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Review

Reactions of alkynes at mononuclear electron-rich transition metal centres

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I. Introduction

Alkynes exhibit a rich coordination chemistry and are increasingly recognized as valuable and versatile reagents for organometallic and organic synthesis [1,2].

Although most of the acetylene-based organic industrial processes have been replaced, mainly refer after the second World War, by olefin-based reactions [2], use of acetylene may become again economically attractive in some cases. It is formed as a by-product in the production of olefins by cracking of heavy petroleum fractions and some of the early processes that became obsolete (e.g., the hydrocyanation of alkynes) [3] may regain interest in view of current developments; alkynes may also find advantageous applications in synthesis of particular compounds (such as 2-substituted pyridines [4]) that are difficult to obtain by other routes. A decrease in the supply of naphtha or in energy costs would also tend to favour some synthetic routes based on acetylene. Furthermore, alkynes have also biological significance, and, e.g., 1-alkynes are substrates of molybdenum-nitrogenase, being reduced to alkenes through a $2e^-/2H^+$ process [5].

Interest in the activation of alkynes by transition metal centres is thus spreading worldwide, and in this review we describe the results we have obtained by using low oxidation state metal sites of the types $\{ML_4\}$ ($M = Mo^0$ or W^0, $L = \frac{1}{2}$dppe (where dppe = $Ph_2PCH_2CH_2PPh_2$) or PMe_2Ph) or $\{ReClL_4\}$, which are also able to bind dinitrogen [6,7]. Since N_2 is commonly a labile ligand, its complexes constitute convenient sources of these centres and have been used in this study as starting materials for the activation of alkynes.

These metal centres have a high electron-rich character, as revealed by the low redox potential of their complexes with ligands such as carbonyl, dinitrogen, or isocyanides, particularly the group 6 d^6 species [8–10]. Moreover, marked π-electron-releasing ability is expected for such centres for metals of the central periodic groups [11]; in this context, the presence of the π-donor chloro ligand at the rhenium(I) sites is particularly relevant. Such a propensity for π-electron donation has been substantiated, by e.g., infrared and X-ray data, and supported by simplified π-MO schemes for derived isocyanide complexes, as well as by their chemical reactions.

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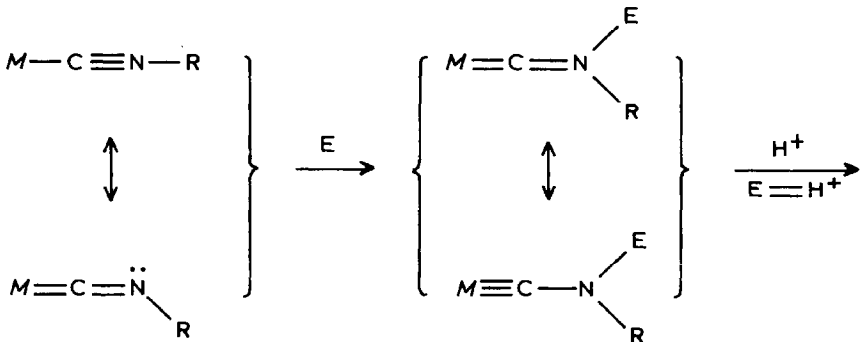


M^{ox} + H_2NR + NH_3 + CH_4 (+C_2, C_3hydrocarbons)

Scheme 1. Activation of isocyanide by an electron-rich binding site (M) with a central group transition metal (E denotes an electrophile such as H^+, R^+, or a Lewis acid).

When ligating any of these d^6 Mo, W or Re sites, isocyanides give ν(CN) bands at very low wavenumbers [9,12,13] (e.g., ca. 1800 cm^{-1} for *trans*-[ReCl(CNMe)(dppe)$_2$]) as a result of the strong π-electron releasing nature of the metal centres. This also accounts for the shortness of the metal–isocyanide carbon bond [14–16] and a possible bending at the nitrogen atom [14] (in agreement with simplified π-MO schemes [17]), as well as for the activation of the isocyanide ligand towards attack by electrophiles (E) to give aminocarbyne products and derived amines, ammonia, and hydrocarbons formed by complete reductive cleavage of the unsaturated CN bond [12,18–22]. This behaviour is indicated by the general scheme 1, and examples illustrating the initial protonation step are given in eqs. 1 and 2 (M = Mo or W; R = alkyl or aryl; HA = HBF_4, HPF_6, $HFSO_3$, etc.).

trans-[ReCl(CNR)(dppe)$_2$] + HA → *trans*-[ReCl(CNHR)(dppe)$_2$]A (1)

trans-[M(CNR)$_2$(dppe)$_2$] + HA → *trans*-[M(CNHR)(CNR)(dppe)$_2$]A (2)

II. 1,3-Hydrogen shift reactions

An unusual metal-centred alkyne rearrangement was observed in the reaction of phenylpropyne (PhC≡CCH_3) with *trans*-[ReCl(N_2)(dppe)$_2$]. Treatment of the latter with this alkyne in refluxing benzene or tetrahydrofuran gave a product shown by single-crystal X-ray diffraction to be the η^2-phenylallene complex *trans*-[ReCl(η^2-H_2-C–C =CHPh)(dppe)$_2$] (eq. 3; Fig. 1a); it was produced by a 1,3-hydrogen migration from the methyl group of the parent alkyne [23].

trans-[ReCl(N_2)(dppe)$_2$] + PhC≡CCH_3 →

trans-[ReCl(η^2-H_2C–C =CHPh)(dppe)$_2$] + N_2 (3)

This was the first allene complex of rhenium to be reported; allene complexes of transition metals are limited in number and are formed mainly with group 8–10 metals [24].

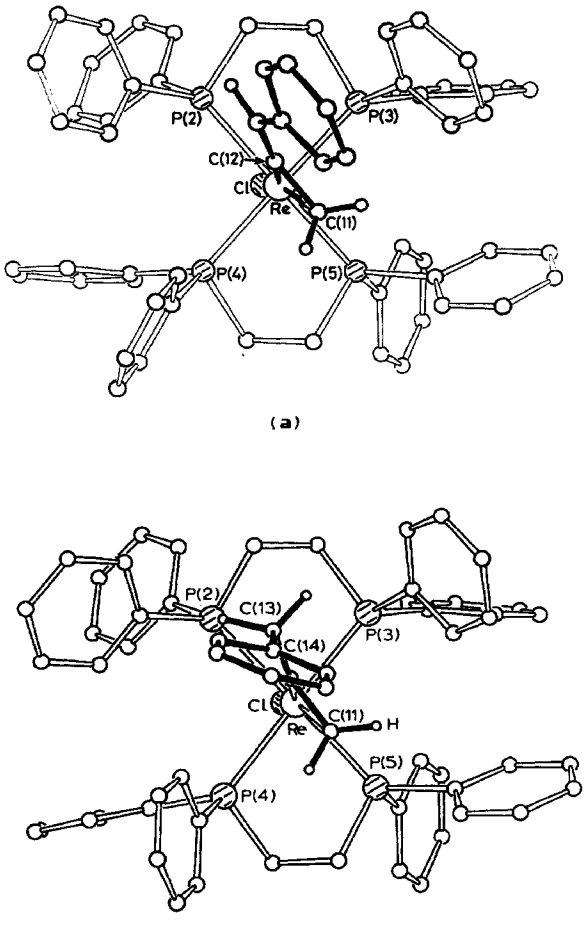


Fig. 1. Molecular structures of the allene complex *trans*-[ReCl{η^2-$H_2\widehat{C-C}$ =CH(Ph)}(dppe)$_2$] (**a**) [23] and of the derived metallacyclopropene (η^2-vinyl) compound *trans*-[ReCl{=C(CH_2Ph)CH_2}(dppe)$_2$][BF_4] (**b**) [36]. Selected distances (with e.s.d.s. in parentheses) are:
For (**a**): Re–C(11) 2.181(6), Re–C(12) 2.087(6), C(11)–C(12) 1.41(1), C(12)–C(13) 1.32(1).
For (**b**): Re–C(11) 2.193(6), Re–C(12) 1.947(6), C(11)–C(12) 1.412(9), C(12)–C(13) 1.500(8) Å.

The allene ligand is planar and has a long bond between the two ligating C atoms (1.41(1) Å) and a short bond between the other two allenic carbons (1.32(1) Å), indicating a considerable σ-bond character in the Re–C_2 moiety and representing one extreme form of allene ligation. However, some double bond character between the Re atom and the internal ligating allene sp^2 carbon is suggested by the relatively short distance (2.087(6) Å) between these atoms.

This metal-centred alkyne–allene conversion is related to the known [25] base-catalysed isomerization of alkynes via an allene intermediate, the electron-rich rhenium site conceivably playing a role corresponding to that of the base in the organic reaction.

A few other examples of this type of alkyne rearrangement involving a metal-centred 1,3-hydrogen migration have been reported for electrophilic alkynes, such as RR′CHC≡CE (E = CO_2Me, CO_2Et or COMe; R, R′ = H or alkyl) at {Mn(η^5-

$C_5H_4Me)(CO)_2\}$ [26] and some arenealkyne chelates of chromium [27]. However, different routes are known [28] for ligating allenes from other ligand precursors.

The detailed mechanisms of these reactions are still unknown, but in the case of the 1,3-hydrogen shift at an alkyne induced by the electron-rich rhenium complex the overall alkyne to allene rearrangement may be rationalized in terms of the orbitals involved in the bonding of the alkyne. Because of the filled pseudo-t_{2g} set of the d orbitals of the electron-rich d^6 $\{ReCl(dppe)_2\}$ centre, a repulsive two-centre four-electron interaction occurs between the filled $\pi_\perp$ orbital of the alkyne (lying in the plane perpendicular to the bond) and the filled metal d_π orbital; such a destabilizing interaction may promote the alkyne to allene conversion, as has been suggested [29] for the alkyne to vinylidene rearrangement at other d^6 metal centres. The alkyne is thus converted into a species in which such a destabilizing effect is no longer present.

Although in the reaction of the dinitrogen complex of rhenium(I) with phenylpropyne an η^2-alkyne complex is conceivably formed as a first step, it was not isolated, and only the more stable allene product was obtained.

III. 1,2-Hydrogen shift reactions

1-Alkynes (RC≡CH) react with the dinitrogen complex *trans*-$[ReCl(N_2)(dppe)_2]$ in refluxing thf to afford vinylidene species, *trans*-$[ReCl(C{=}CHR)(dppe)_2]$ (R = Ph, Et, COOEt, etc.) by N_2 loss from the metal centre and a 1,2-hydrogen shift from the terminal to the adjacent unsaturated carbon atom of the alkyne framework (eq. 4) [30].

$$trans\text{-}[ReCl(N_2)(dppe)_2] + RC{\equiv}CH \rightarrow trans\text{-}[ReCl(C{=}CHR)(dppe)_2] + N_2 \qquad (4)$$

The structure of the phenyl vinylidene complex (R = Ph) has been confirmed by an X-ray study (Fig. 2). The Re–C(carbene) bond length (2.046(8) Å) and the distance between the α- and β-carbon atoms of the vinylidene ligand (1.308(16) Å) are consistent with a Re=C and a C=C double bond, respectively.

As in the case of the above-mentioned alkyne to allene rearrangement, no alkyne

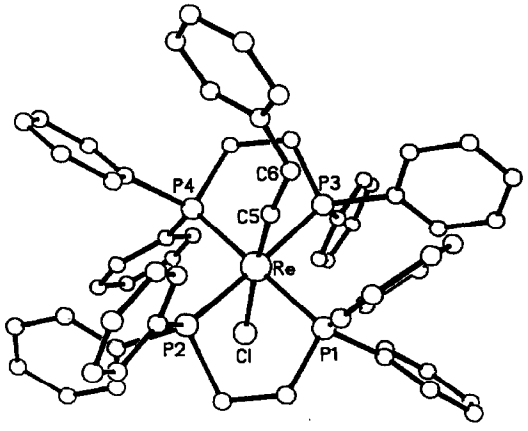


Fig. 2. Molecular structure of the phenyl vinylidene complex *trans*-$[ReCl(C{=}CHPh)(dppe)_2]$ [30]. Selected distances are: Re–C(5) 2.046(8), C(5)–C(6) 1.308(16) Å.

intermediate complex was isolated, and the repulsive d_{π}(metal)–$\pi_{\perp}$(alkyne) interaction is again thought to promote the alkyne to vinylidene conversion, as suggested [29] for related W^0-d^6 complexes.

The formation of vinylidene complexes by 1,2-hydrogen migration at 1-alkynes is known to occur for a variety of activating metal centres, typically of the d^6-ML_5 or cationic T-shaped d^8-ML_3. The mechanism has been investigated [31] by extended Hückel calculations, which suggest that the migration involves a di-hapto to a mono-hapto rearrangement of the alkyne ligand, followed by proton shift from the α to the β carbon. This route has been shown [31] to involve a lower energy than an alternative one that involves the formation of an alkynyl-hydrido intermediate (see the next section).

IV. Hydrogen transfer to the metal

Allene and vinylidene complexes, apparently formed via overall hydrogen-migration reactions within the carbon chain of the alkyne, are not the only observed products of the reactions of alkynes with our rhenium system(s). For example in the reactions of 1-alkynes with *trans*-$[ReCl(N_2)(dppe)_2]$ or the related *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ complex, alkynyl compounds were also observed, e.g., $[Re(C{\equiv}CR)_2(dppe)_2]Cl$ (formed as a minor product in the preparation of the corresponding vinylidene complex), *trans*-$[ReF(C{\equiv}CPh)(dppe)_2]^+$ (formed in the presence of $TlBF_4$) and $[ReCl(C{\equiv}CPh)_2(PMe_2Ph)_3]$ (eq. 5) [32].

$$\textit{trans}\text{-}[ReCl(N_2)(PMe_2Ph)_4] + 2PhC{\equiv}CH \rightarrow [ReCl(C{\equiv}CPh_2)_2(PMe_2Ph)_3] + N_2 + H_2 + PMe_2Ph \quad (5)$$

These reactions involve oxidative additions to the metal of the terminal C–H bond of 1-alkynes and in the case of rhenium centres, commonly give only low yields of products. This type of oxidative addition reaction is typically observed with *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W), which upon reaction with 1-alkynes under irradiation with W-filament light, give, e.g., *cis*-$[WH(C{\equiv}CCO_2Me)(dppe)_2]$, $[MH_2(C{\equiv}CR)_2(dppe)_2]$ (R = Ph, CO_2Me or CO_2Et) (eq. 6), and *trans*-$[M(C{\equiv}CR)_2(dppe)_2]$ [33]. The molecular structures have been authenticated by X-ray studies for $[WH_2(C{\equiv}CCO_2Me)_2(dppe)_2]$ [34] and *trans*-$[Mo(C{\equiv}CPh)_2(dppe)_2]$ [33].

In contrast to the rhenium system, no vinylidene or allene complex was obtained

$$\textit{trans}\text{-}[M(N_2)_2(dppe)_2] + 2RC{\equiv}CH \rightarrow [MH_2(C{\equiv}CR)_2(dppe)_2] + 2N_2 \quad (6)$$

by simple reaction of alkyne with any of the group 6 metal(0) dinitrogen complexes. The easier oxidation of the latter [8,9,13] and the higher tendency to lose N_2, compared with the rhenium(I) species, as well as the absence of a strong π-donor ligand (such as Cl, which is present at Re, and would help to stabilize the metal–carbon multiple bonds) are possible factors favouring the C–H oxidative addition at Mo^0 or W^0 rather than the hydrogen migration within the alkyne C framework with formation of metal–carbon multiple bonds which is the typical type of reaction at the $\{ReCl(dppe)_2\}$ site.

Nevertheless, there is no evidence that any of our alkynyl-hydride complexes can undergo conversion into a vinylidene species, in keeping with the results of the above-mentioned theoretical calculations. Vinyledenes and alkynyl hydrides appear to be formed through distinct pathways at these centres. However, alkynyl hydride species may be intermediates in the formation of vinylidene from alkyne complexes in other systems, for example those involving a neutral d^8 metal centre [35].

V. Protonation of alkyne-derived ligands

The alkyne-derived allene and vinylidene ligands activated by the $\{ReCl(dppe)_2\}$ centre, as well as ligating alkynyl at $\{M(dppe)_2\}$ (M = Mo or W), can undergo attack by protic acid. Hence, e.g., by reaction with HBF_4, *trans*-$[ReCl(\eta^2\text{-}H_2C\text{–}C{=}CHPh)(dppe)_2]$ and *trans*-$[ReCl(C{=}CHPh)(dppe)_2]$ are converted into the corresponding cationic metallacyclopropene [or η^2(3e)-vinyl] complex *trans*-$[ReCl\{{=}C(CH_2PhC)H_2\}(dppe)_2][BF_4]$ (eq. 8) [36] or alkylidyne compound *trans*-$[ReCl(\equiv C\text{–}CH_2Ph)(dppe)_2][BF_4]$ (eq. 9) [37]. In a related reaction $[WF(\equiv C\text{–}CH_2CO_2Me)(dppe)_2]$ is formed by protonation of $[WH_2(C{\equiv}CCO_2Me)_2(dppe)_2]$ (reaction (10) [34].

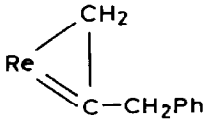
$$trans\text{-}[ReCl(\eta^2\text{-}H_2C\text{–}C{=}CHPh)(dppe)_2] + HBF_4 \rightarrow trans\text{-}[ReCl\{{=}C(CH_2Ph)CH_2\}(dppe)_2][BF_4] \quad (7)$$

$$trans\text{-}[ReCl(C{=}CHPh)(dppe)_2] + HBF_4 \rightarrow trans\text{-}[ReCl(\equiv C\text{–}CH_2Ph)(dppe)_2][BF_4] \quad (8)$$

$$[WH_2(C{\equiv}CCO_2Me)_2(dppe)_2] \xrightarrow{HBF_4} [WF(\equiv C\text{–}CH_2CO_2Me)(dppe)_2] \quad (9)$$

In all these products with metal–carbon multiple bonds, a stabilizing effect results from the presence in the *trans* position of a π-electron donor halide ligand.

The product of reaction 7 appears to represent the first reported metallacyclopropene complex of rhenium, and its structure has been authenticated by X-ray crystallography (Fig. 1b) [36]. The dimensions of the metallacyclopropene ring agree with the formulation



the expected double-bond character of the bond between rhenium and the internal C atom of the ligand being confirmed by the length of this bond (1.947(6) Å). Compared to that for the parent allene complex, there is clearly the expected elongation of the exocyclic C–C distance (from 1.32(1) to 1.500(8) Å) and the twisting of the phenyl group away from the plane of the metallacyclo ring (Fig. 1), in keeping with the sp^2 to sp^3 hybridization change at the exocyclic carbon (in the β position relative to the metal), as the result of proton attack.

The observed protonation of the allene ligand (eq. 7) constitutes a novel route to metallacyclopropene (η^2-vinyl) complexes based on activation of the allene by an

electron rich metal centre, towards the electrophilic attack. This route contrasts with the previously known pathways [38,39] for metallacyclopropene species which involve nucleophilic attack at an alkyne behaving as a 4- or a 3-electron donor to a metal centre in a higher oxidation state and being much less electron-rich than the rhenium(I) site.

The protonation at either the allene, vinylidene, or alkynyl ligands in our complexes (eqs. 7–9) occurs at the β-position (relative to the metal), as was observed [12,18–22] for the reactions of ligating isocyanides (Scheme 1 and eqs. 1 and 2) to give aminocarbyne complexes. Electrophilic β-additions to vinylidene [40] or to alkynyl [41] species have been described by other authors for various systems, but since this type of reaction had not been previously demonstrated for an allene it was further investigated by extended Hückel calculations [36], the results of which were in agreement with the observed site of protonation. These studies indicate that the HOMO, although formally metal *d*-centered (54%), is delocalised over the carbon framework of the allene group and has a substantial (36%) contribution from the p_y orbital of the allene carbon in the β-position (relative to the metal). The proton prefers to attack this C atom, with a highly directional *p* orbital, rather than the coordinatively saturated metal with a rather diffuse electronic density [36]; protonation is frontier-orbital rather than charge controlled, as was observed for nucleophilic attack at various Fischer-type carbene [42] and carbyne [43] ligands.

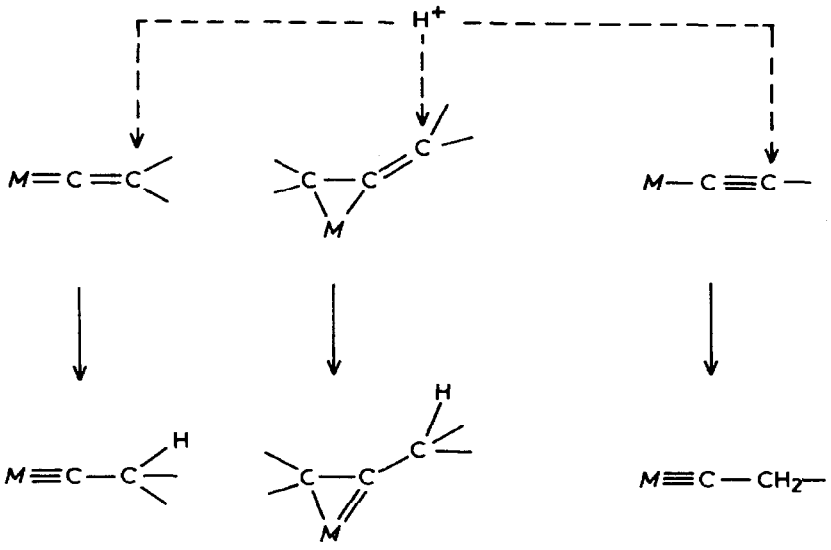
Only a few metallacyclopropene (η^2-vinyl) compounds are known, and they have not been fully studied, but they are conceivably intermediates in insertion reactions of alkynes and in their metal-centred oligomerisation and cyclisation with species such as CO or CNR [39]; the η^2-vinyl ligands may exhibit fluxional behaviour in solution [44], and may rearrange to carbyne, carbene, allene and η^3-allylic complexes [38]. It has also been suggested [36] that metallacyclopropene compounds may be intermediates in the enzymatic reduction [5] of allenes to propenes.

VI. Concluding remarks

Electron-rich metal centres of heavier transition metals of the central groups of the periodic table in low oxidation states, (e.g., d^6 Mo^0, W^0 or Re^I), induce hydrogen migration reactions at terminal alkynes or at phenylpropyne to yield products that are activated towards β-protonation. The nature of the species derived from the alkynes is determined by a combination of different factors, such as the electron-richness of the metal site and the π-donor character and lability of its ligands.

In keeping with the extensive π-electron releasing ability of the $\{ReCl(dppe)_2\}$ site and with the high tendency of the metal to form multiple bonds to carbon, vinylidene and allene species are formed by a 1,2- or 1,3-hydrogen shift along the carbon framework of the alkyne, whereas hydrido-alkynyl complexes are formed by oxidative addition of C–H bonds of a terminal alkyne to the $\{M(dppe)_2\}$ centres (M = Mo or W), which are more readily oxidizable than the Re^I site and do not bear a π-donor halide ligand.

In all cases, the alkyne-derived vinylidene, allene, or alkynyl ligands are activated towards β-electrophilic attack (Scheme 2) to afford alkylidyne or metallacyclopropene species, which are stabilized by the high π-electron releasing character of the metal centre, promoted by a halide in a position *trans* to the multiple bonded organic ligand. This type of activation represents a novel process for η^2-vinyl



Scheme 2. Activation of alkyne-derived vinylidene, allene and alkynyl ligands towards protonation at the β position.

ligands. Further studies are needed to test the generality of these observations and to investigate the reactions of the alkyne-derived species, the mechanisms involved, and their synthetic applications.

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