Manganese Complex Containing a Bidentate 2,2-Dicyanovinylphosphonato Ligand Formed by a Novel Variant of the Michaelis–Arbusov Reaction; the *X*-Ray Crystal Structure of $[\{(NC)_2C{=}CP(O)\}(OCHMe_2)_2Mn(CO)_2(Ph_2PCH_2CH_2PPh_2)]$

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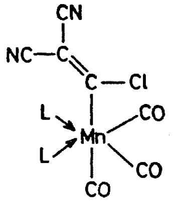
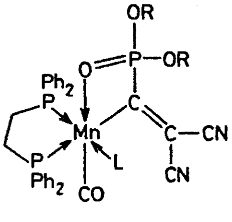
Summary U.v. irradiation of *fac*-$[(NC)_2C{=}C(Cl)Mn(CO)_3(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with excess of tri-isopropyl phosphite results in elimination of both isopropyl chloride and carbon monoxide to give $[(NC)_2C{=}CP(O)(OCHMe_2)_2Mn(CO)_2(dppe)]$ which is shown by *X*-ray diffraction to contain a bidentate 2,2-dicyanovinylphosphonato ligand bonded to the manganese both through a vinylic carbon and the phosphoryl oxygen to give a four-membered MnCPO chelate ring.

Reactions of $[(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5]$[1] with trialkyl phosphites under mild conditions result in a novel chlorine shift from carbon to molybdenum to give the terminal dicyanovinylidene complexes $[C_5H_5Mo\{P(OR)_3\}_2\{C{=}C(CN)_2\}Cl]$.[2] Similar reactions of $[(NC)_2C{=}C(Cl)Mn(CO)_5]$[1] with trialkyl phosphites result in substitution of two carbonyl groups with retention of the 1-chloro-2,2-dicyanovinyl ligand to give *fac*-$[(NC)_2C{=}C(Cl)Mn(CO)_3\{P(OR)_3\}_2]$ derivatives [I: L = $P(OR)_3$].[3] We have now found that u.v. irradiations of the related complex *fac*-$[(NC)_2C{=}C(Cl)Mn(CO)_3(dppe)]$ (I: L_2 = dppe = $Ph_2PCH_2CH_2PPh_2$)[3] with trialkyl phosphites result in further carbonyl substitution accompanied by alkyl chloride elimination to give novel chelating 2,2-dicyanovinylphosphonato derivatives in an unusual variant of the Michaelis–Arbusov reaction.[4]

A tetrahydrofuran solution of *fac*-$[(NC)_2C{=}C(Cl)Mn(CO)_3(dppe)]$ (I: L_2 = dppe) was irradiated with an excess (10:1 mole ratio) of tri-isopropyl phosphite for 10 h. Removal of solvent followed by chromatography on alumina in dichloromethane–hexane gave a *ca.* 20% yield of an orange crystalline product, m.p. 171–174 °C (decomp.), ν(CO) in CH_2Cl_2 at 1955 and 1885 cm^{-1}, indicated by elemental analyses (C, H, N, and mol. wt. in benzene) to have the stoicheiometry $[(NC)_2C{=}CP(O)(OPr^i)_2Mn(CO)_2(dppe)]$. This reaction thus can be represented by the equation (R = Pr^i): $[(NC)_2C{=}C(Cl)Mn(CO)_3(dppe)] + (RO)_3P \rightarrow [(NC)_2C{=}C\text{-}P(O)(OR)_2Mn(CO)_2(dppe)] + CO + RCl$. In order to determine the nature of the apparent di-isopropyl 2,2-dicyanovinylphosphonato ligand in this complex, its structure was determined by single crystal *X*-ray diffraction.



(I)



(II)

The complex $[(NC)_2C{=}CP(O)(OPr^i)_2Mn(CO)_2(dppe)]$ forms monoclinic crystals from dichloromethane–hexane at −20 °C: space group $P2_1/n$; a = 17·419(4) Å, b = 12·560(3) Å, c = 18·164(9) Å, β = 109·10(4)°, Z = 4. Least squares refinement with Mn, P, N, and O atoms treated anisotropically and all C atoms isotropically using the 2631 observed reflections (R = 0·061, R_w = 0·062) indicates the structure depicted in the Figure which corresponds to (II) ($L = CO$, $R = Pr^i$). The most novel feature of this structure is the chelating di-isopropyl 2,2-dicyanovinylphosphonato ligand which is bonded to the manganese through both a vinylic carbon [Mn–C(1) = 1·957 Å] and the phosphoryl oxygen [Mn–O(1) = 2·157 Å] forming a four-membered chelate ring with angles C(1)–Mn–O(1), Mn–O(1)–P(1), O(1)–P(1)–C(1), and P(1)–C(1)–Mn of 74·8, 92·7, 100·3, and 92·0°, respectively. The phosphonato phosphorus atom P(1), arising from the tri-isopropyl phosphite ligand, thus is not directly bonded to the manganese [Mn–P(1) = 2·680 Å]. The remaining co-ordination positions of the manganese atom are occupied by the ditertiary phosphine [Mn–P(2) = 2·334 Å and Mn–P(3) = 2·305 Å] and two carbonyl groups [Mn–C(5) = 1·758 Å and Mn–C(6) = 1·799 Å]. The vinylic carbon atom and the two ditertiary phosphine phosphorus atoms occupy meridional positions in $[(NC)_2C{=}CP(O)(OPr^i)_2Mn(CO)_2(dppe)]$ (II: $L = CO$, $R = Pr^i$) as contrasted with facial positions in the *fac*-$[(NC)_2C{=}C(Cl)Mn(CO)_3(dppe)]$ starting material (I: L_2 = dppe) indicating a rearrangement of the ligands around the manganese atom during the photochemical reaction with tri-isopropyl phosphite.†

Important spectroscopic properties of $[(NC)_2C{=}CP(O)(OCHMe_2)_2Mn(CO)_2(dppe)]$ (II: $L = CO$, $R = Pr^i$) include the ν(P–O) frequency at 1145 cm^{-1}, two cyano ^{13}C resonances at δ 116·3 (d, *J* 46 Hz) and 113·9 p.p.m. (d, *J* 23 Hz) indicating non-equivalent CN groups, two broad ^{31}P resonances at −75·0 and −70·2 p.p.m. (relative to 85% H_3PO_4) from the non-equivalent ditertiary phosphine phosphorus atoms broadened by the ^{55}Mn quadrupole, and a sharp ^{31}P resonance at −24·3 p.p.m. (d, *J* 29 Hz) from the phosphonate phosphorus atom which is little affected by the quadrupole broadening of the ^{55}Mn to which it is not directly bonded. The ^1H n.m.r. spectrum of $[(NC)_2C{=}CP(OPr^i)_2Mn(CO)_2(dppe)]$ exhibits doublet (*J* 6 Hz) isopropyl methyl resonances at δ 1·40, 0·80, and 0·68 of approximate relative intensities 2 : 1 : 1, respectively. This indicates that in one of the isopropyl groups the two diastereotopic methyl groups have distinctly different chemical shifts whereas in the other isopropyl group the chemical shifts of the two diastereotopic methyl groups are too close to be resolved. Inspection of the structure of this complex (Figure) reveals that the methyl groups in the isopropyl group *cis* to the ditertiary phosphine P(2) can approach within *ca.* 4 Å of one of the benzene rings of the ditertiary phosphine and therefore be significantly affected by the ring current whereas the methyl groups in the isopropyl group ***trans*** to the ditertiary phosphine P(2) are too far from any benzene rings to be affected by their ring currents. This could account for the differences in the chemical shifts of the diastereotopic methyl groups in the two isopropyl groups.

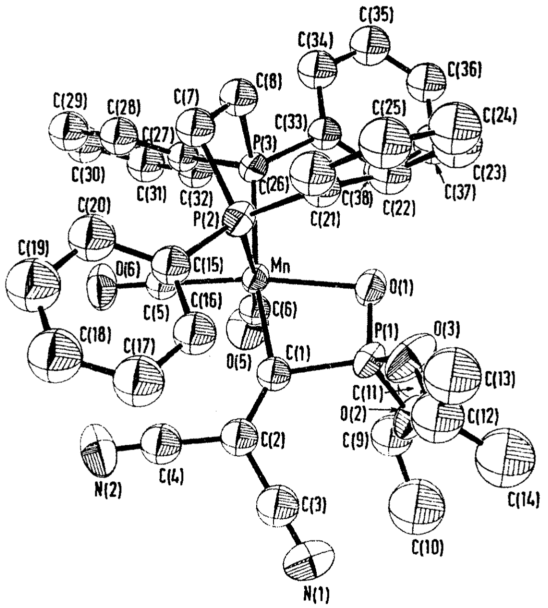


FIGURE. ORTEP drawing of the structure of $[(NC)_2C{=}CP(O)(OPr^i)_2Mn(CO)_2(Ph_2PCH_2CH_2PPh_2)]$

Several other manganese carbonyl derivatives containing similar chelating 2,2-dicyanovinylphosphonato ligands have also been prepared. Metallation of the dialkyl phosphites $(RO)_2P(O)H$ (R = Me or Et) with t-butyl-lithium followed by u.v. irradiation of the resulting lithium derivatives with *fac*-$[(NC)_2C{=}C(Cl)Mn(CO)_3(dppe)]$ in tetrahydrofuran solution produces the orange complexes $[(NC)_2C{=}CP(O)(OR)_2Mn(CO)_2(dppe)]$ (II: $L = CO$, R = Me or Et) which are the methyl and ethyl analogues of the isopropyl derivative depicted in the Figure. U.v. irradiation of *fac*-$[(NC)_2C{=}C(Cl)Mn(CO)_3(dppe)]$ (I: L_2 = dppe) with excess of trimethyl or triethyl phosphite in tetrahydrofuran solution proceeds further than the corresponding reaction with tri-isopropyl phosphite described above to give the corresponding monocarbonyls $[(NC)_2C{=}CP(O)(OR)_2Mn(CO)(dppe)P(OR)_3]$ (II: $L = P(OR)_3$, R = Me or Et), ν(CO): at 1855 ± 3 cm^{-1}, ν(P=O) at 1134 ± 4 cm^{-1}, again containing the same type of chelating 2,2-dicyanovinylphosphonato ligands.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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