Metal Complexes with Terminal Dicyanomethylenecarbene Ligands formed by Chlorine Migration Reactions

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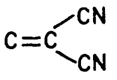
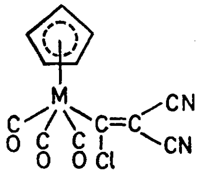
Summary Reactions of the 1-chloro-2,2-dicyanovinyl derivatives $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (M = Mo and W) with trivalent phosphorus and related ligands result in migration of chlorine from carbon to the transition metal to give products of the type $C_5H_5ML_2[C{=}C(CN)_2]Cl$ [M = Mo and W; L = Ph_3P, Ph_3As, Ph_3Sb, $(MeO)_3P$, $(EtO)_3P$, and $(PhO)_3P$] containing a terminal dicyanomethylenecarbene ligand.

We recently reported[1] two isomers of the complex $(C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ containing a bridging dicyanomethylenecarbene (I) ligand. This Communication describes the first metal complexes containing a terminal dicyanomethylenecarbene ligand (I). The complexes were obtained unexpectedly by migration of chlorine from an olefinic carbon atom to the metal atom in certain 1-chloro-2,2-dicyanovinyl metal derivatives.[1]



(I)

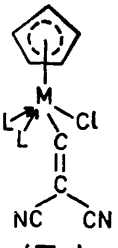


(II)

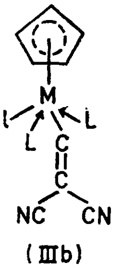
Reaction of the 1-chloro-2,2-dicyanovinylmolybdenum derivative $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ (II; M = Mo) with triphenylphosphine in boiling octane or other inert solvent results in the unexpected displacement of all of the carbonyl groups to give the orange carbonyl-free complex $(NC)_2C{=}CClMo(PPh_3)_2(C_5H_5)$ [m.p. 162—164° (decomp).,† yield *ca.* 75%]. Its ^1H n.m.r. spectrum ($CDCl_3$ solution) exhibits aryl and π-cyclopentadienyl resonances in the expected positions and relative intensities (6:1) for the indicated stoicheiometry. However, the π-cyclopentadienyl resonance was unexpectedly complex consisting of two 1:2:1 triplets (*J ca.* 2·2 Hz) of *ca.* 4:1 relative intensities at τ 4·91 and 5·16, respectively. This suggests that $(NC)_2C{=}CClMo(PPh_3)_2(C_5H_5)$ consists of a mixture of two isomers. Isomerism leading to similar n.m.r. effects has been shown to be possible for numerous $C_5H_5MA_2BC$ compounds,[2] *e.g.* $C_5H_5Mo(CO)_2[P(NMe_2)_3]I$[3] and $C_5H_5Mo(NO)[P(OPh)_3]I_2$;[4] similar isomerism is not possible for a $C_5H_5MA_2B$ compound. Accordingly $(NC)_2C{=}CClMo(PPh_3)_2(C_5H_5)$ is formulated as a mixture of the two $C_5H_5MA_2BC$ isomers (IIIa) and (IIIb)(M = Mo; L = Ph_3P) containing the first example of a terminal dicyanomethylenecarbene ligand. In structures (IIIa) and (IIIb) the central molybdenum atom possesses the favoured 18-electron rare gas configuration whereas in an alternative formulation of $(NC)_2C{=}CClMo(PPh_3)_2(C_5H_5)$ as a $C_5H_5MA_2B$ complex in which the 1-chloro-2,2-dicyanovinyl group is retained, the central molybdenum atom would have only a 16-electron configuration.

The reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ (II; M = Mo) with triphenylphosphine under fairly mild conditions thus results in the conversion of the 1-chloro-2,2-dicyanovinyl group into co-ordinated chloride and terminal dicyanomethylenecarbene ligands through a novel migration of the chlorine from the vinylic carbon to the molybdenum atom. Such reactions of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ (II; M = Mo) with ligands containing trivalent phosphorus and its heavier congeners to give dicyanomethylenecarbene complexes of the type $C_5H_5MoL_2[C{=}C(CN)_2]Cl$ (III; M = Mo) appear to be fairly general. Similar compounds (III; M = Mo) have been prepared with triphenylarsine, triphenylstibine, and the phosphites $(RO)_3P$ (R = Me, Et, and Ph) as ligands (L).†

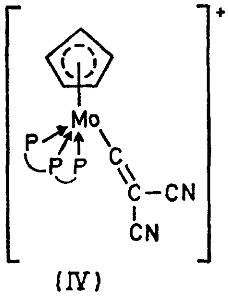
The reaction of the potentially chelating tritertiary phosphine[5] $Ph(CH_2CH_2PPh_2)_2$ (Pf–Pf–Pf) with $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ (II; M = Mo) in boiling octane results not only in displacement of the three carbonyl groups but also of the chlorine to give a 61% yield of the cation $[C_5H_5Mo(Pf\text{–}Pf\text{–}Pf)C{=}C(CN)_2]^+$ (IV) best isolated as its yellow-orange hexafluorophosphate salt† $[C_5H_5Mo(Pf\text{–}Pf\text{–}Pf)C{=}C(CN)_2][PF_6]$ (decomp. 270°). The cation (IV) exemplifies a terminal dicyanomethylenecarbene ligand in the absence of co-ordinated chloride and provides the final unambiguous evidence for the presence of dicyanomethylenecarbene ligands rather than 1-chloro-2,2-dicyanovinyl groups in the compounds of stoicheiometry $(NC)_2C{=}CClMoL_2C_5H_5$ discussed here.



(IIIa)



(IIIb)



(IV)

The reaction of triphenylphosphine with the 1-chloro-2,2-dicyanovinyltungsten compound[1] $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ (II; M = W) was somewhat more sluggish than the corresponding reaction with its molybdenum analogue, in accord with the greater stability of tungsten–carbon relative to molybdenum-carbon bonds.[6] Nevertheless, the reaction between $(NC)_2C{=}C(Cl)W(CO)_3C_5H_5$ (II; M = W) and

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† These new compounds gave correct elemental analyses for at least C, H, and N.

triphenylphosphine in boiling xylene (11 h) gave a 34% yield of yellow-orange $C_5H_5W(PPh_3)_2[C{=}C(CN)_2]Cl$ [(III; M = W, L = Ph_3P), m.p. 166—168° (decomp.)†] again with complete displacement of the three carbonyl groups. However, a second product from this reaction is the known[7] $C_5H_5W(CO)_2PPh_3Cl$, apparently formed by migration of chlorine from the vinylic carbon to the tungsten atom followed by loss of the dicyanomethylenecarbene ligand.

This work was partially supported by the Office of Naval Research.

(*Received, 23rd June* 1972; *Com.* 1095.)

[1] R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, 1972, **94**, 1784.
[2] J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, 1970, **92**, 5852.
[3] R. B. King, *Inorg. Chem.*, 1963, **2**, 936.
[4] R. B. King, *Inorg. Chem.*, 1967, **6**, 30.
[5] R. B. King, P. N. Kapoor, and R. N. Kapoor, *Inorg. Chem.*, 1971, **10**, 1841.
[6] R. B. King, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 905.
[7] P. M. Treichel, K. W. Barnett, and R. L. Shubkin, *J. Organometallic Chem.*, 1967, **7**, 449.