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Reactions of Rh(PNP) pincer complexes with terminal alkynes: homocoupling through a ring or not at all†

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Through use of a bespoke macrocyclic variant, we demonstrate a novel approach for tuning the reactivity of rhodium PNP pincer complexes that enables formation of conjugated enynes from terminal alkynes, rather than vinylidene derivates. This concept is illustrated using *tert*-butylacetylene as the substrate and rationalised by a ring-induced switch in mechanism.

The transition metal-mediated coupling of terminal alkynes into conjugated enynes is an attractive and atom-economic method for the preparation of conjugated enynes.[1,2] Whilst this is a conceptually simple reaction, the formal addition of the C(sp)–H bond of one alkyne across the C≡C bond of another is a process that can and often does result in mixtures of different 1,3-enyne isomers by virtue of head-to-tail (*gem-*) and/or head-to-head coupling (*E-* and *Z-*). In this context, the application of rigid *mer*-tridentate "pincer" ligands is particularly notable, with a number of systems capable of producing one enyne isomer with high fidelity.[3,4] With regards to the work presented herein, the underlying mechanisms of these reactions invoke distinct pathways involving either alkyne insertion into a M–H bond ("hydrometallation") or formation of a metal vinylidene intermediate ("vinylidene"; Scheme 1).[1]

As part of our work exploring the chemistry of phosphine-based pincer complexes of rhodium,[5,6] we recently discovered that reaction of complex **I** with *tert*-butylacetylene resulted in the reversible formation of the vinylidene derivative **II** (Scheme 1).[7] The corresponding alkynyl hydride was not observed, but species of this nature are established intermediates in alkyne/vinylidene tautomerisation reactions of rhodium(I) complexes.[8,9] Whilst this complex is in principle an intermediate in the generation of *t*BuC≡CCHCH*t*Bu *via* the

vinylidene mechanism, in the presence of excess *tert*-butylacetylene we can confirm no homocoupling occurs, even upon prolonged heating at 80 °C in the weakly coordinating solvent 1,2-difluorobenzene (DFB).[10] Having previously noted interesting effects when terminal alkyne coupling reactions are performed through the annulus of a macrocyclic ancillary ligand,[4] we speculated that use of an appropriately designed PNP variant could destabilise the formation of vinylidene derivatives relative to the corresponding alkynyl hydride, and in doing so "switch on" the capacity to promote terminal alkyne homocoupling reactions. We herein present work evaluating this hypothesis using reactive rhodium(I) fragments **1**, featuring PNP pincer ligands with P-donors that are either
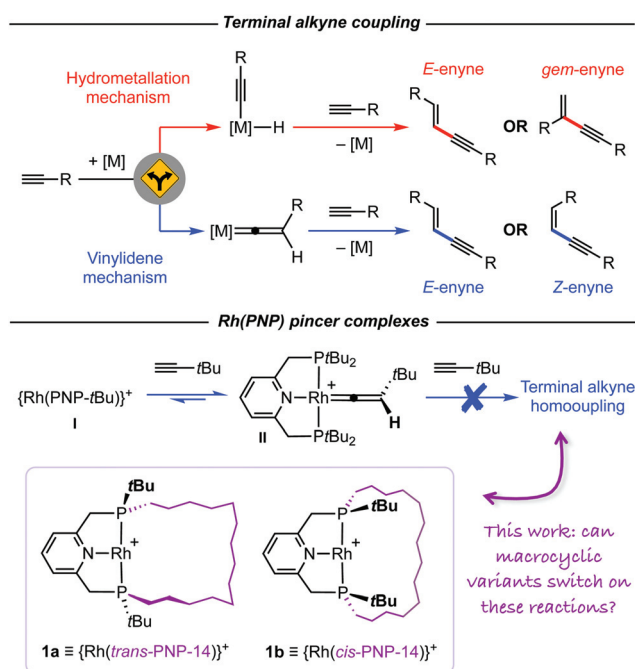
Scheme 1 Terminal alkyne coupling reactions promoted by rhodium pincer complexes.

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trans- or *cis*-substituted with a tetradecamethylene linker (Scheme 1).[5] The linker traverses the coordination plane in **1a**, counteracting formation of a vinylidene derivative, but is skewed to one side in **1b**. The latter therefore represents a strictly isoelectronic control for the former (*vide infra*).

Emulating the method used in the synthesis of **II**, substitution of $[Rh(COD)_2][BAr^F_4]$ (COD = 1,5-cyclooctadiene, Ar^F = 3,5-$(CF_3)_2C_6H_3$) in DFB was chosen to access the organometallic chemistry of the target pincer complexes **1a** and **1b**.[7] Coordination of the macrocyclic pincer ligands is rapid and quantitative at RT, conferring $[Rh(PNP-14)(\eta^2\text{-COD})]^+$ (**1a'** δ_{31P} 57.4, 45.9, $^2J_{PP}$ = 312 Hz, $^1J_{RhP}$ = 131, 138 Hz resp.; **1b'** δ_{31P} 46.8, $^1J_{RhP}$ = 134 Hz) as the exclusive rhodium derivatives in solution by ^1H and ^{31}P NMR spectroscopy. Generation of $[\{Rh(PNP-14)\}_2(\mu_2-\eta^2{:}\eta^2\text{-COD})]^{2+}$ **1''** under equilibrium is also implied, as these dications are ultimately the products obtained upon crystallisation in both cases (see ESI† for solid-state structures). Going forward, generation of **1'** *in situ* proved most expedient and addition of excess HC≡C*t*Bu (2.5 equiv.) at RT afforded the corresponding vinylidene derivatives $[Rh(PNP-14)(CCH\mathit{t}Bu)]^+$ **2** in quantitative spectroscopic yield (Scheme 2), but under disparate timeframes. Complex **2a** was formed within 5 min, but **2b** required 42 h; indicating more strongly bound COD in this case. The formation of **2** are marked by distinctive deep green (**2a**)/blue (**2b**) colours in solu-

tion and exhibit ^{31}P resonances at δ 58.6, 50.8 (**2a**, $^2J_{PP}$ = 312 Hz) and 50.1 (**2b**) that are coupled to ^{103}Rh ($^1J_{RhP}$ = 137–142 Hz). The vinylidene ^{13}C resonances were located in both cases (**2a** δ 323.7; **2b** δ 328.9) and are in good agreement with that of **II** (δ 317.5) and, moreover, other related rhodium precedents.[7,9,11]

In line with the hypothesis, **2a** is characterised by low solution stability and we have so far been unsuccessful in isolating it from solution. In the presence of an excess of terminal alkyne, however, slow conversion into interpenetrated *E*-enyne complex **3a** was observed *in situ* by NMR spectroscopy at RT (Scheme 2). This product was more expediently obtained by heating the reaction at 80 °C for 16 h, isolated in 87% yield, and fully characterised (δ_{31P} 56.6, 51.0, $^2J_{PP}$ = 393 Hz, $^1J_{RhP}$ = 133, 129 Hz resp.; Rh-alkyne, 2.042(5) Å). For comparison, treatment of **1a'** with independently synthesised *E*-*t*BuC≡CCHCH*t*Bu in DFB did not afford **3a**, even upon heating at 80 °C,[12] indicating that it can only result from homocoupling directly through the ring. Emulating **II**, **2b** exhibits excellent solution-phase stability, was readily isolated in the solid state (90%), and showed no onward reaction with terminal alkyne (1.5 equiv.) upon prolonged thermolysis at 80 °C (16 h; Scheme 2). Inspection of the solid-state structure of **2b** corroborates the formation of the vinylidene, with the Rh=C (1.822(6) Å) and C=C bonds (1.319(9) Å) in good agree-
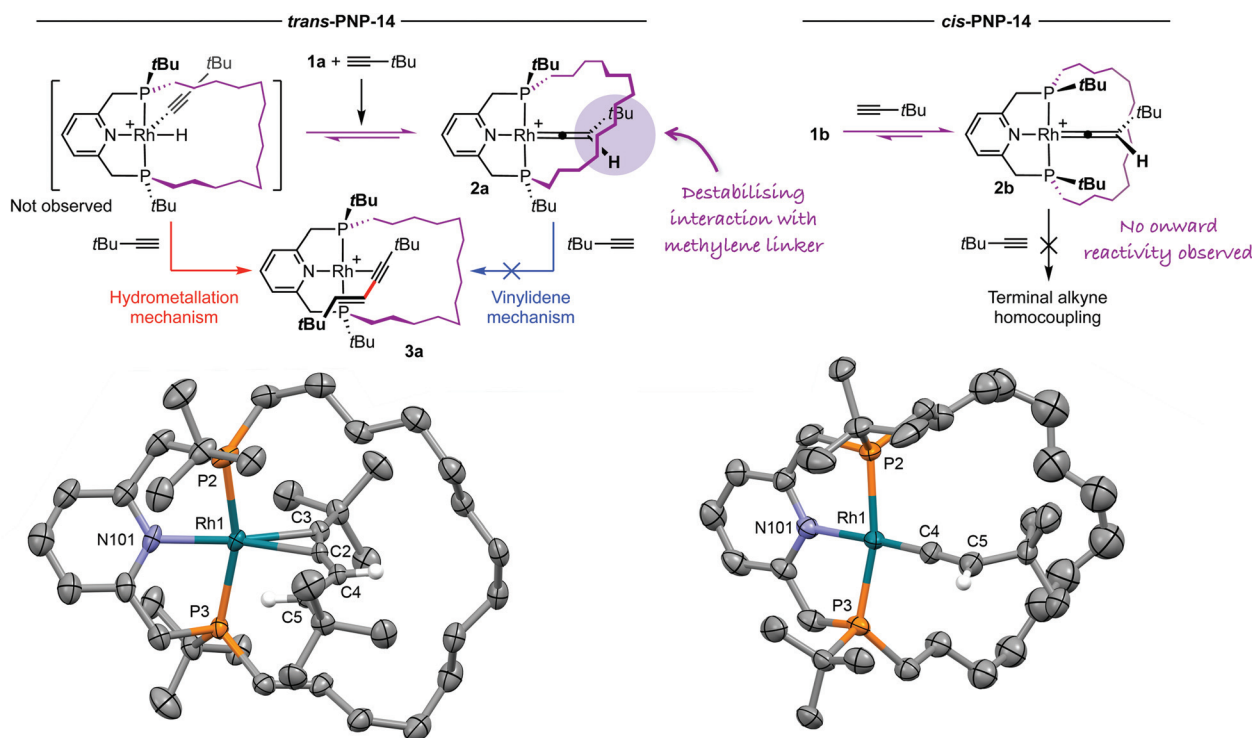
Scheme 2 Terminal alkyne coupling reactions promoted by rhodium pincer complexes. Reactions in DFB at RT unless otherwise stated. Solid-state structures of **3a** (not unique, Z' = 2) and **2b**: thermal ellipsoids drawn at 30% probability, minor disordered components (1 × *t*Bu group, **3a**; methylene chain, **2b**), anions, and most hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): **3a**, Rh1–P2, 2.316(2); Rh1–P3, 2.323(2); Rh1–N101, 2.080(7); P2–Rh1–P3, 161.16(9); Rh1–Cnt(C2,C3), 2.042(5); C2–C3, 1.258(10); C2–C4, 1.431(10); C4–C5, 1.319(10); N101–Rh1–Cnt(C2,C3), 178.6(3); C2–C4–C5, 125.5(7); py-Rh–C≡C twist, 59.6(5); **2b**, Rh1–P2, 2.2801(15); Rh1–P3, 2.2698(14); Rh1–N101, 2.116(5); Rh1–C4, 1.822(6); C4–C5, 1.311(9); C5–C6, 1.491(9); P2–Rh1–P3, 166.73(6); N101–Rh1–C4, 177.8(2); Rh1–C4–C5, 177.5(6); C4–C4–C6, 127.0(7). Cnt = centroid.

ment with those of **II**, and demonstrates the disposition of the methylene strap to one side of the complex; distinctly remote from the vinylidene, with all the RhCCHtBu{$\underline{C}$H$_3$}⋯$\underline{C}$H$_2$ contacts over 4 Å.

To gain deeper insight into the mechanism associated with the formation of **3a**, isotope-labelling experiments were conducted. Heating **2a** with excess DC≡CtBu (10 equiv.) in DFB at 80 °C resulted in extensive D incorporation into both positions of the enyne core of the product (totalling 83% D), indicating that reversible vinylidene formation is fast relative to its onward reactivity (*ca.* 2 × faster). Under the same conditions 54% D incorporation in the vinylidene was observed for **2b**, consistent with slower retro-migration than in **2a**. Supporting this assertion, the irreversible reaction of **2b** with CO forming [Rh(*cis*-PNP-14)(CO)]$^+$ **4b** and liberating HC≡CtBu is appreciably slower than the equivalent reaction of **2a** with CO, which likewise affords [Rh(*trans*-PNP-14)(CO)]$^+$ **4a** and HC≡CtBu.[5] Incidentally, both carbonyl derivatives are characterised by ν(CO) bands at 1997 cm^{-1}, as expected for ligands with equivalent donor properties,[13] and slightly red-shifted to that of [Rh(PNP-tBu)(CO)]$^+$ (1990 cm^{-1}).[5,14]

Based on the observations presented herein – in particular the absence of onward reactivity of **II** and **2b**, requirement for C–C bond formation to occur through the ring, and more facile retro-migration of the vinylidene in **2a** compared to **2b** – the production of **3a** is best reconciled by a hydrometallation mechanism involving steady state formation of a rhodium(III) alkynyl hydride and not a vinylidene mechanism (Scheme 2); as hypothesised. More generally, this work showcases an unconventional approach for tuning the reactivity of pincer ligands[15,16] and provides new insight into how terminal alkyne coupling reactions can be controlled.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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