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Di- and Trivalent Ruthenium Complexes of Chelating, Anionic N-Heterocyclic Carbenes

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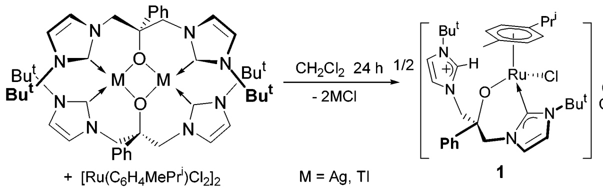
Summary: The reactions of a range of Ru(II) complexes with the anionic alkoxy di-N-heterocyclic carbenes $M[OCPh(CH_2\{1\text{-}C[NCHCHNBu^t]\})_2]$ *(ML; M = Ag, Tl) yield a mixed carbene−imidazolium complex of ruthenium(II),* $[Ru(p\text{-cymene})[OCPh(CH_2\{1\text{-}C[NCHCHNBu^t]\})(CH_2\{1\text{-}CH[NCHCHNBu^t]\}Cl)]Cl$*, and the first trivalent ruthenium N-heterocyclic carbene complex,* $[RuCl_2(PPh_3)(L)]$*, in this case stabilized by the two bound carbene groups.*

The N-heterocyclic carbene (NHC) has earned a special place in the design of organometallic homogeneous catalysts in recent years. It is now used widely as a strongly basic alternative to phosphanes and other supporting ligands in homogeneous ruthenium-based catalytic systems for olefin metathesis, hydrogenation, and atom transfer radical polymerization (ATRP) and cycloisomerization,[1] while some ruthenium NHC complexes exhibit remarkable C−H and C−C bond activation chemistry.[2] To tune the reactivity of NHC derivatives, a range of N-alkyl modified carbenes have been reported which incorporate either chiral or additional donor functional groups.[3] We have prepared ligands that combine this strong, neutral σ-donor NHC group with an adjacent anionic group, the simplest of which, due to its symmetry, is an alkoxide with two pendant N-heterocyclic functional groups L, $[O^-CPh(CH_2\{1\text{-}C[NCHCHNBu^t]\})_2]$.[4] As part of a study of the applicability of this ligand in homogeneous catalysis, we have explored the chemistry of a range of coordination complexes of ruthenium, with the aim of determining the extent to which the additional alkoxide group increases the thermal stability of Ru−NHC adducts and allows the stabilization of more electron deficient, reactive metal centers.[5] The ruthenium(III) carbene fragment is of interest due to the involvement of the Ru(II)/Ru(III) couple in the mechanism of ruthenium complex catalyzed ATRP (atom transfer radical polymerization) catalysis and the implication of the Ru(III) carbene in Gif systems for the selective, catalytic oxidation of alkanes.[6] Recently, a multistep synthesis of a 1,1-binaphthol-derived aryloxy carbene has been used to make enantio- and diastereoselective ruthenium-based olefin metathesis catalysts. The scarcity, but potential utility, of chelating bis-carbenes in ruthenium-catalyzed reactions has also been highlighted recently.[7] The ligand L combines these features—an alcohol functional group and two strongly σ-basic NHC groups—and is made in a one-pot reaction. Herein, we report the reactions of silver and thallium(I) alkoxide salts of this ligand to form a stable Ru(II) complex and the first trivalent ruthenium carbene complex.

Treatment of a dichloromethane solution of $[Ru(p\text{-cymene})Cl_2]_2$ with stoichiometric [AgL] at room temperature affords a precipitate of silver chloride and a dark red-brown solution, from which a red-brown microcrystalline solid may be isolated after addition of hexanes (eq 1). This complex still contains the coordinated arene and initially contains one free and one bound NHC group of the ligand L. However, the pendant NHC group is strongly basic and picks up the elements of HCl to afford the imidazolium salt of the carbene complex; the red-brown microcrystalline complex $[Ru\{HL\}(p\text{-cymene})Cl]Cl$ (**1**) is isolated in an overall yield of 79%.[17] The analogous reaction of $[Ru(p\text{-cymene})Cl_2]_2$ with the thallium analogue [TlL],[18] also affords **1**, after removal of TlCl and recrystallization from dichloromethane. The reaction between $[Ru(p\text{-cymene})Cl_2]_2$ and [AgL] in thf affords the same complex, showing that the chlorinated solvent is not necessary to provide the halogen counterion for the unbound NHC



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group. The yield of the reaction carried out in thf is lower, 52%, so in the absence of chlorinated solvent the ruthenium dichloride starting material is a sacrificial chloride source, providing slightly more than one molar equivalent of chloride. In this reaction, the protonation of the pendant NHC group is too rapid to allow any heating of the solution which could effect the substitution of the arene by the pendant NHC group.[7b]

The bound carbene is identified in the ^{13}C NMR spectrum at the characteristically high-frequency shift of 172.1 ppm. However, the spectrum also shows a resonance at 146.3 ppm, characteristic of an imidazolium CH carbon. The ^{1}H NMR spectrum shows a singlet at 9.95 ppm, corresponding to one imidazolium proton in the product, and a doublet resonance for each of the backbone CH_2 protons of the ligand, according to the asymmetry of the ligand. Electrospray mass spectrometry shows an ion with *m*/*z* 651, corresponding to $[Ru(C_{10}H_{14})\{HL\}Cl]^+$, indicating that one of the imidazol-2-ylidene groups has been reprotonated.

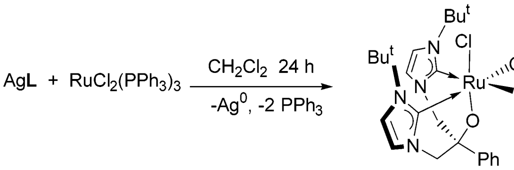
In addition to providing a common oxidative route to metal chlorides, the abstraction of a chloride from chlorinated solvents is also found for simple N,N′-dialkyl carbenes. These can react with CCl_4 and $C_2H_2Cl_4$ to substitute the 4,5-imidazole hydrogen atoms with chlorides and the 2-position with chloride or dichloromethyl groups.[8] The formation of **1** occurs in highest yield in dichloromethane with no evidence of chlorination of the NHC ring. Characterized ruthenium alkoxide complexes are rare; the only previously reported alkoxide-containing N-heterocyclic carbene complex is a *tert*-butoxide analogue of Grubbs' second-generation metathesis catalyst, $[Ru(OBu^t)_2CH_2[1\text{-}C[NCHCHNMes])Cl_2(PCy_3)_2({=}CHPh)]$.[9]

The fact that this complex reprotonates the imidazolium group in preference to the alkoxide contrasts with the recent report of a Ru(II) complex of the bidentate carbene alcohol $[Ru(HOCH_2CH_2[1\text{-}C[NCHCHNMes])Cl_2(py)_2({=}CHPh)]$, which was not deprotonated to the alkoxide but instead formed a complex in which the alcohol displaces one chloride anion from the inner coordination sphere.[10] The isolation of **1** shows that the alkoxide group is a most suitable ligand for Ru(II) in these systems, provided a suitable precursor is available.

The use of ruthenium NHC complexes as homogeneous catalysts in imidazolium-based ionic liquid media has attracted much attention recently, as imidazolium salts have been shown to be capable of acting both as solvent and ligand precursors for a dissolved ruthenium complex: for example, in diene and enyne metathesis catalysis.[11] We find that **1** is as soluble in the ionic liquid $[BMIM]PF_6$ (BMIM = *n*-butylmethylimidazolium cation) as it is in toluene but dissolves completely into the ionic liquid layer when treated with a 1:1 mixture of toluene and $[BMIM]PF_6$.

As an alternative route to a ruthenium alkoxide complex with two bound NHC groups, Ru(II) precursors with other ancillary ligands were addressed. No tractable products could be isolated from the reaction of the solvate $[RuCl_2(DMSO)_4]$ with uninegative metal salts of L. We also note that Grubb's "first generation" olefin metathesis promoter, $[RuCl_2(PCy_3)_2({=}CHPh)]$, does not react with [AgL].[19]

However, the reaction between $[RuCl_2(PPh_3)_3]$ and 1 equiv of [AgL] in dichloromethane at 20 °C affords a dark, heavy precipitate and a dark green-brown (dichroic) solution. Recrystallization of the filtrate from dichloromethane/hexanes affords a microcrystalline green-brown complex characterized as the trivalent $[Ru\{L\}Cl_2(PPh_3)]$ (**2**) in 67% yield (eq 2).[20] The eliminated dark precipitate, assumed to be silver metal, gives a negative test for halide (titration with silver nitrate), confirming this. Electrospray mass spectrometry of **2** shows a molecular fragment with an *m*/*z* value of 775, corresponding to $[Ru\{L\}PPh_3Cl_2]^+$. The broadened ^{1}H NMR spectrum indicates a paramagnetic product.



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To the best of our knowledge, this is the first trivalent ruthenium complex of an N-heterocyclic carbene, the higher oxidation state being stabilized in part by the hard alkoxide group and by the two NHC groups, which are most suitable for the stabilization of electron-deficient metals.[12]

The solution magnetic moment of **2** (Evans' method) is 2.2 μ_B, in the range observed for low-spin d^5 Ru(III) complexes.[13] An EPR spectrum of **2** shows the electron centered at ruthenium(III), and the rhombicity of the spectra indicate the asymmetry of the electronic environment at the $^{2}T_{2g}$ ruthenium(III) metal center, with approximate *g* values $g_{11} = 2.50$, $g_{22} = 2.16$, and $g_{33} = 1.89$ measured, and evidence of hyperfine coupling to one ^{31}P $I = {}^1/_2$ nucleus in the g_{11} ($A_{11} = 189$ G) and g_{33} ($A_{33} = 44$ G) regions.

It is notable that the oxidation of Ru(II) to Ru(III) by [AgL] only occurs for the phosphine-substituted system **2** and not for the *p*-cymene adduct under the same reaction conditions.[21] The oxidation potential of [AgL] is markedly lower than that of simple silver salts but clearly high enough to explain the oxidation to form **2**. A cyclic voltammogram of [AgL] in dichloromethane shows an oxidation at +0.404 V and in thf shows an oxidation at +0.107 V.[14] The $Ag^{+/0}$ couple is +0.65 V in CH_2Cl_2 and +0.41 V in thf.[15] The $E°_{ox}$ value for the bis(carbene) complex **2** in thf is −0.036 V; this is also remarkably low, compared with other Ru(III) organometallic complexes and the monodentate NHC adducts $[Ru(p\text{-cymene})Cl_2(NHC)]$ ($E°_{ox}$ in the range 0.61−0.67 V),[1c] confirming the strongly stabilizing effect of the two Lewis basic NHC groups on the higher oxidation state.

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Unfortunately, raising the potential in this solvent/electrolyte system results in stripping at the electrode at +0.224 V; thus, we were unable to identify any Ru(IV) chemistry in this solvent/electrolyte system.

The oxidation potential for the Ru(II) center in the precursor $[Ru(p\text{-cymene})Cl_2]_2$ is +0.48 V (measured in thf);[16] this is too high to be oxidized by [AgL]. If during the reaction to form **1** the second NHC group never coordinates, the higher oxidation potential of the Ru(III)/Ru(II) couple in that system prevents it from being oxidized by [AgL].

In conclusion, the strongly electron-donating, tridentate bis(carbene) alkoxide ligand $[O^-CPh(CH_2\{1\text{-}C[NCHCHNBu^t]\})_2]$ effectively stabilizes new complexes of Ru(II) and Ru(III); a mixed carbene−imidazolium complex has been isolated in which the oxygen ligand binds in preference to chloride and can be made from silver(I) or thallium(I) alkoxy carbene precursors. The two carbene donors that stabilize the silver alkoxide carbene transfer reagent, rendering it a poor oxidant, also allow easy access to the first trivalent ruthenium N-heterocyclic carbene complex.

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Supporting Information Available: Text and figures giving full synthetic and characterization data for the complexes and cyclic voltammetric and EPR spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] Data for **1** are as follows. ^{13}C NMR ($CDCl_3$): δ 172.1 (NCN), 146.3 (NCHN). Anal. Found (calcd) for $RuC_{33}H_{46}N_4OCl_2\cdot 2CH_2Cl_2$: C, 49.38 (49.08); H, 5.78 (5.88); N, 6.47 (6.54). MS (ES): *m*/*z* 651 ($[M - Cl]^+$, 100%). Mp: 145−146 °C dec.

[18] Thallium NHC complexes are also rare, but the stability and ease of synthesis of this suggests that this is due to their toxicity rather than any instability. Synthesis of TlL: to a suspension of H_2LCl in thf was added 2 molar equiv of TlCp and the mixture stirred for 18 h. The yellow supernatant was extracted and evaporated to dryness under reduced pressure to yield the complex as used here. The salt could be isolated pure by recrystallization from thf. Isolated yield: 47%. ^1H NMR ($CDCl_3$): δ 7.77 (s, 2H), 7.35 (m, 5H), 7.10 (s, 2H), 4.00 (d, *J* = 12 Hz, 2H), 3.87 (d, *J* = 12 Hz, 2H), 1.58 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 163.8. MS (ES): *m*/*z* 583 (M^+).

[19] Anticipated to form the complex [RuCl{L}(=CHPh)], no reaction was observed in common organic solvents, even to the point at which the complexes decompose after prolonged reflux in THF.

[20] Data for **2** are as follows. ^{31}P NMR ($CDCl_3$): δ 26.8. MS (FAB): *m*/*z* 775 ($[M - Cl]^+$, 100%). Anal. Found (calcd) for $RuC_{41}H_{46}N_4OCl_2P$: C, 60.46 (60.51); H, 5.52 (5.70); N, 6.82 (6.88).

[21] Conditions: electrolyte $[NBu_4][PF_6]$, 0.5 M in thf, 0.4 M in CH_2Cl_2, all potentials quoted vs Fc^+/Fc.