A Novel Route to Metallacyclopropene (η²-Vinyl) Complexes from Alkynes: Synthesis and X-Ray Crystal Structure of *trans*-[ReCl{=C(CH₂Ph)CH₂}(Ph₂PCH₂CH₂PPh₂)₂][BF₄]

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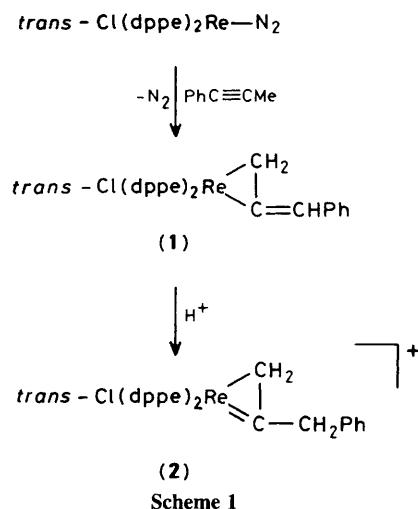[d] *Department of Chemistry and Materials Science Centre, Cornell University, Ithaca, N.Y. 14853, U.S.A.*

Treatment of the allene complex *trans*-[ReCl(H₂C–C=CHPh)(dppe)₂] (dppe = Ph₂PCH₂CH₂PPh₂) with acids, HA (A = BF₄ or PF₆), in CH₂Cl₂ or tetrahydrofuran gives the metallacyclopropene (η²-vinyl) complex *trans*-[ReCl{=C(CH₂Ph)CH₂}(dppe)₂][A] whose structure (A = BF₄) has been authenticated by X-ray crystallography; the site of protonation is in agreement with extended Hückel calculations which show, in the HOMO, a high electronic density on the allene carbon atom which is not directly bonded to the metal.

There is increasing interest in the synthesis and reactions of compounds with metal–carbon multiple bonds, particularly when derived from alk-1-yne complexes whose conversion into vinylidene complexes is well documented.[1] Metallacyclopropene (η²-vinyl) compounds, M=C(R)–C<, although few are known to date, are also products of metal-promoted reactions of alkynes, through intra- or inter-molecular nucleophilic attack at a ligating alkyne.[2,3] These compounds are possible reaction intermediates in insertion, oligomerisation, and co-cyclisation reactions of alkynes.[2] The possibility of their rearrangement into carbyne-type species has also been demonstrated.[3]

During our studies of the activation of nitrogenase substrates at electron-rich dinitrogen-binding metal centres, we have observed a novel route for the conversion of an alkyne into a metallacyclopropene (η²-vinyl) species by electrophilic attack on an alkyne-derived allene ligand.

We have already reported[4] the metal-promoted 1,3-hydrogen migration of PhC≡CMe in its reaction with *trans*-[ReCl(N₂)(dppe)₂] (dppe = Ph₂PCH₂CH₂PPh₂) to give the allene complex *trans*-[ReCl(H₂C–C=CHPh)(dppe)₂] (1), Scheme 1. A related rearrangement has been reported[5] for some areneacetylene complexes of chromium.

trans - Cl(dppe)₂Re—N₂

−N₂ | PhC≡CMe

trans - Cl(dppe)₂Re⟨CH₂ | C=CHPh

(1)

H⁺

trans - Cl(dppe)₂Re⟨CH₂ | C—CH₂Ph ⟩⁺

(2)

Scheme 1

We now report that the allene ligand of (**1**), activated by the electron-rich {ReCl(dppe)₂} centre, undergoes electrophilic attack by acids (HA) (A = BF₄ or PF₆) in CH₂Cl₂ or tetrahydrofuran (thf), at 20 °C, to afford the first metalla-cyclopropene (η²-vinyl) complex of rhenium, *trans*-[ReCl{=C(CH₂Ph)ĊH₂}(dppe)₂][A] (**2**, A = BF₄ or PF₆) as pink, diamagnetic crystals in high yield. In the ¹³C{¹H} n.m.r. spectrum (CD₂Cl₂, 298 K), the carbene carbon [Re=C(12) of Figure 1] resonance is observed at δ 258.2.

The molecular structure of (**2**, A = BF₄) has been authenticated by *X*-ray crystallography and the complex cation is shown in Figure 1.†

The conformation of the rhenium complex cation (**2**) is very similar to that of the rhenium–allene complex (**1**),⁴ but the dimensions of the ReC₂ ring system show a contrasting pattern of bonding. The Re–C(12) distance in (**2**) [1.947(6)Å] is much shorter than Re–C(11) [2.193(6) Å] and the corresponding distance in (**1**) [2.087(6) Å], and is indicative of an Re=C(12) double bond. The C–C bond lengths in the ligand and the location and satisfactory refinement of the hydrogen atoms on both the benzylic, C(13), and terminal, C(11), carbon atoms confirm the co-ordination bonding arrangements shown in Scheme 1.

The electronic factors driving the protonation of the allene complex were investigated by means of extended Hückel
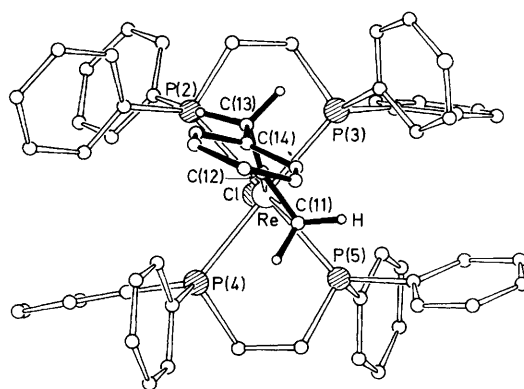
Figure 1. View of the Re-complex cation of (**2**), *trans*-[ReCl{=C(CH₂Ph)ĊH₂}(dppe)₂]⁺, in the same projection as that shown for (**1**) in ref. 4. Selected dimensions (with e.s.d.s in parentheses): Re–C(11) 2.193(6), Re–C(12) 1.947(6), Re–P(2) 2.487(2), Re–P(3) 2.457(2), Re–P(4) 2.490(2), Re–P(5) 2.509(2), Re–Cl 2.440(2), C(11)–C(12) 1.412(9), C(12)–C(13) 1.500(8), C(13)–C(14) 1.511(9) Å; P(2)–Re–P(5) 164.5(1), P(3)–Re–P(4) 175.3(1), C(11)–C(12)–C(13) 130.0(6), C(12)–C(13)–C(14) 118.0(5)°.
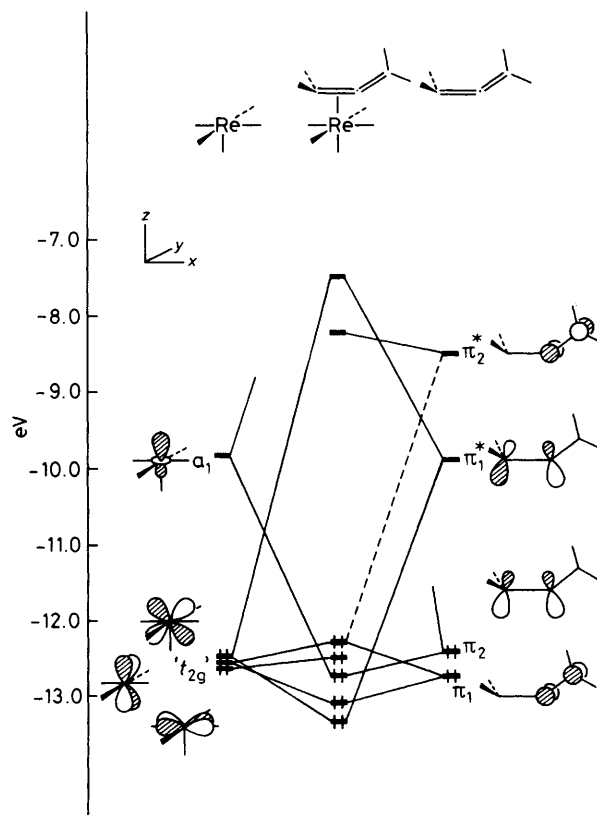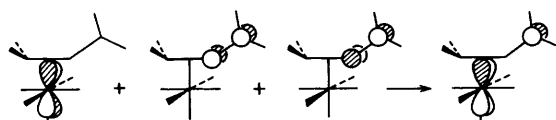

Figure 2. A molecular orbital diagram for a model of the allene complex *trans*-[ReCl(H₂C–C=CHPh)(dppe)₂].

calculations.⁸ Figure 2 is the molecular orbital diagram of the system before protonation. The interactions are typical of those for an alkene binding to a transition metal fragment.⁹

The point of interest is the composition of the HOMO. Although formally metal d-centered (d_{yz}), this orbital turns out to be delocalised over the carbon framework of the allene unit with a substantial contribution (36%) from the p_y orbital of C_γ. The rest of the HOMO is made up of Re-d_{xy}/d_{yz} (54%) and C_β-p_y (10%). The high density on C_γ can be explained using standard perturbation theoretical arguments: d_{yz} (along

Scheme 2

with d_{xy}) mixes with π_1 to produce the HOMO, which is antibonding between Re and C_β. A crucial feature of this orbital is the subsequent mixing of π_2^* with it, which reduces the Re–C_β antibonding character (dashed line in Figure 2). This requirement diminishes the contribution from C_β and reinforces that from C_γ as summarised in Scheme 2.

On the basis of simple frontier orbital concepts, a proton approaching the allene complex will protonate either the metal atom, which is co-ordinatively saturated, with rather diffuse electronic density, or the γ carbon atom with a highly directional and electron rich p orbital. The carbon atom is protonated. The protonation is predicted to be easier if d_{yz} is high in energy; that is, with a strong π-donor *trans* to the allene, as in the complex discussed here.

Calculations on (**1**) predict a shorter bond between Re and C_β than between Re and C_α, in agreement with the structure. The overlap populations (computed with identical distances) are 0.373 and 0.286 electrons for Re–C_β and Re–C_α respectively. From Figure 2 it can be seen that the partial double bond character of the Re–C_β bond is a consequence of the second order mixing shown in Scheme 2; there is more Re–C_β bonding character in the second M.O. (in-phase mixture of d_{yz} and π_1) than there is antibonding character between these atoms in the HOMO.

The two main steps in the conversion of an alkyne into an η^2-vinyl ligand (alkyne isomerisation to a ligating allene[4] and its subsequent protonation) are induced by the relatively high electron-rich character and the π-electron releasing nature of the $\{ReCl(dppe)_2\}$ centre, and the tendency of rhenium to form multiple bonds to carbon.

Electrophilic attack at the β-carbon (relative to Re) of the allene ligand converts it from a two- into a three-electron donor, as also has been observed for ligating isocyanides[10,11] and alkyne-derived vinylidene ligands[1] at related metal centres, to give carbyne-type complexes.

Both alkynes and allenes are known substrates of nitrogenase[12] and although the mechanisms of their reductions (to alkenes, *etc.*) have not been ascertained, η^2-vinyl compounds of the type described in this work are conceivable intermediates in these reductions.

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