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Capture of mechanically interlocked molecules by rhodium-mediated terminal alkyne dimerisation†

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The transition metal-mediated dimerisation of terminal alkynes is an attractive and atom-economic method for preparing conjugated 1,3-enynes. Using a phosphine-based macrocyclic pincer ligand, we demonstrate how this transformation can be extended to the synthesis of novel, hydrocarbon-based interlocked molecules: a rotaxane by 'active' metal template synthesis and a catenane by sequential 'active' and 'passive' metal template procedures.

Introduction

Coordination chemistry is a prominent feature of contemporary methods for constructing mechanically interlocked molecules, such as rotaxanes and catenanes.[1] Active metal template synthesis has emerged as a particularly effective strategy, exploiting a metal to position and covalently fuse the precursor fragments together in an entangled arrangement (Fig. 1A).[2] Whilst this strategy has been successfully implemented using a variety of metal-mediated transformations, the overwhelming majority of examples are based on copper-mediated alkyne–azide cycloaddition reactions (I) or Glaser couplings (II) in combination with bidentate nitrogen-based macrocycles.[2,3]

As part of our work exploring the organometallic chemistry of terminal alkyne dimerisation reactions[4] promoted by macrocyclic pincer complexes (Fig. 1B),[5,6] we speculated that this transformation could be adapted into an active metal template procedure for the preparation of mechanically interlocked 1,3-enynes (III). We herein describe the preparation of hydrocarbon-based rotaxane **1** and catenane **2** derived from the phosphine-based macrocyclic pincer ligand PNP-14 (Fig. 2).[7] Despite the widespread use of phosphine ligands in organo-transition metal chemistry and homogenous catalysis,[8] this constitutes the first application in active metal template synthesis of mechanically interlocked molecules.

Results and discussion

Using a protocol developed previously for rhodium(I) *E*-enyne complex **0** (Fig. 1B),[6,9] rotaxanate **3** and pseudo-rotaxanate **4** were obtained in quantitative spectroscopic yield upon treatment of $[Rh(PNP\text{-}14)(\eta^2\text{-}COD)]^+$ (COD = cyclooctadiene; δ_{31P} 57.4/45.9, $^2J_{PP} = 312$ Hz, $^1J_{RhP} \sim 135$ Hz) with the novel bulky aryl stoppered terminal alkyne $HC{\equiv}C(CH_2)_6C(4\text{-}tBuC_6H_4)_3$ and methylene-spaced ene–yne $HC{\equiv}C(CH_2)_{13}CH{=}CH_2$, respectively, in the weakly coordinating solvent 1,2-difluorobenzene (DFB) at room temperature (Fig. 2).[10] The new rhodium derivatives present ^{1}H NMR resonances at δ 6.95/5.94 (**3**) and 7.01/5.98 (**4**) with $^3J_{HH}$ coupling constants of ~15 Hz that are diagnostic for coordinated *E*-enynes, whilst the C_1 symmetry of the molecules is manifested in the observation of inequivalent ^{31}P NMR resonances at δ 58.6/54.9 (**3**) and 56.9/53.1 (**4**) that are coupled to ^{103}Rh ($^1J_{RhP} = 128$ Hz) and display *trans* $^2J_{PP}$ coupling constants of ~393 Hz.[11] Subsequent treatment of **4** with

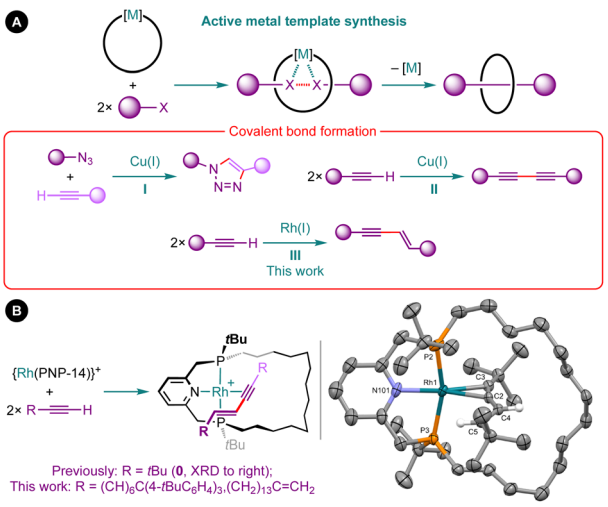

Fig. 1 (A) Active metal template synthesis of interlocked molecules and (B) terminal alkyne dimerisation reactions promoted by macrocyclic rhodium(I) PNP pincer complexes. Solid-state structure of complex **0** shown with thermal ellipsoids drawn at 30% probability and most H-atoms omitted.

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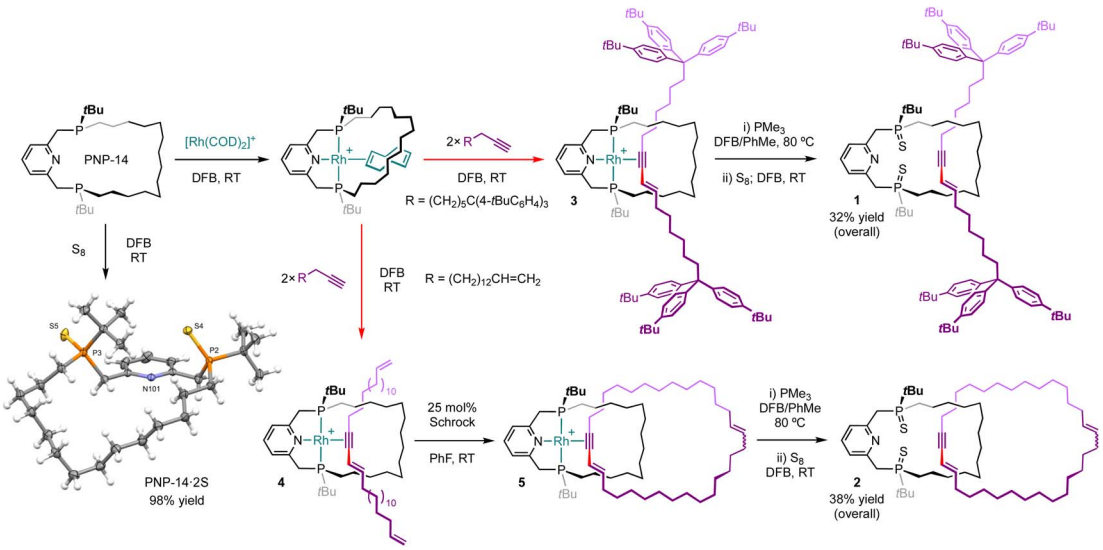

Fig. 2 Synthesis of rotaxane **1** and catenane **2**. $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ counterions omitted for clarity and solid-state structure of PNP-14·2S shown with thermal ellipsoids drawn at 50% probability.

25 mol% Schrock's catalyst (CAS: 139220-25-0) at room temperature enabled capture of catenate **5** by ring closing olefin metathesis, with complete conversion confirmed after monitoring the reaction *in situ* for 5 days at room temperature using ^{1}H and ^{31}P{^{1}H} NMR spectroscopy and (tandem) ESI-MS.

Removal of rhodium from **3** and **5** was achieved by heating with excess PMe_3 (20 equiv.) to give the corresponding rotaxane (**1′**, δ_{31P} 2.42/0.92) and catenane (**2′**, δ_{31P} 1.46/0.78), alongside $[Rh(PMe_3)_4]^+$ as the rhodium-containing by-product.[12] To facilitate isolation, **1′** and **2′** were converted into the corresponding phosphine sulphides **1** and **2** by treatment with S_8 which were thereafter obtained in 32% and 38% overall yield (from PNP-14) following purification on silica. Formation of the new interlocked molecules was corroborated by analysis of isolated materials using NMR spectroscopy and ESI-MS. Threading of the enyne breaks the C_2 symmetry of the macrocycle and this desymmetrisation is evident in both the ^{1}H and ^{31}P{^{1}H} NMR spectra of **1** (δ_{31P} 63.71/63.65) and **2** (δ_{31P} 63.6/63.5), alongside perturbation of the macrocycle resonances relative to independently isolated PNP-14·2S (δ_{31P} 64.7, NMR stack plots provided in the ESI†). The interlocked nature of **1** and **2** was also substantiated by high resolution tandem mass spectrometry experiments,[13] whereby selective fragmentation of the $[M + H]^+$ ions (**1**, 1584.1321, calcd 1584.1339 *m*/*z*; **2**, 982.7566, calcd 982.7549 *m*/*z*) gave the $[M + H]^+$ ion of PNP-14·2S (542.3154/542.3159, calcd 542.3167 *m*/*z*) as the major species in both cases.

Conclusions

These results serve as proof of principle for the application of transition mediated terminal alkyne dimerisation reactions in the synthesis of mechanically interlocked molecules, whilst also demonstrating how phosphine-based functional groups can be integrated into the structure of these intriguing molecules.

Experimental section

All manipulations were performed under an atmosphere of argon using Schlenk and glove box techniques unless otherwise stated. Glassware was oven dried at 150 °C overnight and flame-dried under vacuum prior to use. Molecular sieves were activated by heating at 300 °C *in vacuo* overnight. Fluorobenzene and 1,2-difluorobenzene (DFB) were pre-dried over Al_2O_3, distilled from calcium hydride and dried twice over 3 Å molecular sieves.[10] CD_2Cl_2 was freeze–pump–thaw degassed and dried over 3 Å molecular sieves. THF and dioxane were distilled from sodium/benzophenone and stored over 3 Å molecular sieves. DMSO was freeze–pump–thaw degassed and dried up to five times and finally stored over 3 Å molecular sieves. $SiMe_4$ was distilled from liquid Na/K alloy and stored over a potassium mirror. Other anhydrous solvents were purchased from Acros Organics or Sigma-Aldrich, freeze–pump–thaw degassed and stored over 3 Å molecular sieves. PMe_3 in toluene and 1,6-dibromohexane were freeze–pump–thawed degassed and dried twice over 3 Å molecular sieves before use. Schrock's catalyst (CAS: 139220-25-0) was recrystallised from $SiMe_4$ at −30 °C before use. *n*BuLi was titrated before use.[14] $Br(CH_2)_6C(4\text{-}tBuC_6H_4)_3$,[15] 15-bromo-1-pentadecene,[16] $[Rh(COD)_2][BAr^F{}_4]$,[17] and PNP-14[7] were synthesized according to published procedures. All other reagents are commercial products and were used as received. NMR spectra were recorded on Bruker spectrometers under argon at 298 K unless otherwise stated. Chemical shifts are quoted in ppm and coupling constants in Hz. NMR spectra in DFB were recorded using an internal capillary of C_6D_6. High resolution (HR) ESI-MS and MS/MS were recorded on Bruker Maxis Plus instrument. Microanalysis was performed at the London Metropolitan University by Stephen Boyer.

Preparation of $HC{\equiv}C(CH_2)_6C(4\text{-}tBuC_6H_4)_3$

A suspension of $Br(CH_2)_6C(4\text{-}tBuC_6H_4)_3$ (290 mg, 504 μmol) in DMSO (5 mL) was treated dropwise with THF until

homogeneous. A suspension of HC≡CLi·$H_2N(CH_2)_2NH_2$ (51.0 mg, 554 μmol) in THF (5 mL) was then added and the resulting suspension heated at 130 °C for 48 h. The reaction was quenched by addition of H_2O (2 mL) and the product extracted into CH_2Cl_2 (3 × 5 mL). The combined organic extracts were washed with brine (2 × 10 mL), dried over $MgSO_4$ and then concentrated *in vacuo* to give an oily white solid. Purification using a silica plug (hexane → 1 : 1 hexane : CH_2Cl_2) afforded the product as a white solid. Yield: 220 mg (422 μmol, 84%; mp. 142–143 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (d, $^3J_{HH}$ = 8.4, 6H, *m*-Ar), 7.14 (d, $^3J_{HH}$ = 8.4, 6H, *o*-Ar), 2.48–2.52 (m, 2H, $Ar_3CC\underline{H}_2$), 2.13 (td, $^3J_{HH}$ = 7.1, $^4J_{HH}$ = 2.6, 2H, $C\underline{H}_2C{\equiv}CH$), 1.91 (t, $^4J_{HH}$ = 2.6, 1H, C≡CH), 1.44 (pent, $^3J_{HH}$ = 7.1, 2H, $C\underline{H}_2CH_2C{\equiv}CH$), 1.25–1.36 (m, 4H, 2×$CH_2$), 1.30 (s, 27H, *t*Bu), 1.05–1.12 (m, 2H, CH_2).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 148.2 (s, *t*Bu$\underline{C}$), 145.0 (s, *i*-Ar), 129.0 (s, *o*-Ar), 124.5 (s, *m*-Ar), 84.9 (s, $\underline{C}{\equiv}CH$), 68.2 (s, $C{\equiv}\underline{C}H$), 55.5, (s, $Ar_3\underline{C}$), 40.7 (s, $Ar_3C\underline{C}H_2$), 34.4 (s, *t*Bu{C}), 31.5 (s, *t*Bu{CH_3}), 30.1 (s, CH_2), 28.8 (s, CH_2), 28.7 (s, $\underline{C}H_2CH_2C{\equiv}CH$), 25.7 (s, CH_2), 18.5 (s, $\underline{C}H_2C{\equiv}CH$).

HR ESI-MS (positive ion 4 kV): 559.3684 ($[M + K]^+$, calcd 559.3701) *m*/*z*.

Preparation of $HC{\equiv}C(CH_2)_{13}CH{=}CH_2$

A suspension of 15-bromo-1-pentadecene (1.22 g, 4.24 mmol) and HC≡CLi·$H_2N(CH_2)_2NH_2$ (0.41 g, 4.45 mmol) in 1,4-dioxane-DMSO (10 : 5 mL) was stirred at 120 °C for 16 h. The reaction was quenched by addition of H_2O (15 mL) and product extracted into hexane (3 × 15 mL). The combined organic extracts were washed with brine (2 × 10 mL), dried over $MgSO_4$ and then concentrated *in vacuo* to give an off-white oily wax. The analytically pure compound was obtained as a colourless wax by repeated column chromatography (silica, hexane; R_f = 0.37). Yield: 244 mg (1.04 mmol, 25%; mp. 43–48 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.81 (ddt, $^3J_{HH}$ = 16.9, 10.2, 6.7, 1H, $H_2C{=}C\underline{H}$), 4.99 (ddt, $^3J_{HH}$ = 16.9, $^2J_{HH}$ = 2.2, $^4J_{HH}$ = 1.6, 1H, $\underline{H}_2C{=}CH$), 4.93 (ddt, $^3J_{HH}$ = 10.2, $^2J_{HH}$ = 2.2, $^4J_{HH}$ = 1.3, 1H, $\underline{H}_2C{=}CH$), 2.18 (td, $^3J_{HH}$ = 7.1, $^4J_{HH}$ = 2.6, 2H, $C\underline{H}_2C{\equiv}CH$), 2.01–2.07 (m, 2H, $H_2C{=}CHC\underline{H}_2$), 1.94 (t, $^4J_{HH}$ = 2.6, 1H, $C{\equiv}C\underline{H}$), 1.52 (pent, $^3J_{HH}$ = 7.6, 2H, $C\underline{H}_2CH_2C{\equiv}CH$), 1.33–1.43 (m, 4H, 2×$CH_2$), 1.22–1.33 (m, 16H, 8×$CH_2$).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.4 (s, $H_2C{=}\underline{C}H$), 114.2 (s, $H_2\underline{C}{=}CH$), 85.0 (s, $\underline{C}CH$), 68.2 (s, $C{\equiv}\underline{C}H$), 34.0 (s, $CH_2{=}CH\underline{C}H_2$), 29.80 (s, 2×$CH_2$), 29.76 (s, 2×$CH_2$), 29.7 (s, 2×$CH_2$), 29.31 (s, CH_2), 29.27 (s, CH_2), 29.1 (s, CH_2), 28.9 (s, CH_2), 28.7 (s, CH_2), 18.6 (s, $\underline{C}H_2C{\equiv}CH$).

Anal. calcd for $C_{17}H_{30}$ (234.43 g mol^{-1}): C, 87.10; H, 12.90; N, 0.00. Found: C, 86.99; H, 13.02; N, 0.00.

Preparation of rotaxane 1

A solution of [Rh(PNP-14)(η^2-COD)][BAr^F_4] (8.3 μmol, generated *in situ* from [$Rh(COD)_2$][BAr^F_4] and PNP-14 as previously described[9]) in DFB (0.5 mL) was treated with $HC{\equiv}C(CH_2)_6C(4\text{-}tBuC_6H_4)_3$ (9.5 mg, 18.2 μmol) and stirred at RT for 5 min. Volatiles were removed *in vacuo* to afford **3** as an orange foam upon removal of volatiles. Crude **3** was then dissolved in DFB (330 μL) and treated with a solution of PMe_3 in toluene (170 μL, 1 M, 170 μmol) and the resulting solution heated at 80 °C for 5 days. Volatiles were removed *in vacuo* and the residue extracted with hexane. The resulting orange oil was treated with S_8 (12.6 mg, 49.1 μmol) in DFB (0.5 mL) and stirred at RT for 16 h. Finally, removal of the volatiles *in vacuo* and purification by preparative TLC (silica; 9 : 1 CH_2Cl_2 : MeOH; R_f = 0.4–0.5) afforded the product as a white solid. Yield: 4.2 mg (2.7 μmol, 32%; mp 112 °C).

Data for 3

^{1}H NMR (500 MHz, CD_2Cl_2, selected data): δ 7.76 (t, $^3J_{HH}$ = 7.9, 1H, *p*-py), 7.33 (d, $^3J_{HH}$ = 7.9, 1H, *m*-py), 7.31 (d, $^3J_{HH}$ = 7.9, 1H, *m*-py), 6.95 (dt, $^3J_{HH}$ = 14.6, $^3J_{HH}$ = 6.9, 1H, C≡CCH=C$\underline{H}$), 5.94 (d, $^3J_{HH}$ = 15.3, 1H, C≡C$\underline{C}$H=CH), 1.31 (s, 12H, *t*BuC), 1.30 (s, 38H, *t*BuC), 0.93 (d, $^3J_{PH}$ = 12.3, 9H, P*t*Bu), 0.89 (d, $^3J_{PH}$ = 12.3, 9H, P*t*Bu).

$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 58.6 (dd, $^2J_{PP}$ = 394, $^1J_{RhP}$ = 129, 1P), 54.9 (dd, $^2J_{PP}$ = 394, $^1J_{RhP}$ = 127, 1P).

^{1}H NMR (400 MHz, DFB, selected data): δ 7.55 (t, $^3J_{HH}$ = 8.0, 1H, *p*-py), 5.99 (d, $^3J_{HH}$ = 15.0, 1H, C≡CC$\underline{H}$=CH), 1.12–1.17 (m, 54H, *t*BuC), 0.82–0.89 (m, 18H, P*t*Bu).

$^{31}P\{^1H\}$ NMR (162 MHz, DFB): δ 56.1 (dd, $^2J_{PP}$ = 393, $^1J_{RhP}$ = 129, 1P), 52.5 (dd, $^2J_{PP}$ = 393, $^1J_{RhP}$ = 127, 1P).

Data for 1′

$^{31}P\{^1H\}$ NMR (162 MHz, PhF, selected data): δ 2.42 (s, 1P), 0.92 (s, 1P).

Data for 1

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, $^3J_{HH}$ = 7.6, 1H, *m*-py), 7.41 (t, $^3J_{HH}$ = 7.6, 1H, *p*-py), 7.24 (d, $^3J_{HH}$ = 8.6, 6H, *m*-Ar), 7.23 (d, $^3J_{HH}$ = 8.6, 6H, *m*-Ar), 7.13 (d, $^3J_{HH}$ = 8.3, 12H, 2×*o*-Ar), 7.12 (obscured, 1H, *m*-py), 6.17 (dt, $^2J_{HH}$ = 16.0, $^3J_{HH}$ = 6.9, 1H, C≡CCH=C$\underline{H}$), 5.95 (dt, $^2J_{HH}$ = 16.0, $^4J_{HH}$ = 2.0, 1H, C≡CC$\underline{H}$=CH), 3.84 (app t, $^2J_{PH}$ = $^2J_{HH}$ = 13.9, 1H, py$C\underline{H}_2$), 3.60 (dd, $^2J_{HH}$ = 14.1, $^2J_{PH}$ = 11.1, 1H, py$C\underline{H}_2$), 3.37 (app t, $^2J_{PH}$ = $^2J_{HH}$ = 13.7, 1H, py$C\underline{H}_2$), 3.35 (dd, $^2J_{HH}$ = 13.8, $^2J_{PH}$ = 11.3, 1H, py$C\underline{H}_2$), 2.45–2.53 (m, 4H, 2×$Ar_3CC\underline{H}_2$), 2.18–2.28 (m, 1H, $C\underline{H}_2C{\equiv}CCH{=}CH$), 2.02–2.16 (m, 4H, $C{\equiv}CCH{=}CHC\underline{H}_2$ [δ 2.11, 2H] + PCH_2 [δ 2.08, 1H] + $C\underline{H}_2C{\equiv}CCH{=}CH$ [δ 2.07, 1H]), 1.80–1.94 (m, 5H, CH_2), 1.11–1.68 (m, 34H, CH_2), 1.292 (s, 27H, *t*BuC), 1.290 (s, 27H, *t*BuC), 1.24 (d, $^3J_{PH}$ = 15.6, 18H, 2×P*t*Bu), 0.98–1.11 (m, 4H, 2×$Ar_3CCH_2C\underline{H}_2$).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 153.6 (dd, $^2J_{PC}$ = 6, $^4J_{PC}$ = 1, *o*-py), 153.5 (d, $^2J_{PC}$ = 7, *o*-py), 148.2, (s, *t*Bu$\underline{C}$), 148.1 (s, *t*Bu$\underline{C}$), 145.03 (s, *i*-Ar), 144.97 (s, *i*-Ar), 143.4 (s, $C{\equiv}CCH{=}\underline{C}H$), 135.6 (s, *p*-py), 128.96 (s, *o*-Ar), 128.95 (s, *o*-Ar), 124.53 (s, *m*-Ar), 124.50 (s, *m*-Ar), 123.4 (br, *m*-py), 123.3 (br, *m*-py), 113.3 (s, $C{\equiv}C\underline{C}H{=}CH$), 92.3 (s, $\underline{C}{\equiv}CCH{=}CH$), 82.1 (s, $C{\equiv}\underline{C}CH{=}CH$), 55.43 (s, $Ar_3\underline{C}$), 55.39 (s, $Ar_3\underline{C}$), 40.83 (s, $Ar_3C\underline{C}H_2$), 40.80 (s, $Ar_3C\underline{C}H_2$), 37.1 (d, $^1J_{PC}$ = 42, py$\underline{C}H_2$), 36.3 (d, $^1J_{PC}$ = 41, py$\underline{C}H_2$), 35.3 (d, $^1J_{PC}$ = 47, P*t*Bu{C}), 35.2 (d, $^1J_{PC}$ = 47, P*t*Bu{C}), 34.4 (s, 2×*t*Bu$\underline{C}${C}), 33.3 (s, $C{\equiv}CCH{=}CH\underline{C}H_2$), 31.6 (s, 2×*t*Bu$\underline{C}${$CH_3$}), 31.2 (d, $^2J_{PC}$ = 15, 2×CH_2), 30.8 (s, CH_2), 30.6 (s, CH_2), 28.8–30.0 (m, 12×CH_2), 28.2 (d, $^1J_{PC}$ = 48, PCH_2), 27.7 (d, $^1J_{PC}$ = 47, PCH_2), 26.1 (s,

2×$Ar_3CCH_2\underline{C}H_2$), 25.8 (s, 2×P*t*Bu{$CH_3$}), 23.8 (d, $^3J_{PC}$ = 4, CH_2), 23.2 (d, $^3J_{PC}$ = 4, CH_2), 21.0 (s, $\underline{C}H_2C{\equiv}CCH{=}CH$).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 63.71 (s, 1P), 63.65 (s, 1P).

HR ESI-MS (positive ion, 4 kV): 1584.1321 ($[M + H]^+$, calcd 1584.1339) *m*/*z*.

HR ESI-MS/MS (positive ion; 120 eV @ +1584): 542.3154 ($[PNP\text{-}14{\cdot}2S + H]^+$, calcd 542.3167) *m*/*z*.

Preparation of catenane 2

A solution of [Rh(PNP-14)(η^2-COD)][BAr^F_4] (10.7 μmol, generated *in situ* from [$Rh(COD)_2$][BAr^F_4] and PNP-14 as previously described[9]) in DFB (0.5 mL) was treated with $HC{\equiv}C(CH_2)_{13}CH{=}CH_2$ (194 μL, 116 mM, 22.5 μmol) and stirred at RT for 5 min. Volatiles were removed *in vacuo* to afford **4** as an orange oil. Crude **4** was dissolved in fluorobenzene (10 mL) and treated with 25 mol% Schrock's catalyst in 5 mol% portions (0.4 mg, 0.52 μmol) daily over 5 days and periodically assayed by ESI-MS. Volatiles were removed *in vacuo* to afford **5** as an orange oil. Crude **5** was then dissolved in DFB (300 μL) and treated with a solution of PMe_3 in toluene (200 μL, 1 M, 200 μmol) and the resulting solution heated at 80 °C for 5 days. Volatiles were removed *in vacuo* and the residue extracted with hexane. The resulting orange oil was treated with S_8 (12.6 mg, 49.1 μmol) in DFB (0.5 mL) and stirred at RT for 16 h. Finally, removal of the volatiles *in vacuo* and purification by preparative TLC (silica; 9 : 1 CH_2Cl_2 : MeOH; R_f = 0.4–0.5) afforded the product as a colourless oil. Yield: 3.7 mg (3.8 μmol, 38%).

Data for 4

^1H NMR (500 MHz, CD_2Cl_2, selected data): δ 7.77 (t, $^3J_{HH}$ = 7.8, 1H, *p*-py), 7.36 (overlapping d, $^3J_{HH}$ = 7.9, 2H, *m*-py), 7.01 (dt, $^3J_{HH}$ = 14.6, $^3J_{HH}$ = 6.9, 1H, $C{\equiv}CCH{=}C\underline{H}$), 5.98 (d, $^3J_{HH}$ = 15.3, 1H, $C{\equiv}C\underline{C}H{=}CH$), 5.82 (ddt, $^3J_{HH}$ = 16.8, $^3J_{HH}$ = 9.8, $^3J_{HH}$ = 6.7, 2H, $C\underline{H}{=}CH_2$), 4.98 (d, J_{HH} = 17, 2H, $CH{=}C\underline{H}_2$), 4.91 (d, J_{HH} = 10, 2H, $CH{=}C\underline{H}_2$), 3.37–3.51 (m, 4H, py$C\underline{H}_2$), 0.97 (d, $^3J_{PH}$ = 12.3, 9H, *t*Bu), 0.91 (d, $^3J_{PH}$ = 12.2, 9H, *t*Bu).

$^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 56.9 (dd, $^2J_{PP}$ = 394, $^1J_{RhP}$ = 129, 1P), 53.1 (dd, $^2J_{PP}$ = 394, $^1J_{RhP}$ = 127, 1P).

^1H NMR (400 MHz, DFB, selected data): δ 8.09–8.15 (m, 8H, Ar^F), 7.53 (obscured t, $^3J_{HH}$ = 8.2, p-py), 7.49 (br, 4H, Ar^F), 6.04 (d, $^3J_{HH}$ = 15.4, 1H, $C{\equiv}CC\underline{H}{=}CH$), 5.82 (dt, $^3J_{HH}$ = 15.4, $^3J_{HH}$ = 8.3, $C\underline{H}{=}CH_2$), 4.80–4.98 (m, 2H, $CH{=}C\underline{H}_2$), 0.87 (app t, J_{PH} = 12.8, 18H, *t*Bu).

$^{31}P\{^1H\}$ NMR (121 MHz, DFB): δ 56.5 (dd, $^2J_{PP}$ = 394, $^1J_{RhP}$ = 128, 1P), 52.1 (dd, $^2J_{PP}$ = 394, $^1J_{RhP}$ = 127, 1P).

HR ESI-MS (positive ion, 4 kV): 1048.7587, ($[M]^+$, calcd 1048.7398) *m*/*z*.

Data for 5

^1H NMR (400 MHz, CD_2Cl_2, selected data): δ 7.79 (t, $^3J_{HH}$ = 8.3, 1H, *p*-py), 7.36 (br d, $^3J_{HH}$ = 7.3, 2H, *m*-py), 7.03 (br, 1H, $C{\equiv}CCH{=}C\underline{H}$), 6.00 (d, $^3J_{HH}$ = 16, 1H, $C{\equiv}C\underline{C}H{=}CH$), 5.39 (br, 2H, CH=CH), 3.43 (br, 4H, py$C\underline{H}_2$), 0.98 (d, $^3J_{PH}$ = 11, 9H, P*t*Bu), 0.92 (d, $^3J_{PH}$ = 12, 9H, P*t*Bu).

$^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 56.7 (d, $^2J_{PP}$ = 394, $^1J_{RhP}$ = 129, 1P), 53.3 (d, $^2J_{PP}$ = 393, $^1J_{RhP}$ = 127, 1P).

^1H NMR (400 MHz, DFB, selected data): δ 8.09–8.15 (m, 8H, Ar^F), 7.49 (br, 4H, Ar^F), 6.01 (br d, $^3J_{HH}$ = 14.4, 1H, $C{\equiv}CC\underline{H}{=}CH$), 5.35 (br, 2H, CH=CH), 3.30 (br, 4H, py$C\underline{H}_2$), 0.88 (br d, $^3J_{PH}$ = 12, 9H, *t*Bu), 0.83 (br d, $^3J_{PH}$ = 10, 9H, *t*Bu).

$^{31}P\{^1H\}$ NMR (121 MHz, DFB): δ 56.6 (d, $^2J_{PP}$ = 394, $^1J_{RhP}$ = 129, 1P), 52.5 (d, $^2J_{PP}$ = 393, $^1J_{RhP}$ = 127, 1P).

HR ESI-MS (positive ion, 4 kV): 1020.7092, ($[M]^+$, calcd 1020.7085) *m*/*z*.

HR ESI-MS2 (positive ion, 70 eV @ +1020): 578.2543 ($[\{Rh(PNP\text{-}14)\}\text{-}H_2]^+$, calcd 578.2546) *m*/*z*.

Data for 2′

$^{31}P\{^1H\}$ NMR (162 MHz, DFB, selected data): δ 1.46 (s, 1P), 0.78 (s, 1P).

Data for 2

^1H NMR (500 MHz, $CDCl_3$): δ 7.45–7.54 (m, 2H, py), 7.20 (br d, $^3J_{HH}$ = 5.2, 1H, py), 6.22 (dt, $^3J_{HH}$ = 16.0, $^3J_{HH}$ = 7.0, 1H, $C{\equiv}CCH{=}C\underline{H}$), 5.98 (dt, $^3J_{HH}$ = 16.1, $^4J_{HH}$ = 2.0, 1H, $C{\equiv}CC\underline{H}{=}CH$), 5.36–5.39 (m, 2H, CH=CH), 3.88 (app t, J_{PH} = J_{HH} = 14, 1H, py$C\underline{H}_2$), 3.59–3.69 (m, 1H, CH_2), 3.41 (app t, J_{PH} = J_{HH} = 13, 2H, py$C\underline{H}_2$), 2.04–2.41 (m, 6H, CH_2), 1.89–1.99 (m, 9H, CH_2), 1.38–1.47 (obscured m, ~16H, CH_2), 1.25–1.35 (m, ~65H, CH_2 + P*t*Bu).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 153.5–153.8 (m, py), 143.3 (s, $C{\equiv}CCH{=}\underline{C}H$), 135.7 (s, py), 130.54 (s, CH=CH), 130.46 (s, CH=CH), 123.4 (s, py), 123.3 (s, py), 113.6 (s, $C{\equiv}C\underline{C}H{=}CH$), 92.5 (s, $\underline{C}{\equiv}CCH{=}CH$), 82.1 (s, $C{\equiv}\underline{C}CH{=}CH$), 37.2 (d, $^1J_{PC}$ = 42, py$\underline{C}H_2$), 36.5 (d, $^1J_{PC}$ = 41, py$\underline{C}H_2$), 35.5 (d, $^1J_{PC}$ = 23, P*t*Bu{C}), 35.1 (d, $^1J_{PC}$ = 24, P*t*Bu{C}), 32.8 (s, CH_2), 32.1 (s, CH_2), 32.4 (s, CH_2), 31.2 (s, CH_2), 29.9 (s, CH_2), 29.2–29.8 (m, multiple CH_2), 29.2 (s, CH_2), 29.12 (s, CH_2), 29.09 (s, CH_2), 29.07 (s, CH_2), 28.88 (s, CH_2), 28.86 (s, CH_2), 28.7 (s, CH_2), 28.3 (s, CH_2), 27.9 (s, CH_2), 27.6 (s, CH_2), 25.77 (s, P*t*Bu{CH_3}), 25.75 (s, P*t*Bu{CH_3}), 23.8 (d, $^3J_{PC}$ = 4, CH_2), 23.3 (d, $^3J_{PC}$ = 4, CH_2), 22.9 (s, CH_2), 20.8 (s, CH_2).

$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 63.6 (s, 1P), 63.5 (s, 1P).

HR ESI-MS (positive ion, 4 kV): 982.7566, ($[M + H]^+$, calcd 982.7549) *m*/*z*.

HR ESI-MS2 (positive ion, 60 eV @ +982): 542.3159 ($[PNP\text{-}14{\cdot}2S + H]^+$, calcd 542.3167) *m*/*z*.

Preparation of PNP-14·2S

A solution of PNP-14 (8.5 mg, 17.8 μmol) in DFB (0.5 mL) was treated with S_8 (1.2 mg, 4.68 μmol) and stirred at RT for 16 h. Volatiles were removed, and the resulting residue washed with methanol (2 × 0.5 mL) and then dried *in vacuo* to afford the product as a white microcrystalline solid. Yield: 9.4 mg (17.3 μmol, 97%; mp. 139–140 °C).

^1H NMR (500 MHz, $CDCl_3$): δ 7.59 (t, $^3J_{HH}$ = 7.8, 1H, *p*-py), 7.35 (d app t, $^3J_{HH}$ = 7.8, J_{PH} = 2, 2H, *m*-py), 3.49 (app t, $^2J_{PH}$ = $^2J_{HH}$ = 13, 2H, py$C\underline{H}_2$), 3.43 (app t, $^2J_{PH}$ = $^2J_{HH}$ = 14, 2H, py$C\underline{H}_2$), 1.99–2.10 (m, 2H, PCH_2), 1.68–1.86 (m, 4H, PCH_2 [δ 1.80, 2H] + CH_2), 1.24–1.58 (m, 22H, CH_2), 1.17 (d, $^3J_{PH}$ = 15.9, 18H, *t*Bu).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 153.7 (dd, $^2J_{PC}$ = 8, $^4J_{PC}$ = 2, *o*-py), 136.6 (t, $^4J_{PC}$ = 2, *p*-py), 123.4 (app t, J_{PC} = 3, *m*-py), 38.9

(d, $^{1}J_{PC} = 39$, py$\underline{C}H_2$), 34.8 (d, $^{1}J_{PC} = 47$, *t*Bu{C}), 30.2 (d, $^{2}J_{PC} = 15$, CH_2), 27.9 (s, CH_2), 27.80 (s, CH_2), 27.79 (s, CH_2), 27.7 (s, CH_2), 26.3 (d, $^{1}J_{PC} = 47$, PCH_2), 25.3 (s, *t*Bu{CH_3}), 22.4 (d, $^{3}J_{PC} = 4$, CH_2).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 64.7 (s).

HR ESI-MS (positive ion, 4 kV): 542.3160 ($[M + H]^+$, calcd 542.3167) *m*/*z*.

Conflicts of interest

There are no conflicts to declare.

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