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Synthesis of a rhodium(III) dinitrogen complex using a calix[4]arene-based diphosphine ligand

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The synthesis and characterisation of the rhodium(III) dinitrogen complex [Rh(2,2′-biphenyl)(CxP1-N1)] are described, where CxP1 is a trans-spanning calix[4]arene-based diphosphine and the dinitrogen ligand is projected into the cavity of the macrocycle.

Activation of dinitrogen by coordination to a transition metal is a process of immense biological and technological importance, helping to weaken the otherwise formidably strong nitrogen–nitrogen triple bond (D0 = 946 kJ mol−1) through M–N→π N-back donation.1,2 Molecular dinitrogen complexes have been reported for most of the transition elements but mononuclear d6 systems have been the most heavily investigated. However, no well-defined rhodium(III) examples have been described.3 This paucity presumably reflects an incompatibility between the weak d-donating, poor π-accepting character of dinitrogen and the relatively high oxidation state of the second-row transition metal.

Inspired by the use of donor-functionalised cavitands as ligands in the literature and as part of our work exploring the chemistry of low-coordinate group 9 complexes supported by the high trans influence ancillary ligand 2,2′-biphenyl (biph),4,5 we became intrigued by the prospect of using a cavitand-based ligand to isolate a labile rhodium(III) dinitrogen complex.6 To this end, synthesis of [Rh(biph)(NxP1)(N2)][Al(OR)3] (1-N2, R2 = C(CF3)3; Fig. 1A) was targeted, reasoning that the previously reported diphosphine ligand CxP1 would position the (Rh(biph))4 fragment across the upper rim of the constituent calix[4]arene scaffold and in doing so favour coordination of the small diatomic over solvent molecules. Only polynuclear and dinuclear derivatives of CxP1 have been reported previously.7 We herein describe the in situ synthesis and characterisation of 1-N2 through dehydrogenation of the corresponding rhodium(III) aqua complex 1-ΟΗ2, which can be obtained in 44% isolated yield by ligand substitution of trans-

[Rh(biph)][PPh3]2(ΟΗ2)][Al(ΟR)3]2 (2-ΟΗ2) with CxP1 in THF at room temperature (Fig. 1A).

In CD3Cl solution, isolated 1-ΟΗ2 is characterised by time-averaged Cα symmetry and a doublet 31P resonance at 13.2 (J1PN = 120 Hz) at 298 K. Coordination of water within the calix[4]arene cavity is evidenced by a singlet 2H resonance at δ 0.84, which was washed out upon shaking with D2O and is significantly shielded relative to free water (δ 1.53) and 2-ΟΗ2 (δ 2.44). Crystals of 1-ΟΗ2 suitable for analysis by single crystal X-ray diffraction were obtained from CH3Cl2-hexane and demonstrate that the metal adopts a square pyramidal coordination geometry with the CxP1 ligand bound with near ideal trans geometry (P20–Rh1–P40 = 171.90(2)°) in the solid state (Fig. 1B).

The coordinated water ligand is projected into the calix[4]arene cavity with a Rh1–O1 bond distance of 2.2046(14) Å and approximately linear C15–Rh1–O1 angle of 172.17(8)°. The formally vacant coordination site of the metal centre is sterically occluded by two phenyl groups of the CxP1 ligand, with carbon contacts >3.4 Å suggesting that any stabilisation by agostic bonding is minimal.8 In any case, these phenyl groups complete the encapsulation of the aqua ligand, which is contained within an almost uninterupted van der Waals surface defined by the components of 1.

Treatment of 1-ΟΗ2 with an excess of the potent drying agent [ZrCp2Me2]9 in CD3Cl under an atmosphere of dinitrogen resulted in smooth conversion into a 6:5 dynamic equilibrium mixture of new rhodium(III) CxP1 complexes we assign as 1-N2 (δ31P 16.1, J1PP = 117 Hz) and 1-DCM (δ31P 4.4, J1PP = 117 Hz) within 24 h at room temperature. These assignments were substantiated by freeze-pump-thaw degassing the solution to remove dinitrogen and a control reaction carried out under an atmosphere of argon, both of which resulted in exclusive formation of 1-DCM. Highlighting the decisive role of the calix[4]arene scaffold, the spectroscopic characteristics of the bis(triphenylphosphine) analogue trans-[Rh(biph)][PPh3]2(k1-CIC6H4Cl)][Al(OR)3]2 (2-DCM) remain unchanged under an atmosphere of dinitrogen. Encouraged by these findings, the reaction between 1-ΟΗ2 and [ZrCp2Me2] was repeated under an atmosphere of dinitrogen in the more weakly coordinating

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solvent fluorobenzene.\textsuperscript{10} Consistent with our interpretation so far, 1-N\textsubscript{2} (\(\delta_{13}^{\text{CP}} 16.0; 1^{\text{J}}_{\text{Rh1P}} = 116 \text{ Hz}\)) was the only dehydration product observed by NMR spectroscopy.\textsuperscript{11} Subsequent analysis of 1-N\textsubscript{2} by solution-phase IR spectroscopy provided direct evidence for coordination of dinitrogen. A very low intensity signal was observed at 2290 cm\(^{-1}\) and is tentatively assigned to the v(N=N) band. This band is red-shifted relative to free N\textsubscript{2} (2330 cm\(^{-1}\)), but considerably higher frequency than previously reported for terminal group 9 examples (1910–2236 cm\(^{-1}\)). \textsuperscript{1,3} The assignment is supported by exposure of the sample to air, which resulted in disappearance of the v(N=N) band and formation of 1-OH\textsubscript{2} within 5 seconds, slow evaporation of the solvent and analysis of the residue by ATR-IR spectroscopy within a dinitrogen filled glovebox, and computational analysis.

Despite numerous attempts, our efforts to isolate analytically pure samples of 1-N\textsubscript{2} from solution were frustrated by the extremely strong affinity of 1 for water, resulting in contamination of samples with 1-OH\textsubscript{2} by reaction with adventitious water.\textsuperscript{12} In one instance we were, however, able to obtain a single crystal of 1-N\textsubscript{2} suitable for analysis by X-ray diffraction, by slow diffusion of hexane into a CH\textsubscript{2}Cl\textsubscript{2} solution of 1-N\textsubscript{2} generated in situ using [ZrCp\textsubscript{2}Me\textsubscript{2}]\textsuperscript{+} (Fig. 1B). The dinitrogen ligand was readily located from the Fourier difference map, was freely refined with 100% crystallographic occupancy, and there is no evidence for significant disorder (Fourier peaks <0.5 eÅ\(^{-3}\)). Whilst this crystal was not representative of the bulk of the sample, it is the first structurally characterised example of a rhodium(III) dinitrogen complex. The solid-state structure of 1-N\textsubscript{2} is isomorphous to 1-OH\textsubscript{2} and the bulk geometric features of the [Rh(biph)(C\textsubscript{6}P\textsubscript{3}OPr\textsubscript{2})\textsuperscript{2}]\textsuperscript{+} fragment are consequently similar. There are, however, statistically significant perturbations to the metal-centred metrics. For instance, the Rh1–N1 bond length observed is substantially longer than all these examples (2.160(2) Å). As for the aqua derivative, the Rh1–N1 bond length observed is fluxional in solution on the NMR time scale, adopting time-averaged C\textsubscript{2v} symmetry in solution at 298 K. We attempted to probe coordination of dinitrogen by \textsuperscript{15}N NMR spectroscopy using an isotopically enriched sample in fluorobenzene, but only free dinitrogen was observed. Presumably ligand exchange is fast on the timescale of the NMR experiment at 298 K.

To help delineate the role of the calix[4]arene scaffold, a DFT-based energy decomposition analysis was performed in...
combination with natural orbital for chemical valence (EDA-NOCC; PBE-D3(BJ)/TZ2P-ZORA level of theory) using minimum energy structures of 1-L and 2-L (L = H2O, N2, DCM; optimised at the PBE-D3(BJ)/def2-SVP level of theory).14 Consistent with our hypothesis that Cpx₂ destabilises solvent over dinitrogen coordination, the calculated bond dissociation energies (ΔE_diss) decrease in the order H₂O (89.6) > DCM (71.3) > N₂ (68.6) for the (triphenylphosphine) complexes 2-L, but H₂O (118.9) > N₂ (81.9) >> DCM (33.9) for 1-L. Dichloromethane is not only too large to be accommodated within the calix[4]arene scaffold in 1, but requires a destabilising conformational change to permit metal coordination adjacent to the upper rim of the macrocycle (ΔE_prep = +50.7, cf. +16.4 kJ·mol⁻¹ for 2). The interaction between 1-L and dinitrogen is characterised by a greater extent of σ-donation (ΔE_L=M = 42.8%) than π-back bonding (ΔE_M=π = 44.6%) and no meaningful covariant interactions with the cavity were identified from the NOCCV analysis (Fig. S37). This net charge transfer to the metal is unusual for dinitrogen complexes observed in the condensed phase (ΔE_ferm = +21.0 eV).


Conflicts of interest
The authors declare no conflicts of interest.

Notes and references