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Formation of $[Ru(NHC)_4(\eta^2\text{-}O_2)H]^+$: An Unusual, High Frequency Hydride Chemical Shift and Facile, Reversible Coordination of O_2

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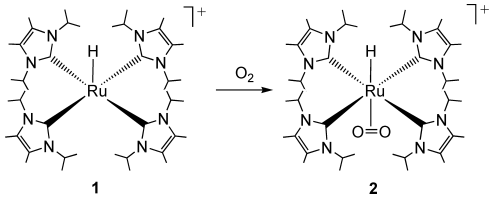
The coordination and activation of dioxygen by transition metal complexes continues to be the focus of considerable interest in attempts to develop new, atom economical oxidation catalysts for organic synthesis.[1] N-heterocyclic carbenes (NHCs) are very promising ligands in this field due to their ability to support high-oxidation state metal complexes with strong $M-C_{NHC}$ bonds which should enhance stability under oxidizing conditions.[2] However, the rational design of any new NHC based catalysts first requires a fundamental understanding of how O_2 interacts with different M−NHC fragments and the impact of oxygen coordination/activation on their chemical and structural properties. We now report an experimental and computational study on the reaction of the tetrakiscarbene ruthenium cation $[Ru(I^iPr_2Me_2)_4H]^+$ (**1**, $I^iPr_2Me_2$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) with oxygen which affords the η^2-O_2 hydride species $[Ru(I^iPr_2Me_2)_4(\eta^2\text{-}O_2)H]^+$ (**2**, eq 1). **2** displays (i) a very facile, reversible O_2 coordination and (ii) an unexpectedly positive hydride chemical shift, and both these features can be predicted and explained by density functional theory (DFT) calculations.



1 **2** (1)

Addition of 1 atm of O_2 at room temperature to C_5D_5N or CD_2Cl_2 solutions of **1**$[BAr_4^F]$ (BAr_4^F = $B\{(3,5\text{-}CF_3)_2C_6H_3\}_4$) resulted in an instantaneous color change from purple to pink with the formation of a single new product, **2**$[BAr_4^F]$. While those regions of the ^1H NMR spectrum associated with the NHC were very similar for both colored solutions (**1** and **2** displayed nonequivalent ^{i}Pr and backbone methyl ^1H resonances due to the perpendicular arrangement of the imidazol-2-ylidene rings with respect to the plane defined by the four carbene C-atoms and the metal center), the addition of O_2 led to the complete disappearance of the very low frequency hydride resonance of **1** at δ −41.2 and formation of a new resonance of integral one at δ +4.8. While the high frequency of this signal suggested initially that **2** could be the hydroperoxy cation, $[Ru(I^iPr_2Me_2)_4(OOH)]^+$,[3] we have been able to exclude this possibility by a combination of structural, spectroscopic, and computational studies. The molecular structure of **2** (Figure 1) clearly shows a side-on bound O_2 molecule, with O−O and Ru−O distances of 1.354(5) and 2.088(3)/2.087(3) Å.[4] This immediately excludes an η^1-OOH structure, although the intrinsic difficulty in structurally locating hydrogen atoms meant an η^2-OOH structure could not be ruled out. Firm evidence for the formulation of **2** as an η^2-dioxygen hydride complex came from the IR spectrum, which displayed a clear Ru−H stretch at 1992 cm^{-1} (*c.f.* 2054 cm^{-1} for **1**)[5] along with a lower frequency band at 1047 cm^{-1} assigned to the O−O stretch ($^{18}O_2$ labeling shifted this to 992 cm^{-1}, close to the calculated value of 987 cm^{-1}). The T_1(min) value of 124 ms (400 MHz, 216 K) measured for the resonance at δ +4.8 was comparable to the values found for the hydride signals of **1** (δ −41.2: 98 ms, 400 MHz, 204 K) and $[Ru(I^iPr_2Me_2)_4(CO)H][BAr_4^F]$ (**3**$[BAr_4^F]$) (δ −3.1: 137 ms, 400 MHz, 222 K). Moreover, the *J*-resolved $^1H-^{13}C$ HMBC spectrum of **2** (220 K) revealed a coupling constant of 5.2 Hz between the δ +4.8 signal and the ^{13}C carbene resonance at δ 176, a value comparable to those recorded in **1** (5.0 Hz) and **3** (4.8 Hz). Finally, $^1H-^1H$ NOESY data revealed a strong contact between the hydride signal at δ +4.8 and one of the two ^{i}Pr methine CH resonances.

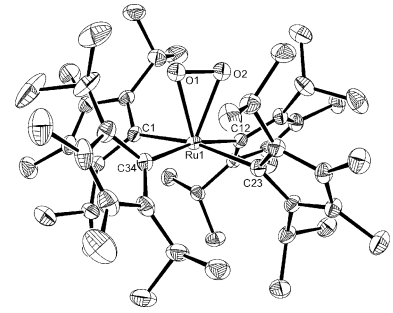


Figure 1. Molecular structure of **2**. Thermal ellipsoids are shown at the 30% probability level, and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ru(1)−O(1) 2.088(3), Ru(1)−O(2) 2.087(3), Ru(1)−C(1) 2.171(4), Ru(1)−C(12) 2.176(4), Ru(1)−C(23) 2.162(4), Ru(1)−C(34) 2.138(4), O(1)−O(2) 1.354(5).

DFT calculations[6] on **2** confirmed the *trans*-H-Ru-(η^2-O_2) structure with no minimum corresponding to the alternative five-coordinate η^2-OOH form being located.[7] The details of the computed structure also agree well with experiment (Ru−O(av) = 2.11 Å, O−O = 1.37 Å, Ru−C(av) = 2.19 Å, Ru−H = 1.61 Å); **2** is therefore a rare example of a dioxygen adduct with an unusually short O−O distance.[4,8] Quantitative formation of **2** was shown by ^1H NMR spectroscopy to occur upon addition of O_2 to **1** at temperatures as low as 193 K. Moreover, the coordinated O_2 ligand proved to be only weakly bound and, in stark contrast to other M(η^2-O_2) species,[9] could be removed by simple freeze−pump−thaw degassing of solutions of **2**. The reversible coordination of O_2 even took place in the solid state; exposing solid **1** to 1 atm of O_2 at 298

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K led to the same purple to pink color change associated with formation of **2**, while application of a vacuum regenerated purple **1** (IR spectroscopy confirmed the transformation). This remarkably reversible oxygen coordination prompted us to compute the energy profile for $^3O_2$ addition to **1** (Figure 2). This is initiated by the barrierless formation of triplet *trans*-[Ru(^{i}Pr$_2$Me$_2$)$_4$(η^1-O$_2$)H]$^+$ (^{3}**2**, E = +0.5 kcal/mol) with a Ru−O−O angle (θ) of 161.5°.[10] Reducing θ in ^{3}**2** to give singlet **2** (denoted hereafter ^{1}**2**) revealed the presence of a second triplet state, ^{3}**2b** (E = +7.0 kcal/mol, θ = 109.9°). ^{3}**2b** was shown to link ^{3}**2** and ^{1}**2** via crossover points at $\theta \approx 125°$ and 90°, respectively. For the latter a triplet-singlet minimum energy crossing point (MECP) was located[11] (θ = 91.1°, E = 12.0 kcal/mol), and this represents the barrier to interconversion between ^{3}**2** and ^{1}**2**. Figure 2 also maps how charge density transfers from Ru to O_2 in forming ^{1}**2**. The most significant change occurs in forming ^{3}**2**, and this, along with computed spin densities,[12] suggests this species (and ^{3}**2b**) are correctly formulated as Ru^{III}-superoxo complexes. Formation of ^{1}**2** then sees a further partial reduction of the {O$_2$} moiety.

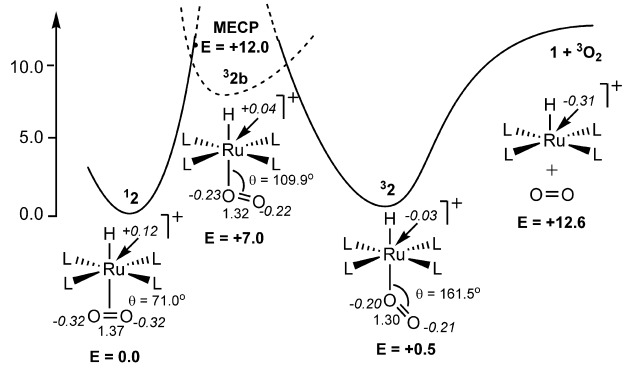

Figure 2. Computed energy profile (kcal/mol) for the addition of $^3O_2$ to **1** with potential energy curves for variation of the Ru−O−O angle, θ, in ^{3}**2**, ^{3}**2b**, and ^{1}**2** (L = ^{i}Pr$_2$Me$_2$). Also shown are values for θ and O−O distances (Å, degrees, plain text) and natural atomic charges at Ru and O (italics).

Overall, the O_2 addition profile for **1** is similar to that described for PdL$_2$/O$_2$ systems,[13] except for the involvement of the second triplet state (^{3}**2b**) in the present case. The highly reversible nature of O_2 binding to **1** is reflected in the Ru−O$_2$ binding energy which was computed to be only 12.6 kcal/mol, while the computed free energy change is only 3.5 kcal/mol (in favor of $^3O_2$ + **1**). This low binding energy may reflect the less electron-releasing nature of square-pyramidal d^6 {ML$_5$} fragments over C_{2v} d^{10} {ML$_2$} species; however, we believe the steric bulk of the ^{i}Pr$_2$Me$_2$ ligand is a key factor here: with [Ru(IMe$_4$)$_4$(η^2-O$_2$)H] (IMe$_4$ = 1,3,4,5-tetramethylimidazol-2-ylidene) the computed O_2 binding energy increases to 27.4 kcal/mol, while for [Ru(^{i}Pr$_2$P(CH$_2$)$_2$P^{i}Pr)$_2$(η^2-O$_2$)H]$^+$ a value of 24.1 kcal/mol is obtained.[4]

DFT calculations were also performed to probe the unusual positive chemical shift associated with the hydride ligand of **2**,[14,15] which contrasts markedly with the more standard negative chemical shifts reported for the phosphine analogues [Ru(P−P)$_2$(η^2-O$_2$)H]$^+$ (P−P = R$_2$P(CH$_2$)$_2$PR$_2$, R = ^{i}Pr, Cy: δ −5.9).[4] Calculations on both ^{1}**2** and [Ru(^{i}Pr$_2$P(CH$_2$)$_2$P^{i}Pr)$_2$(η^2-O$_2$)H]$^+$ satisfactorily reproduce these differences with δ_{calc} = +5.3 and −4.5, respectively. Partitioning of the various components of these computed chemical shifts indicate that the diamagnetic and spin−orbit terms are approximately constant in the NHC and P−P systems. The major difference arises from the paramagnetic term that yields a high frequency 5.3 ppm contribution in **2** but a low frequency 5.6 ppm in [Ru(^{i}Pr$_2$P(CH$_2$)$_2$P^{i}Pr$_2$)$_2$(η^2-O$_2$)H]$^+$.

In summary, we have shown that the NHC complex **1** reacts with O_2 to afford the η^2-dioxygen hydride complex **2** which displays unusual and very different chemical and spectroscopic properties to the related phosphine derivatives. Efforts to alter the coordinating ability of derivatives of **1** through manipulation of sterics by changing the N-substituents on the NHC ligands are currently underway.

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Supporting Information Available: Spectroscopic data for **1**−**3**, X-ray structures of **1** and **3**, X-ray files (CIF format) for **1**−**3** (CCDC 713540−713542). Computed Cartesian coordinates and energies; full refs 6 and 14. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Attempted optimization led instead to an η^1-OOH geometry which was 1.4 kcal/mol higher in energy than the *trans*-H-Ru-(η^2-O$_2$) form.
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