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New Oxypyridinate Paddlewheel Ligands for Alkane-Soluble, Sterically-Protected Ru₂(II,III) and Ru₂(II,II) Complexes

Tristan R. Brown, Josephine P. Lange, Michael J. Mortimer, and John F. Berry*®

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, Wisconsin 53706, United States

Supporting Information

ABSTRACT: The paddlewheel complex $Ru_2(chp)_4Cl$ (1-Cl, chp = 6-chloro-2-oxypyridinate), upon reduction with Zn, has been previously shown to dimerize to $[Ru_2(chp)_4]_2$ (2), blocking further chemistry at the Ru₂(II,II) axial site [Inorg. Chem. 2015, 54, 8571-8589]. Functionalization of the chp ligand at the 3 and 5 positions with either bromine (dbchpH = 3,5-dibromo-6-chloro-2pyridone) or trimethylsilyl (TMS) groups (dsichpH = 6-chloro-3,5bis(trimethylsilyl)-2-pyridone) allows for the preparation of the $Ru_2(II,II)$ paddlewheel complexes $Ru_2(dbchp)_4$ (3) and $Ru_2(dsichp)_4$ (6), respectively, neither of which shows evidence of dimerization. Though the utilization of 3 is limited due to



insolubility, complex 6 is soluble even in typically non-coordinating solvents, forming a stable κ^{1} -axial adduct in CH₂Cl₂ (6- CH_2CI_2) and showing evidence of an axial interaction with *n*-decane. The first example of an axially free $Ru_2(II,II)$ complex with a ³A ground state is observed upon crystallization of 6 from benzene ($6-C_6D_6$). Complex 6 is accessed via Zn reduction of $Ru_2(dsichp)_4Cl$ (4-Cl), which along with $Ru_2(dsichp)_4N_3$ (4-N₃), show similar structural and electronic properties to their non-TMS-substituted analogues, 1-Cl and 1-N₃. Photolysis of 4-N₃ in frozen solution generates $Ru_2(dsichp)_4N$ (5); no N atom transfer to PPh₃ is observed upon room temperature photolysis in fluid solution.

1. INTRODUCTION

Diruthenium paddlewheel complexes have recently been used in several examples of catalytic or stoichiometric reactions involving group transfer or small molecule activation.¹⁻¹⁰ In pursuit of new platforms for these types of reactions, we have explored low-valent chemistry of Ru₂ complexes with the wellknown^{11,12} 6-chloro-2-oxypyridinate (chp) ligand by reduction of $\operatorname{Ru}_2(\operatorname{chp})_4\operatorname{Cl}(1-\operatorname{Cl})$ in the presence of neutral L ligands.¹³ We found that $Ru_2(chp)_4$ is competitively bound by either L or by a neighboring $Ru_2(chp)_4$ unit, leading to aggregation into a tetrametallic structure 2 (Scheme 1). This dimerization reaction precludes the binding of many important substrates of interest,¹⁴⁻¹⁶ so we present here an approach to sterically disfavor the dimerization of Ru₂(II,II) complexes.

The proclivity of the known Ru₂(II,II) paddlewheel complexes to bind axial ligands can be divided into three distinct categories based on their nominal electronic ground





states in C₄ symmetry: ³A, hybridized ³A/³E (Jahn–Teller distorted to ³A" in C_s symmetry), and ¹A.¹³ The ¹A complexes often eschew axial coordination but have been known to bind π -acceptor ligands.^{17,18} On the other hand, the ³A complexes (e.g., $\operatorname{Ru}_2(\operatorname{OAc})_{4^{j}}^{19} \operatorname{Ru}_2(\operatorname{chp})_4$) strongly favor axial coordination by any available σ -donor. The single experimentally observed example of a ³A/³E hybrid, displaying a bent Ru-Ru–P angle that allows mixing of the δ^* and π^* orbitals, was formed upon coordination of PPh₃ to $Ru_2(chp)_4$. While a wide variety of axially-coordinated substrates could theoretically be available to the ³A-type complexes with carboxylate or pyridinate equatorial ligands, in practice, aggregation outcompetes axial coordination of all but the strongest σ -donors. For example, Zn reduction of $Ru_2(chp)_4Cl$ (1-Cl) in tetrahydrofuran (THF) predominantly yields $[Ru_2(chp)_4]_2$ (2, Scheme 1) alongside a small amount of the solvent adduct $\operatorname{Ru}_{2}(\operatorname{chp})_{4}(\operatorname{THF})^{13}$ Inhibition of this dimerization is thus a priority to test the limits of axial coordination and smallmolecule activation chemistry by Ru₂(II,II) centers.

On the basis of the structure of 2, we hypothesized that the addition of substituents to the 3-position of the chp ligand would prevent the chp lone pair from being able to coordinate, while keeping the Ru₂ axial site available to bind L ligands (Chart 1). Thus, we report the synthesis and characterization of two new pyridones, dbchpH (dbchpH = 3,5-dibromo-6-

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Chart 1. Steric Inhibition of Dimerization^a



^{*a*}Out-of-plane ligands are omitted for clarity.

chloro-2-pyridone) and dsichpH (dsichpH = 6-chloro-3,5bis(trimethylsilyl)-2-pyridone), for use as equatorial ligands in nondimerizing M_2 paddlewheel complexes (Chart 2). Preparation and characterization of the new complexes $Ru_2(dsichp)_4Cl$ (4-Cl) and $Ru_2(dsichp)_4N_3$ (4-N₃) are described. These complexes are alkane-soluble, sterically protected analogues to 1-Cl²⁰ and $Ru_2(chp)_4N_3$ (1-N₃)^{6,21} respectively. The photoreactivity of 4-N₃ is compared to that of 1-N₃. We also report reduction of 4-Cl to $Ru_2(dsichp)_4$ (6), which allows us to examine the coordination chemistry and properties of $Ru_2(II,II)$ complexes that have been sterically protected against dimerization.

Chart 2. Compounds Discussed

Ligands	Diruthenium Complexes
chpH	<u>Prior Work</u> 1-CI : Ru ₂ (chp) ₄ Cl
	1-N ₃ : Ru ₂ (chp) ₄ N ₃
dbchpH	2 : [Ru ₂ (chp) ₄] ₂
Br Br	<u>This</u> <u>Work</u> 3: Ru-(dbcbb)
	4-CI: Ru₂(dsichp)₄Cl
dsichpH TMS:TMS	4-N ₃ : Ru ₂ (dsichp) ₄ N ₃
	5: Ru ₂ (dsichp) ₄ N
H H	6-CH₂Cl₂ : Ru ₂ (dsichp) ₄ (κ^{1} -CH ₂ Cl ₂)
TMS = trimethylsilyl	6-C₆D₆ : Ru₂(dsichp)₄•C ₆ D ₆
	6-OH ₂ : Ru ₂ (dsichp) ₄ (OH ₂)
	6-dec : Ru ₂ (dsichp) ₄ • <i>n</i> -decane

2. EXPERIMENTAL SECTION

2.1. General. Except where otherwise noted, all syntheses, product isolations, and characterizations were carried out under a dry N_2 atmosphere using established Schlenk techniques or in a glovebox. All solvents used in air-free conditions were dried, purified, and degassed according to standard techniques. *N*-Bromosuccinimide (NBS, 10 g) was recrystallized from water prior to use. The preparations of new equatorial ligands, dbchpH and dsichpH are described in the Supporting Information. Lithium diisopropylamide (LDA) was

purchased as a 1 M solution in THF/hexanes from Sigma-Aldrich and used as provided. Chlorotrimethylsilane (TMSCl) was distilled from CaH₂ and degassed prior to use. The 6-chloro-2-pyridone (chpH) ligand was recrystallized from hexanes prior to use. Ru₂(OAc)₄Cl was prepared as previously described²² with important modifications.¹³ Photolysis of samples of 4-N₃ was performed in a Rayonet RPR-200 photochemical reactor using 350 nm mercury vapor lamps.

Safety Note: Although we did not have any issues with the preparation of $4-N_{3}$, it should be noted that metal azide complexes are potentially explosive.

2.2. Preparation of Ru₂ Compounds. 2.2.1. Generation of $Ru_2(dbchp)_4$ (3). Starting from Ru₂(OAc)₄Cl (150 mg, 0.317 mmol), LiCl (140 mg, 3.29 mmol), and dbchpH (728 mg, 2.53 mmol), a procedure similar to the synthesis of 1-Cl¹ was used to generate bright red-orange solids containing Ru₂(dbchp)₄. Insolubility precluded isolation of this compound in pure form. MALDI-TOF (m/z): 1348 [M]⁺.

2.2.2. Preparation of $Ru_2(dsichp)_4CI$ (4-Cl). $Ru_2(OAc)_4CI$ (800 mg, 1.69 mmol), LiCl (744 mg, 17.6 mmol), and dsichpH (1.85 g, 6.75 mmol) were dried under a vacuum at 80 °C for 1 h in a 200 mL Schlenk flask fitted with a Soxhlet extractor and condenser containing anhydrous K_2CO_3 (2 g) in a cellulose thimble. Toluene (100 mL) was added, and the mixture was heated to reflux at 150 °C for 72 h. The mixture was filtered and washed with cold toluene (20 mL), and the filtrate was evaporated to dryness. An orange side-product was removed from these solids by washing with minimal cold hexanes (about 40 mL), leaving the desired product as a dark purple powder. Yield: 1.05 g (46.8%). UV-vis ($C\hat{H}_2Cl_2$, λ_{max} nm (\bar{e} , \bar{M}^{-1} cm⁻¹)): 963 (360), 717 (1500), 554 (7200), 453 (2100), 398 (2800). MALDI-TOF (m/z): 1294 $[M - Cl]^+$, 1329 $[M]^+$. χT (CDCl₃, 297.1 K): 1.77 emu K mol⁻¹. ¹H NMR (500 MHz, C_6D_6): δ (ppm) = 30.42 (br, 4H), 5.19 (br, 36H), 1.22 (br, 36H). ²⁹Si NMR (100 MHz, C_6D_6): δ (ppm) = -216.92. Anal. Calcd for $C_{44}H_{76}N_4O_4Cl_5Si_8Ru_2$: C 39.76, H 5.76, N 4.22. Found: C 39.68, H 5.69, N 4.08.

2.2.3. Preparation of $Ru_2(dsichp)_4N_3$ (4-N₃). 4-Cl (500 mg, 0.376 mmol) and NaN₃ (2.45 g, 37.6 mmol) were dissolved in MeOH/ CH₂Cl₂ (4 mL/50 mL) in a 100 mL round-bottom flask, open to air. This purple mixture was protected from light, sealed, and stirred for 24 h, resulting in a blue-purple supernatant over white solids. The solvent was removed, and the solids were extracted with 100 mL CH₂Cl₂. The resulting filtrate was evaporated to dryness and then washed with MeCN (10 mL) and MeOH (100 mL), leaving the desired product as a dark blue-purple powder. Yield: 341 mg (67.9%). UV–vis (CH₂Cl₂, λ_{max} nm (ε , M⁻¹ cm⁻¹)): 590 (7000), 531 (8300), 371 (5900). IR (ATR, cm⁻¹): 2016 cm⁻¹ (N₃ stretch). MALDI-TOF (m/z): 1294 [M – N₃]⁺, 1308 [M – N₂]⁺. ¹H NMR (500 MHz, C₆D₆): δ (ppm) = 30.25 (br, 4H), 4.84 (br, 36H), 1.20 (br, 36H). ²⁹Si NMR (100 MHz, C₆D₆): δ (ppm) = –212.22. Anal. Calcd for C₄₄H₇₆N₇O₄Cl₄Si₈Ru₂: C 39.56, H 5.74, N 7.34. Found: C 39.86, H 5.79, N 6.95.

2.2.4. Preparation of $Ru_2(dsichp)_4(\kappa^1-CH_2Cl_2)$ (**6-CH₂Cl₂**). 4-Cl (200 mg, 0.151 mmol) and Zn powder (492 mg, 7.52 mmol) were placed in a 3-neck Schlenk flask, fitted with a filter stick and receiving flask via an elbow joint. Freshly-distilled CH2Cl2 (45 mL) was added by syringe, and the mixture was stirred for 2 days. Once orange crystals had begun to precipitate, the dark orange-brown mixture was filtered, and the receiving flask containing the filtrate was immediately stored at -20 °C. After 2 weeks, the light purple supernatant was removed by air-free filtration, leaving the desired product as orangebrown crystals. The product was dried in vacuo for 2 h prior to being collected. Yield: 94 mg (45%). UV-vis (CH₂Cl₂, λ_{max} nm (ϵ , M⁻¹ cm⁻¹)): 751 (210), 485 (920) 384 (3200). MALDI-TOF (*m*/*z*): 1294 [M - CH₂Cl₂]⁺. χ T (CD₂Cl₂, 297.2 K): 1.28 emu K mol⁻¹. ¹H NMR (500 MHz, C_6D_6): δ (ppm) = 8.87 (br, 4H), 4.34 (br, 36H), 4.26 (s, 2H), 0.04 (br, 36H). ²⁹Si NMR (100 MHz, C_6D_6): δ (ppm) = 10.69, -18.36. Anal. Calcd for C₄₅H₇₈N₄O₄Cl₆Si₈Ru₂: C 39.20, H 5.70, N 4.06. Found: C 38.96, H 5.58, N 4.05.

2.2.5. Generation of $Ru_2(dsichp)_4$: C_6D_6 (6- C_6D_6). In a glovebox, 6-CH₂Cl₂ (5 mg, 0.004 mmol) and C_6D_6 (2 mL) were combined in a

Tal	ble	1.	Crystal	llographic	: Data
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	4-Cl	$4-\text{Cl}\cdot(\text{hexane})_{1.85}^{a}$	4-N ₃	6-CH ₂ Cl ₂	6-C ₆ D ₆
empirical formula	Ru ₂ (dsichp) ₄ Cl	$Ru_2(dsichp)_4Cl \cdot (C_6H_{14})_{1.85}$	$Ru_2(dsichp)_4N_3$	$Ru_2(dsichp)_4(CH_2Cl_2)$	$Ru_2(dsichp)_4 \cdot C_6D_6$
formula weight	1329.19	1488.62	1335.77	1378.67	1377.89
temperature, K	100(1)	100(1)	100(1)	100(1)	100(1)
λ, Å	1.54178	0.71073	0.71073	0.71073	0.71073
crystal system	tetragonal	monoclinic	tetragonal	tetragonal	tetragonal
space group	P4/ncc	C2/c	P4/n	P4/n	P4/n
<i>a,</i> Å	17.3360(8)	38.492(1)	17.038(6)	16.985(6)	17.018(4)
<i>b,</i> Å	17.3360(8)	20.9916(5)	17.038(6)	16.985(6)	17.018(4)
<i>c,</i> Å	21.794(1)	23.5526(7)	11.281(5)	11.570(5)	11.560(5)
α , deg	90	90	90	90	90
β , deg	90	126.180(1)	90	90	90
γ, deg	90	90	90	90	90
volume, Å ³	6549.8(7)	15361.0(7)	3275(3)	3338(3)	3348(2)
Ζ	4	8	2	2	2
$ ho_{ m calc}$ g cm ⁻³	1.348	1.149	1.355	1.372	1.367
$R_{1}^{b} w R_{2}^{c} [I \ge 2\sigma(I)]$	0.0253, 0.0658	0.0363, 0.0796	0.0298, 0.0701	0.0340, 0.0743	0.0967, 0.2535
$R_{1}^{b} w R_{2}^{c}$ [all data]	0.0289, 0.0684	0.0589, 0.0904	0.0457, 0.0754	0.0479, 0.0790	0.1053, 0.2571

^{*a*}Two diffuse components, corresponding to the total 1.85 hexane molecules per asymmetric unit, were excluded from the crystallographic refinement. ${}^{b}R_{1} = \Sigma ||F_{0}| - |F_{c}||/\Sigma |F_{0}|$. ${}^{c}wR_{2} = [\Sigma [w(F_{0}^{2} - F_{c}^{2})^{2}]/\Sigma [w(F_{0}^{2})^{2}]]^{1/2}$, $w = 1/[\sigma^{2}(F_{0}^{2}) + (aP)^{2} + bP]$, where $P = [\max(0 \text{ or } F_{0}^{2}) + 2(F_{c}^{2})]/3$.

vial. This mixture was heated to reflux while stirring, and then filtered, yielding an orange solution. After 9 days in a sealed vial at room temperature, the solution had separated into a colorless supernatant over orange crystals, which were then analyzed by single-crystal X-ray diffraction. Low yields and severe air sensitivity precluded further isolation or characterization.

2.2.6. Generation of $Ru_2(dsichp)_4$ (6) in n-decane. In a glovebox, 4-Cl (30 mg, 0.023 mmol), KC₈ (3 mg, 0.02 mmol), and n-decane (20 mL) were combined in a vial. This dark purple mixture was stirred for 4 days and filtered. The orange filtrate was concentrated to 6 mL and then stored at -25 °C. After 1 month, several orange crystals were observed and then analyzed by single-crystal X-ray diffraction. Low yields and extreme air sensitivity precluded further isolation or characterization.

2.3. Physical Measurements. NMR spectra were collected on a 400 MHz Bruker Avance III with a SmartProbe, or a 500 MHz Bruker Avance III with a DCH cryoprobe, Prodigy probe, or BBFO probe. Magnetic susceptibility measurements were obtained from the Evans method.^{23,24} Though this method is described already in the literature, the definition of $\Delta \nu$ is unclear in the early reports leading to persistent sign ambiguities, and we therefore include a description of the method as used here. The equation for sample mass susceptibility neglecting the density correction is

$$\chi_{\rm g} = \frac{3\Delta\nu}{4\pi\nu m} + \chi_{\rm c}$$

where χ_0 is the mass susceptibility of the solvent (cm³ g⁻¹), *m* is the mass concentration of the solute (g cm⁻³), ν is the instrument frequency (Hz), and $\Delta \nu = \nu_{para} - \nu_{ref}$ (ν_{ref} being the proton shift (Hz) of (CH₃)₄Si in the inner capillary used as a reference, and ν_{para} being the proton shift (Hz) of (CH₃)₄Si in the presence of the paramagnetic analyte). Applying the necessary diamagnetic corrections (χ_D),²⁵ the paramagnetic susceptibility χ_P (in units of cm³ mol⁻¹; note 1 emu = 1 cm³) of the analyte is thus given by

$$\chi_{\rm p} = \frac{3\Delta\nu}{4\pi\nu M} - \frac{MW_{\rm solvent}}{MW_{\rm analyte}} \cdot \chi_{\rm D}({\rm solvent}) - \chi_{\rm D}({\rm analyte})$$

where M is the concentration of the analyte (in mol cm⁻³) and MW refers to the molecular weights.

Electron paramagnetic resonance (EPR) measurements were carried out on a Bruker EleXsys E500 EPR spectrometer, equipped with a Super Hi-Q resonator and an ESR900 continuous flow liquid helium cryostat. Measurement conditions were 9.3769 GHz (4-Cl),

9.3834 GHz (4-N₃), 9.3856 GHz (5), 4.000 G modulation amplitude, 4000 G center field, 8000 G sweep width, 2.00 mW power, 327.68 ms time constant, 35 dB gain (4-Cl, 4-N₃), 45 dB gain (5) at 6 K. UVvis measurements were carried out using freshly prepared solutions of the metal complexes with a miniature BLUE-Wave UV/vis dip probe with a tungsten-krypton light source, and a 10 mm path length tip. Fourier transform infrared (FTIR) spectra were measured on a Bruker Tensor 27 spectrometer using an ATR module (no matrix). Matrixassisted laser desorption/ionization (MALDI) and electrospray ionization (ESI) mass spectrometry data were recorded at the Mass Spectrometry Facility of the Chemistry Department Instrumentation Center of the University of Wisconsin-Madison, using an anthracene matrix on a Bruker Ultraflex III time-of-flight (TOF) mass spectrometer in positive ion mode, equipped with a SmartBeam laser, and a Shimadzu LCMS-2010A, respectively. The elemental analyses were performed by Midwest Microlab, LLC in Indianapolis, IN, USA. Cyclic voltammetry measurements were made using a BASi-Epsilon potentiostat, using a scan rate of 100 mV/s, a glassy-carbon working electrode, a Ag/AgNO3 reference electrode, and a 0.1 M [Bu₄N][PF₆] supporting electrolyte, and then referenced to the Fc/ Fc⁺ couple. Thermogravimetric analysis (TGA) was carried out on a TA Instruments TGA Q-500 build model 203 using the TA Instruments Universal Analysis 2000 software package.

2.4. X-ray Structure Determinations at 100 K. Suitable single crystals of 4-Cl and 4-N₃ were selected under oil and air. Suitable crystals of $6-CH_2Cl_2$ and $6-C_6D_6$ were suspended in Krytox fluorinated oil in a glovebox, prior to selection under a stream of argon. The crystals were attached to the tip of a MiTeGen MicroMount and mounted in a stream of cold nitrogen at 100(1)K and centered in the X-ray beam using a video monitoring system. The crystal evaluation and data collection were performed on a Bruker Quazar APEX-II diffractometer (4-Cl·N(hexane)_{1.85}, 4-N₃, 6-CH₂Cl₂, 6-C₆D₆) with Mo K α radiation ($\lambda = 0.71073$ Å) or a Bruker SMART APEX-II diffractometer (4-Cl) with Cu K α (λ = 1.54178 Å) radiation. The data were collected using a routine to survey an entire sphere of reciprocal space and were indexed by the SMART program.²⁶ The structures were solved via direct methods and refined by iterative cycles of least-squares refinement on F^2 followed by difference Fourier synthesis using the SHELX2013 suite of programs.²⁷ All hydrogen atoms were included in the final structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The details concerning X-ray crystallographic structure solutions and refinement are given in Table 1. For each structure

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except **6-C**₆**D**₆, the model was refined to a low wR_2 value (<0.10 for all data in each case). The quality of the data modeled as **6-C**₆**D**₆ ($wR_2 = 0.26$) was limited by extensive twinning in the best available crystal.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of New Pyridone Ligands, dbchpH (3), dsichpH (4), and 5-sichpH (5). We initially reasoned that a bromine atom in the 3 position of each chp ligand of $Ru_2(chp)_4$ would be sufficient to disrupt the dimeric structure displayed by 2. Applying the generalized pyridone dibromination methods developed by Meana et al.,²⁸ we treated 6-chloro-2-pyridone (chpH) with N-bromosuccinimide (NBS, 2 equiv) in refluxing MeCN, affording bromination of the 3 and 5 positions. Adding the hot, orange reaction mixture to excess 1 M HCl precipitated out the protonated product, which was collected and recrystallized from benzene, giving 3,5-dibromo-6-chloro-2-pyridone (dbchpH) in good yields. Dibromination was indicated by ESI-MS, elemental analysis, and ¹H NMR spectroscopy (Figure S1), and the 3,5-regioisomer was confirmed through ¹H-¹³C HMBC spectroscopy (Figure S3).

Under the same reaction conditions used to synthesize 1- Cl_{0}^{6} we attempted to substitute the acetate ligands of Ru₂(OAc)₄Cl by refluxing with Hdbchp and LiCl for 3 days in toluene through a Soxhlet apparatus containing a thimble with excess K_2CO_3 (eq 1).²⁹ Analogous to the synthesis of $Ru_2(chp)_4Cl$, we anticipated $Ru_2(dbchp)_4Cl$ as a purple solid. However, Hdbchp behaved as a reducing agent, giving instead a bright orange-red solid more consistent with formulation as the $Ru_2(II,II)$ complex $Ru_2(dbchp)_4$ (3) (MALDI-TOF (m/ z): 1348 [M]⁺). Notably, MALDI-TOF mass spectrometry showed no evidence of dimeric species $[Ru_2(dbchp)_4]_2$ (MALDI-TOF (m/z, calcd.): 2695 [M]⁺). Only a signal at m/z = 1348 corresponding to the $[Ru_2(dbchp)_4]^+$ ion was observed, supporting our hypothesis that substituting the 3position of each equatorial ligand would inhibit dimerization (Figure 1). This solid was collected by filtration and washed with toluene, diethyl ether, dichloromethane, and methanol, but the poor solubility of the desired product precluded further purification or reaction chemistry.

$$\begin{array}{c} \operatorname{Ru}_{2}(\operatorname{OAc})_{4}\operatorname{Cl} + 4 \operatorname{equiv}_{or}^{\operatorname{dbchpH}} \\ \xrightarrow{\operatorname{Soxhlet}, K_{2}\operatorname{CO}_{3}} \operatorname{Ru}_{2}(\operatorname{dbchp})_{4}(3) \\ \xrightarrow{\operatorname{toluene, LiCl}} \operatorname{Ru}_{2}(\operatorname{dschp})_{4}\operatorname{Cl}(4-\operatorname{Cl}, 47\% \operatorname{yield}) \end{array}$$
(1)

To achieve enhanced solubility, we sought to install a trimethylsilyl (TMS) group in the 3-position of each equatorial ligand. Using a silvlation method developed by Schlosser et al.,³⁰ we treated chpH with 5 equiv of lithium diisopropylamide (LDA) at -78 °C, and quenched overnight with excess chlorotrimethylsilane (TMSCl), followed by 1 M HCl (Scheme 2). We found that this method gave better regioselectivity than comparable procedures involving nbutyllithium, yet still generated a mixture of products. After removal of the resulting oils by distillation, ¹H NMR spectroscopy indicated the presence of the products dsichpH, 5-sichpH, 3-sichpH, and 4-sichpH in a 57.1%/20.4%/16.2%/ 6.4% ratio (Figure S4). Recrystallization from acetonitrile removes 4-sichpH from this mixture, and the remaining products are separated by column chromatography, giving both dsichpH and 5-sichpH in useful yields.



Figure 1. MALDI-MS of 3 (blue), compared to 2 (green).





The ¹H NMR spectrum for each TMS substitution product displays three signals in CD₃OD. The disubstituted product is indicated by the presence of two 9-proton trimethylsilyl singlets (0.35 ppm, 0.27 ppm) and one 1-proton singlet in the aryl region (7.65 ppm). 4-sichpH exhibits one 9-proton singlet (0.29 ppm) and two 1-proton singlets (6.85 ppm, 6.69 ppm). Both 3-sichpH and 5-sichpH exhibit one 9-proton singlet (0.28 and 0.35 ppm, respectively) and two 1-proton doublets (respectively: 7.63 ppm, 6.73 ppm, J = 7.3 Hz; 7.66 ppm, 6.55 ppm, J = 8.5 Hz), but can be distinguished on the basis of their ¹H-¹³C couplings observed through semiselective 2D HMBC (Figure S10).

3.2. Synthesis and Characterization of $Ru_2(dsichp)_4Cl$ (4-Cl) and $Ru_2(dsichp)_4N_3$ (4-N₃). The synthesis of the silylated $Ru_2(II,III)$ complex 4-Cl was attempted under conditions similar to the Soxhlet reaction used to produce 1-Cl, but dsichpH also proved more reducing than chpH, yielding a multicomponent mixture of purple (Ru_2^{5+}) and orange (Ru_2^{4+}) products. Using only 4 equiv of dsichpH rather than 8 minimized formation of the orange products, which were washed out with cold hexanes, resulting in practical yields of 4-Cl. From this product, 4-N₃ is accessible through a salt metathesis under the conditions established for $1-N_3$,^{6,21} with a modified workup including a wash of the isolated blue-purple solids with MeCN and MeOH.

Both 4-Cl and 4-N₃ are air-stable, though 4-N₃ must be protected from light, as photodegradation over several hours can be observed by ¹H NMR spectroscopy. The trimethylsilyl groups of 4-Cl and 4-N₃ significantly enhance their solubility in lower-polarity solvents (e.g., toluene, alkanes) over that of 1-Cl and 1-N₃, while decreasing their solubility in higher-polarity solvents (e.g., MeCN, MeOH, DMSO). X-ray crystallographic studies establish 4-Cl (Figure 2) and 4-N3 (Figure 3) as



Figure 2. X-ray crystal structure of 4-Cl. All atoms are drawn as 50% thermal probability ellipsoids, and all H atoms are omitted for clarity.



Figure 3. X-ray crystal structure of $4-N_3$. All atoms are drawn as 50% thermal probability ellipsoids, and all H atoms are omitted for clarity.

having similar structures to 1-Cl and 1-N₃, respectively. Most of the key bond lengths in the silylated complexes differ from their counterparts in the nonsilylated complexes by only ~0.01 Å (Table 2). As an exception, the Ru–Ru bond is ~0.02 Å longer, and the Ru–Cl bond is ~0.03 Å shorter in 4-Cl, relative to 1-Cl, though these differences are not likely to have chemical significance. Adding TMS groups to the paddlewheel complexes results in smaller N-Ru-Ru- O_{eq} torsion angles. This effect is most notable in 4-N₃, which exhibits an abnormally low torsion angle of 13.46(5)°.

The electronic absorption spectrum of **4-Cl** exhibits similar features to that of **1-Cl**, illustrating the ground state similarities between these two complexes (Figure 4). These features are



Figure 4. Electronic absorption spectra of 1-Cl (black), 4-Cl (blue), and $4-N_3$ (red) in CH_2Cl_2 .

slightly red-shifted by 600-1200 cm⁻¹ for 4-Cl. As the large peak near 550 nm has been previously proposed to be due to a $\pi(O_{eq}) \rightarrow \pi^*$ transition in related systems,^{20,31,32} the bathochromic shift corresponds to a slight destabilization in the supporting ligand orbitals, consistent with electron donation from the trimethylsilyl groups. Due to its interaction with the metal-based δ_{xy} orbital, TMS-imposed destabilization of the $\pi(O_{eq})$ orbital may also lead to the red-shift observed for the $\delta_{xy} \rightarrow \delta_{xy}^*$ transition near 700 nm. The electronic absorption spectrum of 4-N₃ contains features similar to those seen in the spectrum of 4-Cl, but with a significant blue-shift. The Ru-Ru distances for the two complexes are effectively identical, precluding an explanation based on the character of the metal-metal bond.³³ Instead, this effect can be explained in terms of the significantly decreased torsion angle observed in the equatorial ligands of 4-N3. This would allow greater mixing between the $\pi(O_{eq})$ orbital and the metal-based δ symmetry orbitals, such that both the $\pi(O_{ed})/\pi^*$ and $\delta_{xy}/\delta_{xy}^*$ gaps are increased.

Cyclic voltammetry on 4-Cl in CH_2Cl_2 revealed significant differences with respect to 1-Cl (Figure 5). Though 1-Cl possesses a reversible $Ru_2^{5+/4+}$ couple at -0.525 V vs Fc/Fc^{+,1} the comparable event for 4-Cl is irreversible, showing a large cathodic wave at -0.87 V and a smaller anodic wave at -0.37

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for the X-ray Crystal Structures Containing 1, 4, and 6 at 100 $K^{a,b}$

compound	Ru-Ru	Ru–L _{ax}	Ru–O _{eq}	Ru-N _{eq}	Ru-Ru-L _{ax}	N-Ru-Ru-O _{eq}	ref
1-Cl $\operatorname{Ru}_2(\operatorname{chp})_4\operatorname{Cl}\cdot\operatorname{CH}_2\operatorname{Cl}_2$	2.281(1)	2.443(2)	2.002[4]	2.085[4]	180	18.8(n.d.)	18
4-Cl Ru ₂ (dsichp) ₄ Cl	2.2999(4)	2.419(1)	1.989(2)	2.095(2)	180	16.66(6)	this work
4-Cl Ru ₂ (dsichp) ₄ Cl·(hexane) _{1.85}	2.2950(2)	2.4082(5)	1.9916[8]	2.0938[9]	179.21(2)	17.02[3]	this work
$1-N_3 \operatorname{Ru}_2(\operatorname{chp})_4 N_3$	2.2907(2)	2.116(2)	1.9986[7]	2.0933[8]	176.34(5)	17.4[2]	1
4-N ₃ Ru ₂ (dsichp) ₄ N ₃	2.300(1)	2.105(3)	1.986(2)	2.100(2)	180	13.46(5)	this work
$2\text{-}\mathbf{ZnCl}_{2} \ [\mathrm{Ru}_{2}(\mathrm{chp})_{4}]_{2}(\mathrm{ZnCl}_{2})$	2.244[2]	2.224[4]	2.033[4]	2.110[2]	168.55[8]	22.1[2]	11
$6-CH_2Cl_2 Ru_2(dsichp)_4(CH_2Cl_2)$	2.241(2)	2.796(6)	2.015(3)	2.118(8)	169.1(2)	16.1(2)	this work
$6 \cdot \mathbf{C}_{6} \mathbf{D}_{6} \operatorname{Ru}_2(\operatorname{dsichp})_4 \cdot \mathbf{C}_6 \mathbf{D}_6$	2.227(2)	$3.05(2)^{c}$	2.027(6)	2.113(7)	$158.2(4)^{c}$	15.0(3)	this work

"Parentheses denote esds; brackets indicate averaged values. ^bThe labels "ax" and "eq" refer to atoms axially or equatorially coordinated to $Ru_{2\nu}$ respectively. ^c L_{ax} corresponds to the nearest C_6D_6 carbon.



Figure 5. Cyclic voltammogram of 1 mM 4-Cl (black) and 4-Cl + 2 mM $[Bu_4N]Cl$ (red) in CH₂Cl₂, both with 0.1 M $[Bu_4N][PF_6]$, at a scan rate of 100 mV/s.

V. The more negative value of -0.87 V for the Ru₂^{5+/4+} reduction is expected, given the previously discussed destabilization of the δ_{xy} and δ_{xy}^* orbitals in 4-Cl. Repeating the experiment in the presence of 2 equiv of [Bu₄N]Cl nearly eliminates the wave at -0.37 V, suggesting that this event corresponds to oxidation of the species in which the axial chloride has been displaced by the CH₂Cl₂ solvent. Meanwhile, a new irreversible oxidation event appears at 0.70 V. 4-Cl also exhibits a reversible wave at $E_{1/2} = 0.83$ V, which corresponds to the Ru₂^{6+/5+} couple. This couple is not observed for 1-Cl, suggesting that the more electron-rich silylated ligands stabilize the Ru₂(III,III) oxidation state.

4-Cl and 4-N₃ were found to be magnetically similar to 1-Cl and $1-N_3^{6,20}$ each having three unpaired electrons. For 4-Cl, the Evans method provides a χT value of 1.77 emu K mol⁻¹ at 297 K, consistent with an S = 3/2 magnetic ground state (Figure S12). Indeed, 4-Cl (Figure S28) and 4-N₃ (Figure S29) give EPR signals with effective g values of $g_{\perp}g_{\parallel} = 4.305$, 1.955 and $g_1 = 4.435$, $g_2 = 4.165$, $g_3 = 1.95$, respectively, that are characteristic of S = 3/2 spin systems, with $D \gg h\nu$. Modeling the spectra with the appropriate spin Hamiltonian model yields axial electronic g values of $g_{\perp},g_{\parallel} = 2.150, 1.955$ and $g_{\perp},g_{\parallel} = 2.150$, 1.95 for 4-Cl and 4-N₃, respectively. The most notable distinction between these two species is in the E/D value, which is 0 for 4-Cl and 0.02 for 4-N₃, consistent with a lack of rigorous C4 symmetry in the latter compound. 4-N3 is slightly more axial than 1-N₃ (effective g values ${}^{6}g_{1} = 4.38$, $g_{2} =$ 3.975, $g_3 = 1.95$), consistent with greater covalency between Ru and the TMS-substituted equatorial ligands.³⁴

The 4-X type species give ¹H NMR signals that are significantly paramagnetically shifted (Figure 6). Whereas one set of TMS groups appears at nearly the same chemical shift regardless of whether Cl or N₃ is the axial ligand (1.22 ppm vs 1.20 ppm), the other set of TMS groups (5.19 ppm vs 4.84 ppm) and the 4-position hydrogen atom (30.42 ppm vs 30.25 ppm) give signals that are far more paramagnetically shifted, with greater distinctions in shift depending on the axial ligand. These effects are consistent with the idea that 4-Cl and 4-N₃ have the same unpaired electron configuration as 1-Cl, $(\delta^*)^1(\pi^*)^2$, because the singly occupied δ^* orbital mixes with the $\pi(O_{eq})$ orbital, which would put some spin density in the aromatic ring, closer to one TMS group than the other. Hence, the stronger paramagnetic shift is likely experienced by the 3-position TMS group in each case, and the chemical shift distinctions between 4-Cl and 4-N₃ may be based on the same δ^* orbital perturbations observed spectroscopically (see above). Using $^1\mathrm{H}-^{29}\mathrm{Si}$ HMBC, the $^{29}\mathrm{Si}$ shifts were obtained



Figure 6. Overlay of the ¹H NMR spectra of 4-Cl (red) and $4-N_3$ (blue). Peak shifts and integrations are displayed for the spectrum of 4-Cl.

for the 5-position TMS group of 4-Cl and 4-N₃ (-216.9 ppm vs -212.2 ppm), but the downfield TMS crosspeak could not be located.

3.3. Generation of Ru₂(dsichp)₄N (5) from Ru₂(dsichp)₄N₃ (4-N₃). Of interest is whether 4-N₃ exhibits the same capacity for N-N cleavage into $Ru_2 \equiv N$ and N_2 fragments that has been previously observed in similar systems.^{6,35–37} Relative to the comparable values in $1-N_3$, the azide group of 4-N₃ is coordinated with a $\sim 6^{\circ}$ higher Ru– N-N bond angle and exhibits bond lengths indicative of slightly more triple-bond character on the proximal, rather than terminal N–N bond (Table 3). These features might suggest deactivation of 4-N₃ toward N-N cleavage, but the opposite is suggested by the slightly shorter Ru-N bond, an effect that has been suggested to lower the activation barrier to generate M≡ N and N₂ fragments.³⁸ Yet, in the current case, deactivation of the azide group in $4-N_3$ is suggested by thermogravimetric analysis (Figure 7), which shows negligible mass loss for this compound in the 100-150 °C range, where 1-N₃ experiences its first thermolytic degradation event.⁶ For 4-N₃, a thermolytic degradation event that may correspond to the loss of N_2 (2.1%) mass) occurs in the 202-207 °C range, but this is only after another degradation event (possibly loss of a TMS group, 5.5% mass) has occurred below 190 °C. Hence, thermolytic conversion of 4-N₃ to 5 cannot be achieved cleanly.

Comparable to $1-N_{3}$,⁶ photolytic conversion of $4-N_3$ to 5 is demonstrated by MALDI-TOF mass spectrometry, in which the ion $[M - N_2]^+$ (*m*/*z* = 1308) is observed with an intensity dependent on laser power. Treating a frozen CH₂Cl₂ solution of 4-N₃ at 77 K for 8 h with 350 nm light converts the purple complex with a S = 3/2 EPR signal into a light blue S = 1/2species (Figure S30). The g values for this species ($g_1 = 2.40, g_2$ = 2.36, $g_3 = 1.725$) are comparable to those observed for $\operatorname{Ru}_{2}(\operatorname{chp})_{4}N$ ($g_{1} = 2.35$, $g_{2} = 2.155$, $g_{3} = 1.97$), suggesting that this is likely species 5, formed upon photolytic elimination of $N_{\rm 2}.$ The EPR signal for ${\bf 5}$ is significantly more axial than that of $Ru_2(chp)_4N$, further supporting the idea of greater metalequatorial-ligand covalency in the silvlated system, but also suggesting a much less covalency with the axial nitride.³⁴ Hence, we suspect the nitride of 5 to be likely more ionic in character and thus less electrophilic than the nitrides previously described in Ru_2 systems.^{6,37,39}

Table 3.	Comparison	of Bond Length	s (Å) and	l Angles	(deg) o	of the Azide	Groups of	f 1-N ₃ and	4-N ₃ at	100 K
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compound	Ru-NNN	RuN-NN	RuNN-N	Ru-N-NN	ref
1-N ₃ Ru ₂ (chp) ₄ N ₃	2.116(2)	1.197(3)	1.156(3)	123.5(2)	1
4-N ₃ Ru ₂ (dsichp) ₄ N ₃	2.105(3)	1.099(8)	1.21(2)	129.2(4)	this work



Figure 7. Thermogravimetric analysis of 4-N₃, showing the % mass loss as temperature is increased, as well as the derivative of the mass with respect to temperature.

Recently, we investigated room temperature photolysis of 1- N_3 in CH_2Cl_2 in the presence of PPh₃ and an internal standard (PPNCl = bis(triphenylphosphane)iminium chloride), which produced an N atom transfer reaction that results in formation of [H₂NPPh₃]Cl after an HCl workup.⁶ However, attempts to photolyze 4-N₃ under the same conditions show no evidence by ³¹P NMR spectroscopy of any reaction with PPh₃. In the absence of PPh₃, no direct evidence of the formation of 5 is observed during a 4 h photolysis of 4-N₂ at room temperature. Instead, this procedure gives the characteristic ¹H NMR spectrum of reduced $\operatorname{Ru}_2(\operatorname{dsichp})_4(6)$ alongside unidentified side products (that are independent of solvent choice), indicating a net photoreduction of 4-N₂ (Figure S17; vide infra for data on 6). Several potential explanations arise for the mechanistic difference between the photoreactivity of 1-N₂ and 4-N₃. The differing character of the Ru \equiv N bond in 5 may mean that this nitride is not electrophilic enough to accept the phosphine lone pair and form a P-N bond. Alternatively, the additional steric bulk of 5 may prevent bulky PPh₃ from approaching at the appropriate angle for a reaction. In either of these cases, 5 may still be reactive enough to be reductively quenched by other means (e.g., reaction with the equatorial ligand TMS or Cl groups of other complexes). However, another possibility is that the actual photolysis mechanism for 4-N₃ changes between 77 K and room temperature, bypassing 5 in the latter case. Instead of expelling N₂, 4-N₃ may instead be directly photoreduced at room temperature, generating 6 and N₃[•] via homolysis of the axial Ru–N bond, as has been previously observed for high-spin ferric azido complexes.⁴⁰ The existing spectroscopic data do not currently allow us to conclusively distinguish between these two possibilities.

3.4. Synthesis and Characterization of $\operatorname{Ru}_2(\operatorname{dsichp})_4(\kappa^{1}-\operatorname{CH}_2\operatorname{Cl}_2)$ (6-CH₂Cl₂). Whereas the Zn reduction of 1-Cl in CH₂Cl₂ generates the dimer 2-ZnCl₂ (Table 2),¹³ the reduction of 4–Cl using the same conditions yields the orange-brown solvent adduct, 6-CH₂Cl₂, which crystallizes upon cooling. This complex is extremely air-sensitive, rapidly turning reddish-purple upon exposure to even trace amounts of

 O_2 . Though CH_2Cl_2 is expected to be a very weakly coordinating ligand, the strong Lewis acidity of $Ru_2(dsichp)_4$ is illustrated by the fact that **6-CH₂Cl₂** surprisingly retains its solvent ligand *in vacuo*, even upon heating at 50 °C for 24 h, though heating to 100 °C causes decomposition indicated by a color change to dark red.

The thermal stability of this CH_2Cl_2 adduct is remarkable in that the Ru–ClCH₂Cl distance (2.796(6) Å) observed in the X-ray crystal structure of **6-CH₂Cl₂** is not particularly short relative to what has been observed in the few known Ru(CH₂Cl₂) structures (Figure 8).⁴¹⁻⁴⁴ The closest analogue



Figure 8. X-ray crystal structure of 6-CH₂Cl₂. All atoms are drawn as 50% thermal probability ellipsoids, and all H atoms and minor disordered components are omitted for clarity.

to 6-CH₂Cl₂ is the Ru₂(II,III) structure reported by Patmore et. al,⁴² Ru₂(O₂CAr)₄Cl(κ^1 -CH₂Cl₂), which possesses a comparable Ru-ClCH₂Cl distance (2.806(2) Å), but loses its CH₂Cl₂ ligand in vacuo. The unusual stability of 6-CH₂Cl₂ may occur because the pocket that is formed when lining up two $Ru_2(dsichp)_4$ complexes axially in the crystal structure is an optimal size to encapsulate CH_2Cl_2 (Figure 9). The other bond lengths in $6-CH_2Cl_2$ are fairly typical in comparison to the known $\operatorname{Ru}_2(\operatorname{chp})_4(L)$ complexes.¹³ This is not entirely expected, because the hypothetical complex $Ru_2(chp)_4(CH_2Cl_2)$ was predicted by DFT to have a ${}^{3}A/{}^{3}E$ hybrid ground state, caused by π -backbonding into the Cl-CH₂Cl σ^* orbital. A key feature of this ³A/³E hybrid model is an elongated Ru-Ru bond (predicted at 2.288 Å, see Table 4), but the observed Ru-Ru bond length in 6-CH₂Cl₂ (2.241 Å) matches what is expected for a ³A complex with a weakly binding axial ligand. Because of the steric constraints imposed by the TMS groups around the axial site of $Ru_2(dsichp)_4$, the CH2Cl2 ligand of 6-CH2Cl2 adopts a Ru-Cl-C angle of 114.2(9) °, which is well above the 95° in the DFT-predicted structure for the less bulky Ru₂(chp)₄ complex. The steric constraint on this angle likely prevents the backbonding into the Cl–C antibond necessary for the ${}^{3}A/{}^{3}E$ state to form.

The electronic absorption spectrum of $6-CH_2Cl_2$ (Figure S33) is most closely comparable to the previously reported



Article



Figure 9. Orientation of two units of 6-CH₂Cl₂ in the X-ray crystal structure, including all disordered components of the trapped CH₂Cl₂ molecule and surrounding ligands.

series of ³A Ru₂(II,II) adducts of the form Ru₂(chp)₄L.¹³ As seen in that series, a strong ($\sim 3200 \text{ M}^{-1} \text{ cm}^{-1}$) absorption band peaking above $25\,000$ cm⁻¹ (400 nm) extends into the visible range, with a shoulder to this larger band appearing at 485 nm (20 600 cm⁻¹), giving $6-CH_2Cl_2$ its orange-brown appearance. The band at 751 nm $(13\ 300\ \text{cm}^{-1})$ is comparable in intensity (210 M^{-1} cm⁻¹) to a feature in the Ru₂(chp)₄L series that was found to range from 15 400 cm⁻¹ to 17 700 cm⁻¹, and appears to increase in energy with the increasing σ donor capacity of the axial ligand. The significantly lower energy of this band for 6-CH2Cl2 seems to underscore the weak coordination of CH2Cl2. Curiously, no band corresponding to the characteristic $\delta_{xy} \rightarrow \pi^*$ transition of Ru₂(II,II) is seen above 10 000 cm^{-1} in the spectrum of 6-CH₂Cl₂. This is likely due to a red-shift from the added TMS groups destabilizing the δ_{xy} orbital in the same manner described for 4-Cl (see above).

A χT value of 1.28 emu K mol⁻¹ at 297 K was measured for 6-CH₂Cl₂ by the Evans method (Figure S18), indicating an S = 1 system with g = 2.26. This value is within the range of what was observed for Ru₂(chp)₄ with various axial ligands.¹³ By ¹H NMR spectroscopy, $6-CH_2Cl_2$ exhibits dissociation of CH_2Cl_2 in a C_6D_6 solution (Figure S19). The ¹H NMR signals of 6 are paramagnetically shifted, but with a different pattern than observed for the 4-X species. The proton resonances from one set of TMS groups shift upfield (0.04 ppm), while the proton resonances from the other set of TMS groups shift downfield (4.34 ppm). The aromatic protons (8.87 ppm) in 6 experience far less of a paramagnetic shift than in 4-X, because the δ^* orbital of 6 is fully occupied, preventing the mixing of spin

density into the equatorial ligand orbitals that is observed for 4-X. This allows the ²⁹Si resonances for both the upfield (-18.36 ppm) and downfield (10.69 ppm) sets of TMS groups in 6 to be located by ${}^{1}H-{}^{29}Si$ HMBC spectroscopy (Figure S20).

3.5. Generation of Ru₂(dsichp)₄ (6) in Non-Coordinating Solvents. Heating 6-CH₂Cl₂ in C₆D₆ generates an orange solution that, after cooling, yields orange plate-like crystals over several days. These crystals contain 6 with a molecule of C_6D_6 occupying the axial pocket, having replaced the coordinated CH_2Cl_2 molecule (Figure 10). Each of the C_6D_6 carbon atoms



Figure 10. X-ray crystal structure of 6-C₆D₆. All atoms are drawn as 50% thermal probability ellipsoids, and all H atoms, D atoms, and minor disordered components are omitted for clarity.

is at least 3 Å from the Ru₂ axial site, precluding a bonding interaction with the benzene π system. Hence, $6-C_6D_6$ represents an example of a Ru₂ complex without a true axial ligand. In accordance with the structural trans effect,¹³ this axially free structure exhibits the shortest Ru-Ru bond length (2.227(2) Å) ever observed in a Ru₂(II,II) species.

The reduction of 4-Cl with Zn powder does not progress in alkane solvents (n-hexane, isooctane, n-decane) or toluene. However, using 1 equiv of KC8 as the reductant generates orange solutions in each of these solvents within 4 days.⁴⁵ Though the purple Ru₂(II,III) starting material is not fully consumed in any of these reactions, it is poorly soluble in ndecane, allowing convenient isolation of the highly air-sensitive orange solution containing $Ru_2(dsichp)_4$ (6) by filtration. Surprisingly, concentrating this solution by evaporation yields a viscous, dark orange-brown oil, without precipitating any solids, even upon cooling. However, prolonged exposure of an n-decane solution containing 6 to a glovebox atmosphere slowly precipitates 6-OH₂ as red-orange crystals.⁴⁶ In this structure, adduct 6-OH₂ (Figure S26) cocrystallizes with an inverted component that interacts with *n*-decane (6-dec,

Table 4. Comparison of Bond Lengths (Å) and Angles (deg) in the DFT-Predicted Structure of $Ru_2(chp)_4(CH_2Cl_2)^a$ and the X-ray Crystal Structure of 6-CH₂Cl₂ at 100 K

compound	Ru-Ru	Ru-L _{ax}	Ru–O _{eq}	Ru-N _{eq}	Ru-Ru-L _{ax}	N-Ru-Ru-O _{eq}
$\begin{array}{l} Ru_2(chp)_4(CH_2Cl_2) \ (DFT) \\ \textbf{6-CH}_2Cl_2 \ Ru_2(dsichp)_4(CH_2Cl_2) \end{array}$	2.288	2.742	2.025	2.111	176.9	18.6
	2.241(2)	2.796(6)	2.015(3)	2.118(8)	169.1(2)	16.1(2)

^aPreviously reported.¹¹

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Figure S27),⁴⁷ consistent with the relatively high solubility of **6** in alkanes. With a Ru…H distance of approximately 2.8 Å, and a Ru…H–C angle >100°, this interaction consists of, at most, a weak Ru…H–C hydrogen bond.⁴⁸ These results demonstrate the limit of the types of ligands that can interact with the Ru₂ axial site. To our knowledge, Ru₂(II,II) complexes with a ³A ground state have never previously been characterized devoid of axial ligands. The data presented here highlight the extremes that must be reached to characterize such a species.

4. SUMMARY AND CONCLUDING REMARKS

Two new oxypyridinate paddlewheel ligand systems have been developed for metal-metal bonded complexes, using steric protection to inhibit oligomerization, and thus test the limits of coordination chemistry available to Ru₂(II,II). While the 3,5dibrominated ligand dbchp generates a nondimerizing Ru₂ complex with universally poor solubility, the 3,5-disilylated ligand dsichp generates Ru₂ complexes with enhanced solubility in nonpolar solvents, including alkanes. $Ru_2(dsichp)_4Cl$, $Ru_2(dsichp)_4N_3$, and $Ru_2(dsichp)_4(L)$ were characterized and shown to have comparable electronic structures and magnetic properties to Ru₂(chp)₄Cl, $Ru_2(chp)_4N_3$, and $Ru_2(chp)_4(L)$ respectively. Spectroscopic and magnetic evidence establish that TMS-substitution in the 3 and 5 positions increases the metal-ligand covalency. As with $Ru_2(chp)_4N_3$, photolysis of $Ru_2(dsichp)_4N_3$ in frozen solution shows the spectroscopic signatures of a terminal nitrido species, though room temperature photolysis does not evidence N atom transfer to PPh₃. The steric protection afforded to $Ru_2(dsichp)_4$ by the dsichp ligands prevents the type of dimerization seen for $Ru_2(chp)_4$, keeping the $Ru_2(II,II)$ axial site accessible even in weakly coordinating conditions. CH₂Cl₂ forms a thermostable adduct at the highly Lewis acidic axial site of $Ru_2(dsichp)_4$, though this ligand is easily displaced in solution, potentially allowing $Ru_2(dsichp)_4(CH_2Cl_2)$ to be used as a versatile starting material for exploring further reactivity of axially-free Ru₂(II,II) species with small molecules.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b01553.

Additional figures and tables as noted in the text (PDF)

Accession Codes

CCDC 1847469–1847473 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: berry@chem.wisc.edu.

ORCID 6

John F. Berry: 0000-0002-6805-0640

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Corcos, A. R.; Pap, J. S.; Yang, T.; Berry, J. F. A Synthetic Oxygen Atom Transfer Photocycle from a Diruthenium Oxyanion Complex. J. Am. Chem. Soc. 2016, 138, 10032–10040.

(2) Dutta, I.; Sarbajna, A.; Pandey, P.; Rahaman, S. M. W.; Singh, K.; Bera, J. K. Acceptorless Dehydrogenation of Alcohols on a Diruthenium(II,II) Platform. *Organometallics* **2016**, *35*, 1505–1513.

(3) Ring, S.; Meijer, A.; Patmore, N. J. Structural, spectroscopic and theoretical studies of a diruthenium(II,II) tetraformamidinate that reversibly binds dioxygen. *Polyhedron* **2016**, *103*, 87–93.

(4) Thompson, D. J.; Paredes, J. E. B.; Villalobos, L.; Ciclosi, M.; Elsby, R. J.; Liu, B.; Fanwick, P. E.; Ren, T. Diruthenium(II,III) tetracarboxylates catalyzed H_2O_2 oxygenation of organic sulfides. *Inorg. Chim. Acta* **2015**, 424, 150–155.

(5) Goberna-Ferrón, S.; Peña, B.; Soriano-López, J.; Carbó, J. J.; Zhao, H. H.; Poblet, J. M.; Dunbar, K. R.; Galán-Mascarós, J. R. A fast metal-metal bonded water oxidation catalyst. *J. Catal.* **2014**, *315*, 25– 32.

(6) Corcos, A. R.; Long, A. K. M.; Guzei, I. A.; Berry, J. F. A Synthetic Cycle for Nitrogen Atom Transfer Featuring a Diruthenium Nitride Intermediate. *Eur. J. Inorg. Chem.* **2013**, 2013, 3808–3811.

(7) Villalobos, L.; Paredes, J. E. B.; Cao, Z.; Ren, T. *tert*-Butyl Hydroperoxide Oxygenation of Organic Sulfides Catalyzed by Diruthenium(II,III) Tetracarboxylates. *Inorg. Chem.* **2013**, *52*, 12545–12552.

(8) Villalobos, L.; Cao, Z.; Fanwick, P. E.; Ren, T. Diruthenium-(II,III) tetramidates as a new class of oxygenation catalysts. *Dalton Trans.* **2012**, *41*, 644–650.

(9) Harvey, M. E.; Musaev, D. G.; Du Bois, J. A Diruthenium Catalyst for Selective, Intramolecular Allylic C-H Amination: Reaction Development and Mechanistic Insight Gained through Experiment and Theory. J. Am. Chem. Soc. 2011, 133, 17207–17216.

(10) Lee, H. B.; Ren, T. Aerobic oxygenation of organic sulfides using diruthenium activators. *Inorg. Chim. Acta* **2009**, *362*, 1467–1470.

(11) Berry, M.; Garner, C. D.; Hillier, I. H.; Macdowell, A. A.; Clegg, W. Diruthenium(II) Tetrakis-6-methyl-2-oxypyridine, $Ru_2(mph)_4$, and comparisons of the metal-metal bonding in $M_2(mhp)_4$ (M = Mo, Ru, or Rh) Complexes. *Inorg. Chim. Acta* **1981**, *53*, L61–L63.

(12) Cotton, F. A.; Ren, T.; Eglin, J. L. Preparative, Structural, and Magnetic Studies of 2-Hydroxypyridinate Complexes of Diruthenium-(II). J. Am. Chem. Soc. **1990**, 112, 3439–3445.

(13) Brown, T. R.; Dolinar, B. S.; Hillard, E. A.; Clerac, R.; Berry, J. F. Electronic Structure of $Ru_2(II,II)$ Oxypyridinates: Synthetic, Structural, and Theoretical Insights into Axial Ligand Binding. *Inorg. Chem.* **2015**, *54*, 8571–8589.

(14) Fieser, M. E.; Johnson, C. W.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. Dinitrogen Reduction, Sulfur Reduction, and Isoprene Polymerization via Photochemical Activation of Trivalent Bis-(cyclopentadienyl) Rare-Earth-Metal Allyl Complexes. *Organometallics* **2015**, *34*, 4387–4393.

(15) Tolman, W. B. Activation of Small Molecules; Wiley-VCH: Weinheim, 2006.

(16) Vigato, P. A.; Tamburini, S.; Fenton, D. E. The Activation of Small Molecules by Dinuclear Complexes of Copper and Other Metals. *Coord. Chem. Rev.* **1990**, *106*, 25–170.

(17) Cotton, F. A.; Falvello, L. R.; Ren, T.; Vidyasagar, K. Preparation and Structural Characterization of 3 Tetrakis(Triazeno)-Diruthenium Compounds. *Inorg. Chim. Acta* **1992**, *194*, 163–170.

(18) Cotton, F. A.; Ren, T. Preparation and Molecular and Electronic Structures of a New Diamagnetic Diruthenium(II) Complex, Ru₂(para-Tol)NC(H)N(para-Tol)₄. Inorg. Chem. **1991**, 30, 3675–3679.

(19) Lindsay, A. J.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. The Synthesis, Magnetic, Electrochemical, and Spectroscopic Properties of Diruthenium(II,II) Tetra- μ -Carboxylates and Their Adducts -X-Ray Structures of Ru₂(O₂CR)₄L₂ (R = Me, L = H₂O or Tetrahydrofuran R = Et, L = Me₂CO). J. Chem. Soc., Dalton Trans. **1985**, 2321–2326.

(20) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. New Isomeric Form of the $M_2(OC_5H_3NCl)_4$ Core - A Polar Arrangement of the 4,6-Chloro-2-Hydroxypyridinato (chp) Ligands in a Chlorodiruthenium(II,III) Complex, $Ru_2Cl(chp)_4$. *Inorg. Chem.* **1985**, *24*, 1263–1267.

(21) Chen, W. Z.; De Silva, V.; Lin, C.; Abellard, J.; Marcus, D. M.; Ren, T. Azidotetrakis(diarylformamidinate)diruthenium(II,III) compounds: Synthesis, molecular structures and voltammetric properties; Linear free energy relationships in dinuclear compounds VII. *J. Cluster Sci.* **2005**, *16*, 151–165.

(22) Stephenson, T. A.; Wilkinson, G. New Ruthenium Carboxylate Complexes. J. Inorg. Nucl. Chem. **1966**, 28, 2285–2291.

(23) Evans, D. F. The Determination of the Paramagnetic Susceptibility of Substances in Solution by Nuclear Magnetic Resonance. J. Chem. Soc. **1959**, 2003–2005.

(24) Schubert, E. M. Utilizing the Evans Method with a Superconducting NMR Spectrometer in the Undergraduate Laboratory. J. Chem. Educ. **1992**, 69, 62–62.

(25) Bain, G. A.; Berry, J. F. Diamagnetic corrections and Pascal's constants. J. Chem. Educ. 2008, 85, 532–536.

(26) Bruker-AXS (2007–2013), APEX2 (Ver. 2013.2–0), SADABS (2012–1), and SAINT+ (Ver. 8.30C) Software Reference Manuals; Bruker-AXS: Madison.

(27) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

(28) Meana, Á.; Rodríguez, J. F.; Sanz-Tejedor, M. A.; García-Ruano, J. L. Efficient regioselective preparation of monobromo and bromoiodo hydroxy pyridines from dibromoderivatives via brominelithium exchange. *Synlett* **2003**, 1678–1682.

(29) Doyle, M. P.; McKervey, M. A.; Ye, T. Modern Catalytic Methods for Organic Synthesis with Diazo Compounds; John Wiley & Sons, Inc.: New York, 1998.

(30) Schlosser, M.; Rausis, T. The structural proliferation of 2,6difluoropyridine through organometallic intermediates. *Eur. J. Org. Chem.* **2004**, 2004, 1018–1024.

(31) Corcos, A. R.; Roy, M. D.; Killian, M. M.; Dillon, S.; Brunold, T. C.; Berry, J. F. Electronic Structure of Anilinopyridinate-Supported Ru_2^{5+} Paddlewheel Compounds. *Inorg. Chem.* **201**7, *56*, 14662–14670.

(32) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. Syntheses, Molecular Structures, and Properties of 2 Polar Diruthenium(II,III) Complexes of 2-Hydroxypyridine and 2-Anilinopyridine. *Inorg. Chem.* **1985**, 24, 172–177.

(33) Gracia, R.; Adams, H.; Patmore, N. J. Unexpected structural and electronic effects of internal rotation in diruthenium paddlewheel complexes containing bulky carboxylate ligands. *Inorg. Chim. Acta* **2010**, *363*, 3856–3864.

(34) Balagopalakrishna, C.; Kimbrough, J. T.; Westmoreland, T. D. Electronic structural contributions to g values and molybdenum hyperfine coupling constants in oxyhalide anions of molybdenum(V). *Inorg. Chem.* **1996**, *35*, 7758–7768.

(35) Das, A.; Reibenspies, J. H.; Chen, Y. S.; Powers, D. C. Direct Characterization of a Reactive Lattice-Confined Ru_2 Nitride by Photocrystallography. J. Am. Chem. Soc. **2017**, 139, 2912–2915.

(36) Long, A. K. M.; Timmer, G. H.; Pap, J. S.; Snyder, J. L.; Yu, R. P.; Berry, J. F. Aryl C-H Amination by Diruthenium Nitrides in the

Solid State and in Solution at Room Temperature: Experimental and Computational Study of the Reaction Mechanism. J. Am. Chem. Soc. **2011**, 133, 13138–13150.

(37) Long, A. K. M.; Yu, R. P.; Timmer, G. H.; Berry, J. F. Aryl C-H Bond Amination by an Electrophilic Diruthenium Nitride. *J. Am. Chem. Soc.* **2010**, *132*, 12228–12230.

(38) Wiberg, N. Lehrbuch der Anorganischen Chemie, 102 ed.; Walter de Gruyter: Berlin, 2007.

(39) Pap, J. S.; George, S. D.; Berry, J. F. Delocalized Metal-Metal and Metal-Ligand Multiple Bonding in a Linear Ru-Ru-N Unit: Elongation of a Traditionally Short Ru-N Bond. *Angew. Chem., Int. Ed.* **2008**, *47*, 10102–10105.

(40) Song, Y. F.; Berry, J. F.; Bill, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. Iron complexes of new pentadentate ligands containing the 1,4,7-triazacyclononane-1,4-diacetate motif. Spectroscopic, electro-, and photochemical studies. *Inorg. Chem.* **200**7, *46*, 2208–2219.

(41) Bown, M.; Waters, J. M. Dichloromethane - a Bridging Ligand. J. Am. Chem. Soc. **1990**, 112, 2442-2443.

(42) Gracia, R.; Patmore, N. J. Synthesis and Characterisation of Diruthenium Paddlewheel Compounds Bearing 2,6-Di(p-tolyl)-benzoate Ligands. J. Cluster Sci. 2010, 21, 339-350.

(43) Huang, D. J.; Huffman, J. C.; Bollinger, J. C.; Eisenstein, O.; Caulton, K. G. The first η^2 -CH₂Cl₂ adduct of Ru(II): RuH(η^2 -CH₂Cl₂)(CO)((PBu₂Me)-Bu-t)₂ BAr₄' (Ar' = 3,5-C₆H₃(CF₃)₂) and its RuH(CO)((PBu₂Me)-Bu-t)₂⁺ precursor. J. Am. Chem. Soc. **1997**, 119, 7398–7399.

(44) Zhang, J. B.; Barakat, K. A.; Cundari, T. R.; Gunnoe, T. B.; Boyle, P. D.; Petersen, J. L.; Day, C. S. Synthesis of the five-coordinate ruthenium(II) Complexes (PCP)Ru(CO)(L) BAr'₄ {PCP = 2,6-((CH₂PBu₂)-Bu-t)₂C₆H₃, BAr'₄ 3,5-(CF₃)₂C₆H₃, L = η^1 -ClCH₂Cl, η -N₂, or μ -Cl-Ru(PCP)(CO)}: Reactions with phenyldiazomethane and phenylacetylene. *Inorg. Chem.* **2005**, *44*, 8379–8390.

(45) Using excess KC $_8$ dechlorinates the dsichp ligand, as evidenced by the observation of [2-pyridone + H]⁺ ions by ESI-MS.

(46) An alternative assignment for this component is an $\mathrm{Ru}_2(\mathrm{II},\mathrm{III})$ hydroxo complex.

(47) 9(OH₂)_{0.91}·0.89(*n*-decane) crystallized from *n*-decane in the monoclinic space group $P2_1/n$ with unit cell dimensions a = 16.75(2)Å, b = 26.45(3) Å, c = 17.04(2) Å, $\alpha = \gamma = 90^{\circ}$, $\beta = 91.40(2)^{\circ}$ (cell volume = 7550(12) Å³; Z = 4). Least-square refinement yielded R_1 and wR_2 values of 0.0495 and 0.1104 for $I > 2\sigma(I)$ data, and 0.1005 and 0.1337 for all data. The crystal mounting and data collection were carried out similarly to 9-C₆D₆.

(48) Braga, D.; Grepioni, F.; Tedesco, E.; Biradha, K.; Desiraju, G. R. Hydrogen bonding in organometallic crystals 6. X-H—M hydrogen bonds and M—(H-X) pseudo-agostic bonds. *Organometallics* **1997**, *16*, 1846–1856.