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

Thomas M. Hood and Adrian B. Chaplin*

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 alkyne 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 tBuC≡CCHtBu 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 alkyne 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.
trans- or cis-substituted with a tetradecamethylene linker (Scheme 1). 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 ionic electronic control for the former (vide infra).

Emulating the method used in the synthesis of 2, substitution of [Rh(COD)2][BARF] (COD = 1,5-cyclooctadiene, ArF = 3,5-(CF3)2C6H3) in DFB was chosen to access the organometallic chemistry of the target pincer complexes 1a and 1b. Coordination of the macrocyclic pincer ligands is rapid and quantitative at RT, conferring [Rh(PNP-14)(η2-COD)]+ (1a) δRh = 57.4, 45.9, JRhP = 134 Hz) as the exclusive rhodium derivatives in solution by 1H and 31P NMR spectroscopy. Generation of [Rh(PNP-14)(η2-COD)]+ (1a)' in situ proved most expedient and addition of excess HC–Bu in DFB did not afford 1a', even upon heating at 80 °C, indicating that it can only result from homocoupling directly through the ring. Emulating 1a, 1b exhibited excellent solution-phase stability, was readily isolated in the solid state (90%), and showed no onward reaction with terminal alkene (1.5 equiv.) upon prolonged thermolysis at 80 °C (16 h; Scheme 2). Inspection of the solid-state structure of 1b corroborates the formation of the vinylidene, with the Rh=C (1.822(6) Å) and C=C bonds (1.319(9) Å) in good agreement.

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 alkene, however, slow conversion into interpenetrated E-enyne complex 3a was observed in situ by NMR spectroscopy at RT (Scheme 2). This product was more expeditiously obtained by heating the reaction at 80 °C for 16 h, isolated in 87% yield, and fully characterised (δRh = 56.6, 51.0, JRhP = 393 Hz, JRh–C = 133, 129 Hz resp.; Rh-alkyne, 2.042(3) Å). For comparison, treatment of 1a with independently synthesised E=C=CHC=C=CH2 in DFB did not afford 3a, even upon heating at 80 °C, indicating that it can only result from homocoupling directly through the ring. Emulating 1a, 1b exhibited excellent solution-phase stability, was readily isolated in the solid state (90%), and showed no onward reaction with terminal alkene (1.5 equiv.) upon prolonged thermolysis at 80 °C (16 h; Scheme 2). Inspection of the solid-state structure of 1b 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 × 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–P1, 161.16(9); Rh1–C(C2,C3), 2.042(5); C2–C3, 1.258(10); C2–C4, 1.431(10); C4–C5, 1.319(10); N101–Rh1–C(C2,C3), 178.6(3); C2–C4–C5, 125.5(7); py–Rh–C(C2,C3) twist, 59.6(5); 2b, Rh1–P2, 2.280(15); Rh1–P3, 2.269(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 RhCCHBu[CH₃]⋯CH₂ 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=C(Bu) (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)] and liberating HC=C(Bu) is appreciably slower than the equivalent reaction of 2a with CO, which likewise affords [Rh(trans-PNP-14)(CO)] and HC=C(Bu).³ 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-Bu)(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(n) 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 ligands¹⁵,¹⁶ and provides new insight into how terminal alkyn coupling reactions can be controlled.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the European Research Council (ERC, grant agreement 637313) and Royal Society (UF100592, UF150675, A. B. C.) for financial support.

Notes and references


12 In this case, a non-interpentated enyne complex is initially formed (δ₁H 44.3, 36.9, δ₁₀₂ = 408 Hz, δ₁₋₁₀₂ = 131, 128 resp.). Extended thermolysis ultimately results in dehydrogenation of the tetradecamethylene linker alongside generation of E,E-isBuCH⁻CH⁻CHBu from transfer hydrogenation of the enyne. Details are provided in the ESL.†

This methodology can also be used to prepare the phosphinite analogue of 3a, \([\text{Rh}\,(\text{trans-PONOP-14})\,(E-t\text{BuC}\equiv\text{CCHCHBu})][\text{BARF}_4]\) \((\delta_{31P}\;204.5,\;194.5,\;^2J_{PP}\;=\;395\;\text{Hz},\;^1J_{RHP}\;=\;140,\;133\;\text{resp.};\;\text{Rh-alkyne},\;2.061(2)\;\text{Å}).\) Details are provided in the ESI.†