ROYAL SOCIETY OF CHEMISTRY

PAPER

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

Charles E. Ellul, John P. Lowe, Mary F. Mahon, Paul R. Raithby (ID) * and Michael K. Whittlesey (ID) *

$[Ru_3(CO)_{12}]$ reacts at room temperature with *N*-alkyl substituted 6-membered ring N-heterocyclic carbenes (6-NHC) to form $[Ru_3(6\text{-NHC})(CO)_{10}]$ (6-NHC = 6-^{i}Pr **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 $[Ru_4(6\text{-Et})_2(CO)_{11}]$ **3** that is formed along with **2**. The degradation of the 6-^{i}Pr 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 intermediates[7] and the formation of multiply activated carbene ligands.[2b,8]

The group 8 tricarbonyl precursors $[M_3(CO)_{12}]$ (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.* $[Os_3(CO)_{10}(\mu\text{-H})_2]$), 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, $[Ru_3(CO)_{10}(\mu\text{-H})_2]$ has only been generated photochemically[14] and its chemistry explored only to a very limited extent.[15]

We[16] (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 $[Ru_3(CO)_{12}]$ at room temperature to afford novel 46-electron Ru₃ clusters of general formula $[Ru_3(6\text{-NHC})(CO)_{10}]$. 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 = 6ᶦPr, 6-Et, 6-Me)

Infra-red analysis of a reaction of 6-^{i}Pr and $Ru_3(CO)_{12}$ (2 : 1 ratio, Scheme 1) in THF showed replacement of the $\nu(CO)$ 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, $[Ru_3(6\text{-}^iPr)(CO)_{10}]$ (**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,

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK.
E-mail: m.k.whittlesey@bath.ac.uk
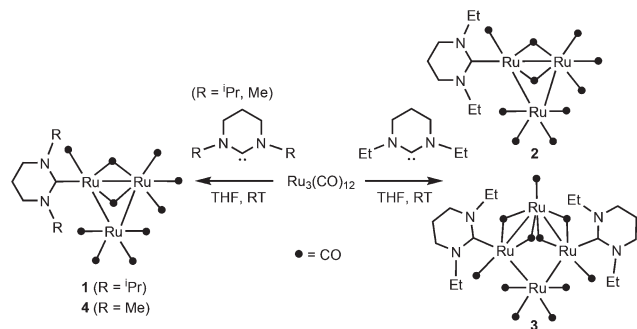
Scheme 1 Summary of the reactivity of [Ru₃(CO)₁₂] with 6-ⁱPr, 6-Me and 6-Et.

Ru(1)–Ru(3) 2.8090(2) Å, Ru(2)–Ru(3) 2.8815(2) Å), a single 6-ⁱPr ligand bound to Ru(1) (Ru(1)–C(11) 2.1178(17) Å) and two asymmetrically bridging CO ligands (Ru(1)–C(2) 1.9791(19) Å, Ru(2)–C(2) 2.125(2) Å, Ru(1)–C(2)–Ru(2) 83.26(7)°; Ru(1)–C(3) 2.0128(19) Å, Ru(2)–C(3) 2.118(2) Å, Ru(1)–C(3)–Ru(2) 82.65(7)°) on the Ru(1)–Ru(2) edge. The two shorter Ru–C(bridging carbonyl) distances are associated with 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 Ru(2), or may alternatively reflect a greater electron density on Ru(1) due to the strongly σ-donating NHC. As anticipated, the carbene ligand lay in the equatorial plane of the Ru₃ core, as is common for the vast majority of nitrogen and phosphorus donor ligands coordinated to Ru₃ triangular clusters, although the dihedral twist between the pyrimidine ring and the Ru₃ core is significantly greater (87.3°) than in either of the 5-membered ring NHC derivatives [Ru₃(IMes)(CO)₁₁] (37.7°; IMes = 1,3-bis(2,4,6-trimethylphenyl) imidazol-2-ylidene)[2b] or [Ru₃(ab-IᵗBu)(CO)₁₁][6a] (9.8°; ab denotes an 'abnormal' (or mesionic) ligated NHC,[21] IᵗBu = 1,3-di-tert-butylimidazol-2-ylidene). As a consequence, the N-ⁱPr 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 [Os₃(CO)₁₀(μ-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 'Ru(μ-CO)₂Ru' 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, [Ru₃(6-Et)(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 Ru₄ cluster, [Ru₄(6-ⁱPr)₂(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
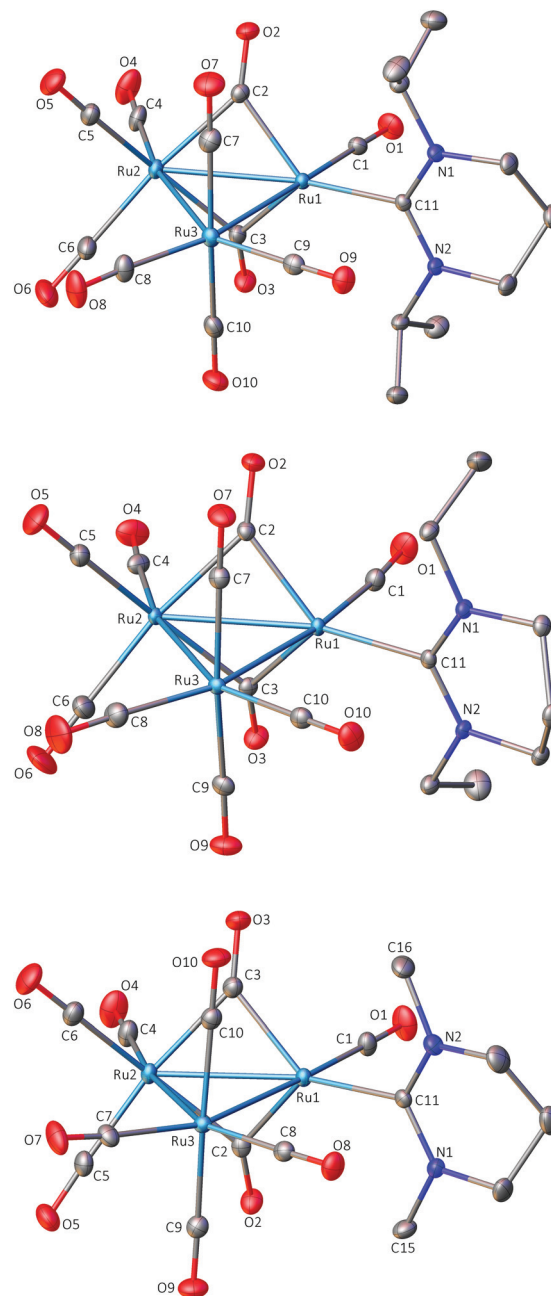
Fig. 1 Molecular structures of **1** (top), **2** (centre) and **4** (bottom). Ellipsoids are shown at 30% probability. The minor disordered component in **3** has been omitted for clarity, as have hydrogen atoms in all cases.

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 NCH₂ protons upon cooling to 235 K.

The molecular geometry of **2** (Fig. 1) is similar to that of **1** with the dicarbonyl-bridged Ru(1)–Ru(2) bond (2.7277(2) Å) being the shortest, while the Ru(1)–Ru(3) and Ru(2)–Ru(3) distances are 2.8018(2) and 2.8644(3) Å. The Ru(1)–C(11) metal–carbene distance is 2.121(2) Å and, as for **1**, the ligand lies close to the equatorial plane of the Ru₃ core. The bridging car-

bonyl ligands display asymmetry (Ru(1)–C(2) 1.993(3) Å, Ru(2)–C(2) 2.121(2) Å, Ru(1)–C(2)–Ru(2) 83.02(9)°; Ru(1)–C(3) 1.985(2) Å, Ru(2)–C(3) 2.115(3) Å, Ru(1)–C(3)–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-^{i}Pr in yielding only the [Ru$_3$(6-NHC)(CO)$_{10}$] product, [Ru$_3$(6-Me)(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 (Ru(1)–Ru(2) 2.7320(3) Å, Ru(1)–Ru(3) 2.8104(3) Å, Ru(2)–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 (Ru(1)–C(11) (carbene) 2.107(3) Å; Ru(1)–C(2) 1.980(3) Å and Ru(1)–C(3) 1.996(3) Å for the two carbonyl bonds). By comparison the bridging-carbonyl Ru(2)–C bond lengths are 2.128(3) Å (Ru(2)–C(2)) and 2.113(3) Å (Ru(2)–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 [Ru$_3$(6-NHC)(CO)$_{10}$] complexes. Given the coordinative unsaturation, we were surprised to find that there was no reaction of [Ru$_3$(6-^{i}Pr)(CO)$_{10}$] with CO (1 atm in THF-d_8), even upon heating to 80 °C. However, exposure of 1 to 1 atm ^{13}CO led to the appearance of a ^{13}C enhanced carbonyl signal at δ 200 in the ^{13}C{^{1}H} NMR spectrum at room temperature (Fig. S11†), implying that although [Ru$_3$(6-^{i}Pr)(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 1992[25] that the insertion of CO and a terminal alkene into the *ortho* C–H position of pyridine was catalysed by [Ru$_3$(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 [Ru$_3$(CO)$_{12}$], achieving instead a more modest 31% average yield.[26] Disappointingly, 1 exhibited lower activity than [Ru$_3$(CO)$_{12}$], as did the coordinatively saturated, abnormally bound 5-membered ring NHC clusters, [Ru$_3$(ab-I^{t}Bu)(CO)$_{11}$][6a] and [Ru$_3$(ab-IAd)(CO)$_{11}$] (IAd = 1,3-bis(adamantyl)imidazol-2ylidene).[6b]

Degradation of 1 through loss of [6-^{i}PrH]$^+$ and 6-^{i}Pr

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 ^{1}H

Table 1 Ru$_3$ cluster catalysed acylation of pyridine^a

Ru precursor	Product yield^b (%)
[Ru$_3$(CO)$_{12}$]	31
1	12
[Ru$_3$(ab-I^{t}Bu)(CO)$_{11}$]	23
[Ru$_3$(ab-IAd)(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 ^{1}H 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-(MeO)$_3$C$_6$H$_3$ as an internal standard.

NMR resonances of 1 and appearance of signals due to the pyridinium cation [6-^{i}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-^{i}PrH]$_2$[Ru$_4$(CO)$_{12}$H$_2$] (Fig. S14†).[28] The di-potassium salt of [Ru$_4$(CO)$_{12}$H$_2$]$^{2-}$ has a hydride chemical shift of δ −19.3.[29]

A likely pathway to [6-^{i}PrH]$^+$ formation involves C–H activation of pyridine by 1,[23a,30] followed by reductive elimination from a resulting {(6-^{i}Pr)RuH} moiety. Support for reductive elimination from such a species came upon reacting 1 with H$_2$ at 60 °C (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 [Ru$_3$(6-NHC) (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, [Ru$_3$(PPh$_3$)$_3$(CO)$_9$] (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 [Ru$_3$(CO)$_{12}$] with N-alkyl substituted, 6-membered ring N-heterocyclic carbenes under very mild conditions. Reactivity studies of the [Ru$_3$(6-NHC)(CO)$_{10}$] complexes carried out using the 6-^{i}Pr 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 [Ru$_3$(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 (^{1}H) and δ 67.6 (^{13}C)). IR spectra were recorded in hexane solution on a Nicolet Nexus spectrometer. Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon, UK. [Ru$_3$(CO)$_{12}$] (Sigma Aldrich) was used as received, while the [PF$_6$]$^-$ salts of [6-^{i}PrH]$^+$, [6-EtH]$^+$ and [6-MeH]$^+$ were prepared according to the literature.[32]

[Ru$_3$(6-^{i}Pr)(CO)$_{10}$] 1

[6-^{i}PrH][PF$_6$] (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, [Ru$_3$(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 × 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%. ^{1}H NMR (500 MHz, 298 K): δ = 3.59 (sept, 2H, $^3J_{HH}$ = 6.50 Hz, CHMe$_2$), 3.40 (m, 2H, NCH$_2$), 3.18 (m, 2H, NCH$_2$), 2.11 (m, NCH$_2$CHH, 1H), 1.88 (m, 1H, NCH$_2$CHH), 1.36 (d, 6H, $^3J_{HH}$ = 6.50 Hz, CHMe$_2$), 1.21 (d, 6H, $^3J_{HH}$ = 6.50 Hz, CHMe$_2$). ^{13}C{^{1}H} NMR (101 MHz, 298 K): δ = 198.7 (s, Ru–C$_{NHC}$), 57.5 (s, NCHMe$_2$), 40.6 (s, NCH$_2$), 21.6 (s, NCH$_2$CH$_2$), 20.6 (s, CHMe$_2$), 20.0 (s, CHMe$_2$). 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. C$_{20}$H$_{20}$N$_2$O$_{10}$Ru$_3$ requires: C, 31.92; H, 2.77; N, 3.60.

[Ru$_3$(6-Et)(CO)$_{10}$] 2 and [Ru$_4$(6-Et)$_2$(CO)$_{11}$] 3

As for 1 but with [6-EtH][PF$_6$] (100 mg, 0.35 mmol), KHMDS (69 mg, 0.35 mmol) and [Ru$_3$(CO)$_{12}$] (111 mg, 0.17 mmol). Combined yield of 2 and 3: 24 mg. Selected spectroscopic data for 2. ^{1}H NMR (500 MHz, 235 K): δ = 3.47 (m, 2H, NCH$_2$CH$_3$), 3.39 (m, 2H, NCH$_2$CH$_3$), 3.26 (m, 4H, NCH$_2$CH$_3$), 2.07 (m, 2H, NCH$_2$CH$_2$), 1.31 (t, 6H, $^3J_{HH}$ = 6.99 Hz, NCH$_2$CH$_3$). ^{13}C{^{1}H} 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, NCH$_2$), 45.1 (s, NCH$_2$), 20.9 (s, NCH$_2$CH$_2$), 13.9 (s, CH$_2$CH$_3$). 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. C$_{18}$H$_{16}$N$_2$O$_{10}$Ru$_3$ 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†).

[Ru$_3$(6-Me)(CO)$_{10}$] 4

As for 1 but with [6-MeH][PF$_6$] (60 mg, 0.23 mmol), KHMDS (46 mg, 0.23 mmol) and [Ru$_3$(CO)$_{12}$] (75 mg, 0.12 mmol) to afford deep-red crystals of 4. Yield 16 mg, 20%. ^{1}H NMR (500 MHz, 298 K): δ = 3.32 (br t, 4H, $^3J_{HH}$ = 4.8 Hz, NCH$_2$), 3.14 (s, 6H, NMe), 2.09 (quint, 2H, $^3J_{HH}$ = 6.0 Hz, NCH$_2$CH$_2$). ^{13}C{^{1}H} NMR (101 MHz, 298 K): δ = 202.7 (s, Ru–C$_{NHC}$), 47.5 (s, NCH$_2$), 43.9 (s, NMe), 21.1 (s, NCH$_2$CH$_2$). 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. C$_{16}$H$_{12}$N$_2$O$_{10}$Ru$_3$ requires: C, 27.63; H, 1.74; N, 4.03.

Reactivity studies of 1

(a) *with C$_5$H$_5$N*: 1 (17.1 mg, 0.023 mmol) was combined with pyridine (7.5 μL, 0.093 mmol) in THF-d_8 in a J. Young's resealable NMR tube and the reaction followed by ^{1}H NMR spectroscopy. (b) *with H$_2$*: 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 (×3), placed under 1 atm H$_2$ and the reaction followed by ^{1}H NMR spectroscopy. (c) *with PPh$_3$*: 1 (6.5 mg, 0.009 mmol) was combined with 3 equiv. PPh$_3$ (6.8 mg, 0.026 mmol) in THF-d_8 in a J. Young's resealable NMR tube and the reaction followed by ^{1}H and ^{31}P NMR spectroscopy.

Catalysis

Solid samples of Ru$_3$ precursors (0.0265 mmol), together with 2,4,6-(MeO)$_3$C$_6$H$_3$ (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 CDCl$_3$ and analysed by ^{1}H 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-Kα radiation, while those for 2, 3 (ESI†) and 4 were obtained using a Cu-Kα source and an Agilent SuperNova instrument. Refinements, achieved using SHELXL[33] *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-^{i}PrH]$_2$[Ru$_4$(CO)$_{12}$H$_2$], ESI) and 1816568 ([Ru$_3$(PPh$_3$)$_3$(CO)$_9$], ESI) respectively.†

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

References

1 (a) G. Hogarth, S. E. Kabir and E. Nordlander, *Dalton Trans.*, 2010, **39**, 6153; (b) J. A. Cabeza and P. García-Álvarez, *Chem. Soc. Rev.*, 2011, **40**, 5389.

2 (a) M. F. Lappert and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 1977, 2172; (b) J. A. Cabeza, I. del Río, D. Miguel and M. G. Sánchez-Vega, *Chem. Commun.*, 2005, 3956; (c) J. A. Cabeza, I. del Río, D. Miguel, E. Pérez-Carreño and M. G. Sánchez-Vega, *Organometallics*, 2008, **27**, 211; (d) J. A. Cabeza, I. del Río, M. Fernández-Colinas, E. Pérez-Carreño, M. G. Sánchez-Vega and D. Vázquez-García, *Organometallics*, 2009, **28**, 1832.

3 (a) M. I. Bruce, M. L. Cole, R. S. C. Fung, C. M. Forsyth, M. Hilder, P. C. Junk and K. Konstas, *Dalton Trans.*, 2008, 4118; (b) C. E. Ellul, O. Saker, M. F. Mahon, D. C. Apperley and M. K. Whittlesey, *Organometallics*, 2008, **27**, 100; (c) J. A. Cabeza, M. Damonte, P. García-Álvarez, A. R. Kennedy and E. Pérez-Carreño, *Organometallics*, 2011, **30**, 826.

4 L. Álvarez-Rodríguez, J. A. Cabeza, P. García-Álvarez, E. Pérez-Carreño and D. Polo, *Inorg. Chem.*, 2015, **54**, 2983.

5 (a) J. Campos, L. S. Sharninghausen, R. H. Crabtree and D. Balcells, *Angew. Chem., Int. Ed.*, 2014, **53**, 12808; (b) L. S. Sharninghausen, B. Q. Mercado, R. H. Crabtree, D. Balcells and J. Campos, *Dalton Trans.*, 2015, **44**, 18403; (c) L. S. Sharninghausen, B. Q. Mercado, C. Hoffmann, X. Wang, J. Campos, R. H. Crabtree and D. Balcells, *J. Organomet. Chem.*, 2017, **849–850**, 17.

6 (a) C. E. Ellul, M. F. Mahon, O. Saker and M. K. Whittlesey, *Angew. Chem., Int. Ed.*, 2007, **46**, 6343; (b) M. R. Crittall, C. E. Ellul, M. F. Mahon, O. Saker and M. K. Whittlesey, *Dalton Trans.*, 2008, 4209.

7 Y. Liu, R. Ganguly, H. V. Huynh and W. K. Leong, *Angew. Chem., Int. Ed.*, 2013, **52**, 12110.

8 (a) J. A. Cabeza, I. del Río, D. Miguel, E. Pérez-Carreño and M. G. Sánchez-Vega, *Dalton Trans.*, 2008, 1937; (b) J. A. Cabeza, I. del Río, D. Miguel and M. G. Sánchez-Vega, *Angew. Chem., Int. Ed.*, 2008, **47**, 1920; (c) J. A. Cabeza and E. Pérez-Carreño, *Organometallics*, 2008, **27**, 4697;

(d) C. Y. Zhang, B. Li, H. B. Song, S. S. Xu and B. Q. Wang, *Organometallics*, 2011, **30**, 3029; (e) J. A. Cabeza, M. Damonte and P. García-Álvarez, *Organometallics*, 2011, **30**, 2371; (f) J. A. Cabeza, M. Damonte and E. Pérez-Carreño, *Organometallics*, 2012, **31**, 8355; (g) J. A. Cabeza, M. Damonte, P. García-Álvarez and E. Pérez-Carreño, *Chem. Commun.*, 2013, **49**, 2813; (h) J. Yan, Z. Han, D. J. Zhang and C. B. Liu, *RSC Adv.*, 2016, **6**, 99625.

9 S. Warratz, L. Postigo and B. Royo, *Organometallics*, 2013, **32**, 893.

10 (a) C. E. Cooke, M. C. Jennings, M. J. Katz, R. K. Pomeroy and J. A. C. Clyburne, *Organometallics*, 2008, **27**, 5777; (b) Y. Liu, R. Ganguly, H. V. Huynh and W. K. Leong, *Organometallics*, 2013, **32**, 7559.

11 For reactions of other Os–CO precursors, see; (a) J. A. Cabeza, I. da silva, I. del Río and M. G. Sánchez-Vega, *Dalton Trans.*, 2006, 3966; (b) J. A. Cabeza, I. del Río, J. M. Fernández-Colinas, E. Pérez-Carreño, M. G. Sánchez-Vega and D. Vázquez-Garciá, *Organometallics*, 2010, **29**, 3828.

12 (a) M. I. Bruce, in *Comprehensive Organometallic Chemistry I*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 4; (b) R. D. Adams and J. P. Selegue, in *Comprehensive Organometallic Chemistry I*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 4; (c) A. J. Deeming, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Elsevier, Oxford, 1995, vol. 7.

13 (a) S. Rivomanana, G. Lavigne, N. Lugan and J.-J. Bonnet, *Inorg. Chem.*, 1991, **30**, 4110; (b) G. Süss-Fink, G. Rheinwald, H. Stoeckli-Evans, C. Bolm and D. Kaufmann, *Inorg. Chem.*, 1996, **35**, 3081; (c) H.-C. Böttcher, H. Thönnessen, P. G. Jones and R. Schmutzler, *J. Organomet. Chem.*, 1996, **520**, 15; (d) M. Graf, K. Merzweiler, C. Bruhn and H.-C. Böttcher, *J. Organomet. Chem.*, 1998, **553**, 371; (e) H.-C. Böttcher, M. Graf, K. Merzweiler, T. Rösel, H. Schmidt and C. Wagner, *Polyhedron*, 2001, **20**, 2011; (f) R. D. Adams, Y. Kan, Q. Zhang, M. B. Hall and E. Trufan, *Organometallics*, 2012, **31**, 50.

14 N. E. Leadbeater, J. Lewis and P. R. Raithby, *J. Organomet. Chem.*, 1997, **543**, 251.

15 N. E. Leadbeater, J. Lewis, P. R. Raithby and M.-A. Rennie, *Polyhedron*, 1998, **17**, 1755.

16 (a) C. J. E. Davies, M. J. Page, C. E. Ellul, M. F. Mahon and M. K. Whittlesey, *Chem. Commun.*, 2010, **46**, 5151; (b) M. J. Page, W. Y. Lu, R. C. Poulten, E. Carter, A. G. Algarra, B. M. Kariuki, S. A. Macgregor, M. F. Mahon, K. J. Cavell, D. M. Murphy and M. K. Whittlesey, *Chem. – Eur. J.*, 2013, **19**, 2158; (c) R. C. Poulten, M. J. Page, A. G. Algarra, J. J. Le Roy, I. López, E. Carter, A. Llobet, S. A. Macgregor, M. F. Mahon, D. M. Murphy, M. Murugesu and M. K. Whittlesey, *J. Am. Chem. Soc.*, 2013, **135**, 13640; (d) L. R. Collins, N. A. Rajabi, S. A. Macgregor, M. F. Mahon and M. K. Whittlesey, *Angew. Chem., Int. Ed.*, 2016, **55**, 15539; (e) S. Pelties, E. Carter, A. Folli, M. F. Mahon,

D. M. Murphy, M. K. Whittlesey and R. Wolf, *Inorg. Chem.*, 2016, **55**, 11006; (*f*) S. Sabater, M. J. Page, M. F. Mahon and M. K. Whittlesey, *Organometallics*, 2017, **36**, 1776; (*g*) W. J. M. Blackaby, S. Sabater, R. C. Poulten, M. J. Page, A. Folli, V. Krewald, M. F. Mahon, D. M. Murphy, E. Richards and M. K. Whittlesey, *Dalton Trans.*, 2018, **47**, 769.

17 (*a*) N. Phillips, J. Rowles, M. J. Kelly, I. Riddlestone, N. H. Rees, A. Dervisi, I. A. Fallis and S. Aldridge, *Organometallics*, 2012, **31**, 8075; (*b*) P. Hauwert, J. J. Dunsford, D. S. Tromp, J. J. Weigand, M. Lutz, K. J. Cavell and C. J. Elsevier, *Organometallics*, 2013, **32**, 131; (*c*) N. Phillips, T. Dodson, R. Tirfoin, J. I. Bates and S. Aldridge, *Chem. – Eur. J.*, 2014, **20**, 16721; (*d*) O. S. Morozov, A. V. Lunchev, A. A. Bush, A. A. Tukov, A. F. Asachenko, V. N. Khrustalev, S. S. Zalesskiy, V. P. Ananikov and M. S. Nechaev, *Chem. – Eur. J.*, 2014, **20**, 6162; (*e*) T. Wurm, F. Mulks, C. R. N. Bohling, D. Riedel, P. Zargaran, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Organometallics*, 2016, **35**, 1070; (*f*) J. J. Dunsford, D. J. Evans, T. Pugh, S. N. Shah, N. F. Chilton and M. J. Ingleson, *Organometallics*, 2016, **35**, 1098; (*g*) Ł. Banach, P. A. Guńka and W. Buchowicz, *Dalton Trans.*, 2016, **45**, 8688; (*h*) A. J. Jordan, C. M. Wyss, J. Bacsa and J. P. Sadighi, *Organometallics*, 2016, **35**, 613.

18 Cabeza and co-workers have reported that pyrimidine and 2-methylpyrimidine add and cyclometallate upon reaction with [Ru₃(CO)₁₂]: (*a*) J. A. Cabeza, I. del Río, E. Pérez-Carreño and V. Pruneda, *Organometallics*, 2011, **30**, 1148; (*b*) J. A. Cabeza, P. García-Álvarez, E. Pérez-Carreño and V. Pruneda, *Chem. – Eur. J.*, 2013, **19**, 3426.

19 J. Li, W. X. Shen and X. R. Li, *Curr. Org. Chem.*, 2012, **16**, 2879.

20 **1** is also formed at a 1 : 1 ratio of [Ru₃(CO)₁₂]: 6-ⁱPr with no IR evidence for any other carbonyl products.

21 M. Albrecht, *Adv. Organomet. Chem.*, 2014, **62**, 111.

22 A. G. Orpen, A. V. Rivera, E. G. Bryan, D. Pippard, G. M. Sheldrick and K. D. Rouse, *J. Chem. Soc., Chem. Commun.*, 1978, 723.

23 (*a*) M. I. Bruce, M. G. Humphrey, M. R. Snow, E. R. T. Tiekink and R. C. Wallis, *J. Organomet. Chem.*, 1986, **314**, 311; (*b*) R. D. Adams and J. H. Yamamoto, *Organometallics*, 1995, **14**, 3704; (*c*) B. K. Maiti, H. Gorls, O. Klobes and W. Imhof, *Eur. J. Inorg. Chem.*, 2011, 1545.

24 A number of groups have reported that [Ru₃(CO)₁₂] does not undergo direct exchange with ¹³CO, although the reaction can be promoted by the addition of some salts or metal additives: (*a*) KH: J. C. Bricker, C. C. Nagel and S. G. Shore, *J. Am. Chem. Soc.*, 1982, **104**, 1444; (*b*) KOMe: D. J. Darensbourg, R. L. Gray and M. Pala, *Organometallics*, 1984, **3**, 1928; (*c*) Cp/Cp*Rh(CO)₂: W. E. Lindsell, C. B. Knobler and H. D. Kaesz, *J. Organomet. Chem.*, 1985, **296**, 209; (*d*) KH/NaBH₄: J. C. Bricker, M. W. Payne and S. G. Shore, *Organometallics*, 1987, **6**, 2545.

25 E. J. Moore, W. R. Pretzer, T. J. O'Connell, J. Harris, L. Labounty, L. Chou and S. S. Grimmer, *J. Am. Chem. Soc.*, 1992, **114**, 5888.

26 This represents the average value from six catalytic runs, including ones in which (i) solutions were prepared both in and out of a glovebox and (ii) different batches of pyridine were used.

27 There was no change by NMR spectroscopy when **1** was heated in just THF-*d*₈ at 70 °C for 4 h.

28 R. Suter, A. A. Bhattacharyya, L.-Y. Hsu, J. A. Krause Bauer and S. G. Shore, *Polyhedron*, 1998, **17**, 2889.

29 K. E. Inkrott and S. G. Shore, *Inorg. Chem.*, 1979, **18**, 2817.

30 B. R. Cockerton and A. J. Deeming, *J. Organomet. Chem.*, 1992, **426**, C36.

31 N. E. Leadbeater and P. R. Raithby, *J. Coord. Chem.*, 2001, **53**, 311.

32 A. Aidouni, S. Bendahou, A. Demonceau and L. Delaude, *J. Comb. Chem.*, 2008, **10**, 886.

33 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **A46**, 467–473; G. M. Sheldrick, *SHELXL-97, a computer program for crystal structure refinement*, University of Göttingen, 1997.

34 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.