The [2 + 2] cycloaddition of alkynes at a Ru–P π-bond†

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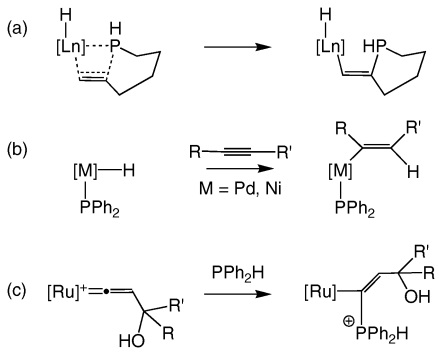
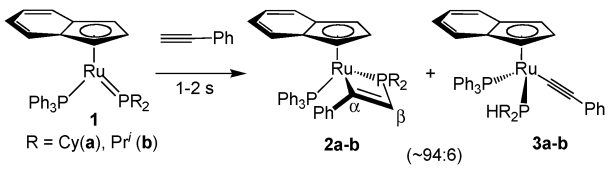
The Ru=P double bond in the 5-coordinate terminal phosphido complex [Ru(η^5-indenyl)(PR$_2$)(PPh$_3$)] undergoes regioselective [2 + 2] cycloaddition with simple and activated alkynes to give metallaphosphacyclobutene complexes. These unusual examples of alkyne insertion into a metal–heteroatom bond represent potentially important intermediates in stereoselective routes to new phosphine reagents and ligands.

Metal-catalyzed addition of the P–H bond in primary or secondary phosphines to alkynes represents a potentially regio- and stereoselective route to important alkenyl phosphine reagents and ligands.[1] Despite the considerable synthetic effort directed toward the development of new chiral phosphine scaffolds, examples of such metal mediated reactions remain quite limited.[2–7] Lanthanide- and calcium-catalyzed intermolecular hydrophosphination of alkynes by PPh$_2$H,[2,3] and intramolecular hydrophosphination of primary alkynyl phosphines,[4] involve insertion of alkyne into the metal–phosphorus bond of a phosphido intermediate (M–PR$_2$), leading to carbon-bound metal phosphine complexes (Scheme 1a). However, such 1,2-insertion of alkynes into a M–P bond has not yet been observed for late metal catalysts. The group 10 metal-catalyzed hydrophosphination of alkynes by PPh$_2$H shows tunable regioselectivity that is rationalized by a mechanism involving alkyne insertion into a M–H bond (Scheme 1b).[5] In this case reductive elimination of a phosphido ligand and the resulting alkenyl ligand is responsible for P–C bond formation. The activity of a series of ruthenium complexes for hydrophosphination of terminal alkynes by PPh$_2$H relies on activation of the alkyne to give a ruthenium vinylidene species that undergoes subsequent nucleophilic attack by free phosphine to form the new P–C bond (Scheme 1c).[6] We recently described [2 + 2] cycloaddition reactions of alkenes at the Ru=PR$_2$ bond of a terminal phosphido ruthenium complex (**1a-b**[8]), and showed that these 1,2-insertion reactions occur *via* a concerted, metathesis-like mechanism.[9] We now report the analogous [2 + 2] cycloaddition reactions of alkynes at **1a-b** to give new phosphametallacyclobutene complexes. These reactions illustrate a new mode of P–C bond formation at late metal centres, and point to new routes to the regio- and stereoselective preparation of alkenyl phosphine reagents and ligands.

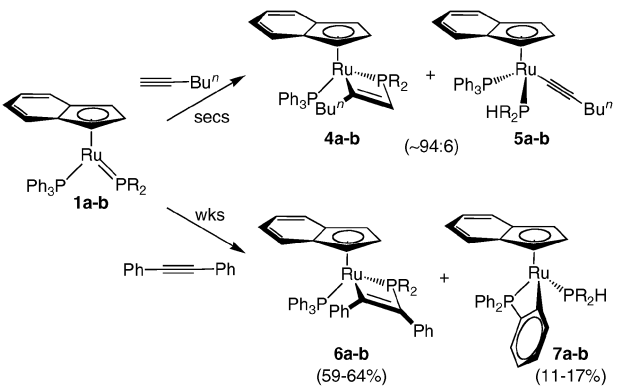


Scheme 1 Examples of metal-catalyzed hydrophosphination of alkynes.

Terminal phosphido complex **1a-b** reacts rapidly and regioselectively with one equivalent of phenylacetylene to give the unusual [2 + 2] cycloaddition product, [Ru(η^5-indenyl)(κ^2-Ph*C*=CH*P*R$_2$)(PPh$_3$)] (**2a-b**, Scheme 2). The phosphametallacyclobutene moiety in **2a-b** shows diagnostic upfield ^{31}P{^{1}H} NMR chemical shifts (−37 ppm (**a**), −27 ppm (**b**)) similar to those previously observed for the four-membered metallacycle in [Ru(η^5-indenyl){κ^2-(*o*-C$_6$H$_4$)PPh$_2$)}(PR$_2$H)] (Scheme 3, **7a-b**).[8b] HSQC NMR for **2a-b** shows ^1J correlations between signals for the distinct olefinic proton on the metallacycle (7.20 ppm (**a**), 7.36 ppm (**b**)) and those due to the β-carbon of the metallacycle (121.2 ppm (**a**), 122.9 ppm (**b**)), which also show large $^1J_{CP}$ coupling (45 Hz (**a**), 44 Hz (**b**)) to



Scheme 2



Scheme 3

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† Electronic supplementary information (ESI) available: PDF with experimental and spectroscopic details. CCDC 765663 and 765664. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c002765k

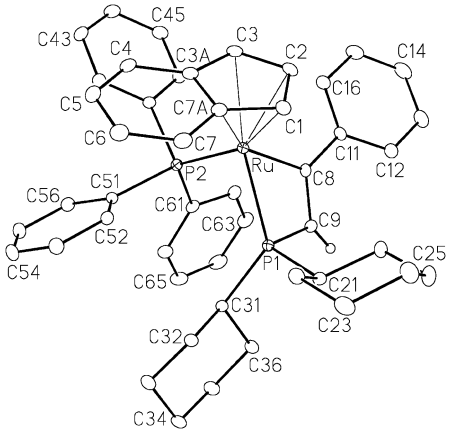

Fig. 1 Molecular structure of **2a**.[15] The hydrogen atom attached to C(9) is shown with arbitrarily small thermal parameters; all other hydrogen atoms are not shown. Selected interatomic distances (Å) and bond angles (°): Ru–P(1) = 2.3323(6), Ru–P(2) = 2.2978(6), Ru–C(8) = 2.065(2), Ru–C* = 1.931, P(1)–C(9) = 1.783(2), C(8)–C(9) = 1.347(3), Δ = 0.12; P(1)–Ru–P(2) = 91.89(2), P(1)–Ru–C(8) = 65.63(6), P(2)–Ru–C(8) = 92.45(6), P(1)–Ru–C* = 135.4, P(2)–Ru–C* = 125.6, C(8)–Ru–C* = 126.9, Ru–P(1)–C(9) = 85.17(7), Ru–C(8)–C(9) = 109.30(15), Ru–C(8)–C(11) = 128.42(15), C(9)–C(8)–C(11) = 122.2(2), P(1)–C(9)–C(8) = 98.80(15).

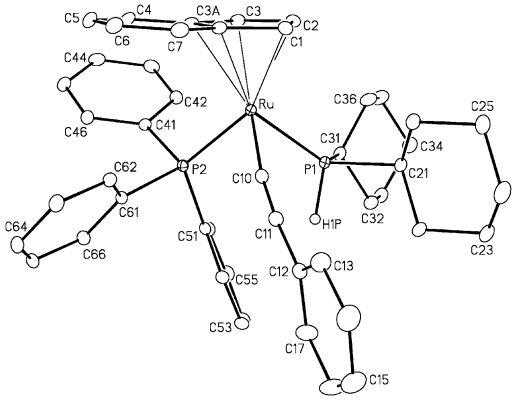

Fig. 2 Molecular structure of **3a**.[15] The hydrogen atom attached to P1 is shown with arbitrarily small thermal parameters; all other hydrogen atoms are not shown. Selected interatomic distances (Å) and bond angles (°): Ru–P(1) = 2.2539(4), Ru–P(2) = 2.2890(4), Ru–C(10) = 2.0143(15), Ru–C* = 1.930, P(1)–H1P = 1.327(18), C(10)–C(11) = 1.219(2), Δ = 0.09; P(1)–Ru–P(2) = 92.553(15), P(1)–Ru–C(10) = 78.79(4), P(2)–Ru–C(10) = 90.46(4), P(1)–Ru–C* = 129.3, P(2)–Ru–C* = 125.6, C(10)–Ru–C* = 126.1, Ru–C(10)–C(11) = 172.82(13), C(10)–C(11)–C(12) = 174.59(17).

the phosphorus contained in the metallacycle and small $^{3}J_{CP}$ coupling (3 Hz (**a**), 2 Hz (**b**)) to the adjacent triphenylphosphine ligand. The ^{13}C signals for the α-carbon (180.3 ppm (**a**), 182.2 ppm (**b**)) show moderate $^{2}J_{CP}$ coupling (25, 15 Hz (**a**); 26, 14 Hz (**b**)) to the two Ru-coordinated phosphorus nuclei.[10] The solid state structure of **2a** (Fig. 1)‡ confirms the regiochemistry of addition, as well as the unsaturated character of the metallacycle: short C(8)–C(9) bond distance (1.347(3) Å) and planarity at the metallated carbon (Σ C(8) ∠ = 359.9°) are observed. The loss of double bond character in the Ru–PCy$_2$ bond is indicated by an increase in the Ru–P(1) bond length in **2a** to 2.3323(6) Å, relative to 2.1589(14) Å in the crystal structure of **1a**.[8b] The small internal bond angle for the metallacycle (P(1)–Ru–C(8) = 65.63(6)°) points to considerable ring strain within this metallacycle.

Along with complex **2a-b**, the reaction of phenylacetylene with **1** consistently produces a small amount of its structural isomer, the alkynyl complex [Ru(C≡CPh)(η^5-indenyl)(PR$_2$H)(PPh$_3$)] (**3a**: 6%; **3b**: 7%), as determined by ^{31}P NMR. The identity of **3a** was confirmed by its independent preparation from the addition of phenylacetylene to [Ru(Cl)(η^5-indenyl)(PCy$_2$H)(PPh$_3$)] in the presence of methanolic KOH.[11] This allowed its characterization by X-ray crystallography (Fig. 2)‡ and solution NMR (ESI†).[12] IR spectroscopy of **3a** showed a strong diagnostic stretch due to the η^1-alkynyl ligand[11] at 2071 cm^{-1} as well as the expected ν_{PH} at 2143 cm^{-1}. The formation of **3a-b** in these reaction mixtures seems reasonable, based on the established P-basicity of **1a-b**,[13] and the relatively high acidity of the terminal proton in phenylacetylene (pK_a(H$_2$O) ≈ 20).[14] The small relative amount of **3a-b** that we observe is interesting: since we have seen no evidence for reversibility of these reactions, we presume that this is a kinetic product distribution, which points to a much higher rate for [2 + 2]-cycloaddition than for deprotonation.

Both simple and internal alkynes also undergo [2 + 2]-cycloaddition reactions with **1a-b**. One equivalent of 1-hexyne adds rapidly and regioselectively to **1a-b** to give [Ru(η^5-indenyl)(κ^2-Bu^n*C*=CH*P*R$_2$)(PPh$_3$)] (**4a-b**, Scheme 3) as the major product, along with a small impurity of the alkynyl isomer, [Ru(C≡CBu^n)(η^5-indenyl)(PR$_2$H)(PPh$_3$)] (**5a-b**), as determined by ^{31}P{^{1}H} NMR. The reaction of one equivalent of diphenylacetylene with **1a-b** was much slower (Scheme 3), but eventually gave up to 64% conversion to the metallacyclic complex [Ru(η^5-indenyl)(κ^2-Ph*C*=CPh*P*R$_2$)(PPh$_3$)] (**6a-b**), as determined by ^{31}P{^{1}H} NMR. As for the terminal alkyne cycloaddition products **2** and **4**, complex **6a-b** showed diagnostic upfield ^{31}P chemical shifts for the phosphorus in the metallacycle (−19 ppm (**a**), −8 ppm (**b**)). However, the longer reaction times resulted in some decomposition to the orthometallated complex **7a-b**,[8b] along with some minor, unidentified by-products.

The formation of phosphametallacyclobutenes **2**, **4**, and **6** is an unusual example of the insertion of alkynes into a well-characterized late M–P bond. It is distinct from the mechanism of P–C bond formation proposed for the lanthanide- and calcium-catalyzed alkyne hydrophosphinations described above, in that this insertion is occurring at a M=PR$_2$ double bond instead of a single bond. In this respect these reactions more closely resemble the observed [2 + 2]-cycloaddition of alkynes at early metal phosphinidene[16] and imido[17] complexes, the latter of which has been shown to be responsible for the N–C bond forming step in the catalytic hydroamination of alkynes by primary amines.[18] Our observation of rapid [2 + 2]-cycloaddition of the electron-rich 1-hexyne, as well as that of the more activated substrate phenylacetylene, suggests that these P–C bond-forming reactions do not rely on a stepwise mechanism involving nucleophilic attack of the basic phosphido ligand at an electrophilic carbon, and this is supported by the high rate of cycloaddition relative to the competing deprotonation of these terminal alkynes. These results, and the much slower rate of cycloaddition we observe

for the internal alkyne diphenylacetylene, are consistent with a possible concerted mechanism, similar to that we observe for the cycloaddition of alkenes at **1a-b**.[9] Further experiments will be required to confirm this and/or to investigate the alternative, conventional migratory insertion, which would require prior coordination of the alkyne ligand at ruthenium.[19] We continue to probe the mechanism of these reactions, to better understand the regioselectivity of the addition of terminal alkynes.

Currently we are investigating conditions allowing cleavage of the Ru–C bond in these metallaphosphacyclobutenes, including putative catalytic hydrophosphination conditions involving excess secondary phosphine and alkyne,[20] and the addition of electrophilic reagents to promote the stoichiometric, stereoselective formation of new alkenyl phosphines. We note also the broader synthetic possibilities that are presented by the α,β-unsaturation in these strained 2-phosphinovinyl metallacycles: addition reactions are envisaged that may allow the systematic elaboration of new tertiary phosphine structures.

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Notes and references

‡ Crystallographic data: yellow crystals of [Ru(η^5-indenyl)-(κ^2-Ph*C*=CH*P*R$_2$)(PPh$_3$)]·0.5C$_6$H$_6$ (**2a**) were obtained *via* slow diffusion of toluene and acetonitrile into a benzene solution of the compound. Crystal data for **2a** (CCDC 765663): $C_{50}H_{53}P_2Ru$, M = 816.93, monoclinic, space group $P2_1/c$ (No. 14), a = 10.1439(9) Å, b = 20.4714(18) Å, c = 19.6785(18) Å, β = 104.5062(14)°, V = 3956.2(6) Å^3, Z = 4, T = 193(1) K, 30 708 reflections measured, 8114 unique (R_{int} = 0.0373) which were used in all calculations, $R_1(F)$ = 0.0302 (6898 reflections with $I \geq 2\sigma(I)$), w$R_2(F^2)$ = 0.0832 (all data). Orange crystals of [Ru(η^5-indenyl)Ru(C≡CPh)(PHCy$_2$)(PPh$_3$)] (**3a**) were obtained *via* slow diffusion of hexanes into a dichloromethane solution of the compound. Crystal data for **3a** (CCDC 765664): $C_{47}H_{50}P_2Ru$, triclinic, space group $P\bar{1}$ (No. 2), a = 9.8234(11) Å, b = 10.0881(11) Å, c = 22.744(2) Å, α = 70.4887(12)°, β = 84.1365 (12)°, γ = 62.9065 (11)°, V = 1888.0 (4) Å^3, Z = 2, T = 173(1) K, 14 796 reflections used in calculations (twinned dataset), $R_1(F)$ = 0.0220 (14 570 reflections with $I \geq 2\sigma(I)$), w$R_2(F^2)$ = 0.0628 (all data).

1 F. Alonso, I. P. Beletskaya and M. Yus, *Chem. Rev.*, 2004, **104**, 3079.
2 K. Takaki, K. Komeyama, D. Kobayashi, T. Kawabata and K. Takehira, *J. Alloys Compd.*, 2006, **408**, 432.
3 M. R. Crimmin, A. G. M. Barrett, M. S. Hill, P. B. Hitchcock and P. A. Procopiou, *Organometallics*, 2007, **26**, 2953.
4 A. M. Kawaoka, M. R. Douglass and T. J. Marks, *Organometallics*, 2003, **22**, 4630.
5 M. A. Kazankova, I. V. Efimova, A. N. Kochetkov, V. V. Afanas'ev, I. P. Beletskaya and P. H. Dixneuf, *Synlett*, 2001, 497.
6 F. Jerome, F. Monnier, H. Lawicka, S. Derien and P. H. Dixneuf, *Chem. Commun.*, 2003, 696.
7 Hydrophosphination strategies to prepare unsaturated phosphine reagents are complemented by efforts to develop metal-catalyzed phosphination of activated vinylic and allylic halides. (*a*) P. Butti, R. Rochat, A. D. Sadow and A. Togni, *Angew. Chem., Int. Ed.*, 2008, **47**, 4878; (*b*) S. R. Gilbertson, Z. Fu and G. W. Starkey, *Tetrahedron Lett.*, 1999, **40**, 8509; (*c*) M. A. Kazankova, E. A. Chirkov, A. N. Kochetkov, I. V. Efimova and I. P. Beletskaya, *Tetrahedron Lett.*, 1999, **40**, 573.
8 (*a*) E. J. Derrah, K. E. Giesbrecht, R. McDonald and L. Rosenberg, *Organometallics*, 2008, **27**, 5025; (*b*) E. J. Derrah, D. A. Pantazis, R. McDonald and L. Rosenberg, *Organometallics*, 2007, **26**, 1473.
9 E. J. Derrah, D. A. Pantazis, R. McDonald and L. Rosenberg, *Angew. Chem., Int. Ed.*, 2010, **49**, 3367.
10 Comparable, downfield ^{13}C chemical shifts for C$_\alpha$ have been observed for other examples of Ru-bound, sp^2 hybridized carbon. In particular, complexes of the generic formula [Ru(η^1-alkenyl)-(η^5-indenyl)L$_2$] (L = tertiary phosphine) show ^{13}C shifts in range ~150–200 ppm, with $^2J_{CP} \approx$ 12–16 Hz. (*a*) M. Bassetti, P. Casellato, M. P. Gamasa, J. Gimeno, C. Gonzalez-Bernardo and B. Martin-Vaca, *Organometallics*, 1997, **16**, 5470; (*b*) V. Cadierno, M. P. Gamasa, J. Gimeno, C. Gonzalez-Bernardo, E. Perez-Carreno and S. Garcia-Granda, *Organometallics*, 2001, **20**, 5177.
11 L. A. Oro, M. A. Ciriano and M. Campo, *J. Organomet. Chem.*, 1985, **289**, 117.
12 Examples of other ruthenium indenyl complexes containing alkynyl ligands: (*a*) M. P. Gamasa, J. Gimeno, B. M. Martinvaca, J. Borge, S. Garciagranda and E. Perezcarreno, *Organometallics*, 1994, **13**, 4045; (*b*) T. Tanase, H. Mochizuki, R. Sato and Y. Yamamoto, *J. Organomet. Chem.*, 1994, **466**, 233; (*c*) V. Cadierno, M. P. Gamasa, J. Gimeno, M. C. Lopez-Gonzalez, J. Borge and S. GarciaGranda, *Organometallics*, 1997, **16**, 4453.
13 Complex **1a-b** rapidly and quantitatively deprotonates acetonitrile (pK_a = 25, R. Stewart, *The Proton: Applications to Organic Chemistry*, Academic Press, Orlando, 1985) to give the secondary phosphine complex [Ru(CH$_2$CN)(η^5-indenyl)(PR$_2$H)(PPh$_3$)] (ref. 8*a*).
14 A. C. Lin, Y. Chiang, D. B. Dahlberg and A. J. Kresge, *J. Am. Chem. Soc.*, 1983, **105**, 5380.
15 Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. C* denotes the centroid of the plane defined by C(7A)–C(1)–C(2)–C(3)–C(3A), and Δ (indenyl slip distortion) is d[Ru–C(7A),C(3A)] − d[Ru–C(1),C(3)].
16 T. L. Breen and D. W. Stephan, *Organometallics*, 1996, **15**, 5729.
17 Examples include: (*a*) A. M. Baranger, P. J. Walsh and R. G. Bergman, *J. Am. Chem. Soc.*, 1993, **115**, 2753; (*b*) E. Blake, D. M. Antonelli, L. M. Henling, W. P. Schaefer, K. I. Hardcastle and J. E. Bercaw, *Organometallics*, 1998, **17**, 718; (*c*) J. L. Polse, R. A. Andersen and R. G. Bergman, *J. Am. Chem. Soc.*, 1998, **120**, 13405; (*d*) B. D. Ward, A. Maisse-Francois, P. Mountford and L. H. Gade, *Chem. Commun.*, 2004, 704.
18 T. E. Muller, K. C. Hultzsch, M. Yus, F. Foubelo and M. Tada, *Chem. Rev.*, 2008, **108**, 3795.
19 The empty coordination site required for alkyne coordination at Ru could arise from loss of planarity at the phosphido ligand, η^5 to η^3 ring-slippage of the indenyl ligand, or dissociation of the triphenylphosphine ligand in **1a-b**. Our previous studies (ref. 8) suggest that adduct formation involving change of the phosphido ligand from a planar, 3e$^-$ donor to a pyramidal, 1e$^-$ donor is too sensitive to the bulk of the incoming donor to allow alkyne coordination. Although hapticity change has been observed for many indenyl complexes, and is commonly invoked to explain associative substitution mechanisms at these complexes, previous studies of the parent complex, [Ru(Cl)(η^5-indenyl)(PPh$_3$)$_2$], indicate that its phosphine substitution reactions proceed dissociatively, with no evidence for formation of η^3-indenyl intermediates, at faster rates than for the corresponding Cp or Cp* derivatives (M. P. Gamasa, J. Gimeno, C. Gonzalez-Bernardo and B. M. Martin-Vaca, *Organometallics*, 1996, **15**, 302). Further control experiments (*e.g.* alkyne addition in the presence of excess PPh$_3$) are required to probe the susceptibility of the triphenylphosphine ligand to substitution by incoming alkyne substrates, although we note that free PPh$_3$ (trace) is observed only in the slow diphenylacetylene reactions.
20 Encouragingly, preliminary experiments show that **2a** is a major ruthenium-containing product formed when catalytic amounts of [Ru(Cl)(η^5-indenyl)(PCy$_2$H)(PPh$_3$)] (the precursor to **1a**) and KOBu^t are added to a 1 : 1 mixture of HPCy$_2$ and PhCCH. However, no free alkenylphosphine hydrophosphination product is observed in this reaction mixture, and we saw no reaction of either excess HPCy$_2$ or excess phenylacetylene with isolated **2a** in separate experiments at RT (see ESI†). More forcing conditions may be required to "turn over" this reaction. Alternatively, the use of less donating and/or bulky substituents at the secondary phosphine may be required. Previous studies have shown that more reactive diaryl (ref. 8*b*) and alkylaryl (G. L. Gibson, *B.Sc. Honour Thesis*, University of Victoria, 2009) analogues of **1a-b** can be generated *in situ*.

