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Review

The beginnings of terminal vinylidene metal complex chemistry through the dicyanomethylene/oxygen analogy: dicyanovinylidene transition metal complexes

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Contents

Abstract

In 1972 the reaction between $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ and triphenylphosphine was found to give the terminal dicyanovinylidene complex $(\eta^5\text{-}C_5H_5)Mo[P(C_6H_5)_3]_2(C{=}C(CN)_2)Cl$. This was the first reported example of a transition metal complex with a terminal vinylidene ligand of any type. This and other related aspects of dicyanovinylidene transition metal chemistry are reviewed.

Keywords: Vinylideneruthenium; Triphenylphosphine; Diphenylketene

1. Introduction

In recent years the chemistry of vinylidene metal complexes has received considerable attention as indicated by the papers in this special issue of *Coordination Chemistry Reviews* as well as a 1998 major review article by Bruce [1]. One of the major driving forces behind this current interest is the application of certain types of terminal vinylideneruthenium complexes in catalysis, particularly that of olefin metathesis reactions [2]. However, the history of vinylidene transition metal complexes dates back nearly forty years although such complexes have remained rather exotic and obscure molecules until recent times.

The first vinylidene transition metal complex to be prepared was the bridging diphenylvinylidene complex $(\mu_2\text{-}Ph_2C{=}C)Fe_2(CO)_8$, which was first reported by Mills and Redhouse [3,4] in 1966 as the product of irradiation of $Fe(CO)_5$ with diphenylketene. Six years later [5] we reported the first terminal vinylidene complexes, namely the dicyanovinylidene complexes $(\eta^5\text{-}C_5H_5)Mo(PR_3)_2[C{=}C(CN)_2]Cl$. The motivation behind this early work was so different than that of modern workers in the field that we did not even think of our complexes as vinylidene complexes. Instead we used the name "dicyanomethylenecarbene" for the unusual ligand in these complexes [5]. This paper examines the rationale based on cyanocarbon chemistry, admittedly naïve in certain respects, which led to the discovery of these first terminal vinylidene complexes. Since a perusal of the Science Citation Index suggests that these unusual cyanovinylidene ligands

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have not been exploited, it appears instructive and useful to review the relevant aspects of cyanocarbon transition metal chemistry after a span of more than 30 years since the original discovery of terminal dicyanovinylidene complexes. This short article updates an account of our work published approximately 30 years ago in the *Annals of the New York Academy of Sciences* [6].

2. Cyanocarbon chemistry

Cyanocarbons are related to hydrocarbons by replacement of all or most of the hydrogen atoms with cyano (nitrile) groups. The emergence of cyanocarbon chemistry as a distinct area of organic chemistry dates back to work at du Pont in the 1950s. Because of the vagaries of industrial clearance of research for publication, the seminal du Pont papers on cyanocarbon chemistry appeared as a cluster of papers in a 1958 issue of the *Journal of the American Chemical Society* [7]. Recently, an excellent short historical account of this early du Pont work on cyanocarbon chemistry was published by Webster, who was one of the key participants in the du Pont group [8].

The following features of cyanocarbon chemistry are of particular interest, especially as contrasted with corresponding hydrocarbon chemistry:

1. Saturated cyanocarbons such as hexacyanoethane [9] and 1,1,2,2-tetracyanoethane [10] are relatively unstable molecules in contrast to the very stable ethane. Such saturated cyanocarbons are even less stable than unsaturated cyanocarbons, which are stabilized by conjugation of the π-orbitals of their cyano groups with those of their carbon-carbon double and/or triple bonds.
2. The electron-withdrawing nature of cyano groups makes cyanocarbons readily reducible to radical anions. For example, tetracyanoethylene can readily be reduced to its radical anion using reducing agents as weak as iodide and even cyanide [11]. The paramagnetism of the stable resulting tetracyanoethylene radical anion has been used by Miller and co-workers [12] to synthesize bulk ferromagnetic organic materials containing tetracyanoethylene and metallocene units.
3. Another consequence of the electron-withdrawing nature of cyano groups is the close analogy between a dicyanomethylene unit and an oxygen atom [13,14]. Examples of this analogy (Fig. 1) are manifested by similarities in some chemical and physical properties of ketones ($R_2C{=}O$) and dicyanomethylene derivatives [$R_2C{=}C(CN)_2$], pyridine N-oxide ($C_5H_5N^+{-}O^-$) and pyridinium *N*-dicyanomethylide [$C_5H_5N^+{-}C^-(CN)_2$], and even CO_3^{2-} and $C[C(CN)_2]_3^{2-}$. The synthesis of terminal dicyanovinylidene metal complexes exploited this analogy to generate unusual transition metal organometallic chemistry.

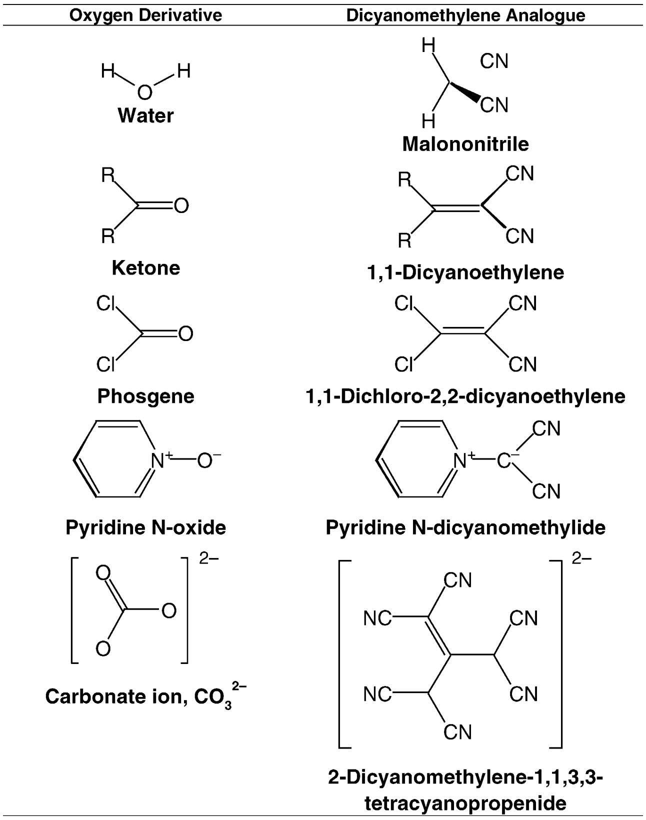

Fig. 1. Examples of the dicyanomethylene/oxygen analogy.

3. Exploitation of the dicyanomethylene/oxygen analogy in transition metal organometallic chemistry

Extension of the dicyanomethylene/oxygen analogy naively suggests a close relationship between the two “bivalent carbon” species dicyanovinylidene $:C{=}C(CN)_2$, and carbon monoxide, CO. We now readily recognize the important difference of CO having π-bonding in two perpendicular planes but $:C{=}C(CN)_2$ having π-bonding only in the plane orthogonal to the molecular plane (Fig. 2). However, back in the early 1970s we did not worry as much about this fundamental molecular orbital difference of the two molecules. Therefore at that time we reasoned that dicyanovinylidene might be a stable molecule like carbon

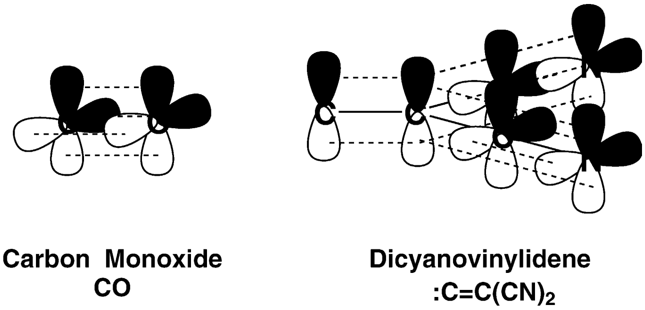

Fig. 2. A comparison of the atomic orbitals for π-bonding in carbon monoxide and dicyanovinylidene.

monoxide. We therefore set out to synthesize this potentially interesting molecule. Since isocyanides, RNC, can be synthesized by dehydration of the corresponding formamides HC(O)NHR by reagents such as phosgene, oxalyl chloride, or phosphorus oxychloride in a basic solvent, we tried an analogous dehydration of alkali metal salts of the enol form of $HC(O)CH(CN)_2$ [15]. However, none of these experiments gave any products that appeared to be free dicyanovinylidene or its further reaction or decomposition products. In addition, attempts to prepare free dicyanovinylidene by the dehydrohalogenation of $(NC)_2C{=}C(H)Cl$ with tertiary amines were also unsuccessful.

Since our attempts to prepare free dicyanovinylidene as a stable entity were unsuccessful, our next goal was the preparation of a transition metal complex of dicyanovinylidene. In this connection we exploited the dicyanomethylene/oxygen analogy in a different manner. Normally vinylic halides are unreactive towards nucleophiles and rarely react with metal carbonyl anions to give σ-vinyl transition metal complexes. However, the dicyanomethylene/oxygen analogy suggests that 2,2-dicyanovinyl chlorides of the general type $(NC)_2C{=}C(R)Cl$ might be highly reactive towards nucleophiles like the corresponding acid chlorides $O{=}C(R)Cl$. In this connection the 2,2-dicyanovinyl chloride found to be of particular importance in dicyanovinylidene chemistry was the dichloride $(NC)_2C{=}CCl_2$, which is the dicyanomethylene analogue of phosgene $O{=}CCl_2$(Fig. 1).

This greatly enhanced reactivity of 2,2-dicyanovinyl chlorides towards nucleophiles was exploited in their reactions with the readily available metal carbonyl anions $(\eta^5\text{-}C_5H_5)M(CO)_3^-$ (M: Mo, W), $Mn(CO)_5^-$, and $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$ to give a range of σ-2,2-dicyanovinyl transition metal derivatives $(NC)_2C{=}C(R)M(CO)_3(\eta^5\text{-}C_5H_5)$ (M: Mo, W; R: H, CN, Cl), $(NC)_2C{=}C(R)Mn(CO)_5^-$ (R: H, CN, Cl), and $(NC)_2C{=}C(H)Fe(CO)_2(\eta^5\text{-}C_5H_5)$ (Fig. 3) [16,17]. These σ-2,2-dicyanovinyl derivatives are rather stable isolable molecules having properties similar to those of other σ-organyl derivatives of the same transition metal carbonyl moieties.

4. Synthesis of dicyanovinylidene metal complexes

4.1. Bridging dicyanovinylidene metal complexes

The cyclopentadienyliron carbonyl anion, $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$, is known to be more nucleophilic than the three other metal carbonyl anions used in this work, namely $(\eta^5\text{-}C_5H_5)M(CO)_3^-$ (M: Mo, W) and $Mn(CO)_5^-$, by factors of 10,000 and more [18]. For this reason the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$ with $(NC)_2C{=}CCl_2$ resulted in some replacement of both chlorine atoms with metal atoms whereas the corresponding reactions of the much less nucleophilic $(\eta^5\text{-}C_5H_5)M(CO)_3^-$ (M: Mo, W) and $Mn(CO)_5^-$ with $(NC)_2C{=}CCl_2$ resulted in the replacement of only a single chlorine atom with a metal atom to give good yields of the corresponding σ-2,2-dicyanovinyl derivatives $(NC)_2C{=}C(Cl)M(CO)_3(\eta^5\text{-}C_5H_5)$ (M: Mo, W) and $(NC)_2C{=}C(Cl)Mn(CO)_5$. The product obtained in low yield (~3%) from the reaction of $(NC)_2C{=}CCl_2$ with $NaFe(CO)_2(\eta^5\text{-}C_5H_5)$ was found to be the bridging dicyanovinylidene complex $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$, isolated as both *cis* and *trans* isomers (Fig. 4) [16,17]. The structure of the *cis* isomer was subsequently confirmed by X-ray crystallography [19].

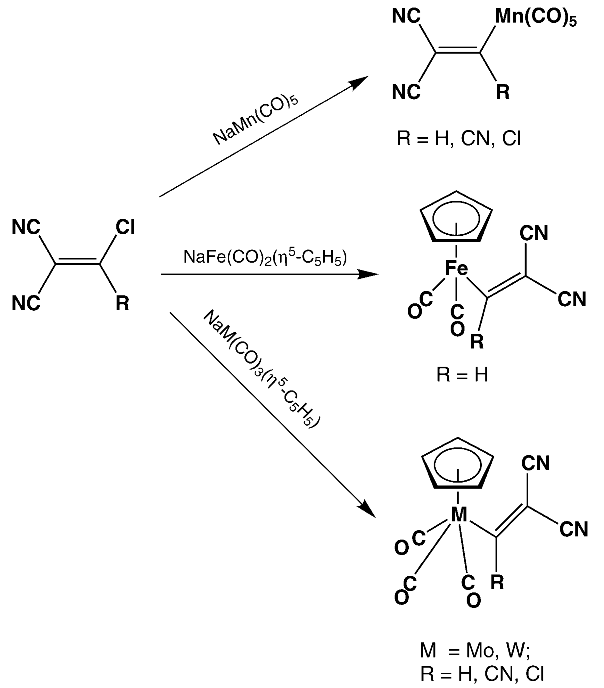

Fig. 3. Reactions of 2,2-dicyanovinyl chlorides with metal carbonyl anions to give σ-2,2-dicyanovinyl transition metal complexes.

The synthesis of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$ from $NaFe(CO)_2(\eta^5\text{-}C_5H_5)$ and $(NC)_2C{=}CCl_2$ is a very direct synthesis but suffers from a very low yield (3%). More recently Bordoni et al. [20] discovered a much higher yield (~50%) synthesis of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$ by reaction of the thiocarbyne complex cation $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSCH_3)]^+$ with the nucleophile $NaCH(CN)_2$ simply obtained from malononitrile (Fig. 5). The thiocarbyne cation starting material can be obtained by methylation of the thiocarbonyl $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CS)$ with methyl trifluoromethanesulfonate.

The bridging dicyanovinylidene isomers *cis*- and *trans*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$ are dicyanomethylene analogues of the well known $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$. As such the following properties of the bridging dicyanovinylidene complexes are of interest:

(1) The *cis*- and *trans*-isomers of the dicyanovinylidene complex $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$ can be readily separated by column chromatography.

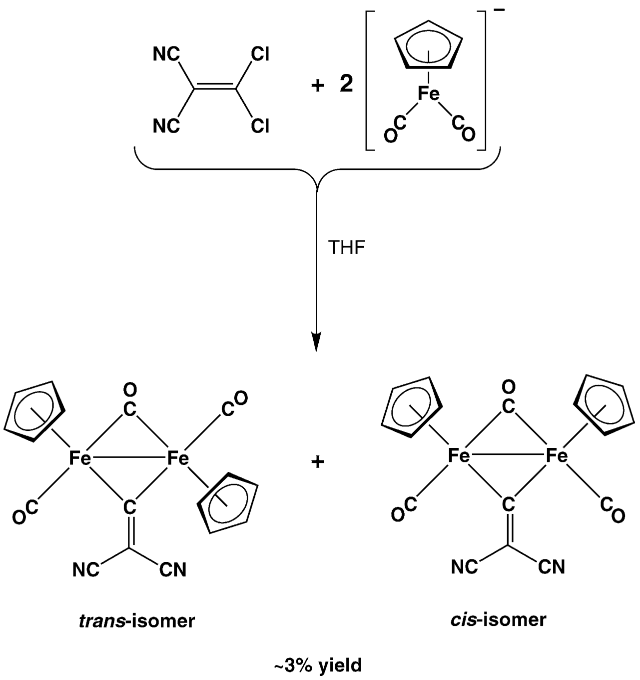

Fig. 4. Preparation of the two stereoisomers of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$ from $NaFe(CO)_2C_5H_5$ and $(NC)_2C{=}CCl_2$.

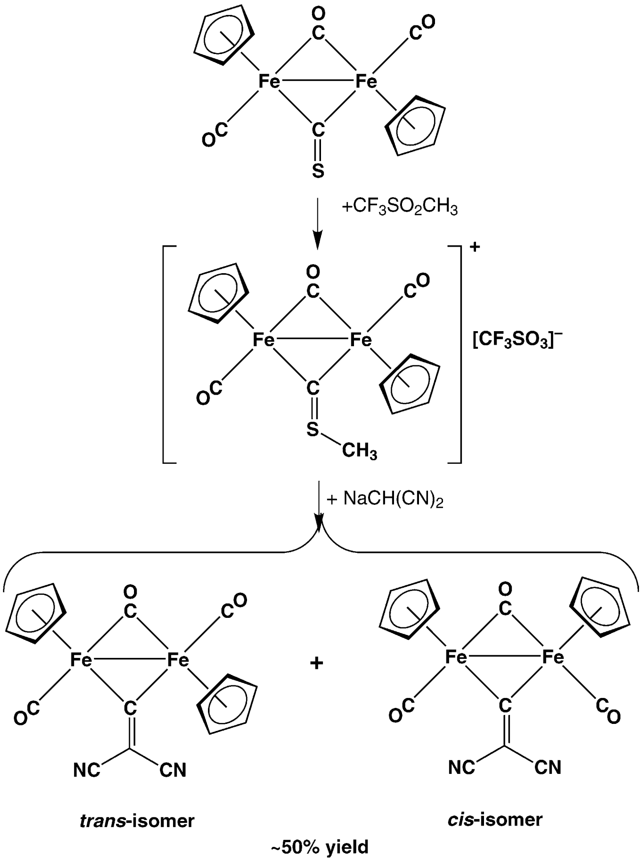

Fig. 5. Preparation of the two stereoisomers of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$ from $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CS)$ by methylation followed by nucleophilic substitution with the malononitrile derivative $NaCH(CN)_2$.

Similar *cis*- and *trans*-isomers of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ are known, [21,22] but they interconvert too easily at room temperature in solution to be separable by column chromatography.

(2) The Fe–Fe bond and bridging dicyanovinylidene system in *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$ is not cleaved by iodine to give a mononuclear product containing a terminal dicyanovinylidene group, such as $(\eta^5\text{-}C_5H_5)Fe(CO)[C{=}C(CN)_2]I$, even under conditions more vigorous than those where the carbonyl analogue $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ reacts with iodine to form mononuclear $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ [23].

(3) The ν(CO) frequencies of *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$, namely 2030, 1989, and 1825 cm^{-1}, are appreciably higher than the corresponding ν(CO) frequencies[21,22] in *cis*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$, namely 1998, 1954, 1810, 1777 cm^{-1}. This indicates that the dicyanovinylidene ligand is an even stronger π-acceptor ligand than the already strong π-acceptor carbonyl ligand, apparently owing to the strong electron-withdrawing properties of its cyano groups.

4.2. Terminal dicyanovinylidene metal complexes

The studies on the bridging dicyanovinylidene complex $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C{=}C(CN)_2]$ (Figs. 4 and 5) indicate extremely strong π-acceptor properties for the bridging dicyanovinylidene ligand. In the case of terminal dicyanovinylidene complexes, this suggests that even a single terminal dicyanovinylidene ligand bonded to a transition metal will deplete its electron density very severely through strong back π-bonding. As a result insufficient electron density is likely to remain on the transition metal for strong π-backbonding to either a second terminal dicyanovinylidene ligand or a carbonyl group to form stable complexes. This suggests that complexes containing two or more terminal dicyanovinylidene ligands or one terminal dicyanovinylidene ligand plus one or more carbonyl groups are likely to be unstable. Thus the prospect of synthesizing terminal dicyanovinylidene complexes such as $Cr[C{=}C(CN)_2]_6$, $Cr(CO)_5[C{=}C(CN)_2]$, or even $(\eta^5\text{-}C_5H_5)Fe(CO)[C{=}C(CN)_2]I$ containing more than one terminal dicyanovinylidene group or a combination of dicyanovinylidene and carbonyl groups appears to be unpromising.

Our success in the early 1970s at synthesizing the first terminal dicyanovinylidene complex and the first vinylidene complex of any type was serendipitous but consistent with the idea that dicyanovinylidene and carbonyl groups are not likely to coexist as ligands to a single transition metal atom in stable metal complexes. Thus the first terminal dicyanovinylidene complexes were found in studies of the substitution reactions of the metal carbonyl complex $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ with trivalent phosphorus ligands. In this connection triphenylphosphine was found to displace all three carbonyl ligands in $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ in boiling dichloromethane (37 °C), which represents unusually mild conditions for complete carbonyl replacement in an $RMo(CO)_3(\eta^5\text{-}C_5H_5)$ derivative. The resulting stable organometallic product has the unusual stoichiometry $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(\eta\text{-}C_5H_5)$, in which three CO groups are replaced by only two triphenylphosphine ligands even though both ligands are normally only two-electron donors. Thus simple electron bookkeeping suggests that conversion of the $(NC)_2C{=}C(Cl)$ group from a one-electron donor in $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ to a three-electron donor of some type is necessary in order to preserve the favored 18-electron configuration in $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(\eta\text{-}C_5H_5)$.

In the early 1970s definitive structure determination by X-ray crystallography of the structure of a metal complex was not as routine as it is now so that "sporting" methods based on various types of spectroscopy were then relied on more heavily for initial structure elucidation. In the case of $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(\eta\text{-}C_5H_5)$ its proton NMR spectrum provided the first clues concerning its structure. The presence of two $\eta^5\text{-}C_5H_5$ resonances of approximate 3:1 relative intensity requires this complex to be a mixture of two stereoisomers. Stereoisomerism leading to similar NMR effects [24] is known to occur for numerous $(\eta^5\text{-}C_5H_5)MA_2BC$ complexes such as $(\eta^5\text{-}C_5H_5)Mo(CO)_2[P(NMe_2)_3]I$ [25] and $(\eta^5\text{-}C_5H_5)Mo(NO)[P(OC_6H_5)_3]I_2$ [26]. Similar isomerism is not possible for a $C_5H_5MA_2B$ complex. This indirect demonstration by NMR that $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(\eta^5\text{-}C_5H_5)$ is an $(\eta^5\text{-}C_5H_5)MA_2BC$ complex rather than an $(\eta^5\text{-}C_5H_5)MA_2B$ complex indicates that the $(NC)_2C{=}CCl$ moiety in this complex occupies two not necessarily adjacent coordination positions rather than only one coordination position of the central molybdenum atom. This is possible if $(NC)_2C{=}CClMo[P(C_6H_5)_3]_2(\eta^5\text{-}C_5H_5)$ is formulated as a mixture of the $(\eta^5\text{-}C_5H_5)MA_2BC$ isomers $(\eta^5\text{-}C_5H_5)Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ (Fig. 6) containing a terminal dicyanovinylidene ligand. This hypothesis was confirmed by an X-ray structure determination on the related trimethyl phosphite complex $(\eta^5\text{-}C_5H_5)Mo[P(OCH_3)_3]_2[C{=}C(CN)_2]Cl$ [27]. In this structure the Mo–C(dicyanovinylidene) distance was found to be only ∼1.83 Å, which is much shorter than the Mo–C(carbonyl) distances of 1.93 to 1.99 Å in molybdenum carbonyl complexes. This is in accord with the stronger π-acceptor characteristics and therefore higher metal-carbon bond order in metal dicyanovinylidene complexes relative to metal carbonyl complexes.

Subsequent to our discovery of $(\eta^5\text{-}C_5H_5)Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ numerous related molybdenum and tungsten terminal dicyanovinylidene complexes have been prepared with the general formula $(\eta^5\text{-}C_5H_5)ML_2[C{=}C(CN)_2]Cl$ by similar reactions of $(NC)_2C{=}C(Cl)M(CO)_3(\eta^5\text{-}C_5H_5)$ with other ligands containing Group 15 trivalent donor atoms (M: Mo, L: $(CH_3)_2C_6H_5P$, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$, $(RO)_3P$ where R: CH_3, C_2H_5, or C_6H_5; M: W, L: $(C_6H_5)_3As$, $(C_6H_5)_3Sb$, $(CH_3O)_3P$, $(C_2H_5O)_3P$) [28]. In contrast to $(\eta^5\text{-}C_5H_5)Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$ most of the other $(\eta^5\text{-}C_5H_5)ML_2[C{=}C(CN)_2]Cl$ complexes were obtained as a single stereoisomer. We were thus lucky that our initial experiments, which led to the discovery of the first terminal dicyanovinylidene metal complexes, were done with triphenylphosphine, which gave an isomer mixture. This allowed us to recognize from the proton NMR spectrum that the product was an $(\eta^5\text{-}C_5H_5)MA_2BC$ rather than an $(\eta^5\text{-}C_5H_5)MA_2B$ derivative, thereby providing the key initial clue to the terminal dicyanovinylidene formulation (Fig. 6).

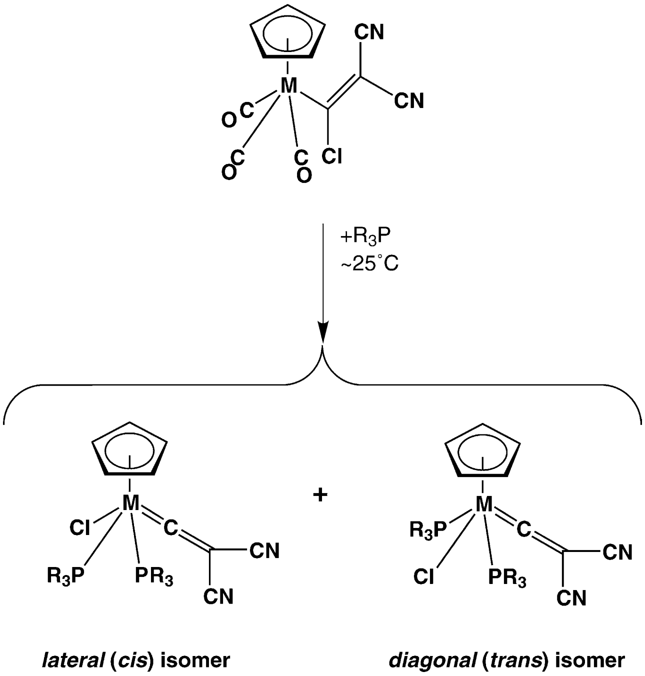

Fig. 6. Preparation of the two stereoisomers of $(\eta^5\text{-}C_5H_5)M(PR_3)_2[C{=}C(CN)_2]Cl$ from $(NC)_2C{=}C(Cl)M(CO)_3(\eta^5\text{-}C_5H_5)$ and trivalent phosphorus ligands (M: Mo or W).

In view of the success in obtaining the terminal vinylidene complexes $(\eta^5\text{-}C_5H_5)ML_2[C{=}C(CN)_2]Cl$ by reactions of $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ with trivalent phosphorus ligands, some reactions of $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ with other potential ligands were also studied. In this connection the reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ with *tert*-butyl isocyanide did not lead to the isolation of a terminal dicyanovinylidene complex analogous to $(\eta^5\text{-}C_5H_5)Mo[P(C_6H_5)_3]_2[C{=}C(CN)_2]Cl$. Instead the products isolated consisted of two stereoisomers of the η^2-tricyanoethylene complex $(\eta^5\text{-}C_5H_5)Mo[CNC(CH_3)_3]_2[\eta^2\text{-}(NC)_2C{=}CHCN]Cl$ as well as a third isomer formulated as a η^3-allylic zwitterionic complex $(\eta^5\text{-}C_5H_5)Mo[(CNC(CH_3)_3][\eta^3\text{-}(NC)_2CC(CN)C{=}NHC(CH_3)_3]$ (Fig. 7) [29]. The structures of these complexes have not yet been de-

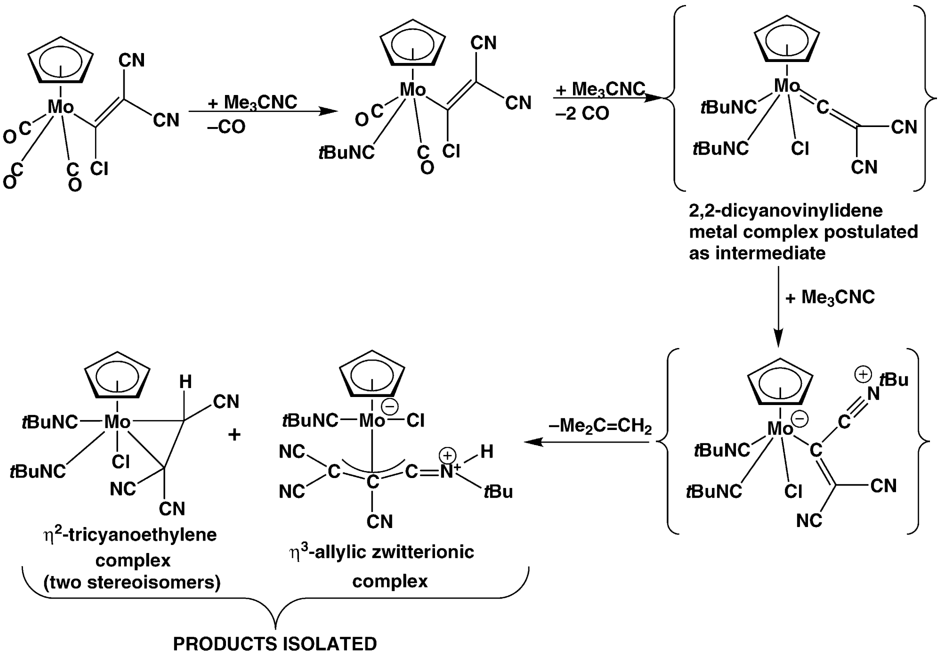

Fig. 7. Reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ with *tert*-butyl isocyanide. Only one of the two stereoisomers of the η^2-tricyanoethylene product is shown for clarity.

termined by X-ray diffraction, largely because of the difficulty in obtaining suitable single crystals of either of the tricyanoethylene isomeric complexes. However, a closely analogous η^2-fumaronitrile complex $(\eta^5\text{-}C_5H_5)Mo[CNC(CH_3)_3]_2[\eta^2\text{-}NCCH{=}CHCN]Cl$ has been obtained by a more rational synthesis, namely the photolysis of $(\eta^5\text{-}C_5H_5)Mo[CNC(CH_3)_3]_2(CO)Cl$ with fumaronitrile (Fig. 8). Comparison of the NMR spectra of the fumaronitrile and tricyanoethylene complexes suggests that these complexes should have analogous structures. Consideration of a possible mechanism for the formation of a tricyanoethylene complex from reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ with *tert*-butyl isocyanide suggests the terminal dicyanovinylidene complex $(\eta^5\text{-}C_5H_5)Mo[CNC(CH_3)_3]_2[C{=}C(CN)_2]Cl$ as a possible reaction intermediate (Fig. 7). However, since *tert*-butyl isocyanide is a weaker π-acceptor than most trivalent phosphorus ligands, the vinylidene carbon atom in $(\eta^5\text{-}C_5H_5)Mo[CNC(CH_3)_3]_2[C{=}C(CN)_2]Cl$ is electron-deficient enough to be susceptible to nucleophilic attack. Such a nucleophilic attack by *tert*-butyl isocyanide on this carbon atom can lead to an intermediate,

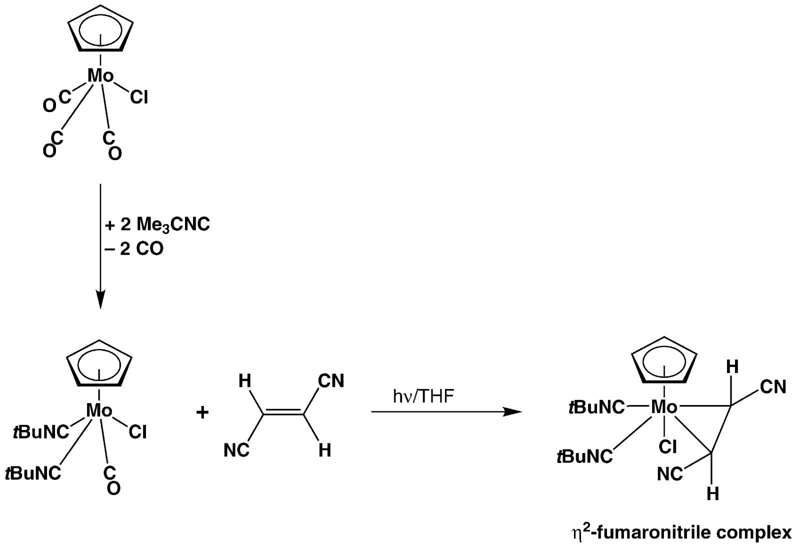

Fig. 8. Preparation of the η^2-fumaronitrile complex $(\eta^5\text{-}C_5H_5)Mo[CNC(CH_3)_3]_2[\eta^2\text{-}NCCH{=}CHCN]Cl$. Again only one stereoisomer is shown for clarity.

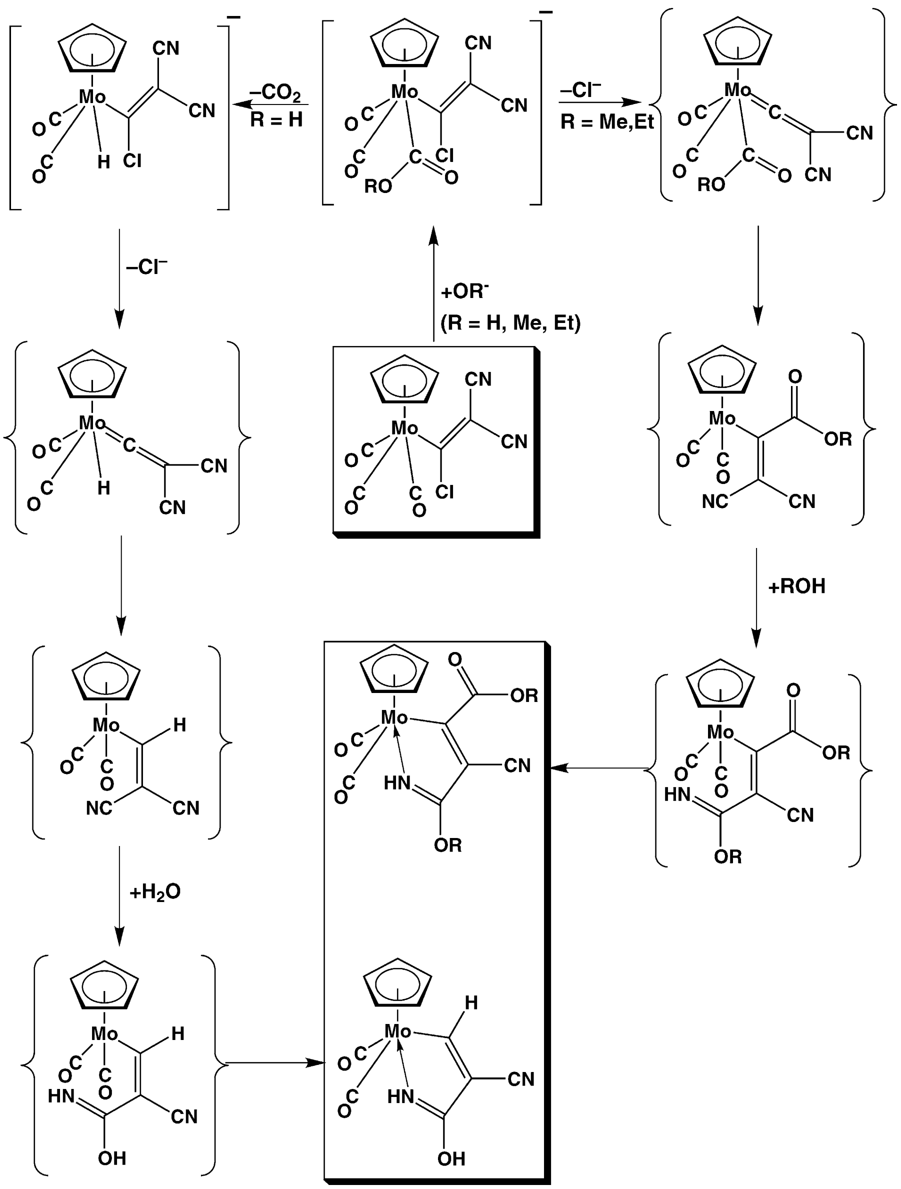

Fig. 9. Reactions of $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ with water and alcohols. The starting material and the isolated products are shown in boxes.

which can undergo loss of isobutene to give the observed η^2-tricyanoethylene and η^3-allylic zwitterionic complexes isolated as products. (Fig. 7).

Reactions of $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ with water and lower alcohols can lead to novel chelates, which may form through intermediate terminal dicyanovinylidene complexes (Fig. 9) [30]. Thus the reaction of $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ with sodium methoxide in methanol converts one of the carbonyl groups to a methoxycarbonyl group followed by loss of chloride. The methoxycarbonyl group in the resulting intermediate, formulated with a terminal dicyanovinylidene ligand, migrates from molybdenum to the vinylidene carbon leading to a coordinately unsaturated 16-electron σ-alkenyl derivative with two cyano and one methoxycarbonyl substituents. Subsequent alcoholysis of one of the cyano groups in this intermediate provides a pendant imino ligand which can then bond to the molybdenum atom to form a five-membered chelate ring leading to the observed coordinately saturated products with the favorable 18-electron configuration for the molybdenum atom.

A closely related reaction occurs upon treatment of $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ with water in the presence of alumina or triethylamine (Fig. 9) [30]. However, in this case the intermediate metallocarboxylic acid undergoes decarboxylation to the corresponding hydride as is typical for carboxyl groups directly bonded to transition metals. Otherwise the reaction pathway appears to be completely analogous leading to a similar type of chelate but with a hydrogen rather than an alkoxycarbonyl substituent.

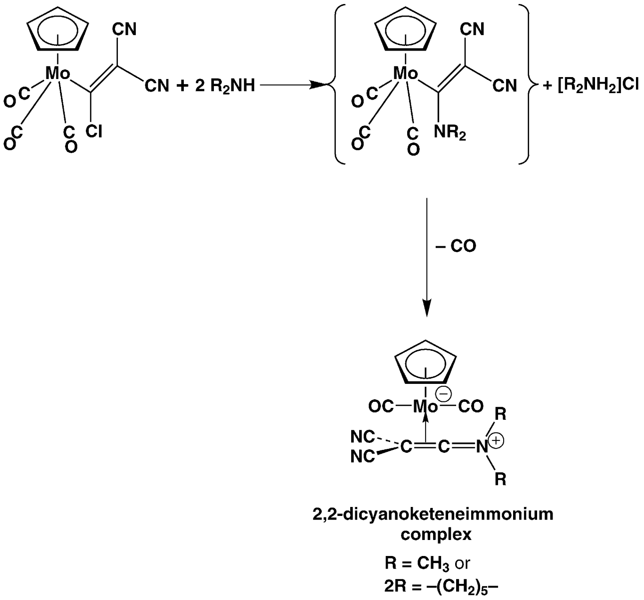

Fig. 10. Reactions of $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ with secondary amines to give 2,2-dicyanoketeneimmonium metal complexes.

Reactions of $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$ with secondary amines (dimethylamine and piperidine) follow still a different course leading to 2,2-dicyanoketeneimmonium molybdenum complexes (Fig. 10) [30]. Again the structures of these products have not yet been determined by X-ray diffraction. However, the ^{13}C and ^1H NMR spectra of these complexes indicate their cyano groups to be equivalent but the two R groups of the R_2N unit to be non-equivalent. This suggests that the C=C double bond rather than the C=N double bond of the 2,2-dicyanoketeneimmonium ligand is bonded to the molybdenum atom.

4.3. Free dicyanovinylidene as a reactive intermediate

We were unable to prepare free dicyanovinylidene as a stable compound as noted above. The question remained whether dicyanovinylidene could be generated as a reactive intermediate. The ability for the 1-chloro-2,2-dicyanovinyl group in complexes of the type $(NC)_2C{=}C(Cl)M(CO)_3(\eta^5\text{-}C_5H_5)$ (M: Mo, W) to become a terminal dicyanovinylidene ligand by migration of chlorine from a vinylic carbon to the central metal atom suggested that simple pyrolysis or photolysis of a 1-chloro-2,2-dicyanovinyl complex might provide a source of free dicyanovinylidene according to the following equation:

$$(NC)_2C = C(Cl)M(CO)_3C_5H_5 \overset{\Delta}{\rightarrow} (NC)_2C = C: + C_5H_5M(CO)_3Cl$$

Such a reaction would be analogous to the generation of dihalocarbenes by pyrolysis of a trihalomethyl mercurial according to the following process [31]:

$$RHgCX_3 \overset{\Delta}{\rightarrow} RHgX + :CX_2$$

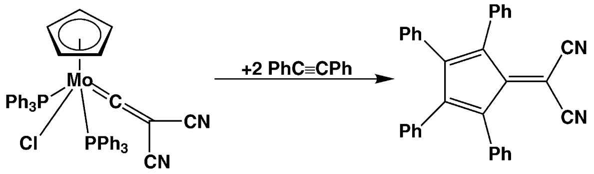

Fig. 11. Preparation of a 6,6-dicyanofulvene by the cyclization of diphenylacetylene with dicyanovinylidene generated by heating $(NC)_2C{=}C(Cl)Mo(CO)_3(\eta^5\text{-}C_5H_5)$.

In this connection we found that pyrolysis of $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ in the presence of diphenylacetylene led to 6,6-dicyano-1,2,3,4-tetraphenylfulvene, which can be formed by the cyclization of two diphenylacetylene units with one dicyanovinylidene unit (Fig. 11) [32]. The resulting fulvene is the dicyanomethylene analogue of tetraphenylcyclopentadienone, which can be formed similarly by cyclization of two diphenylacetylene units with one carbon monoxide unit [33].

5. Future prospects

More than 30 years ago we reported the first dicyanovinylidene transition metal complexes. Such complexes and related polycyanovinyl transition metal derivatives were found to be readily prepared stable organometallic compounds exhibiting interesting chemical reactivity. However, because of changes in the patterns of financial support for our synthetic organometallic chemistry and other related experimental research starting in the late 1970s, we were not able to pursue many of the interesting scientific opportunities afforded by these novel compounds. In fact our research programs have strayed increasingly further from chemical synthesis with the passage of time. In this connection I remain surprised that these interesting and unusual organometallic compounds have received so little attention from other synthetic organometallic chemists throughout the world during the past 30 years. Hopefully, publication of this short rather historically oriented review will stimulate future research on these and related cyanocarbon transition metal compounds.

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