# Reactions of 1-Alkynes with *trans*-[ReCl($N_2$)($Ph_2PCH_2CH_2PPh_2$)$_2$]: Preparation of the Vinylidene Compounds *trans*-[ReCl(=C=CHR)($Ph_2PCH_2CH_2PPh_2$)$_2$] (R = Alkyl or Aryl) and *X*-Ray Structure of *trans*-[ReCl(=C=CHPh)-($Ph_2PCH_2CH_2PPh_2$)$_2$]†

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The vinylidene complexes *trans*-[ReCl(=C=CHR)(dppe)$_2$] (**1**; R = Ph, Et, Bu$^t$, SiMe$_3$, CO$_2$Me, CO$_2$Et, or C$_6$H$_{10}$OH-1; dppe = $Ph_2PCH_2CH_2PPh_2$) have been prepared by reaction of *trans*-[ReCl($N_2$)(dppe)$_2$] with an excess of the appropriate 1-alkyne (HC≡CR), in refluxing tetrahydrofuran (thf) or under tungsten-filament light (in thf or toluene). The *X*-ray structural analysis of (**1**; R = Ph) has been performed.

Although well defined carbene complexes of rhenium are increasing in number,[1] they are still very few compared to those known for the related Group 6 (Mo or W) metals. Moreover, the former generally contain metal sites with a relatively electron-poor character, either with a high formal metal oxidation state as, *e.g.*, in [Re(≡CBu$^t$)(=CHBu$^t$)(C$_5$H$_5$N)$_2$I$_2$],[2] or involving carbonyl and/or cyclopentadienyl ligands, *e.g.* in [Re(η-C$_5$H$_5$)(=C=CHPh)(CO)$_2$][3] or [ReCl{C(OH)Me}(CO)-($N_2$)(PPh$_3$)$_2$].[4]

During our studies on the co-ordination chemistry of unsaturated carbon species at $N_2$-binding sites we have succeeded in preparing rhenium (and related molybdenum or tungsten) complexes with metal–carbon multiple bonds involving the electron-rich M(dppe)$_2$ (M = Mo, W, or Re; dppe = Ph$_2$-PCH$_2$CH$_2$PPh$_2$) metal centres.

In earlier work, we have prepared series of isocyanide or nitrile complexes of the types *trans*-[ReCl(L)(dppe)$_2$] (L = CNR[5] or NCR[6]) or *trans*-[M(CNR)$_2$(dppe)$_2$] (M = Mo or W)[7] and shown these ligands to be activated towards β-electrophilic attack (*e.g.* by H$^+$).[6,8–10]

The study of the behaviour of alkynes at these metal centres was also initiated and although for the Group 6 metal sites the main reaction detected[11] was oxidative addition of C–H from a terminal alkyne (RC≡CH) to form alkynyl-hydride and alkynyl compounds, at the ReCl(dppe)$_2$ site the alkynes undergo isomerisation reactions involving hydrogen migrations. Thus, a metal-centred 1,3-hydrogen shift at phenylpropyne (PhC≡CMe) occurs upon reaction of this alkyne with *trans*-[ReCl($N_2$)(dppe)$_2$] to give the allene complex *trans*-[ReCl(η$^2$-H$_2$C–C=CHPh)(dppe)$_2$][12] which undergoes β protonation to form a metallacyclopropene (η$^2$-vinyl) derivative, *trans*-[ReCl{=C(CH$_2$Ph)CH$_2$}(dppe)$_2$]$^+$.[13] Moreover, 1-alkynes are also activated by the rhenium(I) centre to afford the vinylidene complexes *trans*-[ReCl(=C=CHR)(dppe)$_2$]; a preliminary account of this study has appeared[14] and herein we describe it in detail.

## Results and Discussion

*Vinylidene Complexes.*—Treatment of the dinitrogen complex *trans*-[ReCl($N_2$)(dppe)$_2$] with an excess of the appropriate 1-alkyne HC≡CR in refluxing tetrahydrofuran (thf) or at ambient temperature (in thf or toluene) but under tungsten-filament light, under argon, gives the corresponding vinylidene complex *trans*-[ReCl(=C=CHR)(dppe)$_2$] (**1**; R = Ph, Et, Bu$^t$, SiMe$_3$, CO$_2$Me, CO$_2$Et, or C$_6$H$_{10}$OH-1) [equation (1)].

$$\textit{trans}\text{-[ReCl(N}_2\text{)(dppe)}_2] + \text{HC≡CR} \longrightarrow \textit{trans}\text{-[ReCl(=C=CHR)(dppe)}_2] + \text{N}_2 \quad (1)$$

As might be expected in view of its π-electron acceptor character, the vinylidene ligand is *trans* to the strongest net electron-donor co-ligand, Cl (see below). This type of stabilizing effect has also been recognized in related systems with metal–carbon multiple-bonded ligands, such as the allene complex *trans*-[ReCl(η$^2$-H$_2$C–C=CHPh)(dppe)$_2$],[12] its derived metallacyclopropene compound (formed by protonation)[13] and the aminocarbynes *trans*-[ReCl(CNHR)(dppe)$_2$]$^+$.[8,9]

In their i.r. spectra (Table 1) complexes (**1**) have strong bands in the *ca.* 1 660—1 530 cm$^{-1}$ range which are assigned to ν(C=C) of the vinylidene ligand or to ν(CO) in the methyl or ethyl propiolate derivatives (R = CO$_2$Me or CO$_2$Et). For the latter complexes, two strong bands are observed in the 1 660—1 615 cm$^{-1}$ range, possibly resulting from coupled ν(C=O) and ν(C=C) vibrations; other characteristic (ester–CO) bands appear at 1 270 and 1 225 cm$^{-1}$ (R = CO$_2$Me) or at 1 270 and 1 210 cm$^{-1}$ (R = CO$_2$Et). Corresponding i.r. stretching bands have also been reported for related vinylidene complexes, such as [Ru(η-C$_5$H$_5$)(=C=CHCO$_2$Me)(PPh$_3$)$_2$]$^+$ [at 1 727, 1 263, and 1 241 cm$^{-1}$ assigned to ν(C=O), and at 1 650 cm$^{-1}$ due to ν(C=C)].[15]

For complex (**1**; R = SiMe$_3$ or C$_6$H$_{10}$OH-1) two ν(C=C) bands are also detected, in the 1 575—1 545 cm$^{-1}$ range, possibly arising from two isomers (see below).

The $^{31}$P-{$^1$H} n.m.r. spectra of complexes (**1**) (Table 2) show singlets in the δ *ca.* 108—131 p.p.m. range, upfield from

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† *trans*-Bis[1,2-bis(diphenylphosphino)ethane]chloro(phenylvinylidene)rhenium.

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

**Table 1.** Physical data for vinylidene complexes *trans*-[ReCl(=C=CHR)(dppe)$_2$] (**1**)

| R | Colour | I.r. (cm$^{-1}$)$^a$ ν(C=C) or ν(C=O) | Analysis$^b$ (%) | |
|---|---|---|---|---|
| | | | C | H |
| Ph | Red | 1 532s | 64.9 (64.4)$^c$ | 5.4 (5.2)$^c$ |
| Et | Brown | 1 595s | 63.3 (63.0)$^c$ | 5.8 (5.5)$^c$ |
| $Bu^t$ | Red | 1 585m | 63.2 (63.3) | 5.7 (5.3) |
| $SiMe_3$ | Green | 1 570s<br>1 545s | 62.8 (63.1)$^d$ | 6.1 (6.5)$^d$ |
| $CO_2Me^e$ | Dark red | 1 645s<br>1 660 (sh) | 60.7 (61.0) | 5.1 (4.8) |
| $CO_2Et^f$ | Brownish red | 1 635s<br>1 615s | 61.2 (61.3) | 4.9 (4.9) |
| $C_6H_{10}OH$-1 | Dark brown | 1 575s<br>1 550s | 62.7 (63.0) | 5.6 (5.3) |

[a] In Nujol mull. [b] Required values in parentheses. [c] With thf of crystallisation. [d] With 2thf and pentane of crystallisation. [e] Other characteristic ν(ester-CO) bands are observed at 1 270ms and 1 225wm cm$^{-1}$. [f] Other characteristic ν(ester-CO) bands are observed at 1 270ms and 1 210w cm$^{-1}$.

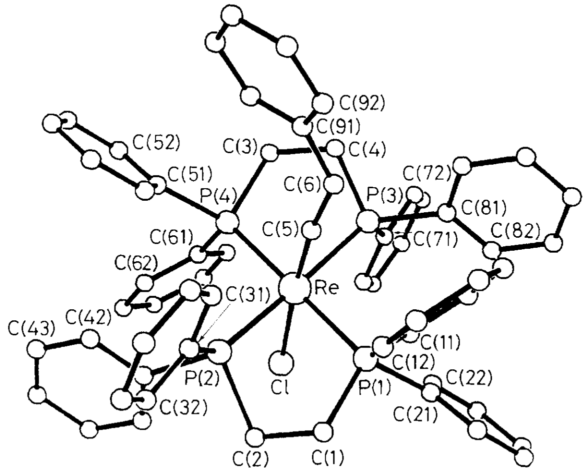

**Figure.** The molecular structure of *trans*-[ReCl(=C=CHPh)(dppe)$_2$] (**1**, R=Ph)

P(OMe)$_3$, in agreement with a *trans* geometry for the dppe ligands.

In the $^1$H n.m.r. spectra of complexes (**1**) (Table 2) a complex resonance occurs at considerable high field (δ *ca.* −0.8 to 1.6 relative to SiMe$_4$, the lower-field limit corresponding to the vinylidene species with the electron-withdrawing ester groups). It is assigned to the β-proton of the vinylidene ligand, C=CHR. For (**1**; R = Ph, $Bu^t$, CO$_2$Et, or C$_6$H$_{10}$OH-1) its structure is resolved into a quintet due to coupling to the four equivalent phosphorus nuclei[$^4J$(HP) = 3.7—5.4 Hz].

The other expected $^1$H resonances for each of the ligating vinylidene groups are also observed. Hence, *e.g.* for C=CH*Ph*, the *ortho*-phenyl proton resonance occurs as a doublet [$^3J$-(HH) = 6.4 Hz] at δ 5.83, whereas a multiplet at δ 6.68—6.37 is assigned to the *meta* and the *para* protons. For C=CH*Et*, the methylene proton resonance occurs as a quintet (7.3 Hz) at δ 1.66, as a result of a partial overlap of two quartets, due to coupling to both the methyl and the C=C*H*Et protons; the methyl proton resonance is a triplet (7.3 Hz) at δ 0.42 and its coupling with the methylene protons has been established by decoupling experiments. The characteristic quartet:triplet (7.2 Hz) pattern is observed for C=CHCO$_2$*Et* at δ 3.65 and 0.96, whereas the expected singlets for C=CHCO$_2$*Me* and C=CH*Bu*$^t$ occur at δ 3.08 and 0.55, respectively. However, for complex (**1**; R = SiMe$_3$), in C$_6$D$_6$, the singlets observed at δ 1.39 and 1.06 (integrating for 3 and 6 protons, respectively) are assigned to two *trans* isomers, possibly corresponding to two orientations of the vinylidene plane relative to the P atoms, in agreement with the occurrence of two singlets in the $^{31}$P-{$^1$H} n.m.r. spectrum [at δ 111.0 and 115.0 p.p.m. upfield from P(OMe)$_3$, the former with double the intensity of the latter].

For complex (**1**; R = C$_6$H$_{10}$OH-1) the $^1$H n.m.r. resonances of the cyclohexanol group are not resolved but, since the resonance of the proton in β position clearly occurs as the expected (broad) quintet, the intramolecular addition of the hydroxyl group to the α-carbon of the vinylidene ligand [known to occur[16] in some reactions of other hydroxyalkynes, HC≡C(CH$_2$)$_n$OH ($n$ = 2 or 3), with metal sites, to give cyclic alkoxycarbene complexes] does not appear to occur in our system. Although only one singlet resonance [at 109.5 p.p.m. upfield from P(OMe)$_3$] is observed in the $^{31}$P-{$^1$H} n.m.r. spectrum, the detection of two strong i.r. ν(C=C) bands (1 575 and 1 550 cm$^{-1}$) suggests the occurrence of two isomers, possibly corresponding to two distinct orientations of the cyclohexanol group.

In the $^{13}$C-{$^1$H} n.m.r. spectra (Table 2), although low solubility and decomposition in common solvents has hindered the detection of the expected[15,17] low-field carbene–carbon resonance, it was observed for ligating *C*=CHCO$_2$Et and *C*=CHBu$^t$ as unresolved multiplets centred at δ 284.7 and 296.9 p.p.m. downfield from SiMe$_4$ (in CD$_2$Cl$_2$), respectively. The assignment of the β-carbon resonance, C=*C*HR, was based on its conversion into the expected[18] doublet in the $^1$H-undecoupled spectrum. Hence, *e.g.* for the C=CHCO$_2$Et ligand, the β-carbon resonance, C=*C*HCO$_2$Et, is a singlet at δ 98.64 p.p.m. which, in the fully proton-coupled spectrum, splits to a doublet [$J$(CH) = 157 Hz], whereas the γ-carbon (carbonyl group), C=CH*C*O$_2$Et, resonates at δ 167.2 p.p.m. and remains a singlet in the undecoupled spectrum; all these $^{13}$C resonances underwent a downfield shift relative to those of free ethyl propiolate whose $^{13}$C n.m.r. spectrum exhibits resonances at δ 75.66, 75.17, and 153.03 p.p.m. for the 1-, 2-, and 3-C atoms (H*C*≡CCO$_2$Et, HC≡*C*CO$_2$Et, and HC≡C-*C*O$_2$Et), respectively.

In the $^{13}$C-{$^1$H} n.m.r. spectrum of complex (**1**; R = CO$_2$Me) the C=CHCO$_2$Me ligand displays β- and γ-carbon resonance patterns which are identical to those of the analogous C=CHCO$_2$Et ligand (Table 2).

The molecular structure of the phenylvinylidene complex (**1**; R = Ph) (thf solvate) has been confirmed by an *X*-ray diffraction analysis and is depicted in the Figure; selected bond lengths and angles are listed in Table 3 and atomic co-ordinates in Table 4. The phenylvinylidene ligand is planar and lies in the plane defined by the metal, the choride ligand, and two of the phosphorus atoms [P(1) and P(4)]. A slight bending at the carbene-carbon is observed, as occurs in other cases.[15,17,18]

As expected, the Re–C(carbene) distance [2.046(8) Å] is shorter than the Re–C single bond length (2.297 Å).[19] Nevertheless, it is slightly longer than those quoted for $[(\eta\text{-}C_5H_5)(OC)_2Re\{C{=}C(Ph)C(Ph){=}CH_2\}Re(CO)_2(\eta\text{-}C_5H_5)]$ [1.90(2) Å][3] (where π-density delocalisation may occur along the Re=C and the butadiene group) and the $\eta^2$-vinyl (cyclic carbene) complex *trans*-$[ReCl\{{=}C(CH_2Ph)CH_2\}(dppe)_2][BF_4]$ [1.947(6) Å][13] (with Re in a higher oxidation state). However, it is considerably longer than those observed for the Re–C(carbyne) bond in *trans*-$[ReCl(CNHR')(dppe)_2][BF_4]$ [1.80(3) or 1.802(4) Å, for R′ = Me[8] or H[9], respectively]. The bond length between the α-and the β-carbon atoms [C(5)–C(6)] of the ligating vinylidene [1.31(2) Å] is in agreement with a C=C double bond, being close to those known[15,17,20] for other vinylidene complexes. The angle at the β-carbon [125.5(15)°] is as expected for $sp^2$ hybridisation at this atom.

Complexes (**1**) are susceptible to protonation which occurs at the β-carbon of the vinylidene ligand to give carbyne complexes, such as *trans*-$[ReCl({\equiv}CCH_2R)(dppe)_2][BF_4]$ (R = Ph or $Bu^t$) derived from treatment of the corresponding vinylidene compounds by $[Et_2OH][BF_4]$.[21] These reactions will be published in detail separately, and parallel the activation

**Table 2.** Proton, $^{31}P\text{-}\{^1H\}$, and $^{13}C\text{-}\{^1H\}$ n.m.r. data for the vinylidene complexes *trans*-$[ReCl({=}C{=}CHR)(dppe)_2]$ (**1**)

| | $^1H$ N.m.r.[a,b] | | | $^{31}P\text{-}\{^1H\}$ N.m.r.[a,c] | $^{13}C\text{-}\{^1H\}$ N.m.r.[a,b] | |
|---|---|---|---|---|---|---|
| R | δ | Integration | Assignment | δ | δ | Assignment |
| Ph | 7.8—6.8 (m) | 40 | Ph(dppe) | 109.8 (s) | 135.1—120.2 (m) | Ph(dppe + vinylidene) |
| | 6.68—6.37 (m) | 3 | *meta* + *para* phenyl protons (vinylidene) | | 68.50 (s) | $CH_2$(thf)[e] |
| | 5.83 (d)[d] | 2 | *ortho* phenyl protons (vinylidene) | | 26.68 (s, br) | $CH_2$(dppe) |
| | 3.73 (m) | 4 | $CH_2$(thf)[e] | | 26.36 (s) | $CH_2$(thf)[e] |
| | 3.1—2.3 (m, br) | 8 | $CH_2$(dppe) | | | |
| | 1.87 (m) | 4 | $CH_2$(thf)[e] | | | |
| | 0.93 (qnt)[f] | 1 | C=C*H*Ph | | | |
| Et | 7.3—7.0 (m) | 40 | Ph(dppe) | 109.6(s) | | |
| | 3.68 (m) | 4 | $CH_2$(thf)[g] | | | |
| | 2.70 (m, br) | 4 | $CH_2$(dppe) | | | |
| | 2.56 (m, br) | 4 | | | | |
| | 1.82 (m) | 4 | $CH_2$(thf)[g] | | | |
| | 1.66 (qnt)[h] | 2 | $C{=}CHC\mathit{H}_2CH_3$ | | | |
| | 0.42 (t)[i] | 3 | $C{=}CHCH_2C\mathit{H}_3$ | | | |
| | 0.01 (m)[j] | 1 | $C{=}C\mathit{H}CH_2CH_3$ | | | |
| $Bu^t$ | 7.8—6.9 (m) | 40 | Ph(dppe) | 107.9 (s) | 296.9 (m) | *C*=$CHBu^t$ |
| | 3.68 (m) | 2 | $CH_2$(thf)[g] | | 135.2—127.2 (m) | Ph(dppe) |
| | 3.0—2.3 (m) | 8 | $CH_2$(dppe) | | 34.39 (s)[l] | $C{=}CH\mathit{Bu}^t$ |
| | 1.81 (m) | 2 | $CH_2$(thf)[g] | | 32.17 (qnt)[m] | $CH_2$(dppe) |
| | 0.55 (s) | 9 | $C{=}CH\mathit{Bu}^t$ | | 26.1 (s)[n] | $C{=}\mathit{C}HBu^t$ |
| | −0.81 (qnt)[k] | 1 | $C{=}C\mathit{H}Bu^t$ | | | |
| $SiMe_3$[o] | 7.8—6.8 (m) | 40 | Ph(dppe) | 111.0 (s)[p] | | |
| | 3.62 (m) | 8 | $CH_2$(thf)[f] | 115.0 (s) | | |
| | 3.1—2.3 (m, br) | 8 | $CH_2$(dppe) | | | |
| | 1.6—1.3 (m) | 14 | $CH_2$(thf)[q] + $CH_2$(pentane)[r] | | | |
| | 1.39 (s) | 3 | $\frac{1}{3}$ $C{=}CHSi\mathit{Me}_3$ | | | |
| | 1.1—0.9 (m) | 6 | $CH_3$(pentane)[r] | | | |
| | 1.06 (s) | 6 | $\frac{2}{3}$ $C{=}CHSi\mathit{Me}_3$ | | | |
| $CO_2Me$ | 7.6—6.8 (m) | 40 | Ph(dppe) | 109.2 (s) | 167.8 (s) | $C{=}CH\mathit{C}O_2Me$ |
| | 3.70 (m) | 4 | $CH_2$(thf)[e] | | 136.3—127.7 (m) | Ph(dppe) |
| | 3.08 (s) | 3 | $C{=}CHCO_2\mathit{Me}$ | | 98.35 (s) | $C{=}\mathit{C}HCO_2Me$ |
| | 2.9—2.4 (m, br) | 8 | $CH_2$(dppe) | | 68.51 (s) | $CH_2$(thf)[e] |
| | 1.83 (m) | 4 | $CH_2$(thf)[e] | | 49.39 (s) | $C{=}CHCO_2\mathit{Me}$ |
| | 1.6 (m, br) | 1 | $C{=}C\mathit{H}CO_2Me$ | | 32.81 (qnt)[s] | $CH_2$(dppe) |
| | | | | | 26.37 (s) | $CH_2$(thf)[e] |
| $CO_2Et$ | 7.7—6.9 (m) | 40 | Ph(dppe) | 131.1 (s) | 284.7 (m) | $\mathit{C}{=}CHCO_2Et$ |
| | 3.70 (m) | 2 | $CH_2$(thf)[g] | | 167.20 (s) | $C{=}CH\mathit{C}O_2Et$ |
| | 3.65 (q)[t] | 2 | $C{=}CHCO_2C\mathit{H}_2CH_3$ | | 136.0—127.5 (m) | Ph(dppe) |
| | 2.7 (t, br)[u] | 8 | $CH_2$(dppe) | | 98.64 (s)[v] | $C{=}\mathit{C}HCO_2Et$ |
| | 1.5 (qnt, br)[w] | 1 | $C{=}C\mathit{H}CO_2Et$ | | 68.24 (s)[x] | $CH_2$(thf) |
| | 1.81 (m) | 2 | $CH_2$(thf)[g] | | 57.52 (s)[y] | $C{=}CHCO_2\mathit{C}H_2CH_3$ |
| | 0.96 (t)[t] | 3 | $C{=}CHCO_2CH_2C\mathit{H}_3$ | | 32.70 (qnt)[z] | $CH_2$(dppe) |
| | | | | | 26.09 (s)* | $CH_2$(thf) |
| | | | | | 15.54 (s)† | $C{=}CHCO_2CH_2\mathit{C}H_3$ |

**Table 2** (*continued*)

| | $^1$H N.m.r.$^{a,b}$ | | | $^{31}$P-{$^1$H} N.m.r.$^{a,c}$ | $^{13}$C-{$^1$H} N.m.r.$^{a,b}$ | |
|---|---|---|---|---|---|---|
| R | δ | Integration | Assignment | δ | δ | Assignment |
| $C_6H_{10}$-OH-1 | 7.8—6.8 (m) | 40 | Ph(dppe) | 109.5 (s) | | |
| | 3.68 (m) | 4 | $CH_2$(thf)$^e$ | | | |
| | 3.0—2.5 (m) | 8 | $CH_2$(dppe) | | | |
| | 2.5—0.8 (m, br) | 9 (11) | $C_6H_{10}OH$ | | | |
| | 1.82 (m) | 4 | $CH_2$(thf)$^e$ | | | |
| | 0.17 (qnt)‡ | 1 | $C{=}CHC_6H_{10}OH$ | | | |

[a] In $CD_2Cl_2$, unless stated otherwise; s = singlet, d = doublet, t = triplet, q = quartet, qnt = quintet, m = complex multiplet, and br = broad. [b] δ values in p.p.m. relative to internal $SiMe_4$. [c] δ values in p.p.m. upfield from external $P(OMe)_3$. [d] $^3J$(HH) = 6.4 Hz. [e] thf of crystallisation. [f] $^4J$(PH) = 4.9 Hz. [g] 0.5 thf of crystallisation. [h] Quintet as a result of a doublet of quartets, $^3J$(HH) = 7.3 Hz. [i] $^3J$(HH) = 7.3 Hz. [j] Broad septet (*J ca.* 6.5 Hz) resulting from a partial overlap of a triplet [$^3J$(HH) coupling] of quintets [$^4J$(PH)]. [k] $^4J$(PH) = 5.4 Hz. [l] Converts into a quartet [$J$(CH) = 130.7 Hz] in the $^1$H-undecoupled spectrum. [m] Quintet (11.0 Hz) due to virtual coupling to the P nuclei; converts into a broad triplet [$J$(CH) *ca.* 130 Hz] in the $^1$H-undecoupled spectrum. [n] Converts into a doublet [$J$(CH) = 136.4 Hz] in the $^1$H-undecoupled spectrum. [o] In $C_6D_6$; two isomers; $C{=}CHSiMe_3$ resonance was not detected, possibly being buried under those due to thf or pentane of crystallisation. [p] Double intensity of the resonance at δ 115 p.p.m. [q] 2thf of crystallisation. [r] Pentane of crystallisation. [s] Quintet (11.0 Hz) due to virtual coupling to the P nuclei. [t] $^2J$(HH) = 7.2 Hz. [u] Triplet ($J$ = 13 Hz) due to virtual coupling to the $P$ nuclei. [v] Converts into a doublet [$J$(CH) = 156.5 Hz] in the $^1$H-undecoupled spectrum. [w] More clearly observed at −20 °C; $^4J$(PH) = 3.8 Hz. [x] Converts into a triplet [$J$(CH) = 154.4 Hz] in the $^1$H-undecoupled spectrum. [y] Converts into a triplet [$J$(CH) = 145.3 Hz] in the $^1$H-undecoupled spectrum. [z] Quintet (10.8 Hz) due to virtual coupling to the P nuclei; converts into a broad triplet [$J$(CH) = 133.9 Hz] in the $^1$H-undecoupled spectrum. * Converts into a triplet [$J$(CH) = 130.0 Hz] in the $^1$H-undecoupled spectrum. † Converts into a quartet [$J$(CH) = 125.1 Hz] in the $^1$H-undecoupled spectrum. ‡ $^4J$(PH) = 4.5 Hz.

**Table 3.** Selected internuclear distances (Å) and angles (°) for *trans*-[ReCl(=C=CHPh)(dppe)$_2$] (**1**; R=Ph) with estimated standard deviations (e.s.d.s) in parentheses

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Re–P(1) | 2.389(8) | Re–P(2) | 2.402(9) | Re–P(3) | 2.440(8) | Re–P(4) | 2.441(9) |
| Re–Cl | 2.454(3) | Re–C(5) | 2.046(8) | P(1)–C(11) | 1.884(9) | P(1)–C(21) | 1.791(12) |
| P(1)–C(1) | 1.85(2) | P(2)–C(31) | 1.922(8) | P(2)–C(41) | 1.863(12) | P(2)–C(2) | 1.84(2) |
| P(3)–C(71) | 1.760(9) | P(3)–C(81) | 1.875(11) | P(3)–C(4) | 1.86(2) | P(4)–C(51) | 1.925(12) |
| P(4)–C(61) | 1.845(9) | P(4)–C(3) | 1.89(2) | C(1)–C(2) | 1.52(2) | C(3)–C(4) | 1.56(2) |
| C(5)–C(6) | 1.31(2) | C(6)–C(91) | 1.46(2) | | | | |
| P(1)–Re–P(2) | 80.2(3) | P(1)–Re–P(3) | 101.4(3) | P(2)–Re–P(3) | 177.7(2) | P(1)–Re–P(4) | 180.0(2) |
| P(2)–Re–P(4) | 99.7(3) | P(3)–Re–P(4) | 78.7(3) | P(1)–Re–Cl | 88.6(2) | P(2)–Re–Cl | 81.0(2) |
| P(3)–Re–Cl | 100.6(2) | P(4)–Re–Cl | 91.4(2) | P(1)–Re–C(5) | 88.3(4) | P(2)–Re–C(5) | 99.2(4) |
| P(3)–Re–C(5) | 79.3(4) | P(4)–Re–C(5) | 91.7(4) | Cl–Re–C(5) | 176.8(4) | Re–P(1)–C(11) | 117.2(5) |
| Re–P(1)–C(21) | 123.8(5) | Re–P(1)–C(1) | 111.9(6) | C(11)–P(1)–C(1) | 96.5(6) | C(21)–P(1)–C(1) | 105.5(7) |
| Re–P(2)–C(31) | 122.5(4) | Re–P(2)–C(41) | 121.2(5) | Re–P(2)–C(2) | 105.2(6) | C(31)–P(2)–C(2) | 98.1(6) |
| C(41)–P(2)–C(2) | 101.1(7) | Re–P(3)–C(71) | 127.2(5) | Re–P(3)–C(81) | 120.5(5) | Re–P(3)–C(4) | 106.5(6) |
| C(71)–P(3)–C(4) | 100.9(7) | C(81)–P(3)–C(4) | 104.0(6) | Re–P(4)–C(51) | 118.3(5) | Re–P(4)–C(61) | 117.0(5) |
| Re–P(4)–C(3) | 109.5(6) | C(51)–P(4)–C(3) | 97.1(6) | C(61)–P(4)–C(3) | 108.1(7) | P(1)–C(1)–C(2) | 109.4(12) |
| P(2)–C(2)–C(1) | 109.9(11) | P(4)–C(3)–C(4) | 114.2(12) | P(3)–C(4)–C(3) | 108.0(10) | Re–C(5)–C(6) | 166.6(12) |
| C(91)–C(6)–C(5) | 125.5(15) | | | | | | |

towards β-electrophilic attack of other unsaturated species, such as isocyanides,[8–10] nitriles,[6] or phenylallene,[13] when bound to the same rhenium site. Moreover, this type of reactivity of vinylidene species has also been reported[17,18] for other systems.

In the reactions of the supposedly more acidic 1-alkynes (particularly HC≡CCO$_2$Et and HC≡CPh), the crude vinylidene products, as precipitated from the reaction solutions, are often contaminated by minor (and variable) amounts of other products which are clearly detected in the i.r. spectra by their bands at *ca.* 2 000 cm$^{-1}$, in the expected[15,22,23] range for ν(C≡C) of alkynyl ligands, their formation possibly involving the known[11,24] oxidative addition of the terminal C–H alkyne bond. However, they were never obtained in a pure condition.

1,2-*Hydrogen Migration.*—Although the above-mentioned reactions conceivably occur through the co-ordination of the alkyne upon loss of $N_2$, no alkyne complex was isolated. Similar observations have been quoted for the phenylpropyne-to-allene conversion (involving a 1,3-hydrogen migration) at the same metal site[12] as well as for the 1-alkyne-to-vinylidene rearrangement centred at related $d^6$ metal centres, such as in the reactions of *fac*-[W(CO)$_3$(dppe)(thf)] with terminal alkynes which lead to [W(=C=CHR)(CO)$_3$(dppe)].[18]

This may be rationalised by considering a repulsive four-electron $d_\pi$(metal)–$\pi_\perp$(alkyne) interaction,[25] as a result of the filled psuedo-$t_{2g}$ set of the $d^6$ Re atom in the electron-rich ReCl(dppe)$_2$ site. Such a destabilizing rhenium–alkyne interaction would promote the alkyne-to-vinylidene (or to allene) conversion as suggested[18] also for the former rearrangement at other tungsten(0)-$d^6$ complexes, *i.e.* the alkyne would rearrange into a species where such an interaction would not be present.

The 1-alkyne-to-vinylidene conversion occurs through a 1,2-hydrogen migration reaction which, for $d^6$ ML$_5$ or cationic T-shaped $d^8$ metal centres, has been examined by extended-Hückel calculations; they suggest that such a hydrogen migration involves a di- to a mono-hapto slippage of the alkyne ligand, followed by 1,2-proton migration.[26] This route was shown[26] to be energetically favourable relatively to the alternative one through the formation of an intermediate alkynyl-

**Table 4.** Atomic positional parameters (fractional co-ordinates × $10^4$) for compound (**1**; R = Ph) with e.s.d.s. in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Re | 0 | 0 | 0 |
| P(1) | −1 373(8) | 30(6) | 1 219(5) |
| P(2) | −541(7) | 1 531(6) | −192(4) |
| P(3) | 660(8) | −1 506(5) | 204(5) |
| P(4) | 1 403(8) | −28(5) | −1 247(5) |
| Cl | −2 735(5) | −1 246(4) | −1 704(4) |
| C(11) | −28(12) | 843(8) | 2 847(6) |
| C(12) | 441 | 2 021 | 3 422 |
| C(13) | 1 562 | 2 665 | 4 605 |
| C(14) | 2 215 | 2 129 | 5 214 |
| C(15) | 1 745 | 951 | 4 639 |
| C(16) | 624 | 308 | 3 456 |
| C(21) | −2 920(12) | −1 285(7) | 1 209(9) |
| C(22) | −3 484 | −2 381 | 348 |
| C(23) | −4 750 | −3 428 | 261 |
| C(24) | −5 452 | −3 379 | 1 037 |
| C(25) | −4 888 | −2 283 | 1 899 |
| C(26) | −3 622 | −1 236 | 1 985 |
| C(31) | 821(11) | 3 144(6) | 976(7) |
| C(32) | 293 | 3 941 | 904 |
| C(33) | 1 227 | 5 097 | 1 779 |
| C(34) | 2 689 | 5 455 | 2 725 |
| C(35) | 3 217 | 4 658 | 2 797 |
| C(36) | 2 283 | 3 503 | 1 922 |
| C(41) | −1 095(11) | 1 690(8) | −1 603(7) |
| C(42) | 184 | 2 545 | −1 725 |
| C(43) | −138 | 2 698 | −2 765 |
| C(44) | −1 739 | 1 998 | −3 684 |
| C(45) | −3 019 | 1 143 | −3 562 |
| C(46) | −2 697 | 990 | −2 521 |
| C(51) | 3 148(13) | 1 469(8) | −1 042(10) |
| C(52) | 3 885 | 1 485 | −1 800 |
| C(53) | 5 174 | 2 561 | −1 646 |
| C(54) | 5 727 | 3 621 | −735 |
| C(55) | 4 990 | 3 604 | 23 |
| C(56) | 3 700 | 2 528 | −131 |
| C(61) | 79(12) | −830(8) | −2 840(6) |
| C(62) | −157 | −143 | −3 433 |
| C(63) | −1 184 | −686 | −4 633 |
| C(64) | −1 976 | −1 917 | −5 240 |
| C(65) | −1 740 | −2 603 | −4 647 |
| C(66) | −712 | −2 060 | −3 447 |
| C(71) | −423(12 | −3 009(7) | −786(8) |
| C(72) | 252 | −3 711 | −627 |
| C(73) | −550 | −4 877 | −1 454 |
| C(74) | −2 027 | −5 341 | −2 441 |
| C(75) | −2 702 | −4 638 | −2 600 |
| C(76) | −1 900 | −3 472 | −1 772 |
| C(81) | 837(10) | −1 850(7) | 1 523(6) |
| C(82) | −552 | −2 747 | 1 512 |
| C(83) | −434 | −2 966 | 2 512 |
| C(84) | 1 074 | −2 287 | 3 522 |
| C(85) | 2 463 | −1 390 | 3 533 |
| C(86) | 2 344 | −1 171 | 2 533 |
| C(91) | 5 140(10) | 2 453(7) | 2 902(7) |
| C(92) | 6 077 | 3 225 | 4 085 |
| C(93) | 7 712 | 4 147 | 4 492 |
| C(94) | 8 409 | 4 296 | 3 717 |
| C(95) | 7 472 | 3 523 | 2 534 |
| C(96) | 5 838 | 2 601 | 2 126 |
| C(1) | −2 277(17) | 966(11) | 1 100(11) |
| C(2) | −2 465(16) | 1 138(11) | −28(10) |
| C(3) | 2 727(15) | −676(10) | −820(10) |
| C(4) | 2 753(16) | −974(11) | 257(10) |
| C(5) | 2 214(13) | 1 020(9) | 1 479(8) |
| C(6) | 3 423(19) | 1 538(13) | 2 534(12) |
| O | 3 483(44) | 6 907(31) | 5 782(29) |
| C(7) | 3 734(43) | 6 085(29) | 5 891(27) |
| C(8) | 2 529(58) | 5 556(40) | 6 567(37) |
| C(9) | 2 604(35) | 6 600(25) | 7 366(23) |
| C(10) | 2 663(60) | 7 337(42) | 6 511(39) |

hydrido complex derived from oxidative addition of the terminal C–H bond of the 1-alkyne.

Alkynyl-hydrido species were not unambiguously detected in the present study, although they have been recognised as products in the reactions of terminal alkynes with the related complexes *trans*-[M($N_2$)$_2$(dppe)$_2$] (M = Mo or W) which lead to a variety of alkynyl compounds, such as *cis*-[WH(C≡C-$CO_2$Me)(dppe)$_2$].[11] Nevertheless, in all these systems, involving $d^6$ $ML_5$ metal centres, there is no evidence for the direct conversion of an alkynyl-hydrido compound into a vinylidene product, in agreement with the above-mentioned theoretical studies.

## Conclusions

The reactions described in this paper extend the rhenium sites which promote the 1-alkyne-to-vinylidene rearrangement from those which are relatively electron poor, *e.g.* Re(η-$C_5H_5$)(CO)$_2$,[3] to the electron-rich ReCl(dppe)$_2$. In so doing, the latter centre contrasts with the related electron-rich, but more readily-oxidisable sites M(dppe)$_2$ (M = Mo or W) which mainly give products of C–H oxidative addition, such as alkynyl–hydrides.[11]

Nevertheless, some oxidative addition does appear to occur at the rhenium centre and the preferred pathway for these reactions, all of which must involve initial co-ordination of the alkyne (in place of $N_2$) at these sites, appears to depend upon a balance of the electron-richness, π-donor ability, ease of oxidation, and substitution lability of these centres.

Vinylidene complexes have been recognised as intermediates not only in organometallic chemistry but also in some enzymatic processes involving, *e.g.*, the metabolism of some chlorinated hydrocarbons at haem proteins.[17] Such a type of unsaturated carbenes, as exemplified by those of the present study, may also be postulated as plausible intermediates in the reduction of 1-alkynes by nitrogenases.

## Experimental

All air-sensitive materials were handled using standard inert gas-flow or high-vacuum techniques.

The complex *trans*-[ReCl($N_2$)(dppe)$_2$] was prepared by a published method[27] and the 1-alkynes (HC≡CR) were used as purchased from Aldrich (R = Ph, Bu$^t$, $CO_2$Me, $CO_2$Et, or $C_6H_{10}$OH-1), Cambrian Chemicals (R = Et), or Fluorochem (R = $SiMe_3$). The solvents were purified and dried by standard procedures.

Infrared spectra were run in a Perkin-Elmer 683 or 457 instrument, and n.m.r. spectra in a JEOL FX90Q or Bruker 360 spectrometer. The solvents used for n.m.r. measurements were dried and degassed before use.

*Preparations—trans*-[ReCl(=C=CHPh)(dppe)$_2$] (**1**; R = Ph). An excess of PhC≡CH (1.5 $cm^3$, 13.7 mmol) was added to a solution of *trans*-[ReCl($N_2$)(dppe)$_2$] (0.72 g, 0.69 mmol) in thf (350 $cm^3$) and the system was stirred and heated to reflux under argon for *ca.* 8 d. The dark red solution was then concentrated under vacuum and pentane added, always with heating, until appearance of a yellow solid (mainly unreacted starting dinitrogen complex). The solution was filtered and upon concentration and addition of pentane, with heating at *ca.* 50 °C, the complex (**1**; R = Ph), slightly contaminated with possible alkynyl species, separated out as a red solid which was filtered off, washed with thf–pentane, and dried under vacuum. Further crops of these products could be obtained upon concentration and addition of pentane to the mother-liquor. Recrystallisation of the crude solid from thf–pentane afforded complex (**1**; R = Ph) as a red crystalline solid (total *ca.* 0.45 g, 60% yield).

In an attempt to speed up the reaction, the refluxing thf solution was irradiated by a 40-W tungsten-filament bulb (at *ca.* 35 cm), but no increase in the yield of the vinylidene product was obtained. Moreover, this yield decreased drastically by carrying out the reaction in the presence of NaOMe.

Alternatively, complex (**1**; R = Ph) could be obtained in toluene, at ambient temperature and under irradiation from a tungsten-filament bulb. Thus, addition of PhC≡CH (1.3 $cm^3$, 11.8 mmol) to a filtered and stirred solution of *trans*-[ReCl($N_2$)(dppe)$_2$] (0.48 g, 0.46 mmol) in toluene (200 $cm^3$), under argon, followed by irradiation from one 150-W tungsten-filament bulb (at *ca.* 15 cm) for about 5 d, led to a brownish orange solution which was concentrated under vacuum with heating at *ca.* 50 °C. Addition of hexane until the solution became cloudy, followed by filtration, allowed the separation of complex (**1**; R = Ph) (slightly contaminated with a possible alkynyl complex) as aggregates of red crystals which were filtered off, washed with toluene–hexane, and dried under vacuum (*ca.* 0.25 g, 50% yield).

*trans*-[ReCl(=C=CHEt)(dppe)$_2$] (**1**; R = Et). The compound EtC≡CH was bubbled slowly (for *ca.* 10 min) through a thf solution (300 $cm^3$) of *trans*-[ReCl($N_2$)(dppe)$_2$] (0.45 g, 0.43 mmol), prepared under argon, which was then vigorously stirred and irradiated by two 100-W tungsten-filament bulbs for *ca.* 6 d. The reddish brown solution was then concentrated under vacuum, with heating at *ca.* 50 °C, and pentane added to give a greenish brown solid which was separated from the solution. Concentration of the filtered solution followed by addition of pentane resulted in the precipitation of complex (**1**; R = Et) as a dark brown crystalline solid which was filtered off, washed with thf–pentane and acetone, and then dried under vacuum. Further crops of this product could be obtained from the mother-liquor upon concentration and addition of pentane (*ca.* 0.15 g, 35% yield).

*trans*-[ReCl(=C=CHBu$^t$)(dppe)$_2$] (**1**; R = Bu$^t$). The compound Bu$^t$C≡CH (1.0 $cm^3$, 8.2 mmol) was added to a solution of *trans*-[ReCl($N_2$)(dppe)$_2$] (0.50 g, 0.48 mmol) in thf (350 $cm^3$) which was left stirring, under argon, and irradiated by one 150-W tungsten-filament bulb (at a distance of *ca.* 20 cm). After *ca.* 4 d the red solution was concentrated under vacuum at *ca.* 50 °C, and complex (**1**; R = Bu$^t$) precipitated, upon addition of hexane, as a red crystalline solid which was filtered off, washed with thf–hexane, and dried under vacuum. Further crops could be obtained upon concentration and addition of hexane to the mother-liquor (*ca.* 0.37 g, 70% yield).

*trans*-[ReCl(=C=CHSiMe$_3$)(dppe)$_2$] (**1**; R = SiMe$_3$). The synthesis of this complex was carried out under similar experimental conditions to those used for (**1**; R = Ph). The final reaction solution was brownish green and complex (**1**; R = SiMe$_3$) was isolated in *ca.* 30% yield.

*trans*-[ReCl(=C=CHR)(dppe)$_2$] (**1**, R = $CO_2Me$ *or* $CO_2Et$). An excess of RC≡CH [0.6 $cm^3$, 7.2 (R = $CO_2Me$) or 5.9 mmol (R = $CO_2Et$)] was added to a solution of *trans*-[ReCl($N_2$)(dppe)$_2$] (0.42 g, 0.40 mmol) in thf (200 $cm^3$) which was refluxed, with stirring, under argon for *ca.* 6 or 4 d (R = $CO_2Me$ or $CO_2Et$, respectively). The final dark red solution was concentrated under vacuum with heating at *ca.* 50 °C, and pentane was slowly added until a brown solid separated. From the filtered solution (A), complex (**1**; R = $CO_2Et$) with an alkynyl species precipitated as a mixture of a brown powder with red crystalline needles which was recrystallised from thf–pentane to give a brownish red solid (*ca.* 0.20 g, 45% yield).

In the case of the reaction of HC≡CCO$_2$Me, solution (A) was concentrated under vacuum at *ca.* 50 °C and pentane was added until a dark red oil started to form; it was filtered off and complex (**1**; R = $CO_2Me$) precipitated from the solution as aggregates of dark red crystals (*ca.* 0.18 g, 40% yield).

Alternatively, the reactions could be carried out in toluene, at ambient temperature, under tungsten-filament light [see also the preparation of (**1**; R = Ph)].

*trans*-[ReCl(=C=CHC$_6$H$_{10}$OH-1)(dppe)$_2$] (**1**; R = C$_6$H$_{10}$OH-1). A thf (200 $cm^3$) solution of *trans*-[ReCl($N_2$)(dppe)$_2$] (0.50 g, 0.48 mmol) and HC≡CC$_6$H$_{10}$OH-1 (0.57 g, 4.6 mmol) was refluxed under argon, with stirring, for *ca.* 14 d. The final dark brown solution was then concentrated under reduced pressure at *ca.* 50 °C, and a green powder was formed on addition of pentane. The solution was filtered, concentrated again, and pentane was added slowly leading to the precipitation of a dark brown solid which was recrystallised from thf–pentane (*ca.* 0.080 g, 15% yield).

*Crystal Structure Determination of* trans-[ReCl(=C=CHPh)(dppe)$_2$] (**1**; R = Ph).—Crystals of (**1**; R = Ph) were grown from tetrahydrofuran–pentane as red plates and found to contain one molecule of tetrahydrofuran per molecule of the complex. Diffracted intensities were collected (Wyckoff ω scans) at room temperature from a crystal of dimensions *ca.* 0.50 × 0.25 × 0.15 mm on a Nicolet *P*3 diffractometer. Of the total 3 967 intensities ($2\theta \leqslant 45°$), 3 884 with $F \geqslant 4\sigma F$ were used in structure solution and refinement after corrections for Lorentz, polarisation, and *X*-ray absorption effects. The latter was based upon an analytical method using crystal faces.[28]

*Crystal data.* $C_{60}H_{54}ClP_4Re\cdot C_4H_8O$, $M$ = 1 192.7, triclinic, $a$ = 9.901(2), $b$ = 13.569(4), $c$ = 13.132(4) Å, $\alpha$ = 103.56(3), $\beta$ = 107.05(2), $\gamma$ = 114.86(2)°, $U$ = 1 394.3(7) Å$^3$, $Z$ = 1, $D_c$ = 1.42 g cm$^{-3}$, $F(000)$ = 606, space group $P1$, $\mu$(Mo-$K_\alpha$) = 21.18 cm$^{-1}$.

The structure was solved by conventional heavy-atom and Fourier difference methods, and refined by blocked-cascade least squares. The data were relatively poor and accordingly hydrogen atoms were not included and only the heavy atoms (Re, P, and Cl) were refined with anisotropic thermal parameters. Phenyl rings were included as rigid groups (C–C 1.395 Å). As the space group is chiral an enantiomeric refinement of the type suggested by Rogers[29] was carried out. The value of the Rogers' parameter obtained [0.1(3)] suggests that enantiomeric twinning may occur in the crystal. Refinement converged at $R$ = 0.041 ($R'$ = 0.044) and a weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + 0.001 |F_o|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks $\geqslant 1.2$ or $\leqslant -0.5$ e Å$^{-3}$. All calculations were performed on a Data General Eclipse computer using the SHELXTL system of programs.[28] Scattering factors with corrections for anomalous scattering were taken from ref. 30.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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