $(NC)_2C{=}CP(O)(OR)_2Mn(CO)_2(Pf\text{-}Pf)$ with excess trialkyl phosphite $(R'O)_3P$ ($R' = CH_3$ and C_2H_5 but not $(CH_3)_2CH$) result in displacement of one of the two carbonyl groups to give the corresponding monocarbonyls $(NC)_2C{=}CP(O)(OR)_2Mn(CO)(Pf\text{-}Pf)[P(OR')_3]$ ($R = CH_3$, $R' = CH_3$; $R = C_2H_5$, $R' = C_2H_5$; $R = (CH_3)_2CH$, $R' = CH_3$). The spectroscopic properties of these complexes suggest that their (2,2-dicyanovinyl)phosphonato groups $(NC)_2C{=}CP(O)(OR)_2$ are bidentate ligands which are bonded to the metal through both a vinylic carbon atom and a phosphoryl oxygen atom leading to a four-membered Mn–C–P–O chelate ring.

Introduction

The thermal reactions of the 1-chloro-2,2-dicyanovinyl derivatives $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (M = Mo and W) with trivalent phosphorus ligands, including trialkyl phosphites, have been shown[4,5] to result in the replacement of three carbonyl groups with two trivalent phosphorus ligands to give terminal dicyanovinylidene complexes of the general type $C_5H_5M(PR_3)_2[C{=}C(CN)_2]Cl$ (M = Mo and W). In attempts to synthesize analogous dicyanovinylidene complexes of manganese, analogous thermal reactions of $(NC)_2C{=}C(Cl)Mn(CO)_5$ with trivalent phosphorus ligands were investigated.[1] However, such thermal reactions were found to result only in the replacement of two carbonyl groups by the trivalent phosphorus ligand to give complexes of the type *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3(PR_3)_2$, containing an intact 1-chloro-2,2-dicyanovinyl group.

In view of the limited types of products obtained from thermal reactions of $(NC)_2C{=}C(Cl)Mn(CO)_5$ with trivalent phosphorus ligands, we began an investigation of photochemical reactions of $(NC)_2C{=}C(Cl)Mn(CO)_5$ and *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3L_2$ derivatives[1] with trivalent phosphorus ligands. Our idea was that such photochemical reactions would lead to more extensive CO substitution by the trivalent phosphorus ligand accompanied by rearrangement of the 1-chloro-2,2-dicyanovinyl group to the dicyanovinylidene ligand. However, up to the present time such reactions have not given any dicyanovinylidene complexes of manganese but instead have resulted in the isolation of other types of unusual and interesting cyanocarbon manganese carbonyl derivatives. This paper describes the preparation and properties of a series

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Table I. Infrared Spectra of the [(2,2-Dicyanovinyl)phosphonato]manganese Carbonyl Derivatives

compd[a]	infrared spectrum, cm^{-1} ν(CN)[b]	ν(CO)[b]	ν(C=C)[c]	ν(P=O)[c]
$(NC)_2C{=}CP(O)(OMe)_2Mn(CO)_2$(Pf-Pf)	2220 m, 2212 m	1960 s, 1890 s	1472 m	1130 m
$(NC)_2C{=}CP(O)(OMe)_2Mn(CO)[P(OMe)_3]$(Pf-Pf)	2210 m, 2198 m	1858 s	1421 m	1130 m
$(NC)_2C{=}CP(O)(OEt)_2Mn(CO)_2$(Pf-Pf)	2223 m, 2216 m	1961 s, 1884 s	1473 m	1143 m
$(NC)_2C{=}CP(O)(OEt)_2Mn(CO)[P(OEt)_3]$(Pf-Pf)	2206 m, 2199 m	1852 s	1430 s	1138 m
$(NC)_2C{=}CP(O)(O\text{-}i\text{-}Pr)_2Mn(CO)_2$(Pf-Pf)	2220 m, 2212 m	1955 s, 1885 s	1465 m	1145 m
$(NC)_2C{=}CP(O)(O\text{-}i\text{-}Pr)_2Mn(CO)[P(OMe)_3]$(Pf-Pf)	2208 m, 2196 m	1856 s	1425 m	1145 m
$(NC)_2C{=}CP(O)(OMe)_2Mn(CO)[P(OMe)_3]_3$	2206 m, 2191 m	1868 s	1431 s	1132 s

[a] Me = methyl, Et = ethyl, *i*-Pr = isopropyl, Pf-Pf = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. [b] The infrared ν(CN) and ν(CO) frequencies were measured in CH_2Cl_2 solutions. [c] The infrared ν(C=C) and ν(P=O) frequencies were measured in KBr pellets.

Table II. Proton NMR Spectra of the [(2,2-Dicyanovinyl)phosphonato]manganese Carbonyl Derivatives

compd[a]	proton NMR spectrum,[b,c] τ C_6H_5	$P(O)(OR)_2$	$P(OR)_3$
$(NC)_2C{=}CP(O)(OMe)_2Mn(CO)_2$(Pf-Pf)	~2.5 m	6.15 d (11), 6.80 d (11)	
$(NC)_2C{=}CP(O)(OMe)_2Mn(CO)[P(OMe)_3]$(Pf-Pf)	2.33 br, d, 2.61 br, d	6.10 d (11), 6.90 d (11)	6.54 d (11)
$(NC)_2C{=}CP(O)(OEt)_2Mn(CO)_2$(Pf-Pf)	~2.5 m	CH_2: 5.82 br, p (7) CH_3: 8.64 t (7), 9.27 t (7)	
$(NC)_2C{=}CP(O)(OEt)_2Mn(CO)[P(OEt)_3]$(Pf-Pf)	2.19 d, 2.71 d	CH_2: 5.73 br, t, 6.24 br, t CH_3: 8.65 t (7), 9.40 t (7)	CH_2: 6.24 br, t CH_3: 8.99 t (7)
$(NC)_2C{=}CP(O)(O\text{-}i\text{-}Pr)_2Mn(CO)_2$(Pf-Pf)	~2.5 d	CH: 5.3 m CH_3: 8.60 d (6), 9.20 d (6), 9.32 d (6)	
$(NC)_2C{=}CP(O)(O\text{-}i\text{-}Pr)_2Mn(CO)[P(OMe)_3]$(Pf-Pf)	2.6 m	CH: 5.4 m CH_3: 8.60 d (6), 8.64 (7), 9.05 d (7), 9.39 d (6)	6.57 d (10)
$(NC)_2C{=}CP(O)(OMe)_2Mn(CO)[P(OMe)_3]_3$		*d*	~6.2 m

[a] Me = methyl, Et = ethyl, *i*-Pr = isopropyl, Pf-Pf = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. [b] d = doublet, t = triplet, p = quintet, m = multiplet, br = broad, dd = double doublet; coupling constants in hertz are given in parentheses. [c] The resonances from the CH_2 groups of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ were too weak and broad to be unequivocally identified. [d] The signals from these protons could not be distinguished from those of $(CH_3O)_3P$.

of (2,2-dicyanovinyl)phosphonato complexes of the general type $(NC)_2C{=}CP(O)(OR)_2MnL_4$ (R = alkyl group; L = CO and various trivalent phosphorus ligands) originally obtained by the photochemical reactions of trialkyl phosphites with *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3L_2$ derivatives. Such reactions clearly must result in the elimination of the alkyl chloride RCl and therefore represent variants of the Michaelis–Arbusov reaction[6-8] of alkyl halides with trialkyl phosphites according to eq 1. This new manganese cyanocarbon chemistry can

$$R'X + (RO)_3P \rightarrow RX + R'P(O)(OR)_2 \qquad (1)$$

be represented schematically by this equation (1) where $R' = (NC)_2C{=}C{-}MnL_n$. However, the proximity of a transition metal to the carbon atom bearing the halogen involved in the Michaelis–Arbusov reaction[6-8] introduces some unusual features which are not found in Michaelis–Arbusov reactions of trialkyl phosphites with simple organic halides.

Experimental Section

Microanalyses were performed by Atlantic Microanalytical Laboratory, Atlanta, Ga. Molecular weights were determined in benzene solution using a Mechrolab Model 301 vapor pressure osmometer located in the laboratory of Professor G. E. Boyd at the University of Georgia. Melting and decomposition points were determined in capillaries and are uncorrected.

Infrared spectra (Table I) were recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated against the 1601-cm^{-1} band of polystyrene film. Proton NMR spectra (Table II) were recorded on a Varian T-60 spectrometer at 60 MHz. Carbon-13 NMR spectra (Table III) were recorded on a Jeolco PFT-100 spectrometer operating at 25.0349 MHz with proton noise decoupling and a deuterium lock using a 2-s repetition rate. Carbon-13 chemical shifts (δ) are given relative to internal tetramethylsilane with positive numbers referring to downfield chemical shifts. The proton and carbon-13 NMR spectra were run in $CDCl_3$ solutions. Phosphorus-31 NMR spectra (Table IV) were taken in CH_2Cl_2 solutions and recorded at 40.3 MHz on the 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 external 85% phosphoric acid with positive numbers indicating upfield chemical shifts.

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.[9] The remaining organophosphorus compounds used in this work were commercial products. The manganese derivatives *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) and *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3[P(OCH_3)_3]_2$ were prepared by a combination of published procedures[1,10-13] using commercial $CH_3C_5H_4Mn(CO)_3$ (Ethyl Corp., New York, N.Y.), malononitrile (Kay-Fries Chemicals Inc., New York, New York) and the $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ as raw materials.

Reaction of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with Excess Trimethyl Phosphite. A mixture of 2.56 g (4.0 mmol) of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf), 5.0 mL (5.3 g, 42 mmol) of trimethyl phosphite, and 80 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 36 h. Solvent was then removed from the deep red reaction mixture at 25 °C (25 mm). The dark red residue was chromatographed on an alumina column in dichloromethane solution. The chromatogram was first developed with 1:1 dichloromethane–hexane. The yellow band which separated was eluted with 1:1 dichloromethane–hexane. Evaporation of this eluate gave a negligible amount of material which was discarded. Further development and elution of the chromatogram with dichloromethane gave an orange band which was eluted with dichloromethane. Evaporation of this eluate at 25 °C (25 mm) followed by rechromatography of the residue on alumina using similar eluants as in the original chromatography and recrystallization of the red residue from a mixture of dichloromethane and pentane at -20 °C gave 0.82 g (26% yield) of dark red crystalline $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)$(Pf-Pf)$[P(OCH_3)_3]$, mp 168–174 °C dec. Anal. Calcd for $C_{36}H_{39}MnN_2O_7P_4$: C, 54.7; H, 4.9; N, 3.5; Cl, 0.0. Found: C, 53.7; H, 5.1; N, 3.4; Cl, 0.0.

Reaction of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with Excess Triethyl Phosphite. A mixture of 1.28 g (2.0 mmol) of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf), 4.1 mL (3.9 g, 24 mmol) of triethyl

Table III. Carbon-13 NMR Spectra of the [(2,2-Dicyanovinyl)phosphonato]manganese Carbonyl Derivatives

	carbon-13 NMR spectrum,[b] δ			
compd[a]	Pf-Pf[c]	CN	$(NC)_2C^*{=}C$[d]	OR
$(NC)_2C{=}CP(O)(OMe)_2Mn(CO)_2$-(Pf-Pf)	C_6H_5: 127–137 m CH_2: 30.0 dd (26, 17), 27.2 dd (24, 14)	116.2 d (43), 113.6	90.4 br	54.1, 53.3
$(NC)_2C{=}CP(O)(OMe)_2Mn(CO)$-$[P(OMe)_3]$(Pf-Pf)	C_6H_5: 127–142 m CH_2: 31.8 dd (28, 13), 30.2 dd (18, 11)	118.6 d (46), 117.5 br	83.9 d (9)	54.2 d (7), 52.4 d (7), 51.8
$(NC)_2C{=}CP(O)(OEt)_2Mn(CO)_2$-(Pf-Pf)	C_6H_5: 128–138 m CH_2: 30.0 dd (28, 16), 27.3 br, t (~20)	116.2 d (44), 113.9 d (24)	90.0 br	CH_2: 63.7 br, t CH_3: 16.3 br, 15.6 br
$(NC)_2C{=}CP(O)(OEt)_2Mn(CO)$-$[P(OEt)_3]$(Pf-Pf)	C_6H_5: 127–144 m CH_2: 31.4 m	118.6 d (46), 116.7 d (21)	83.6 d (11)	CH_2: 53.2 d (6), 61.9 d (10), 60.0 d (9) CH_3: 16.1 br, 15.2 br
$(NC)_2C{=}CP(O)(O\text{-}i\text{-}Pr)_2Mn(CO)_2$-(Pf-Pf)	C_6H_5: 128–138 m CH_2: 31.0 dd (29, 17), 26.9 dd (18, 11)	116.3 d (46), 113.9 d (23)	89.4 d (8)	CH: 73.6 d (9), 72.8 d (6) CH_3: 24.1, 23.5
$(NC)_2C{=}CP(O)(O\text{-}i\text{-}Pr)_2Mn(CO)$-$[P(OMe)_3]$(Pf-Pf)	C_6H_5: 126–144 m CH_2: 31.5 m	*e*	83.8 d (9)	CH: 73.0 d (12), 71.4 d (6) CH_3: 52.3 d (8), 24.4, 23.5
$(NC)_2C{=}CP(O)(OMe)_2Mn(CO)$-$[P(OMe)_3]_3$		118.5 br	85.9 br	53.6, 52.9, 51.8

[a] Me = methyl, Et = ethyl, *i*-Pr = isopropyl, Pf-Pf = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. [b] d = doublet, dd = double doublet, t = triplet, m = multiplet, br = broad; unlabeled resonances were apparent singlets; coupling constants in hertz are given in parentheses. [c] In view of the (expected) complexity of the phenyl carbon-13 resonances, no attempts were made to assign peaks to individual phenyl carbon atoms. [d] The olefinic carbon atom directly bonded to manganese did not give an observable carbon-13 resonance. [e] These resonances were not unequivocally observed.

Table IV. Phosphorus-31 NMR Spectra of the [(2,2-Dicyanovinyl)phosphonato]manganese Carbonyl Derivatives

	phosphorus-31 NMR spectrum,[b] ppm		
compd[a]	Pf-Pf	$P(O)(OR)_2$	$P(OR)_3$
$(NC)_2C{=}CP(O)(OMe)_2Mn(CO)_2$(Pf-Pf)	−75.7 br, −70.4 br	−28.3 d (32)	
$(NC)_2C{=}CP(O)(OMe)_2Mn(CO)[P(OMe)_3]$(Pf-Pf)	−80.9 dd (115, 22), −66.6 br, d (73)	−29.3 d (32)	−169.6 br
$(NC)_2C{=}CP(O)(OEt)_2Mn(CO)_2$(Pf-Pf)	−76.0 br, −73.0 br	−25.8 d (30)	
$(NC)_2C{=}CP(O)(OEt)_2Mn(CO)[P(OEt)_3]$(Pf-Pf)	−82.3 dd (112, 25), −65.5 t (28)	−27.6 d (32)	−165.1 br
$(NC)_2C{=}CP(O)(O\text{-}i\text{-}Pr)_2Mn(CO)_2$(Pf-Pf)	−75.0 br, −70.2 br	−24.3 d (29)	
$(NC)_2C{=}CP(O)(OMe)_2Mn(CO)[P(OMe)_3]_3$		−31.0 d (37)	−178.8 br, −167.9 br

[a] Me = methyl, Et = ethyl, *i*-Pr = isopropyl, Pf-Pf = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. [b] d = doublet, dd = double doublet, t = triplet, br = broad; coupling constants in hertz are given in parentheses.

phosphite, and 40 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 24 h. Isolation of product by a procedure similar to that given above for $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)$(Pf-Pf)$[P(OCH_3)_3]$ gave 0.61 g (36% yield) of dark orange $(NC)_2C{=}CP(O)(OC_2H_5)_2Mn(CO)$(Pf-Pf)$[P(OC_2H_5)_3]$, mp 140–145 °C dec. Anal. Calcd for $C_{41}H_{49}MnN_2O_7P_4$: C, 57.2; H, 5.7; N, 3.2; Cl, 0.0; mol wt 860. Found: C, 57.5; H, 5.7; N, 3.2; Cl, 0.0; mol wt 827.

Reaction of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with Excess Triisopropyl Phosphite. A mixture of 2.56 g (4.0 mmol) of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf), 8.0 mL (7.7 g, 37 mmol) of triisopropyl phosphite, and 80 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 10 h. Solvent was then removed from the dark red reaction mixture at 25 °C (25 mm). The dark red oil was chromatographed on an alumina column in dichloromethane solution. The chromatogram was first developed with 2:3 dichloromethane–hexane. The yellow band which separated was eluted with 2:3 dichloromethane–hexane. Evaporation of this eluate gave a negligible amount of material and therefore was discarded. Further development and elution with 1:1 dichloromethane–hexane gave successively two orange bands. Evaporation of the eluate from the second orange band gave a trace amount of material which was discarded. Evaporation of the eluate from the first orange band at 25 °C (25 mm) gave an orange residue. Recrystallization of this residue from a mixture of dichloromethane and hexane gave 0.56 g (19% yield) of orange crystalline product. A second recrystallization from a mixture of dichloromethane and hexane at −20 °C gave 0.48 g of red-orange crystalline $(NC)_2C{=}CP(O)[OCH(CH_3)_2]_2Mn(CO)_2$(Pf-Pf), mp 171–174 °C dec. Anal. Calcd for $C_{38}H_{38}MnN_2O_5P_3$: C, 60.8; N, 5.1; N, 3.7; Cl, 0.0; mol wt 750. Found: C, 60.2; H, 5.2; N, 3.6; Cl, 0.0; mol wt 777.

Reaction of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3[P(OCH_3)_3]_2$ with Excess Trimethyl Phosphite. A mixture of 1.0 g (2.0 mmol) of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3[P(OCH_3)_3]_2$, 2.0 mL (2.1 g, 17 mmol) of trimethyl phosphite, and 40 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 48 h. Solvent was then removed from the reaction mixture at 25 °C (25 mm). The oily brown residue was chromatographed on an alumina column in dichloromethane solution. A small yellow band was eluted with 2:3 dichloromethane–hexane. Evaporation of the eluate gave a negligible amount of material and therefore was discarded. Two orange bands were eluted with 1:1 dichloromethane–hexane. These could not be separated and so were collected together. The eluate was evaporated to dryness at 25 °C (25 mm). The residue was rechromatographed on an alumina column in dichloromethane solution. A small yellow band was eluted with 1:4 dichloromethane–hexane. This eluate gave a negligible amount of material and therefore was discarded. A dark orange band was then eluted with 2:3 dichloromethane–hexane. Evaporation of this eluate to dryness at 25 °C (25 mm) gave a negligible amount of material which was discarded. The major orange band was then eluted with 1:1 dichloromethane–hexane. The eluate was evaporated to dryness at 25 °C (25 mm). The residue was recrystallized from a mixture of dichloromethane and hexane at −20 °C to give 0.162 g (13% yield) of orange-red crystalline $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)[P(OCH_3)_3]_3$, mp 146–148 °C dec. Anal. Calcd for $C_{16}H_{33}MnN_2O_{13}P_4$: C, 30.0; H, 5.1; N, 4.4; Cl, 0.0. Found: C, 30.2; H, 5.0; N, 4.3; Cl, 0.0.

Reaction of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with $LiP(O)(OCH_3)_2$. A stirred solution of 0.23 mL (0.28 g, 2.5 mmol) of $(CH_3O)_2P(O)H$ in 50 mL of tetrahydrofuran was treated with 1.5 mL (2.7 mmol) of a 1.8 M pentane solution of *tert*-butyllithium. After 30 min of stirring, 0.96 g (1.5 mmol) of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) was added. The resulting mixture was exposed to ultraviolet irradiation for 2 h. Solvent was then removed from the deep red reaction mixture at 25 °C (25 mm). The residue was extracted with 150 mL of dichloromethane in two portions. These extracts were filtered through Celite. The filtrate was evaporated to dryness at 25 °C (25 mm). The residue was chromatographed on an alumina column in dichloromethane solution. The orange band of product was eluted with 3:2 dichloromethane–hexane. The eluate was evaporated to dryness at 25 °C (25 mm). The orange residue was recrystallized from a mixture of dichloromethane and hexane at −20 °C to give 0.42 g (41% yield) of orange crystalline $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)_2$(Pf-Pf), mp 174–179 °C dec. Anal. Calcd for $C_{34}H_{30}MnN_2O_5P_3$: C, 58.8; H, 4.3; N, 4.0; Cl, 0.0. Found: C, 58.9; H, 4.5; N, 3.8; Cl, 0.4.

Reaction of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with $LiP(O)(OC_2H_5)_2$. A solution of $LiP(O)(OC_2H_5)_2$ prepared from 0.32 mL (0.34 g, 2.5 mmol) of $(C_2H_5O)_2P(O)H$ and 1.5 mL (2.7 mmol) of 1.8 M *tert*-butyllithium in pentane in 50 mL of tetrahydrofuran was treated with 0.96 g (1.5 mmol) of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf). The resulting mixture was exposed to ultraviolet irradiation for 2 h. Isolation of product by a procedure essentially similar to that given above for $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)_2$(Pf-Pf) gave 0.64 g (59% yield) of orange $(NC)_2C{=}CP(O)(OC_2H_5)_2Mn(CO)_2$(Pf-Pf), mp 188–193 °C dec. The analytical sample was recrystallized from a mixture of 1:1 dichloromethane–toluene and pentane at −20 °C. Anal. Calcd for $C_{36}H_{34}MnN_2O_5P_3$: C, 59.8; H, 4.7; N, 3.9; Cl, 0.0; mol wt 722. Found: C, 60.1; H, 4.9; N, 3.7; Cl, 0.3; mol wt 701.

Reaction of *fac*-$(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)_2$(Pf-Pf) with Trimethyl Phosphite. A mixture of 0.20 g (0.28 mmol) of $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)_2$(Pf-Pf), 2.0 mL (2.1 g, 17 mmol) of trimethyl phosphite, and 40 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 4 h. Solvent was then removed from the dark red reaction mixture of 25 °C (25 mm). The dark red oil was chromatographed on an alumina column in dichloromethane solution. A small yellow band was eluted with 1:1 dichloromethane–hexane. This band contained only a small amount of material and was discarded. The major orange band was eluted with 4:1 dichloromethane–hexane. The eluate was evaporated to dryness at 25 °C (25 mm). The red residue was recrystallized from a mixture of dichloromethane and pentane at −20 °C to give 0.16 g (72% yield) of dark red $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)$(Pf-Pf)$[P(OCH_3)_3]$, mp 171–176 °C dec, identified by its infrared and proton NMR spectra.

Reaction of $(NC)_2C{=}CP(O)(OC_2H_5)_2Mn(CO)_2$(Pf-Pf) with Triethyl Phosphite. A mixture of 0.35 g (0.48 mmol) of $(NC)_2C{=}CP(O)(OC_2H_5)_2Mn(CO)_2$(Pf-Pf), 1.7 mL (1.6 g, 8.2 mmol) of triethyl phosphite, and 40 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 5 h. Isolation of product by a procedure essentially identical with that given above for $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)$(Pf-Pf)$[P(OCH_3)_3]$ gave 0.22 g (53% yield) of dark orange $(NC)_2C{=}CP(O)(OC_2H_5)_2Mn(CO)$(Pf-Pf)$[P(OC_2H_5)_3]$, mp 143–148 °C dec, identified by its infrared and proton NMR spectra.

Reaction of $(NC)_2C{=}CP(O)[OCH(CH_3)_2]_2Mn(CO)_2$(Pf-Pf) with Trimethyl Phosphite. A mixture of 0.12 g (0.16 mmol) of $(NC)_2C{=}CP(O)[OCH(CH_3)_2]_2Mn(CO)_2$(Pf-Pf), 2.0 mL (2.1 g, 17 mmol) of trimethyl phosphite, and 40 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 3.5 h. Solvent was then removed from the red-orange reaction mixture at 25 °C (25 mm). The oily residue was chromatographed on an alumina column in dichloromethane solution. The orange band was eluted with 7:3 dichloromethane–hexane. The eluate was evaporated to dryness at 25 °C (25 mm). The orange residue was recrystallized from a mixture of 1:1 dichloromethane–toluene and pentane at −20 °C to give 0.031 g (30% yield) of red $(NC)_2C{=}CP(O)[OCH(CH_3)_2]_2Mn(CO)$(Pf-Pf)$[P(OCH_3)_3]$, mp 145–148 °C dec. Anal. Calcd for $C_{40}H_{47}MnN_2O_7P_4$: C, 56.7; H, 5.5; N, 3.3. Found: C, 56.0; H, 5.4; N, 3.2.

Reaction of $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)$(Pf-Pf)$[P(OCH_3)_3]$ with CO. Carbon monoxide was bubbled into a solution of 0.5 g (0.63 mmol) of $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)$(Pf-Pf)$[P(OCH_3)_3]$ in 60 mL of tetrahydrofuran while being irradiated with ultraviolet light. After 27 h, no further change occurred in the infrared spectrum, which indicated an approximately 3:2 mixture of a dicarbonyl and a monocarbonyl, respectively, in the reaction mixture. Solvent was then removed from the orange reaction mixture at 25 °C (25 mm). The red residue was chromatographed on an alumina column in dichloromethane solution. A yellow band was eluted with 7:3 dichloromethane–hexane. The eluate was evaporated to dryness at 25 °C (25 mm). The residue was recrystallized from a mixture of dichloromethane and pentane at −20 °C to give 0.070 g (16% yield) of $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)_2$(Pf-Pf), mp 174–179 °C dec, identified from its infrared and proton NMR spectra. An orange band was eluted next with dichloromethane. The eluate was evaporated to dryness at 25 °C (25 mm). The residue was crystallized from a mixture of dichloromethane and pentane at −20 °C to give 0.039 g (7.8% yield) of unreacted $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)$(Pf-Pf)$[P(OCH_3)_3]$.

Reaction of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with Trimethyl Phosphite in a 1:1 Mole Ratio. A mixture of 0.64 g (1.0 mmol) of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf), 0.125 mL (0.131 g, 1.06 mmol) of trimethyl phosphite, and 35 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 3.5 h. The resulting deep red reaction mixture was evaporated to dryness at 25 °C (25 mm). The dark red residue was chromatographed on an alumina column in dichloromethane solution. A yellow band was first eluted with 4:1 dichloromethane–hexane. Evaporation of the eluate followed by crystallization of the residue from a mixture of dichloromethane and hexane at −20 °C gave 0.060 g (9% yield) of orange $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)_2$(Pf-Pf), mp 171–173 °C dec, identified by its infrared and proton NMR spectra. An orange band was eluted next with 19:1 dichloromethane–tetrahydrofuran. The eluate was evaporated to dryness at 25 °C (25 mm). The residue was crystallized from a mixture of dichloromethane and hexane at −20 °C to give 0.152 g (19% yield) of dark red $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)$(Pf-Pf)$[P(OCH_3)_3]$, mp 172–174 °C dec, identified by its infrared and proton NMR spectra.

Results

The photochemical reaction of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with excess triisopropyl phosphite was found to give an orange crystalline product indicated by its two ν(CO) frequencies to be a dicarbonyl. However, elemental analyses, including the absence of chlorine, indicated the stoichiometry $(NC)_2C{=}CP(O)[OCH(CH_3)_2]_2Mn(CO)_2$(Pf-Pf) rather than the expected stoichiometry $(NC)_2C{=}C(Cl)MnP[OCH(CH_3)_2]_3(CO)_2$(Pf-Pf) which would result if the triisopropyl phosphite simply replaced a carbonyl group. The photochemical reaction of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with triisopropyl phosphite thus appears to proceed according to eq 2 corresponding to a new variant of the Michaelis–Arbusov reaction which results in the formation of a (2,2-dicyanovinyl)phosphonato complex.

$$(NC)_2C{=}C(Cl)Mn(CO)_3(\text{Pf-Pf}) + [(CH_3)_2CHO]_3P \rightarrow (NC)_2C{=}CP(O)[OCH(CH_3)_2]_2Mn(CO)_2(\text{Pf-Pf}) + CO + (CH_3)_2CHCl \quad (2)$$

The corresponding photochemical reactions of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with the less sterically demanding trimethyl and triethyl phosphites proceed one stage further to give the corresponding monocarbonyls $(NC)_2C{=}CP(O)(OR)_2Mn(CO)$(Pf-Pf)$[P(OR)_3]$ (R = CH_3, C_2H_5) where an intact trialkyl phosphite has replaced an additional carbonyl group. However, the dicarbonyls $(NC)_2C{=}CP(O)(OR)_2Mn(CO)_2$(Pf-Pf) corresponding to the diisopropyl(2,2-dicyanovinyl)phosphonato derivative of eq 2 can be obtained by photolyses of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with the corresponding lithium derivatives $LiP(O)(OR)_2$ (R = CH_3, C_2H_5) according to eq 3. One of the two carbonyl groups in these dicarbonyls (eq 3) can be replaced photochemically by trialkyl phosphites to give products $(NC)_2C{=}CP(O)(OR)_2Mn(CO)$(Pf-Pf)$[P(OR)_3]$ (R = CH_3, C_2H_5) which are identical with the products obtained directly by the ultraviolet irradiation of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with the trialkyl phosphites as discussed above. An unsymmetrical derivative $(NC)_2C{=}CP(O)[OCH(CH_3)_2]_2Mn(CO)$(Pf-Pf)$[P(OCH_3)_3]$ can similarly be obtained by ultraviolet ir-

$$(NC)_2C{=}C(Cl)Mn(CO)_3(\text{Pf-Pf}) + LiP(O)(OR)_2 \rightarrow (NC)_2C{=}CP(O)(OR)_2Mn(CO)_2(\text{Pf-Pf}) + CO + LiCl \quad (3)$$

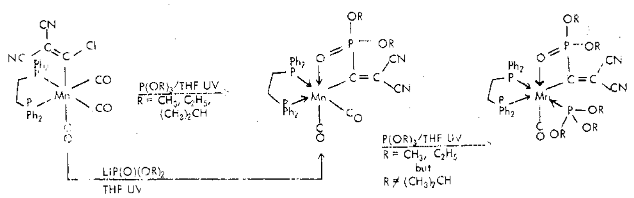


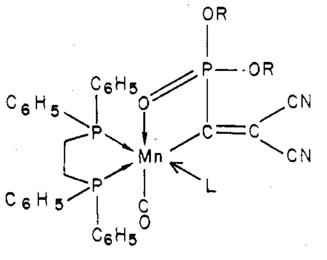
Figure 1. Summary of products isolated from reactions of $(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with phosphite derivatives.

radiation of the diisopropylphosphonato derivative (eq 2) with trimethyl phosphite. These transformations are summarized in Figure 1.

In order to gain an insight into possible reaction mechanisms, the photolysis of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) with trimethyl phosphite was examined in greater detail. Ultraviolet irradiation of equimolar quantities of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf) and trimethyl phosphite was found to give $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)_2$(Pf-Pf) and $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)$(Pf-Pf)$[P(OCH_3)_3]$ as the only two isolable products. Of interest was the failure to obtain the dicarbonyl product $(NC)_2C{=}C(Cl)Mn(CO)_2$(Pf-Pf)$[P(OCH_3)_3]$. This suggests that the (2,2-dicyanovinyl)phosphonato ligand is formed before the carbonyl group is replaced with the trialkyl phosphite. In another experiment the monocarbonyl $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)$(Pf-Pf)$[P(OCH_3)_3]$ was irradiated in the presence of CO. After 27 h, no further change had occurred in the infrared spectrum of the reaction mixture, which indicated a 3:2 equilibrium mixture of the dicarbonyl and the monocarbonyl. This latter experiment indicates that CO replaces the coordinated trimethyl phosphite ligand in $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)$(Pf-Pf)$[P(OCH_3)_3]$ to give $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)_2$(Pf-Pf) rather than a coordinated phosphoryl oxygen of the $(NC)_2C{=}CP(O)(OCH_3)_2$ ligand to give complexes such as $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)_2$(Pf-Pf)$[P(OCH_3)_3]$ or $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)_3$(Pf-Pf).

The ability of *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3L_2$ derivatives to form (2,2-dicyanovinyl)phosphonato derivatives of the type $(NC)_2C{=}CP(O)(OR)_2Mn(CO)_2L_2$ upon photolysis with trialkyl phosphites is not restricted to the di(tertiary phosphine) complex *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3$(Pf-Pf). Thus, the ultraviolet irradiation of the trimethyl phosphite complex[1] *fac*-$(NC)_2C{=}C(Cl)Mn(CO)_3[P(OCH_3)_3]_2$ with excess trimethyl phosphite was found to result in the formation of the (2,2-dicyanovinyl)phosphonato derivative $(NC)_2C{=}CP(O)(OCH_3)_2Mn(CO)[P(OCH_3)_3]_3$ which appears to be completely analogous to the di(tertiary phosphine) complexes depicted in Figure 1.

These new (cyanocarbon)manganese carbonyl derivatives contain a new type of (2,2-dicyanovinyl)phosphonato ligand $(NC)_2C{=}CP(O)(OR)_2$, which must function as a three-electron donor if the manganese atom is to attain the usual 18-electron rare-gas electronic configuration. The ν(P=O) frequencies in the infrared spectra of these (2,2-dicyanovinyl)phosphonato complexes (Table I) appear in the range 1130–1145 cm^{-1} which is considered below the 1210–1325-cm^{-1} range found in uncomplexed phosphoryl derivatives of the type $XP(O)(OR)_2$ (R = alkyl, X = halogen, alkyl, aryl, RO, R_2N, etc.).[14] This lowering of the phosphoryl oxygen frequency in these [(2,2-dicyanovinyl)phosphonato]manganese carbonyl complexes relative to the values expected for an uncomplexed $XP(O)(OR)_2$ ligand suggests that the phosphoryl oxygen is coordinated to manganese in these $(NC)_2C{=}CP(O)(OR)_2Mn(CO)L$(Pf-Pf) complexes in view of the generally observed[15] lowering of ν(P=O) frequencies upon complexation of the phosphoryl oxygen with a metal. This leads to the conclusion that the (2,2-dicyanovinyl)phosphonato ligand in the manganese carbonyl complexes described in this paper functions as a bidentate ligand which is bonded to the manganese atom through both a vinylic carbon and the phosphoryl oxygen. A structure of this type, I (L = CO, R = $CH(CH_3)_2$), has recently been confirmed by X-ray crystallography[16] for $(NC)_2C{=}CP(O)[OCH(CH_3)_2]_2Mn(CO)_2$(Pf-Pf).



I

The NMR spectra of the $(NC)_2C{=}CP(O)(OR)_2Mn(CO)L$(Pf-Pf) derivatives are also in accord with structure I. The proton and carbon-13 NMR spectra indicate nonequivalence of the two alkoxy groups of the $(NC)_2C{=}CP(O)(OR)_2$ ligand in accord with the different environments on each side of the four-membered Mn–O–P–C ring arising from the high asymmetry of the system. In most cases the two diastereotopic[17] methyl groups of each isopropyl group in the isopropyl derivatives $(NC)_2C{=}CP(O)[OCH(CH_3)_2]_2Mn(CO)L$(Pf-Pf) (I: R = $CH(CH_3)_2$, L = CO or $(CH_3O)_3P$) exhibit detectably different chemical shifts. The carbon-13 NMR spectrum (Table III) indicates the nonequivalence of the two cyano groups in the (2,2-dicyanovinyl)phosphonato group required by structure I. Furthermore, both cyano resonances are split appreciably (46 and 23 Hz) by a single phosphorus atom thereby suggesting that exactly one of the four phosphorus atoms in this molecule is within a reasonable coupling distance, i.e., three or less chemical bonds. Such is the case in structure I where the $P(O)(OR)_2$ phosphorus is three chemical bonds from the cyano carbons but the phosphorus atoms of the di(tertiary phosphine) are four chemical bonds from the cyano carbons. Since couplings across trans positions of a carbon–carbon double bond are larger than those across cis positions,[18] the lower field cyano resonance with $|^3J(C{-}P)|$ of 43–46 Hz can be assigned to the cyano group trans to the $P(O)(OR)_2$ substituent. The carbons directly bonded to manganese (i.e., one of the vinylic carbons and the CO groups) are never observed in the carbon-13 NMR spectra, apparently because of excessive quadrupole broadening from the manganese-55.

The phosphorus-31 NMR spectra of the (2,2-dicyanovinyl)phosphonato derivatives (Table IV) exhibit the expected features for structure I. The two phosphorus atoms of the coordinated di(tertiary phosphine) exhibit different chemical shifts in accord with their nonequivalence in structure I. Their resonances are broad suggesting broadening from the quadrupole moment of the manganese-55 nucleus to which both phosphorus atoms of the di(tertiary phosphine) are coordinated. On the other hand, the phosphorus-31 NMR resonance of the $P(O)(OR)_2$ phosphorus is a *sharp* doublet suggesting the absence of quadrupole broadening from the manganese-55 atom. This is in accord with structure I in which the $P(O)(OR)_2$ phosphorus is not directly bonded to the manganese atom. The following additional features were observed in the phosphorus-31 NMR spectra of the trialkyl phosphite complexes $(NC)_2C{=}CP(O)(OR)_2Mn(CO)$(Pf-Pf)$[P(OR')_3]$ (I: L = $(R'O)_3P$): (1) a broad resonance around −170 ppm arising from the coordinated trialkyl phosphite phosphorus which is broadened by the quadrupole moment of the manganese-55 to which it is directly bonded; (2) splitting of one of the di(tertiary phosphine) resonances by 112–115

Hz apparently owing to a large $|^2J(\mathrm{P-P})|$ between this di(tertiary phosphine) phosphorus and the trialkyl phosphite ligand in a trans position. This latter observation is a basis for the indicated stereochemistry (I: $\mathrm{L} = (\mathrm{R'O})_3\mathrm{P}$) for the trialkyl phosphite complexes $(\mathrm{NC})_2\mathrm{C{=}CP(O)(OR)_2Mn(CO)(Pf\text{-}Pf)[P(OR')_3]}$.

The infrared spectra of the (2,2-dicyanovinyl)phosphonato derivatives I (Table I) exhibit the expected ν(CN) frequencies from the two cyano groups, the expected ν(CO) frequencies from the one or two metal carbonyl groups, the expected ν(C=C) from the double bond of the 2,2-dicyanovinyl group, and the ν(P=O) from the phosphoryl group in the $\mathrm{P(O)(OR)_2}$ unit. Substitution of CO by a weaker π-acceptor trialkyl phosphite leads to the expected decreases in the infrared ν(CN) and ν(C=C) frequencies of the 2,2-dicyanovinyl group by 10–20 and 40–50 $\mathrm{cm^{-1}}$, respectively, in accord with the expected increase in electron density available for the π^* antibonding orbitals in these multiple bonds of the cyanocarbon ligand when the other ligands remove less electron density from the metal atom through retrodative bonding.

Discussion

The reactions described in this paper appear to represent the first examples of Michaelis–Arbusov reactions of trialkyl phosphites with the carbon–halogen bonds of organic halides containing a participating metal atom in the side chain. They thus contrast with previous examples of Michaelis–Arbusov reactions in transition-metal organometallic chemistry which involve a metal–halogen bond in organometallic halides of the types $\mathrm{C_5H_5Mo(CO)_3X}$[19] and $\mathrm{C_5H_5Re(CO)_2X_2}$[20] rather than a carbon–halogen bond. Furthermore, the Michaelis–Arbusov reactions described in this paper, as exemplified by eq 2, involve not only reaction of the trialkyl phosphite at the carbon–halogen bond of the 1-chloro-2,2-dicyanovinyl group but also displacement of one carbonyl group. They thus appear to proceed only under ultraviolet irradiation, which apparently is required for removal of this carbonyl group. In contrast to the monodentate one-electron donor $\mathrm{P(O)(OR)_2}$ ligands found in the products obtained from the Michaelis–Arbusov reactions of trialkyl phosphites with $\mathrm{C_5H_5Mo(CO)_3X}$[15] and $\mathrm{C_5H_5Re(CO)_2X_2}$,[16] the (2,2-dicyanovinyl)phosphonato ligands in the complexes discussed in this paper function as bidentate ligands which are bonded to the metal through both a vinylic carbon atom and a phosphoryl oxygen atom thereby resulting in a net donation of three electrons to the metal atom. In these various ways the Michaelis–Arbusov reactions discussed in this paper exhibit features not found in previously studied versions of this very fundamental and important reaction in organophosphorus chemistry.

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Registry No. $\mathrm{(NC)_2C{=}CP(O)(OMe)_2Mn(CO)_2(Pf\text{-}Pf)}$, 68081-56-1; $\mathrm{(NC)_2C{=}CP(O)(OMe)_2Mn(CO)[P(OMe)_3](Pf\text{-}Pf)}$, 68108-68-9; $\mathrm{(NC)_2C{=}CP(O)(OEt)_2Mn(CO)_2(Pf\text{-}Pf)}$, 68081-57-2; $\mathrm{(NC)_2C{=}CP(O)(OEt)_2Mn(CO)[P(OEt)_3](Pf\text{-}Pf)}$, 68081-58-3; $\mathrm{(NC)_2C{=}CP(O)(O\text{-}}i\mathrm{\text{-}Pr)_2Mn(CO)_2(Pf\text{-}Pf)}$, 68081-59-4; $\mathrm{(NC)_2C{=}CP(O)(O\text{-}}i\mathrm{\text{-}Pr)_2Mn(CO)[P(OMe)_3](Pf\text{-}Pf)}$, 68081-60-7; $\mathrm{(NC)_2C{=}CP(O)(OMe)_2Mn(CO)[P(OMe)_3]_3}$, 68081-61-8; *fac*-$\mathrm{(NC)_2C{=}C(Cl)Mn(CO)_3(Pf\text{-}Pf)}$, 66705-73-5; *fac*-$\mathrm{(NC)_2C{=}C(Cl)Mn(CO)_3[P(OCH_3)_3]_2}$, 66705-83-7.

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