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Insights into metal–ligand hydrogen transfer: a square-planar ruthenate complex supported by a tetradentate amino–amido-diolefin ligand†

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A four-coordinate, sixteen-electron Ru(0) complex containing the tetradentate diamino-diolefin ligand (\pm)-*trans*-*N,N*-bis(5*H*-dibenzo[*a,d*]cyclohepten-5-yl)-1,2-diaminocyclohexane (*trop*₂dach) has been synthesised. Deprotonation of one amino N–H functional group generates an unprecedented four-coordinate ruthenate species which has been characterised in solution and in the solid state. The newly formed ruthenate complex undergoes intramolecular metal–ligand N–H addition/elimination in solution to generate a transient diamido ruthenium hydride species, as supported by NMR spectroscopy and density functional theory.

In organometallic chemistry, the η^2 -5*H*-dibenzo[*a,d*]cycloheptenyl (η^2 -*trop*) moiety serves as a two-electron π -donor that can be functionalised with nitrogen or phosphorus atoms bound to the sp^3 carbon within the seven-membered ring.^{1,2} In the presence of strong base, amine functionalised *trop* ligands have been shown to stabilise rhodium,^{3–8} iridium,^{9–11} and ruthenium^{12–14} compounds, much owing to the robust π -accepting nature of the olefin ligands (Scheme 1). In addition, the η^2 -olefin CH nuclei are sensitive to changes in their electronic environment, making them useful probes into the overall electronic structure.

Complexes containing the *trop*₂dach (dach = (*R,R*)-1,2-diaminocyclohexane) and *trop*₂dae (dae = 1,2-diaminoethane) ligands have been used as catalysts for “green” chemical transformations (Scheme 1).¹⁵ The iridium complex **B**, generated by deprotonating **A** with strong base, is proposed as an intermediate in the iridium–nitrogen-radical catalyzed oxidation of alcohols, mimicking radical-based metalloenzyme catalysts.¹¹ Recently,



Scheme 1 Reactivity of rhodium and ruthenium amino-olefin ligands with one equivalent strong base. *dme* = 1,2-dimethoxyethane.

the anionic ruthenium hydride complex **D** was found to be an active catalyst for the formation of CO₂/H₂ from 1:1 methanol:water mixtures, with complexes **C** and **D** being proposed as key intermediates within the catalytic cycle.¹² In the presence of base, it is proposed that the ligand backbone of zero-valent Ru complex **C** becomes dehydrogenated and this metal–ligand reactivity/cooperativity plays a key role in the catalytic methanol dehydrogenation process. In related cases, hydrogenation or dehydrogenation of the PNNP ligand backbone of catalysts can lead to catalyst activation,^{16–18} deactivation,^{19–21} or side reaction²² while dehydrogenation of a tridentate PNP ligand allows for the reversible storage/release of two equivalents of hydrogen and change of the spin state.^{23–26}

Four coordinate, sixteen-electron Ru(0) complexes such as **C** remain quite rare and related compounds contain bulky and basic phosphines paired with carbonyl or nitrosyl ligands.^{27–33} In our efforts to expand the coordination chemistry and reactivity of ruthenium amino-olefin complexes, we report the synthesis and characterization of tetradentate amino-olefin Ru(0) and amido-olefin ruthenate complexes (Scheme 2). Our experimental observations and calculations support the ease with which hydrogen can migrate between metal and ligand, which might be operative in the mechanism of methanol dehydrogenation using complexes **C** and/or **D**.

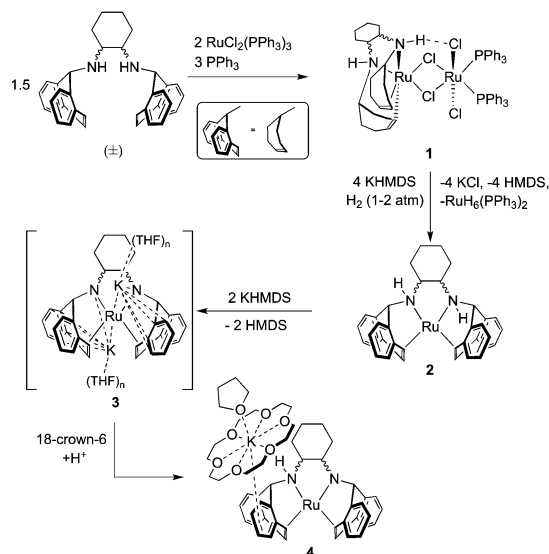
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Scheme 2 Synthesis of compounds 1–4.

Upon reaction of two equivalents of $\text{RuCl}_2(\text{PPh}_3)_3$ with an excess of (\pm)-*trans*-*N,N*-bis(5*H*-dibenzo[*a,d*]cyclohepten-5-yl)-1,2-diaminocyclohexane ((\pm) trop_2dach)³⁴ and PPh_3 , the chloro-bridged bimetallic species **1** precipitates from solution as an analytically pure powder which is insoluble in common organic solvents (Scheme 2). In lieu of solution-state analysis, **1** was characterised by solid-state CP/MAS NMR and single crystal X-ray diffraction (Scheme 1 and Fig. S1, ESI[†]). The solid-state $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** reveals three groups of signals consistent with a coordinated trop_2dach ligand while the ^{31}P NMR contains a broad resonance centred at 53.8 ppm, also consistent with coordinated PPh_3 (see the ESI[†]).

When dimer **1** is heated in the presence of four equivalents of the strong base potassium hexamethyldisilazide (KHMDs) under a hydrogen atmosphere, the pale pink suspension turns deep orange. Analysis of the crude products by ^1H and ^{31}P NMR indicates the presence of two compounds, one whose hydride chemical shift matches the known polyhydride species $\text{RuH}_6(\text{PPh}_3)_2$ ^{35–37} and the other being the zero-valent Ru complex $\text{Ru}(\text{trop}_2\text{dach})$ (**2**, Scheme 1). These products form by a series of steps involving, in no proven order, the precipitation of potassium chloride, the heterolytic splitting of dihydrogen at ruthenium, formation of ruthenium hydrides and hexamethyldisilazane, and the cleavage of the dimer to give the two monometallic products.

Complex **2** was characterised by NMR spectroscopy and single crystal X-ray diffraction (Fig. 1, left). The complex resides in a distorted square planar geometry with one molecule of THF hydrogen bonded to an amine proton ($\text{O1}\cdots\text{H1}$ 2.100 Å). The Ru-centroid bond distances ($\text{Ru1}-\text{ct1}$ = 1.980(4), $\text{Ru1}-\text{ct2}$ = 1.973(5) Å) are significantly shorter than in **1** and the metrical parameters are similar to those of complex **C**.¹²

In the presence of KHMDs and heat, complex **2** does not behave in a manner similar to **C**, which undergoes dehydrogenation at the ethylene bridge between the nitrogen atoms.¹² With two or more equivalents strong base, we observe that the backbone of **2** remains intact, generating a symmetrical species containing



Fig. 1 Molecular structures of **2** (left) and **4** (right) with 30% probability ellipsoids. Only a single enantiomer is shown and most hydrogen atoms have been omitted for clarity. Distances (Å) and angles ($^\circ$): **2**: $\text{Ru1}-\text{N1}$ 2.131(4), $\text{Ru1}-\text{N2}$ 2.129(3), $\text{Ru1}-\text{ct1}$ 1.980(4), $\text{Ru1}-\text{ct2}$ 1.973(5), $\text{C4}-\text{C5}$ 1.423(7), $\text{C19}-\text{C20}$ 1.435(7), $\text{O1}\cdots\text{H1}$ 2.100; $\text{N1}-\text{Ru1}-\text{N2}$ 82.0(2), $\text{ct1}-\text{Ru1}-\text{ct2}$ 98.30(2), $\text{N1}-\text{Ru1}-\text{ct2}$ 92.18(2), $\text{N2}-\text{Ru1}-\text{ct1}$ 92.18(2), $\text{N1}-\text{Ru1}-\text{ct1}$ 163.51(2), $\text{N2}-\text{Ru1}-\text{ct2}$ 162.37(2). **4**: $\text{Ru1}-\text{N1}$ 2.091(5), $\text{Ru1}-\text{N2}$ 1.995(4), $\text{Ru1}-\text{ct1}$ 1.992(4), $\text{Ru1}-\text{ct2}$ 1.997(3), $\text{K1}\cdots\text{ct3}$ 3.221(5), $\text{C7}-\text{C8}$ 1.445(5), $\text{C22}-\text{C23}$ 1.435(5); $\text{N1}-\text{Ru1}-\text{N2}$ 80.2(2), $\text{ct1}-\text{Ru1}-\text{ct2}$ 98.73(2), $\text{N1}-\text{Ru1}-\text{ct2}$ 90.90(2), $\text{N2}-\text{Ru1}-\text{ct1}$ 90.98(2), $\text{N1}-\text{Ru1}-\text{ct1}$ 167.65(2), $\text{N2}-\text{Ru1}-\text{ct2}$ 169.07(2).

CH_{dach} NMR resonances at 2.09 ppm (^1H) and 74.14 ppm (^{13}C) (see ESI[†]). The same product is observed using the strong base KO^tBu , however reactions were cleaner when using KHMDs. We propose that the solution state structure is the doubly deprotonated $[\text{K}]_2[\text{Ru}(\text{trop}_2\text{dach}-2\text{H})]\cdot(\text{THF})_n$ (**3**), an intimate ion-paired structure that might prevent backbone dehydrogenation. Diamido-olefin rhodium³⁸ and nickel³⁹ complexes containing similar potassium–nitrogen interactions have been structurally characterised while potassium–nitrogen ion pairing has also been observed in other metal–amido type systems.^{40–42} A square planar, dianionic Ru(0) complex $[\text{Li}(\text{THF})_3]_2[\text{Ru}(\text{P}_2)_2]$ with 2,2'-biphosphinine (P_2) ligands was reported where both lithium cations sit directly on top of ruthenium.⁴³

Crystallization of solutions containing **3** in the presence of 18-crown-6 (**18c6**) consistently resulted in reprotonation of one amido nitrogen atom, generating large brown-black crystals of the four-coordinate amidoruthenate complex $[\text{K}(\text{18c6}\cdot\text{THF})][\text{Ru}(\text{trop}_2\text{dach}-\text{H})]\cdot\text{THF}$ (**4**, Fig. 1). The source of proton could be the hexamethyldisilazane that is generated in the preparation of **3**, however its origin is still unclear. The molecular structure shows a shortening of the $\text{Ru}-\text{N}_{\text{amido}}$ bond by about 0.1 Å (1.995(4) Å) with respect to $\text{Ru}-\text{N}_{\text{amino}}$ (2.091(5) Å), with the N_{amido} atom approaching a planar coordination geometry ($\Sigma^\circ = 354.8^\circ$). The complex $[\text{Ru}(\text{NO})(\text{PtBu}_2\text{CH}_2\text{SiMe}_2\text{NSiMe}_2\text{CH}_2\text{PtBu}_2)]$ has a $\text{Ru}-\text{N}_{\text{amido}}$ distance of 2.070(2) Å,⁴⁴ significantly longer than $\text{Ru1}-\text{N2}$ 1.995(4) in **4**. The $\text{K}(\text{18c6})$ cation is capped with one THF molecule and weakly bound to one of the benzo groups on the inside of the trop ligand ($\text{K1}\cdots\text{ct3}$ = 3.221(5) Å).

DFT-calculated (M06/TZVP/TZVPFit)⁴⁵ molecular orbital (MO) and Atomic Polar Tensor (APT) charge analysis of **2** and **4** are presented in Fig. 2. In line with the Dewar–Chatt–Duncanson model for metal–olefin binding,⁴⁶ the degenerate MOs at -0.20 eV for complex **2** predominantly consist of stabilizing interactions between the d_{xz}/d_{yz} and π^* atomic orbitals (AOs) of the η^2 -trop olefin ligands. The next two MOs at -0.18 and -0.16 eV consist of nonbonding



between the metal and ligand during catalytic methanol dehydrogenation. Future efforts will be directed towards synthesizing other functionalised trop₂(diamine) derivatives and investigating these compounds for the catalytic dehydrogenation of alcohols.

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