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Comparative behaviours of phospha-alkynes and alkynes at electron-rich phosphinic metal centres

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Abstract

The coordination chemistry of phospha-alkynes (P≡CR) at electron-rich and sterically hindered {M(diphosphine)$_2$} [M = Mo(0), W(0), Re(I), Fe(II)] centres, in which the P≡CR ligand adopts the very rare and electronically unfavoured end-on (η^1) coordination mode, as well as at the less sterically demanding {Rh(triphos)}$^+$ site, are described and compared with those exhibited by alkynes at the same metal centres. At the former sites, the η^1-P≡CR ligand behaves as a weak π-acceptor and is typically activated to α-nucleophilic addition to give phospha-alkene, phosphine and phosphinidene oxide products, although activation towards electrophilic (protic) addition has also been recognized upon hydrometalation (insertion into a metal–H bond to give a phospha-alkenyl species). At the same metal sites, the η^2-coordination of alkynes is unfavoured (on both electronic and steric grounds) and these substrates undergo rearrangements (H-shifts) towards η^1-bonded alkynyl and vinylidene derivatives, or towards a less sterically demanding η^2-allene species, and these products are activated towards β-electrophilic addition (protonation) on account of their π-electron withdrawal ability which contrasts with the behaviour of the η^1-P-ligated phospha-alkyne and derivatives. The alkyne and phospha-alkyne insertions into an Fe–H bond are also compared, as well as their cycloaddition reactions (cyclotri- and cyclodimerisations, respectively) at the {Rh(triphos)}$^+$ centre which exhibits open coordination sites for η^2-ligation. The above reactions are discussed in terms of both stereochemical and electronic effects.

Keywords: Phospha-alkyne; Phospha-alkene; Phosphine; Fluorophosphine; Phosphinedene oxide; Alkyne; Vinylidene; Alkynyl; Allene; Carbyne; Alkylidyne; Vinyl; Nucleophilic addition; Electrophilic addition; Protonation

1. Introduction

The author acknowledges the invitation that was kindly addressed to him to contribute to this celebratory issue on the occasion of Professor A. Romão Dias' 60th anniversary, in spite of the fact that his research (initially based on the D. Phil. training at the University of Sussex, UK) has developed separately from that of the wide organometallic group that was remarkably established by Professor A.R. Dias.

For this contribution, the selected topic falls within the author's general interest on the activation, by coordination, of small molecules [1], in this particular case phospha-alkynes (P≡CR) and related alkynes (commonly 1-alkynes, HC≡CR) at electron-rich phosphinic dinitrogen-binding metal centres. The study of the comparative behaviours of such unsaturated species would allow to compare the effect on the unsaturated bond of the replacement of the CH group at HC≡CR by the P atom at P≡CR. This would be particularly significant in view of the C–P diagonal relationship, which has been recently recognized in the field of unsaturated-P chemistry, as expressed in the suggestive title of the book 'Phosphorus: The Carbon-Copy' by Dillon, Mathey and Nixon [2].

Both phospha-alkynes [2–4] and alkynes [5] (the former only recently) have led to the development of rich organometallic chemistries and usually bind a metal centre in the dihapto (η^2) or side-on coordination mode (**1**, for the former species). This is in accord with the nature of the HOMO which is of the P≡C or C≡C π-type, respectively. However, the phospha-alkynes would be able, in principle, to utilise not only the triple

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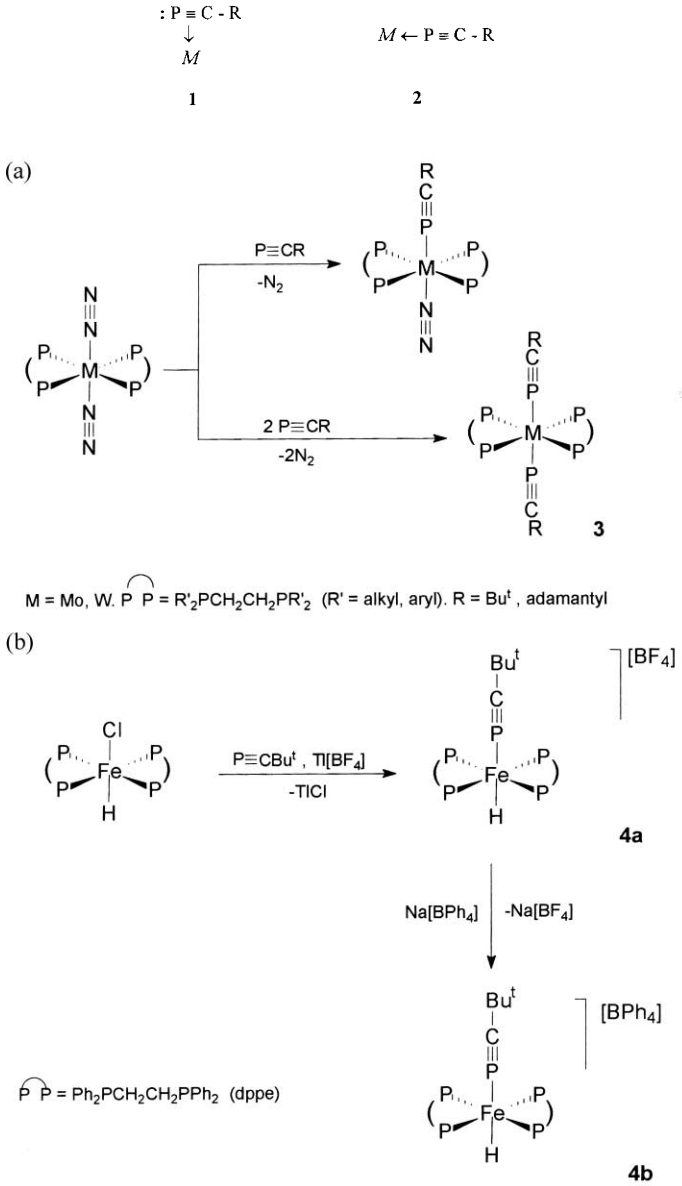
bond but also the P lone-pair electrons (although in an orbital with a significantly lower energy than the HOMO) and in fact they can bind (although rarely) in the η^1 (end-on) fashion (**2**) at a suitable narrow coordination site, in particular of the bulky diphosphinic type {M(diphosphine)$_2$} [6–8] able to accept only linear molecules oriented in such a way.

This unusual coordination mode, stereochemically aided but electronically unfavoured, results in interesting forms of reactivity of the phospha-alkynes which are discussed herein and compared with those observed for alkynes at the same metal-binding sites. The account is based on the author's group contributions (in particular within his collaborations with Professor R.L. Richards and Professor J.F. Nixon, University of Sussex), but related studies by other groups are also discussed.



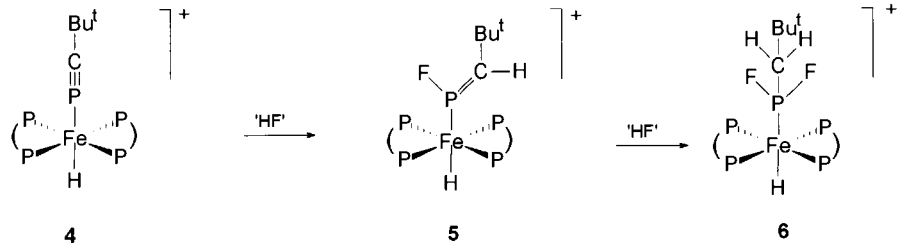
Scheme 1.

2. η^1-Coordination of phospha-alkynes

The η^1-ligation mode of phospha-alkyne ligands has been unambiguously established at an axial position in octahedral-type transition metal complexes containing two bulky *trans*-chelating diphosphine ligands, i.e. in *trans*-[M(N$_2$)(η^1-P≡CR)(R′$_2$PCH$_2$CH$_2$PR′$_2$)] (M = Mo or W, R = ^{t}Bu or adamantyl, R′ = alkyl or aryl) [6], *trans*-[M(η^1-P≡CR)$_2$(R′$_2$PCH$_2$CH$_2$PR′$_2$)$_2$] (**3**) [6] and *trans*-[FeH(η^1-P≡C^{t}Bu)(dppe)$_2$]A (A = BF$_4$ (**4a**) or BPh$_4$ (**4b**)) [7,8]. The Group 6 metal complexes were prepared by replacement of N$_2$, in the corresponding parent dinitrogen complexes, *trans*-[M(N$_2$)$_2$(R′$_2$PCH$_2$CH$_2$PR′$_2$)$_2$], by the phospha-alkyne (Scheme 1a), whereas the iron(II) complex **4a** was derived from *trans*-[FeH(Cl)(dppe)$_2$], the reaction being carried out [7,8] in the presence of Tl[BF$_4$] as the chloride ligand abstractor (Scheme 1b). Further replacement of the [BF$_4$]$^-$ counter-ion in **4a** by [BPh$_4$]$^-$ on reaction with Na[BPh$_4$] afforded the final product **4b** (Scheme 1b) [7]. In all the above binding metal centres, the bulky diphosphines leave only a narrow channel in the axial direction for ligation of the phospha-alkyne which thus coordinates linearly in the η^1(end-on) mode.

The molecular structures of *trans*-[Mo(η^1-P≡CR)$_2$-(R′$_2$PCH$_2$CH$_2$PR′$_2$)$_2$] (**3**, R = adamantly, R′ = Et) [6] and *trans*-[FeH(η^1-P≡C^{t}Bu)(dppe)$_2$][BPh$_4$] (**4b**) [8] were established by single crystal X-ray diffraction analyses which show a rather short P≡C bond length, i.e. 1.520(12) Å for **3** [6] or the even shorter value of 1.512(5) Å for **4b** [7]. The P≡C distance is shorter than the average value of ca. 1.540(4) Å known [9] for free P≡CR ligands and therefore a shortening of the P≡C bond results upon η^1-coordination, as also observed [10] for the P=C bond in the case of phospha-alkenes. This contrasts with the significant lengthening of the P≡C or P=C bonds in phospha-alkyne or phospha-alkene ligands, respectively, that occurs in η^2-bonded complexes [2–4] in agreement with the electron donation from a filled π-bonding orbital of the ligand and eventual electron acceptance by an antibonding π*-orbital.

The shortening upon η^1-coordination of the phospha-alkyne P≡C bond can conceivably be interpreted by analogy with the structurally related unsaturated carbonyl [11], isocyanide [11], dinitrogen and nitrile [12] ligands, where the electron lone pair orbital involved in σ-coordination to the metal has some antibonding character for the unsaturated bond. The observation is also indicative of a modest or even non-existing π-electron accepting ability of the phospha-alkyne since an extensive π-electron backbonding component of the coordination bond (π-electron release from the metal to an empty π*-orbital of the phospha-alkyne) would result in a weakening (elongation) of the P≡C bond (see also the electrochemical studies discussed below).



Scheme 2.

The metal-P (phospha-alkyne) bond distance, 2.305(3) Å for **3** (R = adamantyl, R′ = Et) [6] or 2.148(2) Å for **4b** [7], is shorter than those of metal–P(phosphine), ca. 2433(4) or ca. 2.276(2) Å, respectively, reflecting the smaller sp radius of phosphorus (in the phospa-alkyne) compared with the sp^3 value (in the phosphine).

In the ^{13}C-{^1H}-NMR spectrum of **4b** (CD_2Cl_2) the P≡*C*′Bu resonance (doublet, *J*(CP) 140 Hz) occurs at a chemical shift (δ 183.38) comparable with that of the uncoordinated phospha-alkyne, thus not showing the downfield shift typical for η^2-coordination not only for a two-electron donor [13], but also, and even much more extensively, for a four-electron donor phospha-alkyne [14]. Interestingly, four-electron donor alkynes also exhibit a much lower field ^{13}C resonance for the ligating C atoms [15], compared with the two- or three-electron donor cases.

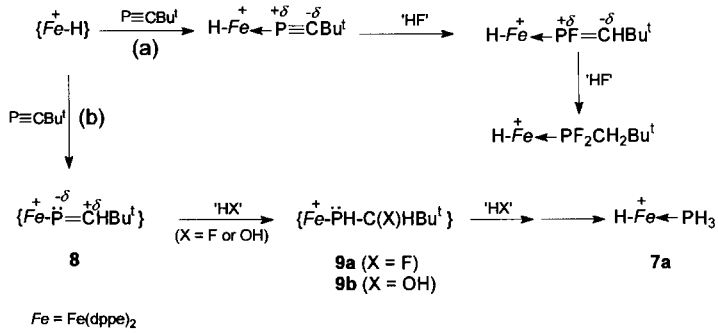
As revealed by a cyclic voltammetric study, *trans*-[FeH(η^1-P≡C′Bu)(dppe)$_2$][BF_4] (**4a**) undergoes a *quasi*-reversible single electron oxidation at $E° = 1.00$ V versus SCE, a value that is rather close to that (1.04 V) of the analogous carbonyl complex *trans*-[FeH(CO)(dppe)$_2$]$^+$ [7]. Thus, the η^1-phospha-alkyne and the CO ligands exhibit a very similar *net* π-electron acceptor minus σ-donor ability, as also indicated by the closeness of the estimated value of the electrochemical P_L ligand parameter (a measure of that net electron ability [17]) for the former ligand, −0.04 V [7], and that of CO ($P_L = 0$ V). Therefore, since the η^1-phospha-alkyne (see above) is not an efficient π-acceptor (in contrast to CO), one concludes that it is also not a strong σ-donor, thus accounting for the scarcity of complexes with this coordination mode. In this respect it resembles dinitrogen ($P_L = -0.07$ V [17]) and behaves as a weaker net electron donor than PPh_3, CNMe or NCMe (with P_L values of −0.35, −0.43 or −0.58 V, respectively [17]).

η^1-Coordination was also suggested [16], on the basis of spectroscopic evidence, for the 'super misityl' phospha-alkyne P≡CR (R = $C_6H_2^tBu_3$-2,4,6) with high steric hindrance at the C atom, in the Ru(0) complex [Ru(η^1-P≡CR)(CO)$_2$(PPh_3)$_2$] whose molecular structure however was not authenticated by X-rays. The complex was obtained by displacement of one PPh_3 ligand at [Ru(CO)$_2$(PPh_3)$_3$], a route also employed for the preparation of related η^2-alkyne complexes [16].

3. Phospha-alkyne reduction to phospha-alkene and phosphine

Treatment of a CH_2Cl_2 solution of *trans*-[FeH(η^1-P≡C′Bu)(dppe)$_2$][BF_4] (**4a**) with HBF_4 forms a mixture of the η^1-fluorophospha-alkene *trans*-[FeH(η^1-PF=CH′Bu)(dppe)$_2$][BF_4] (**5a**) and the difluorophosphine *trans*-[FeH($PF_2CH_2^tBu$)(dppe)$_2$][BF_4] (**6**) complexes, formed upon a sequential addition of 2HF groups across the P≡C bond of the η^1-phospha-alkyne (Scheme 2) [7,8]. These products were isolated as their [BF_4]$^-$ salts (and also as the [$FeCl_2F_2$]$^-$ salt, **5b**, in the former case), fully characterised mainly by multinuclear NMR spectroscopy and, in the latter case, by the single crystal diffraction analysis of *trans*-[FeH(η^1-PF=CH′Bu)(dppe)$_2$][$FeCl_2F_2$] (**5b**) [8] obtained from prolonged attempted recrystallisation of **4a**, from CH_2Cl_2–Et_2O, in the presence of [NH_4][BF_4]–Tl[BF_4]. Similarly to what is observed for the parent η^1-phospha-alkyne complex **4** (see above), the unsaturated (P=C) bond length in the ligated η^1-phospha-alkene in **5b**, 1.66(4) Å, is shorter than that in a free phospha-alkene [18], in contrast with the known [2,3] stretching of such a bond in the case of η^2-coordination.

The above reactions of the η^1-phospha-alkyne (Scheme 2), via formal 'HF' 1,2-additions, suggest the ligand polarity $Fe \leftarrow P(+\delta) \equiv C(-\delta)^tBu$, thus following a nucleophilic attack route at the phospha-alkyne involving F^- attack at the ligated P atom and protonation at the unsaturated C atom—see Scheme 3a, which also includes the binding of the phospha-alkyne to the unsaturated metal centre $\{Fe^+ - H\}$ i.e. {FeH(dppe)$_2$}$^+$ generated by chloride abstraction, by Tl^+, from *trans*-[FeH(Cl)(dppe)$_2$]. Such a 1,2-addition of a protic nucleophile (HF) parallels the observed behaviours of free phospha-alkynes (:P≡CR) which e.g. on reaction with HCl lead to the corresponding phospha-alkenes Cl$\ddot{P}$=CHR [2–4], i.e. the protonation occurs exclusively at the C atom rather than at the P atom in spite of the electron lone pair at the latter.



Scheme 3. (a) Nucleophilic attack route at the phospha-alkyne P. (b) Postulated phospha-alkyne insertion followed by electrophilic attack route.

However, a different pattern of reactivity of the η^1-phospha-alkyne ligand has also been observed in the unexpected formation of the PH_3 complex *trans*-[FeH(PH_3)(dppe)$_2$][BF_4] (**7a**) as a side product in the reaction of *trans*-[FeH(Cl)(dppe)$_2$] with Tl[BF_4]–[NH_4][BF_4] (Scheme 4), besides the abovementioned η^1-phospha-alkyne complex **4a** [7]. Replacement of the [BF_4]$^-$ counter-ion in **7a** by [BPh_4]$^-$ leads to the related *trans*-[FeH(PH_3)(dppe)$_2$][BPh_4] (**7b**) complex [7].

The formation of the PH_3 complex **7a**, which cannot be obtained from the η^1-phospha-alkyne complex **4**, follows a distinct pathway from that discussed above, conceivably involving (Scheme 3b) [7] a postulated phospha-alkenyl intermediate, *Fe*←P̈=CH^{t}Bu (**8**) [*Fe* = Fe(dppe)$_2$] (formed via insertion of P≡C^{t}Bu in the Fe–H bond), containing a nucleophilic P atom, i.e. with a reversed polarization to that observed in the phospha-alkyne complex H-*Fe*$^+$←P≡C^{t}Bu (**4**). The phospha-alkenyl intermediate **8** would undergo protonation at P and nucleophilic attack at C, by HX = 'HF' or H_2O, forming (Scheme 5) *Fe*–P̈H–C(X)H^{t}Bu (X = F (**9a**), OH (**9b**)) which, upon β-H elimination, rearrangement (in the case of HX = H_2O involving the conversion of the enol **9b** into the keto form H-*Fe*←PH_2CO^tBu) and further 'HX' addition would yield the final PH_3 complex **7** on liberation of the corresponding organic products [7].

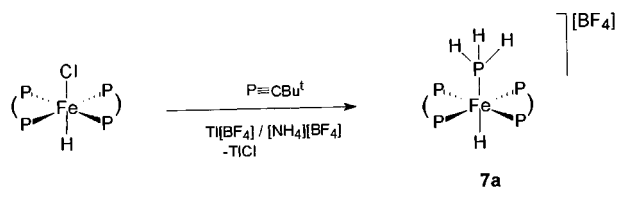
A precedent for the conversion of a phospha-alkyne into a phosphine (a fluorophosphine) ligand via a phospha-alkenyl intermediate has been reported [19] for [RuH(Cl)(CO)(PPh_3)$_3$] which, on treatment with P≡C^{t}Bu followed by CNR (R = $C_6H_3Me_2$-2,6), affords [Ru(Cl)(η^1-P=CH^{t}Bu)(CO)(CNR)(PPh_3)$_2$] (Scheme 6) that is converted into the fluorophosphine complex [Ru(Cl)(PHFCH$_2^t$Bu)(CO)(CNR)(PPh_3)]$^+$ by protonation (HBF_4) followed by nucleophilic addition of 'HF' (added as K[HF_2] or [NBu_4]F).

Scant examples of phospha-alkyne hydrometalations are known [20], and another precedent for the nucleophilic character of the P atom of the derived phospha-alkenyl ligand can be recognized in the alkylation (by CH_3I) of [Ru(Cl)(L)(η^1-P=CH^{t}Bu)(PPh_3)$_2$] (L = CO or CS) to yield the corresponding phospha-alkene complexes [Ru(Cl)(I)(L){η^1-P(CH_3)=CH^{t}Bu}(PPh_3)$_2$] [21].

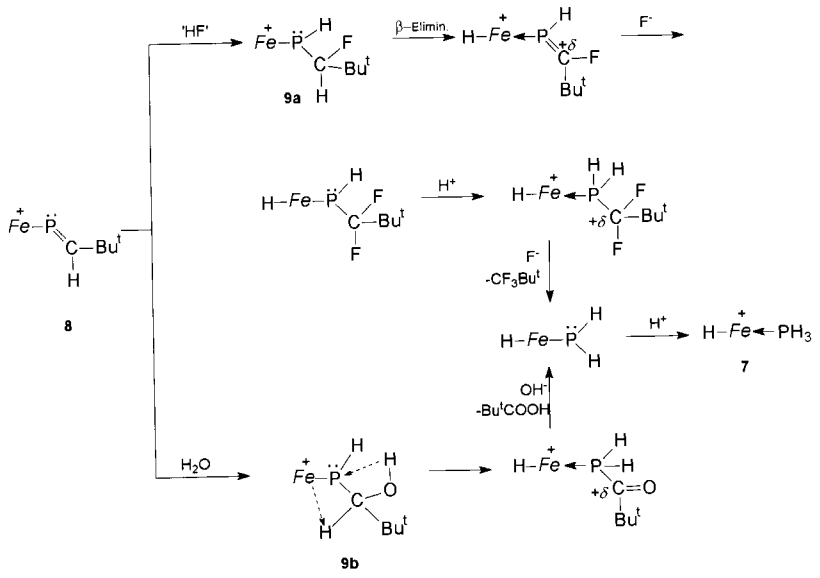
4. Phospha-alkyne hydration to phosphinidene oxide

We have discussed above (Schemes 2 and 3) the 1,2-nucleophilic addition of the protic nucleophile 'HF' to the η^1-ligated phospha-alkyne in a iron(II) centre (complex **4**) to give the η^1-phospha-alkene derivative **5** in which the nucleophile (F^-) added to the P atom and the electrophile (H^+) to the carbon atom. A related 1,2-nucleophilic addition by H_2O as the nucleophile has been observed at the η^1-phospha-alkyne ligating a Re(I) centre (Scheme 7) [22], to give quite a different type of product, a phosphinidene oxide (^{t}BuCH$_2$P=O).

The reaction of the dinitrogen complex *trans*-[ReCl(N_2)(dppe)$_2$] with P≡C^{t}Bu in tetrahydrofuran results in N_2 replacement by the phospha-alkyne to form *trans*-[ReCl((η^1-P≡C^{t}Bu)(dppe)$_2$] (**10**) (the crowded metal centre prevents η^2-coordination) which, upon hydrolysis with traces of moisture, yields the final P-bonded phosphinidene oxide product, *trans*-[ReCl{P(O)CH$_2^t$Bu}(dppe)$_2$] (**11**), whose molecular structure has been established by X-ray diffraction [22]. The P atom of the phosphinidene oxide ligand is trigonal planar with a P=O bond length of 1.499(3) Å and a



Scheme 4.



Scheme 5. Postulated mechanism for the complete P≡C bond cleavage via a phospha-alkenyl intermediate **8**. *Fe* = Fe(dppe)$_2$.

P–Re distance of 2.203(1) Å which is shorter than the Re–P(dppe) distances (average of 2.433(1) Å) in accord with the smaller sp^2-hybridised P radius of the ^{t}BuCH$_2$P=O ligand [22].

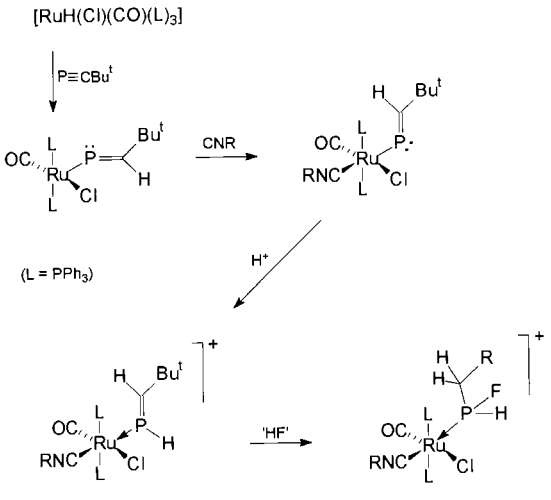
Phosphinidene oxides are rare and highly reactive species and the above reaction provides a novel method for their generation and stabilisation at a transition metal centre. The possibility to extend the method to the formation of other chalcogeno or imido derivatives, RP=X (X = S, Se or NR, respectively) should be further explored.

5. η^2-Phospha-alkyne reactions

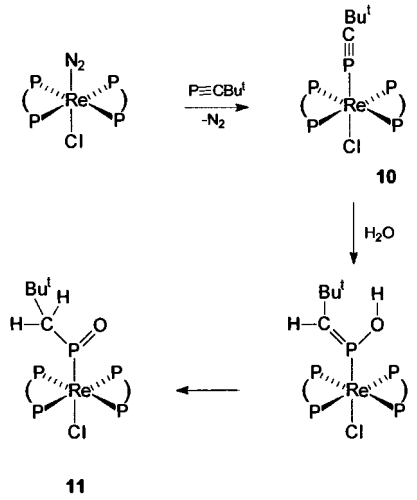
When the steric encumbrance is not sufficient to impose η^1-ligation, the phospha-alkyne ligand binds the metal in the usual η^2-coordination mode [2–4] and presents a different reactivity than that discussed above.

We have observed a rather unusual phospha-alkyne/diazenido (or hydrazido) (P–N) coupling involving two phospha-alkyne molecules and one chelated diazenide (or hydrazide) ligand in the reaction of P≡C^{t}Bu with [ReCl$_2$(NNCOPh)(PPh$_3$)$_2$] in which π-electron delocalization occurs within the chelated ring, thus presenting features of both a benzoyldiazenido(1-) rhenium(III) and a benzoylhydrazido(3-) rhenium(V) species. The reaction with the phospha-alkyne gives, conceivably via an unprecedented template process (Scheme 8), the first η^2-phosphidocarbene complex, [ReCl$_2${η^4-N(NCOPh)-PC^{t}BuPC^{t}Bu}(PPh$_3$)] (**12**), whose molecular structure has been established by a single-crystal X-ray diffraction which also shows some π-delocalisation within the phospha-alkyne and benzoyldiazenido (or benzoylhydrazido)-derived rings [23]. The coupling is surprising in view of the usual stability of the chelating benzoyldiazenido (or benzoylhydrazido) ligand towards electrophilic reagents. No other examples have yet been reported.

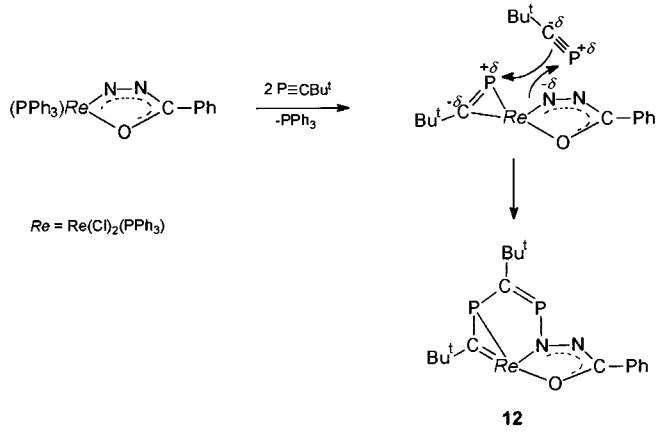
Cyclodimerisation of P≡C^{t}Bu was observed in its reaction with the Rh(I) phosphinic complex [RhCl(triphos)] [triphos = PPh(CH$_2$CH$_2$PPh$_2$)$_2$], in the presence of Tl[BF$_4$] (chloride ligand abstractor), to yield the η^4-1,3-diphosphacyclobutadiene complex [Rh(triphos){η^4-(PC^{t}Bu)$_2$}][BF$_4$] (**13**) (Scheme 9) [24]. The ability of the ring P atoms to bind to other metal centres was tested successfully for {PtCl$_2$(PEt$_3$)} and {W(CO)$_5$}, by reacting **13** with [Pt$_2$Cl$_4$(PEt$_3$)$_2$] or [W(CO)$_5$(THF)], respectively, to form the corresponding diadducts [Rh(triphos) {η^4,η^1-[PtCl$_2$(PEt$_3$)]$_2$-(PC^{t}Bu)$_2$}][BF$_4$] and [Rh(triphos){η^4,η^1-[W(CO)$_5$]$_2$-



Scheme 6.



Scheme 7.



Scheme 8.

$(PC'Bu)_2\}][BF_4]$ [24]. The Pt-monoadduct is obtained upon partial dissociation of the diadduct in CH_2Cl_2 [24].

Cycloaddition reactions of phospha-alkynes at transition metal centres have already been well recognized [2–4,25], leading to a variety of P-containing rings in particular of the η^4-1,3-diphosphacyclobutadiene type at Group 9 metal centres [26,27]. However, in the case of Rh [27e], the yields and the selectivity (a variety of products are usually formed) are normally lower than those exhibited by the above Rh–triphos system.

6. Reactions of alkynes at the same metal centres

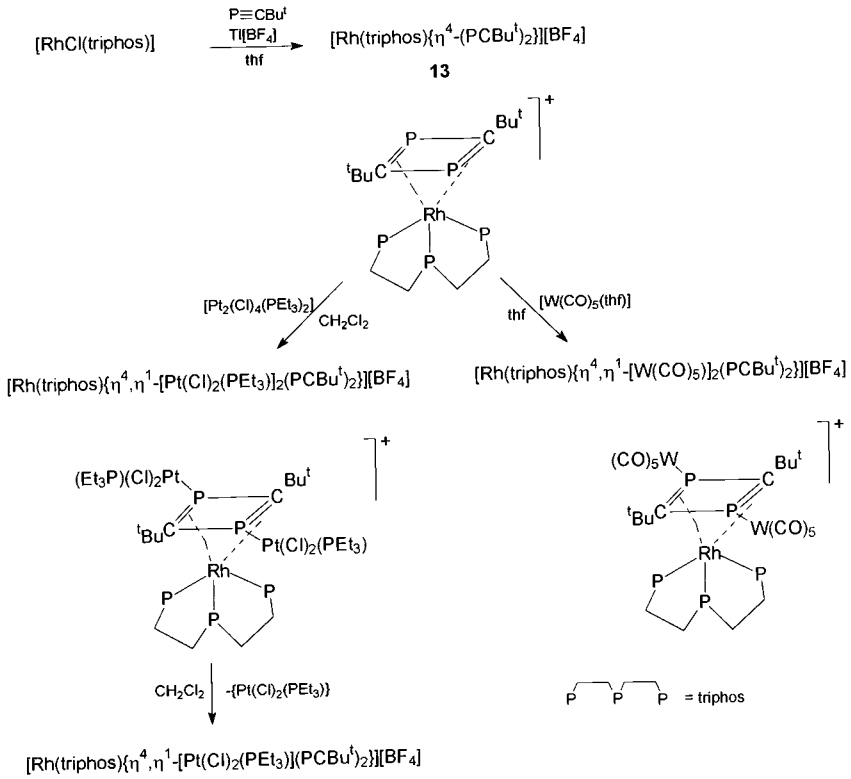
We have also been investigating the reactions of alkynes at electron-rich metal centres and particularly relevant behaviours for comparative purposes with the phospha-alkynes are summarized in Schemes 10–12.

Hence, at the most electron-rich and readily oxidizable $\{M(dppe)_2\}$ (M = Mo or W) centres in *trans*-$[M(N_2)_2(dppe)_2]$ (Scheme 10), C–H oxidative addition reactions of 1-alkynes RC≡CH occur to yield dihydrido–dialkynyl, dialkynyl or trihydrido–alkynyl (for a bulky alkynyl) complexes, i.e. $[MH_2(C{\equiv}CR)_2(dppe)_2]$ (**14**) [28], *trans*-$[M(C{\equiv}CR)_2(dppe)_2]$ (**15**) [28] or $[MoH_3(C{\equiv}C'Bu)(dppe)_2]$ (**16**) [29], respectively, in which the alkynyl ligand is activated towards protonation to form the carbyne or carbene products *trans*-$[WF(\equiv CCH_2R)(dppe)_2]$ (**17**) (R = CO_2Me) [28], *trans*-$[WF(=CHCH_2R)(dppe)_2]^+$ (**18**) (R = Ph) [28] or *trans*-$[MoF(\equiv CCH_2'Bu)(dppe)_2]$ (**19**) (a stable paramagnetic carbyne complex) [30].

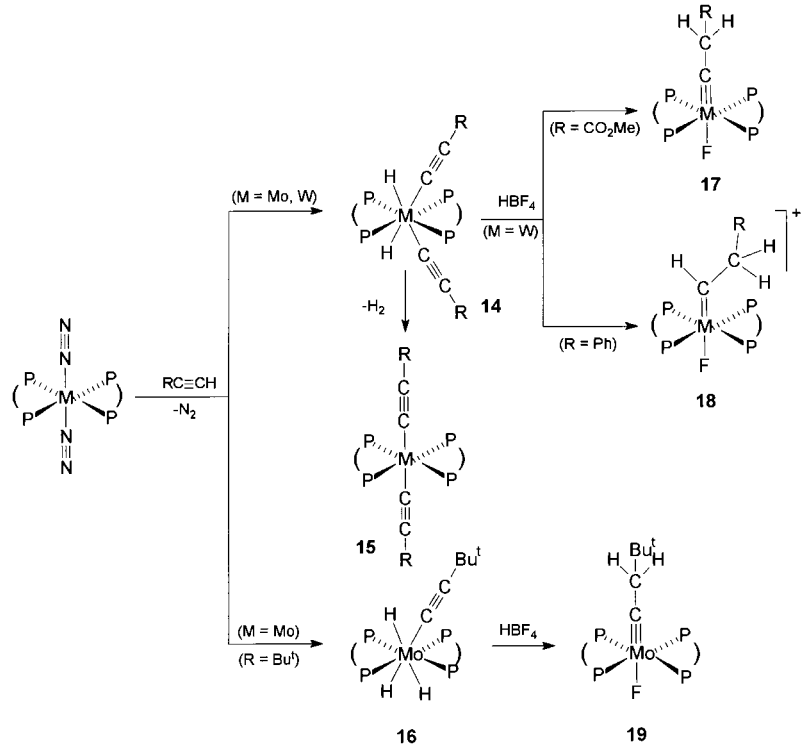
At the $\{ReCl(dppe)_2\}$ metal site, with a not so high electron-richness as the above Mo(0) or W(0) centres, the reactions of RC≡CH or $PhC{\equiv}CCH_3$ (phenyl propyne) with *trans*-$[ReCl(N_2)(dppe)_2]$ proceed (Scheme 11) via 1,2- or 1,3-hydrogen migration, respectively, yielding the vinylidene *trans*-$[ReCl(=C{=}CHR)(dppe)_2]$ (**20**) [31–33] or allene *trans*-$[ReCl(\eta^2\text{-}CH_2{=}C{=}CHPh)(dppe)_2]$ (**21**) [34] complexes which also undergo β-protonation to afford the corresponding carbyne (alkylidyne) *trans*-$[ReX(\equiv CCH_2R)(dppe)_2]^+$ (X = Cl (**22**) or F (**23**)) [31,32,35,36] or η^2-vinyl *trans*-$[ReCl\{C(CH_2)CH_2Ph\}(dppe)_2]^+$ (**24**) [37–39] complexes. The formation of vinylidene complexes via 1,2-H shifts at terminal alkynes is a well-documented reaction [40], as well as their susceptibility to β-protonation and to α-nucleophilic addition.

At the cationic iron(II)-hydride $\{FeH(dppe)_2\}^+$ centre, with a lower electron-richness than the above Mo(0), W(0) or Re(I) ones, methyl propiolate ($HC{\equiv}CCO_2Me$) inserts into the Fe–H bond in its reaction with *trans*-$[FeH(Cl)(dppe)_2]$ in the presence of $Tl[BF_4]$ to yield the vinyl product *cis*-$[Fe(CH{=}CHCOOMe)(dppe)_2][BF_4]$ (**25a**) (Scheme 12a) whose structure was authenticated by X-rays [41]. This alkyne behaviour closely relates to the abovementioned postulated hydrometalation of the phospha-alkyne (Scheme 3b) in its reaction with the same starting hydride complex. The analogous vinyl complex *cis*-$[Fe(CH{=}CHCOOMe)(dmpe)_2]^+$ (**25b**) (dmpe = $Me_2PCH_2CH_2PMe_2$), isolated as the $[BPh_4]^-$ salt, was obtained [42] on treatment of *trans*-$[FeCl_2(dmpe)_2]$ with $HC{\equiv}CCO_2Me$ in the presence of $Na[BH_4]$, conceivably via a hydride intermediate.

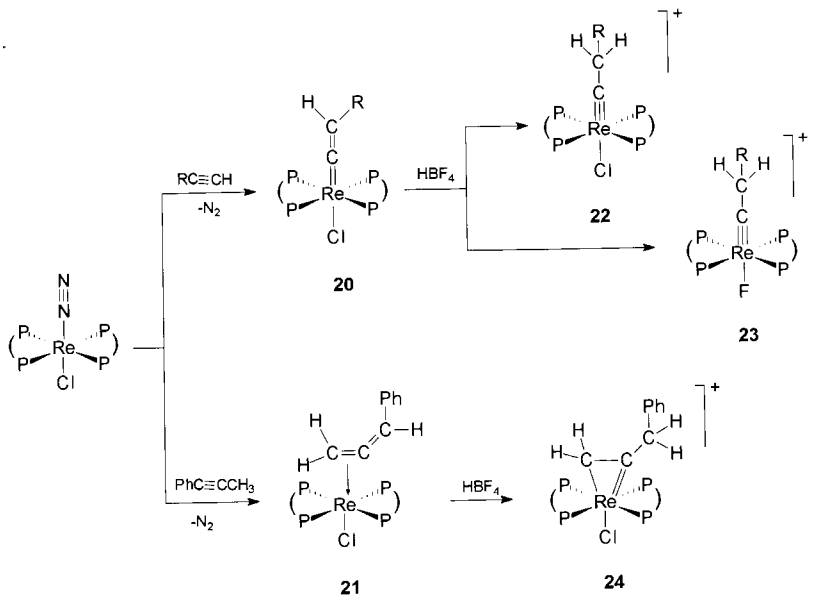
The alkyne-derived alkenyl and vinylidene complexes *trans*-$[FeCl(C{\equiv}CPh)(LL)_2]$ [LL = depe ($Et_2PCH_2CH_2PEt_2$) (**26a**), dmpe (**26b**)] and *trans*-$[FeCl(=C{=}CHPh)(LL)_2]^+$ (LL = depe (**27a**), dmpe (**27b**)), which are interconvertible (by acid–base reaction), have been prepared from the reactions of PhC≡CH with the corresponding *trans*-$[FeCl_2(LL)_2]$ complexes (Scheme 12b) [42], whereas treatment of the dihydrogen complexes *trans*-$[FeH(\eta^2\text{-}H_2)(LL)_2]^+$ with RC≡CH (R = Me, ^{i}Pr or Ph) affords the dialkynyl *trans*-$[Fe(C{\equiv}CR)_2(LL)_2]$ (**28**) complexes which, on protona-



Scheme 9.



Scheme 10.



Scheme 11.

tion, lead to the alkynyl-vinylidene species *trans*-$[Fe(C{\equiv}CR)(=C{=}CHR)(LL)_2]^+$ (**29**) that undergo a coupling process to yield the final butenynyl products $[\overline{Fe(RC{\equiv}C{-}C{=}CHR)}(LL)_2]^+$ (**30**) (Scheme 12c) [43,44]. This acyclic coupling of two alkyne-derived ligands is different from the well established [2–4] (see above) metal-mediated coupling of two phospha-alkyne molecules (cyclodimerisation) which leads to an η^4-1,3-diphosphacyclobutadiene ligand. Although phospha-alkyne coupling has not yet been reported at binding metal centres that induce η^1-ligation of the phospha-alkyne, in view of this coupling of alkyne derivatives it would be worthwhile to attempt their acyclic coupling at such metal sites with potential hydrogen transfer ligands (hydride or dihydrogen).

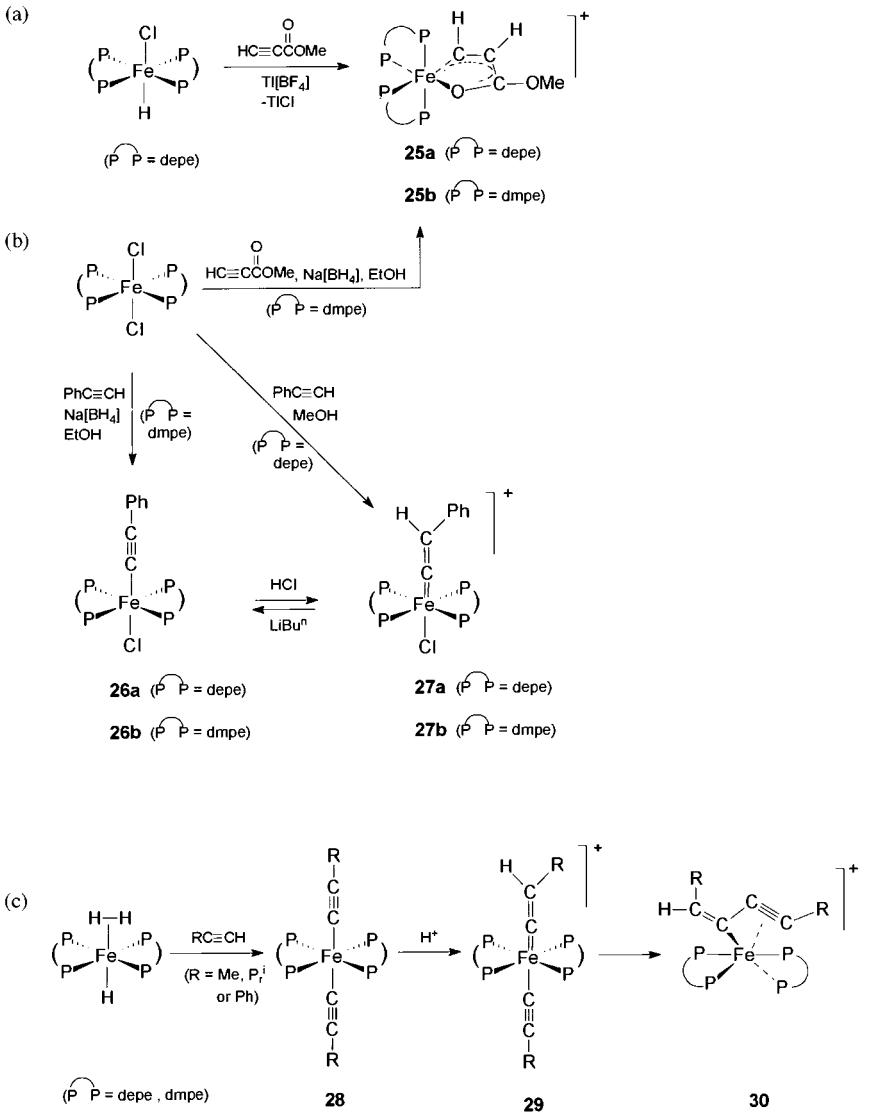
In the above reactions, at electron-rich and sterically hindered metal centres, η^2-RC≡CH complexes have been obtained only rather scantly and the tendency for the formation of end-on (η^1) coordinated derivatives (like alkynyls and vinylidenes), as observed in the case of the phospha-alkyne reactions, is evident. The unfavourable isolation of η^2-alkyne complexes conceivably results not only from steric constrictions at the binding metal site but also from a destabilizing repulsive four-electron d_π(metal)–$\pi_\perp$(alkyne) interaction involving the filled pseudo-t_{2g} set of the d^6 metal atom in the electron-rich binding site [31,33,34,45] which can also constitute a driving force towards the alkyne conversion into another species (e.g. an alkynyl, vinylidene or allene) without such a coordinative destabilisation.

The alkyne-derived ligands are readily activated towards β-electrophilic attack (protonation) as a result of both the extensive π-electron release ability of the metal centre and the capacity of such unsaturated-C ligands to π-acceptance, a behaviour that contrasts with that observed for the weak π-acceptor η^1-phospha-alkyne ligand.

At the less sterically hindered $\{Rh(triphos)\}^+$ centre, alkynes (as phospha-alkynes) can ligate in the η^2-mode and also undergo a cycloaddition reaction [24]. Hence, the products of alkyne cyclotrimerisation, $[Rh(triphos)\{\eta^4\text{-}(HCCR)_3\}][BF_4]$ (**31**) (R = CO_2Me or CO_2Et), are obtained on reaction of HC≡CR with [RhCl(triphos)] in the presence of $Tl[BF_4]$ (Scheme 13) [24]. However, this alkyne behaviour does not follow entirely that observed for the phospha-alkyne (Scheme 9) since no η^4-ligated cyclobutadiene product (which would be the analogous one to the η^4-1,3-diphosphacyclobutadiene **13** complex) was obtained. The preferential formation of the η^4-1,3-diphosphacyclobutadiene ring (product of phospha-alkyne cyclodimerisation) over the cyclobutadiene ring (product of alkyne cyclodimerisation) is known [26a,46] in other metal systems.

7. Concluding remarks

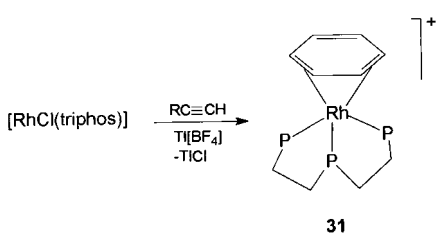
The above-mentioned electron-rich and bulky diphosphinic Mo(0), W(0), Re(I) and Fe(II) centres prefer, on steric grounds, to accept axial linear ligands in the end-on (η^1) coordination rather than in the dihapto mode. In particular, phospha-alkynes bind them in the former and very rare mode, in spite of this being electronically unfavoured in comparison with the latter. In the case of alkynes, the η^2-coordination is both sterically and electronically hampered.



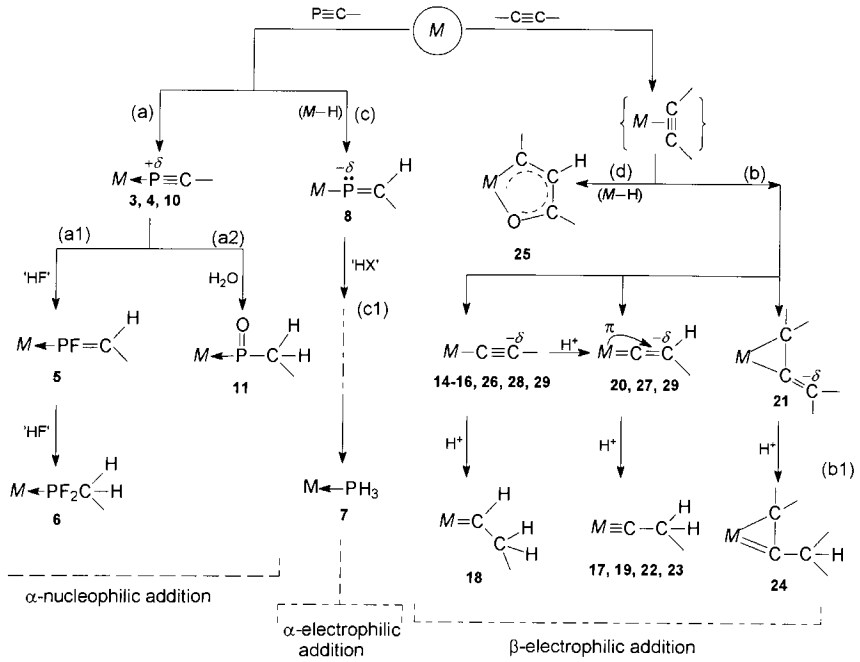
Scheme 12.

Hence, both η^1-phospha-alkynes and η^2-alkynes at such centres are prone to undergo rearrangements or reactions that convert them in coordinatively more stable species (Scheme 14). Since the η^1-P≡CR ligand is *not* an efficient π-electron acceptor, its typical reaction (in complexes **3**, **4** and **10**) consists of the α-nucleophilic addition at the ligated P-atom to form a variety of rare species such as a fluorophospha-alkene (**5**) and a difluorophosphine (**6**) derivative ('HF' as the nucleophile (Scheme 14a1)) or a phosphinidene oxide (**11**) (H_2O as the nucleophile (Scheme 14a2)). The activation to α-nucleophilic attack is well documented for other unsaturated η^1-bonded species such as vinylidenes [40a], nitriles (N≡CR) [47] or isocyanides (C≡NR) [1b,48] when behaving mainly as σ-electron donors (not appreciable π-acceptors) to binding metal centres without a pronounced π-electron release ability. A wide variety of nucleophiles (both protic and aprotic ones) has been successfully applied for these substrates but the extension to phospha-alkynes has not yet been reported. Nevertheless, only short-sized nucleophiles have chances to succeed at the above metal centres in view of the inherent steric constrictions.

In contrast, the unsaturated C-bonded alkyne-derived ligands (vinylidene, allene or alkynyl in complexes **20**, **27**, **29**; **21**; or **14**–**16**, **26**, **28**, **29**, respectively



Scheme 13.



Scheme 14.

(Scheme 14b)) behave as effective π-electron acceptors from the strong π-electron releaser metal centre and are activated towards electrophilic addition (protonation) at the β-C atom which constitutes their typical reaction, leading to a variety of multiple metal–carbon bonded species (carbynes, an η^2-vinyl or a carbene) (in complexes **17**, **19**, **22**, **23**; **24** or **18**, respectively (Scheme 14b1)). Such a type of activation has also been recognized for isocyanides [1a,d,k,49–51], nitriles [1g,j,k,52,53] or dinitrogen [54] when behaving as effective π-electron acceptors from electron-rich binding metal centres, in particular those of Mo(0), W(0) or Re(I) discussed above.

As a result of the α-nucleophilic addition to the η^1-phospha-alkyne or of the β-electrophilic addition to the alkyne-derived species, the unsaturated P=C or C=C bond weakens, but the cleavage of the formers appears to follow a distinct form of reactivity. In fact, the polarity of the P=C bond can be reversed (Scheme 14c) by insertion of the phospha-alkyne into a metal–H bond with resulting development of a nucleophilic character at the P atom (as in complex **8**) which thus becomes susceptible to protonation which is believed to be a key step towards the complete P=C bond rupture (Scheme 14c1). The similar insertion of an alkene into a metal–H bond appears to require the promoting effect of chelation by a second appropriate functional group, as in the derived chelated vinyl–ester complex (**25**) (Scheme 14d).

Both phospha-alkyne and alkyne coupling reactions (cycloadditions) can readily occur at metal centres without sufficient steric hindrance to hamper their dihapto coordination, but with distinct preferences for ring sizes (numbers of coupled molecules). At sterically hindered binding metal centres, in particular with H-ligands, acyclic coupling remains a possibility to be explored.

The results discussed above reflect the versatile coordination chemistry of phospha-alkynes and suggest that, in some cases, it can be related to that of alkynes, although distinctive features are preserved in their behaviours which are determined by a combination of both steric and electronic effects whose full understanding still requires further detailed investigations.

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