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[Ru₃(6-NHC)(CO)₁₀]: synthesis, characterisation and reactivity of rare 46-electron tri-ruthenium clusters†

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[Ru₃(CO)₁₂] reacts at room temperature with *N*-alkyl substituted 6-membered ring *N*-heterocyclic carbenes (6-NHC) to form [Ru₃(6-NHC)(CO)₁₀] (6-NHC = 6-ⁱPr **1**, 6-Et **2** and 6-Me **4**), rare examples of coordinatively unsaturated (46-electron) ruthenium clusters. Complexes **1**, **2** and **4** have been structurally characterised, along with the tetranuclear ruthenium cluster [Ru₄(6-Et)₂(CO)₁₁] **3** that is formed along with **2**. The degradation of the 6-ⁱPr derivative **1** by pyrimidinium salt elimination helped to explain the poor activity of the complex in the catalytic acylation of pyridine.

Introduction

Despite the unquestionable impact that *N*-heterocyclic carbene (NHC) ligands have had on organometallic chemistry over the last 25 years, their application to low-valent metal cluster chemistry has received only limited attention.¹ However, on the basis of what has been observed, it is clear that combining NHCs with metal clusters frequently leads to very interesting observations. Thus, there are examples in which cluster structure is retained upon reaction with one type of NHC substitution pattern,² but cleaved upon only relatively small changes to either the substituents or reaction stoichiometry.^{3,4} In very recent cases, clusters with unusually high NHC content have been identified as catalyst deactivation products.⁵ Arguably of most interest have been the observations of atypical NHC binding modes,⁶ the detection of unprecedented reaction intermediates⁷ and the formation of multiply activated carbene ligands.^{2b,8}

The group 8 tricarbonyl precursors [M₃(CO)₁₂] (M = Fe,⁹ Ru,^{1b,2,3,6,7} Os)^{1b,2c,7,10,11} have proven to be the most fertile area of cluster chemistry for reaction with NHCs, largely due to their ease of accessibility and the well-known differences in properties that are seen upon descending the group.¹² For example, osmium exhibits a willingness to adopt 46-electron counts in some Os₃ clusters (e.g. [Os₃(CO)₁₀(μ-H)₂]), whereas ruthenium shows a greater tendency to maintain coordinative saturation (*i.e.* 48 electrons) meaning that electron-deficient

Ru₃ systems are not very common.¹³ Indeed, [Ru₃(CO)₁₀(μ-H)₂] has only been generated photchemically¹⁴ and its chemistry explored only to a very limited extent.¹⁵

We¹⁶ (and others)¹⁷ have shown that NHCs with a ring size of >5 can be used to stabilise low coordination numbers in a wide range of mononuclear transition metal complexes, but as far as we are aware, reactions between this class of so-called 'ring-expanded carbenes'¹⁸ and transition metal clusters have not been described.¹⁹ Herein, we report that *N*-alkylated, 6-membered ring NHCs (denoted as 6-NHC) react with [Ru₃(CO)₁₂] at room temperature to afford novel 46-electron Ru₃ clusters of general formula [Ru₃(6-NHC)(CO)₁₀]. Their structures, together with studies of reactivity alongside other Ru₃ clusters in catalytic C–H bond functionalisation, are described.

Results and discussion

Synthesis and characterisation of [Ru₃(6-NHC)(CO)₁₀] (6-NHC = 6-ⁱPr, 6-Et, 6-Me)

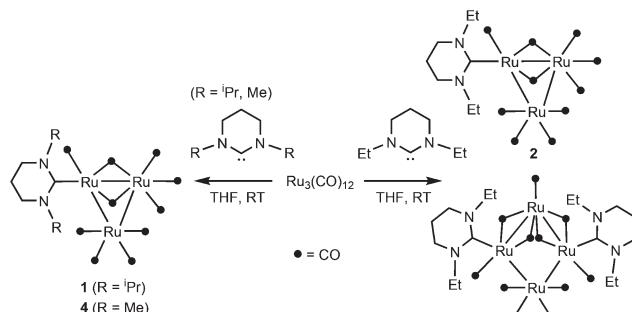
Infra-red analysis of a reaction of 6-ⁱPr and Ru₃(CO)₁₂ (2 : 1 ratio, Scheme 1) in THF showed replacement of the ν(CO) bands, characteristic of the starting material, by a new set of terminal carbonyl stretches between 2084–1963 cm^{−1}, as well as a lower frequency feature at 1802 cm^{−1}, over a period of *ca.* 2.5 days at room temperature. Removal of the solvent, extraction of the red-brown residue into hexane and slow evaporation confirmed that all of the IR bands arose from the formation of a single product, the 46-electron cluster, [Ru₃(6-ⁱPr)(CO)₁₀] (**1**, Scheme 1), which could be isolated as a red crystalline product in 65% yield.²⁰

The X-ray structure of **1** (Fig. 1) revealed an asymmetric arrangement of the three Ru atoms (Ru(1)–Ru(2) 2.7287(2) Å,

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Scheme 1 Summary of the reactivity of $[\text{Ru}_3(\text{CO})_{12}]$ with 6- ^iPr , 6-Me and 6-Et.

$\text{Ru}(1)\text{-Ru}(3)$ 2.8090(2) Å, $\text{Ru}(2)\text{-Ru}(3)$ 2.8815(2) Å, a single 6- ^iPr ligand bound to $\text{Ru}(1)$ ($\text{Ru}(1)\text{-C}(11)$ 2.1178(17) Å) and two asymmetrically bridging CO ligands ($\text{Ru}(1)\text{-C}(2)$ 1.9791(19) Å, $\text{Ru}(2)\text{-C}(2)$ 2.125(2) Å, $\text{Ru}(1)\text{-C}(2)\text{-Ru}(2)$ 83.26(7)°; $\text{Ru}(1)\text{-C}(3)$ 2.0128(19) Å, $\text{Ru}(2)\text{-C}(3)$ 2.118(2) Å, $\text{Ru}(1)\text{-C}(3)\text{-Ru}(2)$ 82.65(7)°) on the $\text{Ru}(1)\text{-Ru}(2)$ edge. The two shorter Ru-C (bridging carbonyl) distances are associated with $\text{Ru}(1)$, which is also bound to the 6- ^iPr ligand; this may result from the carbene exerting less steric pressure than the two carbonyl ligands associated with $\text{Ru}(2)$, or may alternatively reflect a greater electron density on $\text{Ru}(1)$ due to the strongly σ -donating NHC. As anticipated, the carbene ligand lay in the equatorial plane of the Ru_3 core, as is common for the vast majority of nitrogen and phosphorus donor ligands coordinated to Ru_3 triangular clusters, although the dihedral twist between the pyrimidine ring and the Ru_3 core is significantly greater (87.3°) than in either of the 5-membered ring NHC derivatives $[\text{Ru}_3(\text{IMes})(\text{CO})_{11}]$ (37.7°; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene)^{2b} or $[\text{Ru}_3(\text{ab-}^i\text{Bu})(\text{CO})_{11}]$ ^{6a} (9.8°; ab denotes an ‘abnormal’ (or mesionic) ligated NHC,²¹ ^iBu = 1,3-di-*tert*-butylimidazol-2-ylidene). As a consequence, the $\text{N-}^i\text{Pr}$ groups lie in the same plane as the axial carbonyl ligands. The inherent strain of this conformation may be alleviated somewhat by the presence of the μ -CO ligands. The Ru-Ru bond lengths in **1** are reminiscent of the Os-Os bond lengths in $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2]$ where the ‘unsaturated’ dihydrido-bridged bond is substantially shorter, at 2.680(2) Å, than the mean of the other two bonds, at 2.814 Å.²² However, in a series of 48-electron tri-ruthenium clusters containing a ‘ $\text{Ru}(\mu\text{-CO})_2\text{Ru}$ ’ unit, the dicarbonyl-bridged Ru-Ru bond is also shorter than the two unbridged Ru-Ru bonds.²³

Changing to the less bulky 6-Et ligand led to the formation of an analogous product, $[\text{Ru}_3(6\text{-Et})(\text{CO})_{10}]$ (**2**, Scheme 1), albeit in much lower yield. Moreover, the crystallisation of deep red **2** also afforded very small amounts of a second, less intensely coloured product, which upon manual separation, was structurally characterised as the unusual Ru_4 cluster, $[\text{Ru}_4(6\text{-Et})_2(\text{CO})_{11}]$ **3** (Fig. S7†).

The solution IR spectrum of **2** was essentially identical to that of **1**. However, in contrast to the sharp, well-resolved room temperature ^1H NMR spectrum of **1**, the spectrum of **2** comprised of

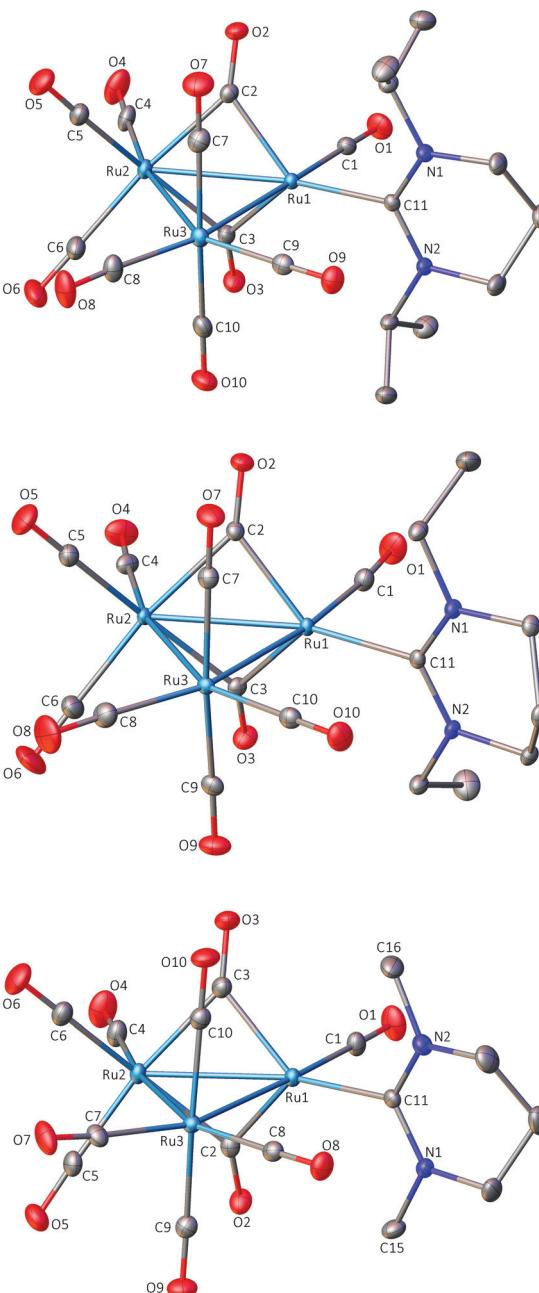


Fig. 1 Molecular structures of **1** (top), **2** (centre) and **4** (bottom). Ellipsoids are shown at 30% probability. The minor disordered component in **3** has been omitted for clarity, as have hydrogen atoms in all cases.

three broad resonances at δ 3.43, 3.27 and 2.07, together with a sharp triplet at δ 1.31. The two higher frequency broad signals resolved into three sharper multiplets (relative integrals of 2 : 2 : 4) for the eight NCH_2 protons upon cooling to 235 K.

The molecular geometry of **2** (Fig. 1) is similar to that of **1** with the dicarbonyl-bridged $\text{Ru}(1)\text{-Ru}(2)$ bond (2.7277(2) Å) being the shortest, while the $\text{Ru}(1)\text{-Ru}(3)$ and $\text{Ru}(2)\text{-Ru}(3)$ distances are 2.8018(2) and 2.8644(3) Å. The $\text{Ru}(1)\text{-C}(11)$ metal-carbene distance is 2.121(2) Å and, as for **1**, the ligand lies close to the equatorial plane of the Ru_3 core. The bridging car-



bonyl ligands display asymmetry ($\text{Ru}(1)\text{-C}(2)$ 1.993(3) Å, $\text{Ru}(2)\text{-C}(2)$ 2.121(2) Å, $\text{Ru}(1)\text{-C}(2)\text{-Ru}(2)$ 83.02(9)°; $\text{Ru}(1)\text{-C}(3)$ 1.985(2) Å, $\text{Ru}(2)\text{-C}(3)$ 2.115(3) Å, $\text{Ru}(1)\text{-C}(3)\text{-Ru}(2)$ 83.36(9)°), again with the shortest Ru-C(bridging carbonyl) distances associated with Ru(1), which is also bound to the carbene ligand.

The N-Me substituted ligand 6-Me behaved similarly to 6-ⁱPr in yielding only the $[\text{Ru}_3(6\text{-NHC})(\text{CO})_{10}]$ product, $[\text{Ru}_3(6\text{-Me})(\text{CO})_{10}]$ **4** (Scheme 1). The carbonyl absorption bands in the IR spectrum of **4** partially merged to give a total of nine bands compared to the eleven bands seen for both **1** and **2**. In the proton NMR spectrum, both the N-Me singlet and NCH_2CH_2 quintet were sharp, while the NCH_2 triplet was noticeably broader, suggestive of fluxionality (*cf.* **2**).

The molecular structure of **4** (Fig. 1) also closely resembles that of **1** and **2** with the three Ru–Ru distances following the same trend ($\text{Ru}(1)\text{-Ru}(2)$ 2.7320(3) Å, $\text{Ru}(1)\text{-Ru}(3)$ 2.8104(3) Å, $\text{Ru}(2)\text{-Ru}(3)$ 2.8688(3) Å), and the same distribution of the carbonyls and the carbene ligand. The asymmetry in the bonding of the two bridging carbonyls is again apparent with the shortest Ru-C(carbonyl) distance being associated with Ru(1) which also has the carbene ligand bonded to it ($\text{Ru}(1)\text{-C}(11)$ (carbene) 2.107(3) Å; $\text{Ru}(1)\text{-C}(2)$ 1.980(3) Å and $\text{Ru}(1)\text{-C}(3)$ 1.996(3) Å for the two carbonyl bonds). By comparison the bridging-carbonyl $\text{Ru}(2)\text{-C}$ bond lengths are 2.128(3) Å ($\text{Ru}(2)\text{-C}(2)$) and 2.113(3) Å ($\text{Ru}(2)\text{-C}(3)$).

Stoichiometric and catalytic reactions of **1** involving CO

The comparatively poor yields of **2** and **4**, as well as the need to manually separate **2** from **3**, led us to use **1** for investigations into the reactivity of the $[\text{Ru}_3(6\text{-NHC})(\text{CO})_{10}]$ complexes. Given the coordinative unsaturation, we were surprised to find that there was no reaction of $[\text{Ru}_3(6\text{-iPr})(\text{CO})_{10}]$ with CO (1 atm in $\text{THF-}d_8$), even upon heating to 80 °C. However, exposure of **1** to 1 atm ¹³CO led to the appearance of a ¹³C enhanced carbonyl signal at δ 200 in the ¹³C{¹H} NMR spectrum at room temperature (Fig. S11†), implying that although $[\text{Ru}_3(6\text{-iPr})(\text{CO})_{10}]$ will not add CO, it can undergo facile CO exchange.²⁴

The stability of **1** to CO led us to test it as a precursor in the catalytic acylation of pyridine (Table 1). Moore and co-workers reported in 1992²⁵ that the insertion of CO and a terminal alkene into the *ortho* C–H position of pyridine was catalysed by $[\text{Ru}_3(\text{CO})_{12}]$ at high pressure (10 atm CO) under forcing conditions (150 °C, 16 h) to give predominantly linear acylation products. In our hands, we were unable to achieve the 65% yield with 1-hexene described by Moore using $[\text{Ru}_3(\text{CO})_{12}]$, achieving instead a more modest 31% average yield.²⁶ Disappointingly, **1** exhibited lower activity than $[\text{Ru}_3(\text{CO})_{12}]$, as did the coordinatively saturated, abnormally bound 5-membered ring NHC clusters, $[\text{Ru}_3(\text{ab-}i\text{Bu})(\text{CO})_{11}]$ ^{6a} and $[\text{Ru}_3(\text{ab-}i\text{Ad})(\text{CO})_{11}]$ (*i*Ad = 1,3-bis(adamantyl)imidazol-2-ylidene).^{6b}

Degradation of **1** through loss of $[6\text{-iPrH}]^+$ and 6-ⁱPr

In an effort to rationalise the poor catalytic activity, **1** was heated in the presence of 4 equiv. pyridine in an NMR tube scale reaction. Warming to 85 °C brought about loss of the ¹H

Table 1 Ru_3 cluster catalysed acylation of pyridine^a

Ru precursor	Product yield ^b (%)
$[\text{Ru}_3(\text{CO})_{12}]$	31
1	12
$[\text{Ru}_3(\text{ab-}i\text{Bu})(\text{CO})_{11}]$	23
$[\text{Ru}_3(\text{ab-}i\text{Ad})(\text{CO})_{11}]$	6

^a Reaction conditions: Ru_3 precursor (0.026 mmol), 1-hexene (0.25 mL), pyridine (7.5 mL), CO (10 atm), 150 °C, 16 h. ^b Yields (average of at least two runs) determined by integration of ¹H NMR product resonances at δ 3.22 and/or δ 1.74 (linear product)²⁵ and δ 4.1 (branched product)²⁵ versus the OMe resonance of $2,4,6\text{-}(\text{MeO})_3\text{C}_6\text{H}_3$ as an internal standard.

NMR resonances of **1** and appearance of signals due to the pyridinium cation $[6\text{-}i\text{PrH}]^+$.²⁷ The presence of low frequency proton signals at δ –15.5 and δ –19.2 suggested that this was partnered with anionic ruthenium carbonyl hydride species and, indeed, an X-ray study of a small number of orange-yellow crystals isolated from the reaction yielded a structure of $[6\text{-}i\text{PrH}]_2[\text{Ru}_4(\text{CO})_{12}\text{H}_2]$ (Fig. S14†).²⁸ The di-potassium salt of $[\text{Ru}_4(\text{CO})_{12}\text{H}_2]^{2-}$ has a hydride chemical shift of δ –19.3.²⁹

A likely pathway to $[6\text{-}i\text{PrH}]^+$ formation involves C–H activation of pyridine by **1**,^{23a,30} followed by reductive elimination from a resulting $\{6\text{-}i\text{Pr}\}\text{RuH}$ moiety. Support for reductive elimination from such a species came upon reacting **1** with H_2 at 60 °C ($\text{THF-}d_8$), which again generated pyrimidinium proton NMR signals, together with hydride signals at δ –12.1 and –12.5, in <1 h.

Further evidence for the low stability of the $[\text{Ru}_3(6\text{-NHC})(\text{CO})_{10}]$ complexes comes from the reaction of **1** with phosphines, where we found that **1** reacted with 1–3 equiv. PPh_3 at 60 °C with complete loss of the starting material and the formation of multiple phosphorus containing species. Efforts to characterise the product mixture led to isolation of just the known phosphine carbonyl cluster, $[\text{Ru}_3(\text{PPh}_3)_3(\text{CO})_6]$ (Fig. S18†),³¹ indicating that **1** also appears to be susceptible to loss of free carbene under quite mild conditions.

Conclusions

The synthesis and structural characterisation of rare examples of 46-electron tri-ruthenium clusters has been achieved upon reacting $[\text{Ru}_3(\text{CO})_{12}]$ with *N*-alkyl substituted, 6-membered ring N-heterocyclic carbenes under very mild conditions. Reactivity studies of the $[\text{Ru}_3(6\text{-NHC})(\text{CO})_{10}]$ complexes carried out using the 6-ⁱPr derivative **1** indicated that loss of the carbene ligand took place upon addition of PPh_3 , mild heating under H_2 or in the presence of pyridine, thereby limiting the potential of these complexes in catalytic applications.

The formation of very different products in the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with 6-NHCs to those formed with 5-membered



ring analogues is notable,^{1b} suggesting that (i) investigations with 6- and/or 7-membered ring NHCs bearing, for example, *N*-aryl substituents, and/or (ii) the use of other group 8 carbonyl clusters as precursors, is worthy of investigation.

Experimental

All manipulations were carried out using standard Schlenk, high vacuum and glovebox techniques using dried and degassed solvents. NMR spectra were recorded on a Bruker Avance 500 and 400 MHz NMR spectrometers and run in THF-*d*₈ (referenced to δ 3.58 (¹H) and δ 67.6 (¹³C)). IR spectra were recorded in hexane solution on a Nicolet Nexus spectrometer. Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon, UK. [Ru₃(CO)₁₂] (Sigma Aldrich) was used as received, while the [PF₆]⁻ salts of [6-ⁱPrH]⁺, [6-EtH]⁺ and [6-MeH]⁺ were prepared according to the literature.³²

[Ru₃(6-ⁱPr)(CO)₁₀]¹

[6-ⁱPrH][PF₆] (108 mg, 0.34 mmol) and KHMDS (66 mg, 0.33 mmol) were stirred in THF for 1 h in a J. Young's resealable ampoule. The suspension was then reduced to dryness, [Ru₃(CO)₁₂] (110 mg, 0.17 mmol) added and the mixture redissolved in THF (6 mL). After stirring at room temperature for 3–4 days, the solvent was removed and the residue extracted exhaustively with warm hexane (4 \times 25 mL). The hexane was removed under vacuum and the residue allowed to slowly evaporate in an argon-filled glovebox from *ca.* 2 mL hexane/THF (90 : 10) to afford deep-red crystalline **1**. Yield 84 mg, 65%. ¹H NMR (500 MHz, 298 K): δ = 3.59 (sept, 2H, ³J_{HH} = 6.50 Hz, CHMe₂), 3.40 (m, 2H, NCH₂), 3.18 (m, 2H, NCH₂), 2.11 (m, NCH₂CHH, 1H), 1.88 (m, 1H, NCH₂CHH), 1.36 (d, 6H, ³J_{HH} = 6.50 Hz, CHMe₂), 1.21 (d, 6H, ³J_{HH} = 6.50 Hz, CHMe₂). ¹³C{¹H} NMR (101 MHz, 298 K): δ = 198.7 (s, Ru-C_{NHC}), 57.5 (s, NCHMe₂), 40.6 (s, NCH₂), 21.6 (s, NCH₂CH₂), 20.6 (s, CHMe₂), 20.0 (s, CHMe₂). IR (cm⁻¹): 2084, 2061, 2041, 2031, 2022, 2009, 2001, 1984, 1976, 1963, 1802 (all ν_{CO}). Analysis found: C, 31.96; H, 2.68; N, 3.73. C₂₀H₂₀N₂O₁₀Ru₃ requires: C, 31.92; H, 2.77; N, 3.60.

[Ru₃(6-Et)(CO)₁₀]² and [Ru₄(6-Et)₂(CO)₁₁]³ **3**

As for **1** but with [6-EtH][PF₆] (100 mg, 0.35 mmol), KHMDS (69 mg, 0.35 mmol) and [Ru₃(CO)₁₂] (111 mg, 0.17 mmol). Combined yield of **2** and **3**: 24 mg. Selected spectroscopic data for **2**. ¹H NMR (500 MHz, 235 K): δ = 3.47 (m, 2H, NCH₂CH₃), 3.39 (m, 2H, NCH₂CH₃), 3.26 (m, 4H, NCH₂CH₃), 2.07 (m, 2H, NCH₂CH₂), 1.31 (t, 6H, ³J_{HH} = 6.99 Hz, NCH₂CH₃). ¹³C{¹H} NMR (126 MHz, 235 K): δ 206.1 (s), 201.0 (s), 199.1 (s), 198.2 (s), 189.5 (s), 186.8 (s), 52.5 (s, NCH₂), 45.1 (s, NCH₂), 20.9 (s, NCH₂CH₂), 13.9 (s, CH₂CH₃). IR (cm⁻¹): 2085, 2061, 2042, 2031, 2022, 2009, 2002, 1984, 1977, 1964, 1803 (all ν_{CO}). Analysis found: C, 30.01; H, 2.20; N, 3.93. C₁₈H₁₆N₂O₁₀Ru₃ requires: C, 29.87; H, 2.23; N, 3.87. Only a few single crystals of

3 could be isolated, restricting characterisation to just an X-ray crystal structure (Fig. S7†).

[Ru₃(6-Me)(CO)₁₀]⁴

As for **1** but with [6-MeH][PF₆] (60 mg, 0.23 mmol), KHMDS (46 mg, 0.23 mmol) and [Ru₃(CO)₁₂] (75 mg, 0.12 mmol) to afford deep-red crystals of **4**. Yield 16 mg, 20%. ¹H NMR (500 MHz, 298 K): δ = 3.32 (br t, 4H, ³J_{HH} = 4.8 Hz, NCH₂), 3.14 (s, 6H, NMe), 2.09 (quint, 2H, ³J_{HH} = 6.0 Hz, NCH₂CH₂). ¹³C{¹H} NMR (101 MHz, 298 K): δ = 202.7 (s, Ru-C_{NHC}), 47.5 (s, NCH₂), 43.9 (s, NMe), 21.1 (s, NCH₂CH₂). IR (cm⁻¹): 2086, 2061, 2043, 2023, 2010, 2003, 1981, 1962, 1806 (all ν_{CO}). Analysis found: C, 28.02; H, 1.66; N, 3.82. C₁₆H₁₂N₂O₁₀Ru₃ requires: C, 27.63; H, 1.74; N, 4.03.

Reactivity studies of **1**

(a) *with C₅H₅N*: **1** (17.1 mg, 0.023 mmol) was combined with pyridine (7.5 μ L, 0.093 mmol) in THF-*d*₈ in a J. Young's resealable NMR tube and the reaction followed by ¹H NMR spectroscopy. (b) *with H₂*: **1** (11.1 mg, 0.015 mmol) was dissolved in THF-*d*₈ in a J. Young's resealable NMR tube, the solution freeze-pump-thaw degassed (\times 3), placed under 1 atm H₂ and the reaction followed by ¹H NMR spectroscopy. (c) *with PPh₃*: **1** (6.5 mg, 0.009 mmol) was combined with 3 equiv. PPh₃ (6.8 mg, 0.026 mmol) in THF-*d*₈ in a J. Young's resealable NMR tube and the reaction followed by ¹H and ³¹P NMR spectroscopy.

Catalysis

Solid samples of Ru₃ precursors (0.0265 mmol), together with 2,4,6-(MeO)₃C₆H₃ (0.0265 mmol) as an internal standard, were weighed into a Parr autoclave inside a glovebox. A solution of 1-hexene (2 mmol) in pyridine (7.5 mL, dried over activated 3 Å molecular sieves) was added by cannula, and the autoclave assembly put together under a flow of argon. After purging twice with CO, the autoclave was pressurised to 10 atm and heated at 150 °C for 16 h. After cooling and depressurising, a small amount of the red-orange solution was diluted with CDCl₃ and analysed by ¹H NMR spectroscopy. Product resonances were assigned by comparison to the literature.²⁵

X-ray crystallography

Data for **1** were collected on a Nonius kappaCCD diffractometer using Mo-K α radiation, while those for **2**, **3** (ESI†) and **4** were obtained using a Cu-K α source and an Agilent SuperNova instrument. Refinements, achieved using SHELXL³³ via Olex2,³⁴ were relatively straightforward and only points of note are mentioned hereafter. In **3** (ESI†), C22 was refined subject to taking 75 : 25 disorder with C22A into account. Meanwhile, the asymmetric unit in **4** was seen to comprise 2 molecules, which differ in the relative orientation of the apical carbene–carbon atoms within the respective molecules to which they belong.

Crystallographic data for all compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1559943 (1), 1559944 (2), 1559945



(3, ESI), 1559946 (4), 1816567 ($[6\text{-}^{\text{i}}\text{PrH}]_2[\text{Ru}_4(\text{CO})_{12}\text{H}_2]$, ESI) and 1816568 ($[\text{Ru}_3(\text{PPh}_3)_3(\text{CO})_9]$, ESI) respectively.[†]

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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