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

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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. 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, but cleaved upon only relatively small changes to either the substituents or reaction stoichiometry. In very recent cases, clusters of general formula [Ru₃(6-NHC)(CO)₁₀] have only been structurally characterised, along with the tetrannuclear ruthenium cluster [Ru₄(6-Et₂)(CO)₁₁] 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.

Results and discussion

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

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], Scheme 1, which could be isolated as a red crystalline product in 65% yield.

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, 

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

We and others 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’ and transition metal clusters have not been described. 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 functionalisation, are described.
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(bonding 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)2 or [Ru3(ab′Bu)[CO]11]α (9.8°; ab denotes an ‘abnormal’ (or mesionic) ligated NHC,21 ab′Bu = 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)3] 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, [Ru4(6-Et)[CO]12] (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-Pr)[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 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 NCH3 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-^1Pr in yielding only the [Ru6(6-NHC)(CO)10] product, [Ru6(ab-IAd)(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 NCH2CH2 quartet were sharp, while the NCH2 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 cyanoboryl 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 [Ru6(6-NHC)(CO)10] complexes. Given the coordinative unsaturation, we were surprised to find that there was no reaction of [Ru6(6-^1Pr)(CO)10] with CO (1 atm in THF-d8), 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 [Ru6(6-^1Pr)(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 ester Ru

<table>
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<th>Table 1 Ru3 cluster catalysed acylation of pyridinea</th>
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<tr>
<td>Ru precursor</td>
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<tr>
<td>[Ru3(CO)12]</td>
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<tr>
<td>1</td>
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<tr>
<td>[Ru3(ab-^1Bu)(CO)11]</td>
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<td>[Ru3(ab-IAd)(CO)11]</td>
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a Reaction conditions: Ru3 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)23 and δ 4.1 (branched product)25 versus the OMe resonance of 2,4,6-(MeO)3C6H3 as an internal standard.

NMR resonances of 1 and appearance of signals due to the pyridinium cation [6-^1PrH]+.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-^1PrH][Ru4(CO)12H2] (Fig. S14†). The di-potassium salt of [Ru4(CO)12H2]2− has a hydride chemical shift of δ −19.3.29

A likely pathway to [6-^1PrH]+ formation involves C–H activation of pyridine by 1,26,29 followed by reductive elimination from a resulting [(6-^1Pr)RuH] moiety. Support for reductive elimination from such a species came upon reacting 1 with H2 at 60 °C (THF-d8), 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 [Ru6(6-NHC)(CO)10] complexes comes from the reaction of 1 with phosphines, where we found that 1 reacted with 1–3 equiv. PPh3, 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, [Ru3(PPh3)3(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 [Ru6(CO)12] with N-alkyl substituted, 6-membered ring N-heterocyclic carbenes under very mild conditions. Reactivity studies of the [Ru6(6-NHC)(CO)10] complexes carried out using the 6-Pr derivative 1 indicated that loss of the carbene ligand took place upon addition of PPh3, mild heating under H2 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 [Ru6(CO)12] with 6-NHCs to those formed with 5-membered

Degradation of 1 through loss of [6-^1PrH]2+ and 6-^1Pr

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
ring analogues is notable,\textsuperscript{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\textsubscript{8} referenced to δ 3.58 (1\textsuperscript{H}) and δ 67.6 (1\textsuperscript{3}C). IR spectra were recorded in hexane solution on a Nicolet Nexus spectrometer. Elemental analyses were performed by Elemental Microanalytical Ltd, Okehampton, Devon, UK. [Ru\textsubscript{3}(CO)\textsubscript{12}] (Sigma Aldrich) was used as received, while the [PF\textsubscript{6}]\textsuperscript{−} salts of [6-PrH]\textsuperscript{+}, [6-EtH]\textsuperscript{+} and [6-MeH]\textsuperscript{+} were prepared according to the literature.\textsuperscript{32}

\[\text{Ru}_3(6-\text{Pr})(\text{CO})_{10} \] 1

[6-PrH][PF\textsubscript{6}] (108 mg, 0.34 mmol) and KHMDS (66 mg, 0.33 mmol) were stirred in THF for 1 h in a J. Young resealable ampoule. The suspension was then reduced to dryness, and the residue allowed to slowly evaporate to afford deep-red crystals of 1. Yield 84 mg, 65%.\textsuperscript{1}H NMR (500 MHz, 298 K): δ = 3.39 (m, 2\text{H}, NC\textsubscript{2}H), 3.26 (m, 4\text{H}, NC\textsubscript{2}H), 21.6 (s, NCH\textsubscript{2}), 45.1 (s, NCH\textsubscript{2}), 20.9 (s, NCH\textsubscript{2}), 13.9 (s, CH\textsubscript{2}). IR (cm\textsuperscript{−1}): 2103, 2086, 2061, 2043, 2023, 2010, 2003, 1981, 1962, 1806 (all ν(CO)). Analysis found: C, 31.96; H, 2.22; N, 3.60.

\[\text{Ru}_3(6-\text{Et})(\text{CO})_{10}\text{a} \] 2 and \[\text{Ru}_4(6-\text{Et})(\text{CO})_{11}\text{b} \] 3

As for 1 but with [6-EtH][PF\textsubscript{6}] (100 mg, 0.35 mmol), KHMDS (69 mg, 0.35 mmol) and [Ru\textsubscript{3}(CO)\textsubscript{12}] (111 mg, 0.17 mmol). Combined yield of 2 and 3: 24 mg. Selected spectroscopic data for 2. \textsuperscript{1}H NMR (500 MHz, 235 K): δ = 3.47 (m, 2\text{H}, NCH\textsubscript{2}CH\textsubscript{3}), 3.39 (m, 2\text{H}, NCH\textsubscript{2}CH\textsubscript{3}), 3.26 (m, 4\text{H}, NCH\textsubscript{2}CH\textsubscript{3}), 2.07 (m, 2\text{H}, NCH\textsubscript{2}CH\textsubscript{3}), 1.31 (t, 6\text{H}, J\textsubscript{HH} = 6.99 Hz, NCH\textsubscript{2}CH\textsubscript{3}). \textsuperscript{13}C\textsuperscript{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\textsubscript{2}), 45.1 (s, NCH\textsubscript{2}), 20.9 (s, NCH\textsubscript{2}), 13.9 (s, CH\textsubscript{2}). IR (cm\textsuperscript{−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\textsubscript{26}H\textsubscript{46}N\textsubscript{2}O\textsubscript{16}Ru\textsubscript{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†).

\[\text{Ru}_4(6-\text{Me})(\text{CO})_{10}\text{a} \] 4

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

Reactivity studies of 1

(a) with C\textsubscript{5}H\textsubscript{5}N: 1 (17.1 mg, 0.023 mmol) was combined with pyridine (7.5 μL, 0.093 mmol) in THF-d\textsubscript{8} in a J. Young’s resealable NMR tube and the reaction followed by \textsuperscript{1}H NMR spectroscopy. (b) with H\textsubscript{2}: 1 (11.1 mg, 0.015 mmol) was dissolved in THF-d\textsubscript{8} in a J. Young’s resealable NMR tube, the solution freeze-pump-thaw degassed (∼3), placed under 1 atm H\textsubscript{2} and the reaction followed by \textsuperscript{1}H NMR spectroscopy. (c) with PPh\textsubscript{3}: 1 (6.5 mg, 0.009 mmol) was combined with 3 equiv. PPh\textsubscript{3} (6.8 mg, 0.026 mmol) in THF-d\textsubscript{8} in a J. Young’s resealable NMR tube and the reaction followed by \textsuperscript{1}H and \textsuperscript{31}P NMR spectroscopy.

Catalysis

Solid samples of Ru\textsubscript{3} precursors (0.0265 mmol), together with 2,4,6-(MeO)\textsubscript{3}C\textsubscript{6}H\textsubscript{4} (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\textsubscript{3} and analysed by \textsuperscript{1}H NMR spectroscopy. Product resonances were assigned by comparison to the literature.\textsuperscript{25}

X-ray crystallography

Data for 1 were collected on a Nonius kappaCCD diffractometer using Mo-K\textsubscript{α} radiation, while those for 2, 3 (ESI\textsuperscript{†}) and 4 were obtained using a Cu-K\textsubscript{α} source and an Agilent SuperNova instrument. Refinements, achieved using SHELXL\textsuperscript{13} via Olex2,\textsuperscript{14} were relatively straightforward and only points of note are mentioned hereafter. In 3 (ESI\textsuperscript{†}), 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).
(3, ESI), 1559946 (4), 1816567 ([6−PrH][Ru3(CO)12H2], ESI) and 1816568 ([Ru3(PPh3)3(CO)5], ESI) respectively.†

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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


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-d8 at 70 °C for 4 h.


