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The Synergy between Theory and Experiment

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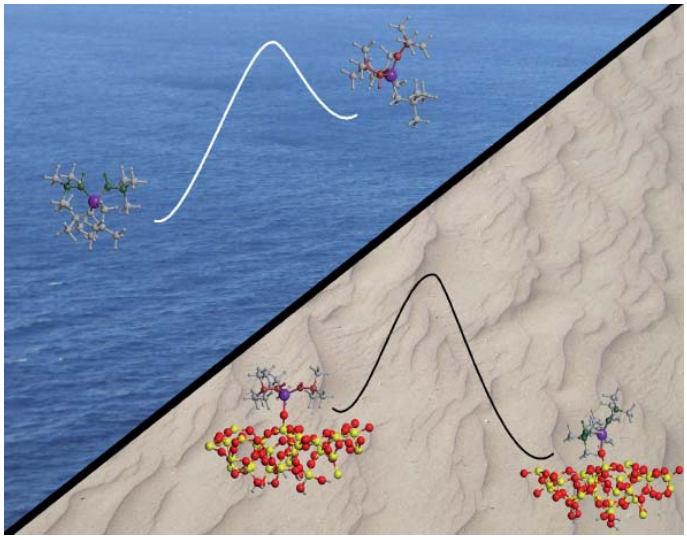

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Synthesis and reactivity of a Ru(I) dimer devoid of π-acid ligands†

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Zinc reduction of $[(Cym)RuCl_2]_2$ gives $[(Cym)RuCl]_2$, (Cym = 1,4-Me^{i}PrC$_6$H$_4$), whose reactivity is evaluated. This Ru^I dimer with two bridging chlorides shows no reactivity towards H_2, N_2, N_2O or methyl triflate, but does add HCl to form $(Cym)_2Ru_2HCl_3$. Attempts to form a monomeric monovalent ruthenium complex with dppm, $Ph_2PCH_2PPh_2$, gives disproportionation to $(Cym)RuCl_2(\eta^1$-dppm) and $(Cym)Ru(\eta^2$-dppm). With terpyridyl, the analogous disproportionation behavior is observed, to form $Ru(terpy)_2^{2+}$ and a zero valent product, which decomposed before it could be isolated. The molecular orbitals, from a DFT calculation, of $[(Cym)RuCl]_2$ show the LUMO to be in a sterically crowded region of the molecule, and thus helps to account for the reactivity targeted for small and more nucleophilic reagents, while the HOMO is accessible to reaction with HCl.

Introduction

A recent publication[1] reported the identification of a side product of reaction of $[(Cym)RuCl_2]_2$ (Cym = 1,4-Me^{i}PrC$_6$H$_4$) with a Ga(I)Cp* reagent as the dimer $[(Cym)RuCl]_2$, **1**, containing a metal–metal bond and thus diamagnetic for the d^7 electron configuration. We ourselves have formed this as a side product of other research, and we desired to provide some more convenient synthesis of this species as a useful new source of anhydrous Ru, in a reduced oxidation state. This synthon might be useful because it incorporates (a) a somewhat unusual oxidation state, carrying reducing power, (b) a metal–metal bond, which may keep together the two metals in any derived product, (c) the potential[2,3] to disproportionate to Ru^0 and Ru^{II} and (d) the leaving group character of cymene, which means that this reagent is, at heart, a synthon for the simple anhydrous unit Ru_2Cl_2. Our interest in a molecule devoid of carbonyl ligands relates to maximizing metal reducing power by avoiding electron withdrawing π-acid ligands. We report here on a convenient synthesis of $[(Cym)RuCl]_2$, together with a survey of its reactivity characteristics, including efforts to break the usual constraint[4–13] of dimeric Ru^I species and to access monomeric Ru^I.

Results

Synthesis of $[(Cym)RuCl]_2$

The reaction of $[(Cym)RuCl_2]_2$ in THF with powdered zinc under argon gives complete conversion within 12 h at 23 °C to a poorly soluble product, which matches the ^{1}H NMR spectra reported for $[(Cym)RuCl]_2$. The spectra show a cymene ring with mirror symmetry. The ESI-MS shows mainly singly charged ions of the parent ion, but also containing water molecules (derived from ESI solvent), presumably attached by hydrogen bonding to the especially electron rich chlorides, to one or both Cl; for the cation fragment which has lost one Cl, only one water molecule is retained.

We have determined the crystal structure of this molecule, crystallized from benzene (Fig. 1), and find it to be the identical phase as that reported.[2] There are no significant differences from the previously reported structure, so we merely comment that it has a folded Ru_2Cl_2 quadrilateral, which leaves one side of each Ru open to reagent attack (Fig. 1). In spite of the length (2.6022 Å) of the Ru–Ru bond, the NMR spectrum of this molecule is normal for a diamagnetic species, and shows no signs of population of a triplet spin state. The molecule is surprisingly poorly soluble in hydrocarbon solvents like benzene and toluene.

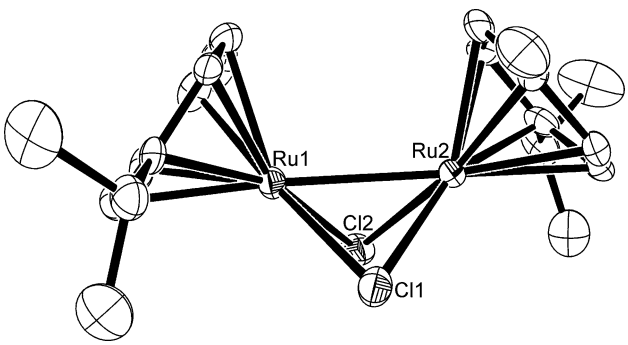

Fig. 1 ORTEP drawing of the non-hydrogen atoms of $[(Cym)RuCl]_2$, showing selected atom labelling. The unlabelled atoms are carbon.

Reactivity

$[(Cym)RuCl]_2$ should have some reactivity associated either with its redox character, or even through heterolytic splitting of the Ru–Ru bond yielding equimolar Ru^{II} and Ru^0. Although the metals are saturated, one side of the $RuCl_2$ plane is sterically open to access by reagents for a chloride bridge-splitting reaction. In fact, there is no reaction, at 23 °C in C_6D_6, on addition of 1 atm of N_2, H_2, N_2O and of equimolar $SiHMe_3$, even after heating 24 h at reflux. Attempts to heterolytically split coordinated H_2, in any unfavorable equilibrium forming an H_2

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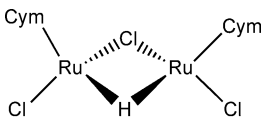
† Electronic supplementary information (ESI) available: ^{1}H NMR spectra of the terpy complexes and details of the X-ray determination. CCDC reference numbers 719526. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b902759a

adduct, by addition of NEt_3 also returned unreacted starting Ru reagent. The complex is recovered unchanged after treatment with equimolar $Me_3SiO_3SCF_3$, where chloride-by-triflate replacement was sought; this suggests that the bridging chlorides are not very nucleophilic, apparently due to their formal positive charge. In addition, in hopes of either coordinating N_2 to the Ru_2 species during reduction, or even effecting disproportionation of Ru into $(Cym)Ru(N_2)_2$ and $(Cym)RuCl_2(N_2)$, the synthetic reaction with Zn was repeated under 1 atm N_2. The product was unchanged, as $[(Cym)RuCl]_2$. We therefore turned to electrophilic and oxidizing reagents, which revealed that reducing power is indeed the center of the reactivity of this Ru(I) compound.

HCl. Adding HCl(etherate) (one mole per mole Ru_2) yields primarily a diamagnetic product which has one set of cymene signals, with no two ring hydrogens equivalent, indicating Ru to be a chiral center. Consistent with this, the ^{i}Pr methyls are also inequivalent. The molecule is a hydride, giving a singlet at −10 ppm. The color lightens in the reaction, and the major product is benzene soluble. No H_2 evolution is visible, nor is there a resonance due to dissolved free H_2. The identity of this product provides evidence that the reactivity of the Ru(I) dimer is both electron rich (oxidizable) and Brønsted basic. Although the product has no mirror plane bisecting the cymene ring, the two ends of the molecule are symmetry related. A possible product structure is shown as **2**, but it could also have the cymenes trans.

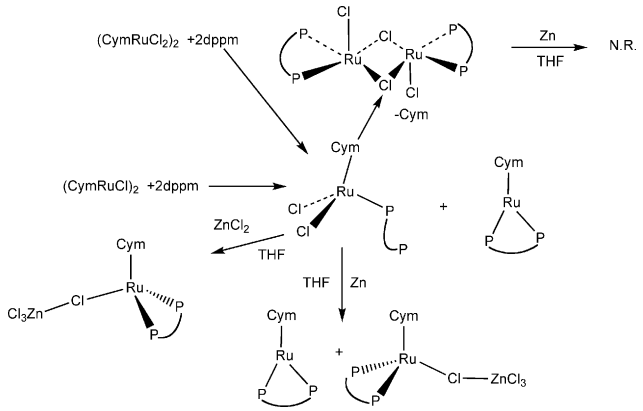


2

In fact, this molecule has been made previously[14] from $[CymRuCl_2]_2$ and H_2 in the presence of base, and the structures of two different polymorphs of $(Cym)_2Ru_2HCl_3$ determined. The structure reported has the cymenes *trans*, and the cell constants for our product are identical to one of those already published. The Ru–Ru distance is 2.96 Å, or an increase of 0.36 Å compared to $[(Cym)RuCl]_2$. This is consistent with loss of a Ru–Ru bond in this $(Ru^{II})_2$ species. It is noteworthy that the Ru–Cl distances are all 2.41 Å, hence, and atypically, not longer to the bridging halide. In $[(Cym)RuCl]_2$ the four Ru–Cl distances are all 2.43 Å.

Reaction with Lewis bases

(a) Bidentate phosphine. Reaction of dppm, $Ph_2PCH_2PPh_2$, with $[(Cym)RuCl]_2$ occurs within time of mixing in benzene to give complete conversion to a 1 : 1 mixture of two diamagnetic compounds, hence not monomeric Ru^I. One of the products has an AX $^{31}P\{^1H\}$ NMR pattern with a small (28 Hz) $J_{PP'}$ value, and the cymene ring hydrogen ^1H NMR is consistent with C_s symmetry. This product (Scheme 1) was confirmed to be $(Cym)RuCl_2(\eta^1$-dppm) by independent synthesis of this molecule from reaction of $[(Cym)RuCl_2]_2$ with dppm and comparison of its NMR spectra. Since this is divalent metal, the second product, with a singlet ^{31}P NMR spectrum and hence C_s symmetry, based on the cymene ring proton NMR, is expected to be zero valent metal, and thus $(Cym)Ru(\eta^2$-dppm), eqn (1). Reaction of $(Cym)RuCl_2(\eta^1$-dppm) with zinc powder in THF (there is no reaction in benzene)

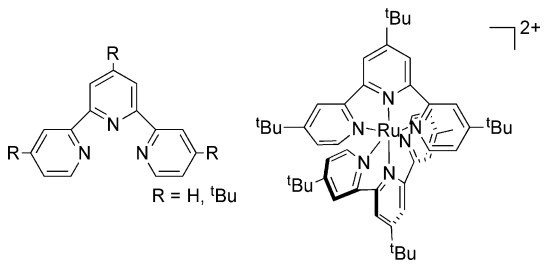


Scheme 1

shows production of this same $(Cym)Ru(\eta^2$-dppm), together with lesser amounts of a C_s symmetry (by ^1H and ^{31}P NMR spectra) product characterized as $(Cym)Ru(\eta^1$-$ZnCl_4)(\eta^2$-dppm) by independent synthesis of this molecule from anhydrous $ZnCl_2$ and $(Cym)RuCl_2(\eta^1$-dppm); this Lewis acid/base reaction is faster than the reduction reaction, which is why it is formed competitively during the zinc metal reduction.

$$2Ru^I \rightarrow Ru^{II} + Ru^0 \quad (1)$$

(b) Pyridine-based chelates. In an attempt to form a monomeric 4-coordinate *mer*-$(imine)_3Ru^ICl$ species, 2,2′:6′,6″ terpyridine (terpy, Scheme 2, R = H) was reacted with the Ru^I dimer, anticipating that this tridentate donor would replace an arene. When terpy was combined with the Ru^I dimer in a 2 : 1 ratio at room temperature in deuterobenzene, there was no reaction between the two, even after a week of stirring. At 50 °C, the color changed from blood red to brown after 12 h, and a dark brown precipitate was observed. ^1H NMR showed that the precipitate was diamagnetic and contained no *p*-cymene, confirming the leaving group behavior of cymene. X-Ray quality crystals were grown from CH_2Cl_2 and showed that two terpy molecules surrounded one Ru^{II} center, with two outer sphere chloride anions (Fig. 2).[15–18]



Scheme 2

A trisubstituted terpyridine ligand was also investigated for better solubility as well as simpler NMR properties: the terpy where R = tert butyl in Scheme 2. This reaction, also performed in a 2 : 1 ratio of ligand to dimer at room temperature in deuterobenzene, showed no reaction and ultimately required temperatures as high as 90 °C to generate an intense orange precipitate in good yields. Upon dissolving the precipitated orange solid in CD_2Cl_2, the ^1H NMR spectrum showed that the product contained only coordinated tri-tert-butyl terpy signals of C_2

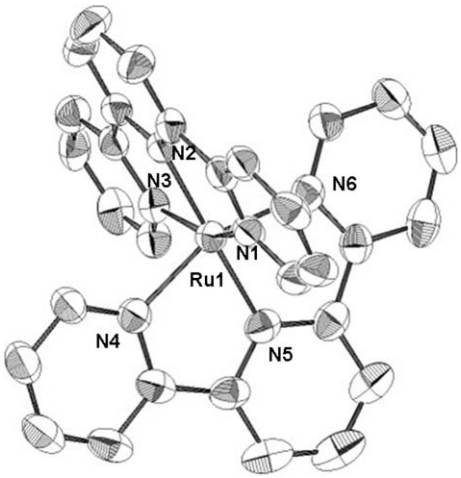


Fig. 2 ORTEP diagram (50% probability) of the non-hydrogen atoms of $Ru(terpy)_2^{2+}$ from its chloride salt; unlabelled atoms are carbon. Selected bond lengths and angles. Ru1–N2 = 1.969(4) Å, Ru1–N5 = 1.973(4) Å, Ru1–N6 = 2.064(4) Å, Ru1–N1 = 2.066(4) Å, Ru1–N3 = 2.070(4) Å, Ru1–N4 = 2.080(4) Å; N1–Ru1–N3 = 158.33(18)°, N2–Ru1–N1 = 78.97(18)°, N2–Ru1–N5 = 177.88(17)°.

symmetry; *p*-cymene was thus again displaced. Single crystals were grown by solvent diffusion of benzene into CH_2Cl_2. While the quality of these crystals was poor, and the diffraction data could not be satisfactorily refined, the connectivity of the solid is unambiguous and is identical to that in Fig. 2. The product is thus $[(^tBu_3\text{-terpy})_2Ru]Cl_2$. ESI-MS shows signals for the parent cation, supporting the X-ray study. This shows that this terpy derivative reacts in a similar manner to terpy, and gives the analogous compound.

Discussion

The modest reducing power of this Ru^I dimer contrasts to that of the Cp*Ru moiety, which has a long history[19,20] of reactivity from the species $[Cp^*RuH_2]_2$. This is perhaps symptomatic of the fact that Cp* is much more electron donating than cymene in the isoelectronic $(Cym)Ru^+$ species, not only because of the ring difference, but also because of the overall charge, which clearly favors electron richness for the less positive species.

Based on a DFT geometry optimization calculation, Fig. 3 shows a fragment MO analysis of the frontier orbitals resulting from interacting two (cymene)RuCl fragments. The six MO's resulting from the *xz*, *yz* and *xy* orbitals are all occupied and contribute no net Ru–Ru bonding. The large splitting of orbitals HOMO107 and LUMO108, a bonding/antibonding pair (Fig. 4), indicates strong bonding, of σ_{RuRu} character, and the double occupancy of 107 comprises the net single bond. As shown in the orbital contour diagram, for each Ru it constitutes the third leg of a three-legged piano stool; it is also a candidate site for electrophilic attack, and thus also for 1-electron oxidation. However, since the σ orbital is strongly stabilized by this interaction, this

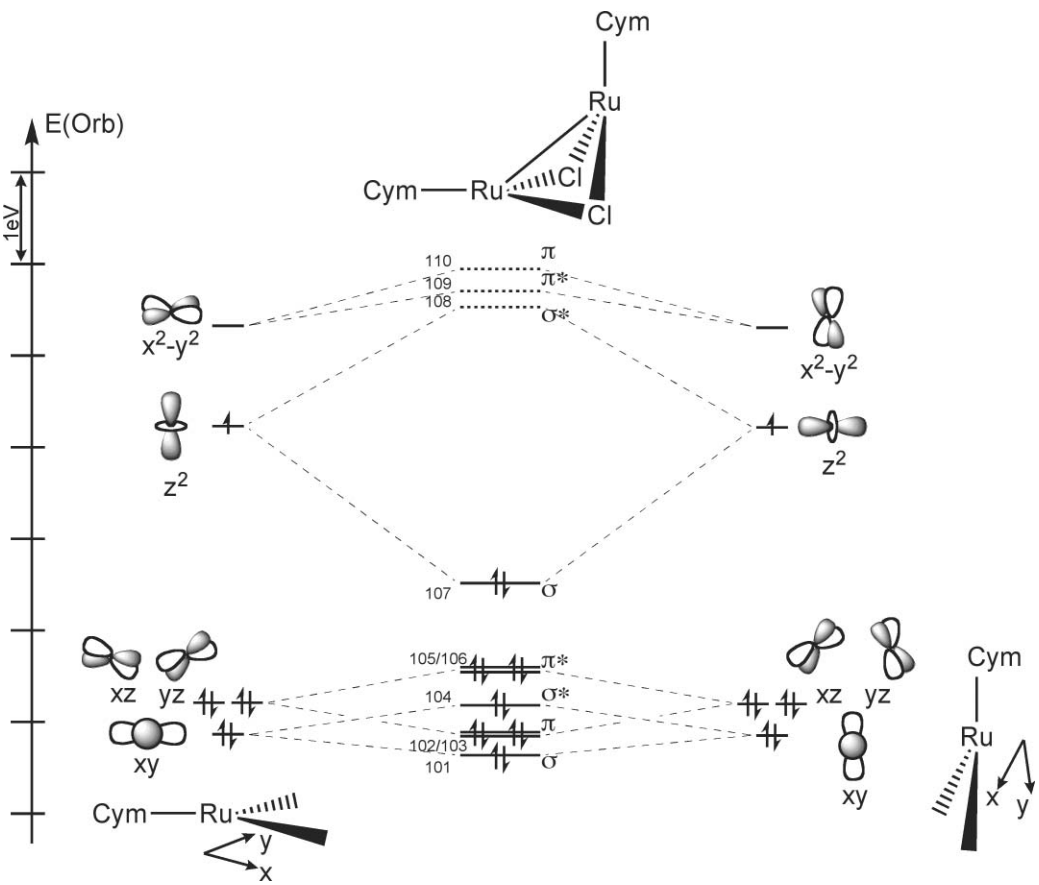


Fig. 3 Frontier orbital energy diagram for $[(Cym)RuCl]_2$ showing their primarily metal-based character.

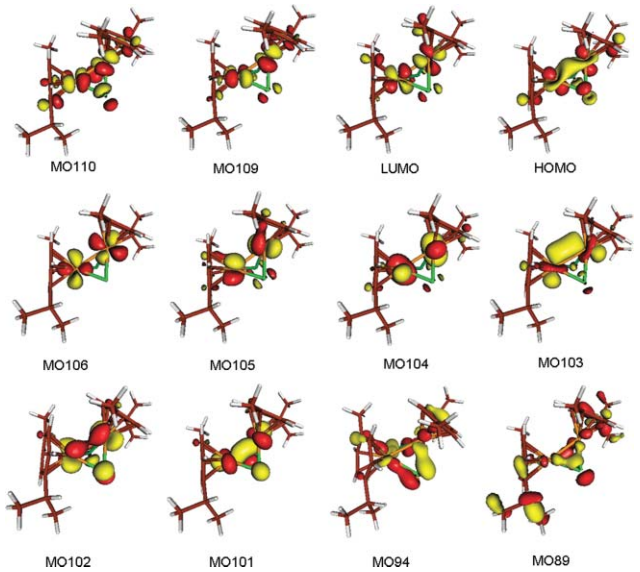


Fig. 4 Selected Kohn–Sham orbitals for $[(Cym)RuCl]_2$ showing primarily metal-based orbitals, Ru–Ru bond (MO 103), chloride participation, and lowest orbitals for nucleophilic attack.

may diminish its reducing power; it lacks the high-lying energy which characterizes a reducing agent. Note also (Fig. 4) the Cl participation in occupied MO's 101, 102 and HOMO107.

The lack of symmetric chloride bridge splitting reactivity towards nucleophiles (*i.e.* making two RuCl monomers), even relatively sterically unencumbered ones, can be traced to the character of the unoccupied MO 110 (Fig 4). This has the Ru–Cl σ* character needed to effect the typical bridge-splitting behavior of an $M_2(\mu\text{-}Cl)_2$ unit, but the main extent of the LUMO lies between the two cymene rings *syn* to the Ru–Ru bond, hence a crowded place. While this alone might not have predicted a lack of reactivity, it surely contributes to the experimental fact. Even the location of the methyl and ^{i}Pr ring substituents in Fig 1 shows this region to be a place to avoid, when ring rotation is facile.

Conclusions

The facile reaction of the dimer with dppm thus shows that disproportionation is preferred over production of radical Ru^I monomers. The facility of this reaction is surely assisted by the fact that each ruthenium in $[(Cym)RuCl]_2$ is bonded to two chlorides, so asymmetric splitting of Ru–Cl bonds as phosphine arrives is enough to accomplish formation of distinct products. It is the dimeric and doubly chloride-bridged character of $[(Cym)RuCl]_2$ that facilitates disproportionation.

With these reactivities established, it becomes clear that the divalent ruthenium product observed with several terpy reagents is not caused by oxidative reaction of Ru^I with CH_2Cl_2, but is inherent to the dimeric reagent. The slow rate of reaction with terpy ligands is thus attributed to the lower basicity of bulky terpy imine nitrogen atoms than of trivalent phosphorus. Moreover, since terpy alone is unsuitable to satisfy the coordination demands of Ru^0 (five coordinate by five N donors), hence the zero valent product is subject to decomposition. Note also that the yields of divalent terpy ruthenium products, ~50%, are consistent with this being disproportionation chemistry.

These results prove the validity of cymene as a leaving group in $[(Cym)RuCl]_2$, being displaced by phosphorus donors and less easily by imines (*i.e.* the terpy ligands, but also bipy and some diimines were evaluated, all with very low conversions after long times at 90 °C in benzene).

Experimental

General

Preparation from a literature source[21] was used to synthesize $[RuCl_2(p\text{-cymene})]_2$, and standard Schlenk or glovebox techniques in inert (argon) atmosphere were used for air sensitive manipulations. All solvents, including deuterated NMR solvents, were dried over and distilled from Na/benzophenone and stored in anaerobic conditions. All other reagents were degassed and/or used as received from commercial vendors. ^{1}H NMR spectra were recorded on either a Varian Unity I400 (400 MHz) instrument or a Varian Gemini 300 (300 MHz). Mass spectra were acquired on a PE-Sciex API III triple quadrupole spectrometer. The zinc powder used in the reduction of $[RuCl_2(p\text{-cymene})]_2$ was stirred in concentrated HCl to remove the oxide outer surface (~5 min). The zinc was then filtered under argon, rinsed with water, and then triple rinsed with THF to wash away any remnant acid or water.

$[RuCl(p\text{-cymene})]_2$. To a round bottom flask containing 0.20 g (0.34 mmol) of $[RuCl_2(p\text{-cymene})]_2$ in 50 mL of THF, a 10 fold excess (0.23 g, 3.4 mmol) of zinc powder was added and the mixture stirred overnight in an argon filled drybox. The resultant air sensitive, blood red solution was dried *in vacuo* and the residue redissolved in C_6H_6, filtered, and dried again. A 5 mg sample of the resultant red-black powder was dissolved in C_6D_6, and the ^{1}H NMR showed the quantitative conversion to $[RuCl(p\text{-cymene})]_2$. ^{1}H NMR (300 MHz, C_6D_6): 5.34 (d, A of AB, $J_{H-H} = 6$ Hz, 2 H, $CH_3\text{-}C_6\mathit{H}_4\text{-}CH(CH_3)_2$), 5.27 (d, B of AB, $J_{H-H} = 5$ Hz, 2 H, $CH_3\text{-}C_6\mathit{H}_4\text{-}CH(CH_3)_2$), 2.13 (septet, $J_{H-H} = 7.5$ Hz, Hz, 1 H, $CH_3\text{-}C_6H_4\text{-}C\mathit{H}(CH_3)_2$)), 1.61 (s, 3 H, $C\mathit{H}_3\text{-}C_6H_4\text{-}CH(CH_3)_2$)), 1.08 (d, $J_{H-H} = 7.5$ Hz, 6 H, $CH_3\text{-}C_6H_4\text{-}CH(C\mathit{H}_3)_2$)). The crystal used for X-ray diffraction structure determination was grown by slow evaporation of a benzene solution. This molecule is highly O_2 sensitive, even as a solid. ESI-MS in THF, where M = $[(Cym)RuCl]_2$: $(M + 2H_2O)^+$ at 577.2, $(M + H_2O)^+$ at 559.3, M^+(v. weak) at 540.6, $(M - Cl + H_2O)^+$ at 523.3 and $(M - Cl)^+$ at 504.3.

Reaction of 1 with 1M HCl in Et_2O. To 5 mg (8.62 μmol) of **1** in C_6D_6, was added 9.8 μL of 1 M HCl in Et_2O and the solution was shaken vigorously as its color turned from blood red to pale red. Yield: 54%. ^{1}H NMR (300 MHz, C_6D_6): 5.67 (d, A of AMXY, $J_{H-H} = 6$ Hz, 2 H, $CH_3\text{-}C_6\mathit{H}_4\text{-}CH\text{-}(CH_3)_2$), 5.54 (d, M of AMXY, $J_{H-H} = 6$ Hz, 2 H, $CH_3\text{-}C_6\mathit{H}_4\text{-}CH\text{-}(CH_3)_2$), 5.33 (d, Y of AMXY, $J_{H-H} = 6$ Hz, 2 H, $CH_3\text{-}C_6\mathit{H}_4\text{-}CH\text{-}(CH_3)_2$), 4.79 (d, X of AMXY, $J_{H-H} = 6$ Hz, 2 H, $CH_3\text{-}C_6\mathit{H}_4\text{-}CH\text{-}(CH_3)_2$), 2.90 (septet, $J_{H-H} = 7.5$ Hz, 2 H, $CH_3\text{-}C_6H_4\text{-}C\mathit{H}\text{-}(CH_3)_2$), 2.16 (s, 6 H, $C\mathit{H}_3\text{-}C_6H_4\text{-}CH\text{-}(CH_3)_2$), 1.42 (d, $J_{H-H} = 7.5$ Hz, 6H, $CH_3\text{-}C_6H_4\text{-}CH\text{-}(C\mathit{H}_3)_2$), 1.37 (d, $J_{H-H} = 7.5$ Hz, 6H, $CH_3\text{-}C_6H_4\text{-}CH\text{-}(C\mathit{H}_3)_2$), −10.30 (s, 1 H, Ru-*H*-Ru). Crystals were grown by layering pentane over a benzene solution of the compound.

Reaction of $(CymRuCl)_2$ with bis-(diphenylphosphino)methane, dppm. To 5 mg of $(CymRuCl)_2$ (9.2 μmol) dissolved in 0.5 mL of C_6D_6, was added 7.0 mg (18.2 μmol) of dppm, which is

a 2 : 1 ligand–dimer ratio. Two products, characterized as (Cym)$RuCl_2(\eta^1$-dppm) and (Cym)Ru(η^2-dppm), are observed within 20 min in a 1 : 1 ratio as indicated by ^{31}P NMR. Attempted crystal growth from this stoichiometry reaction, by evaporation of benzene, resulted only in a black precipitate, apparently due to decomposition of (Cym)Ru(η^2-dppm), whereas the reaction with 4 : 1 ligand–dimer ratio, which showed (spectroscopically) the above products at early reaction time, finally afforded small yellow crystals of *trans*-$Cl_2Ru(dppm)_2$, by slow (4 d) evaporation of benzene solvent at room temperature under inert atmosphere; these were identified by single-crystal X-ray diffraction.

(Cym)$RuCl_2(\eta^1$-dppm). $^{31}P\{^1H\}$ NMR [162.0 MHz, C_6D_6] (δ/ppm): 27.38 (d, $J_{P\text{-}P'}$ = 33.2 Hz) and –27.61 (d, $J_{P\text{-}P'}$ = 33.2 Hz). $^{31}P\{^1H\}$ NMR [162.0 MHz, d^8-THF] (δ/ppm): 26.87 (d, $J_{P\text{-}P'}$ = 29.3 Hz) and –27.44 (d, $J_{P\text{-}P'}$ = 30.1 Hz). ^{1}H NMR [400.1 MHz, C_6D_6] (δ/ppm): 0.68 (d, 7.2 Hz, CH_3(*i*Pr), 6 H); 1.65 (s, CH_3(cymene), 3 H); 2.54 (sept, 7.2 Hz, CH(*i*Pr), 1 H); 4.11 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, PC(H_2)P, 2 H); 4.80 (d, 6.0 Hz, CH(cymene), 2 H); 4.88 (d, 5.6 Hz, CH(cymene), 2 H). ^{31}P decoupling studies established that the CH_2 multiplicity was due to coordinated and free P. ^{1}H NMR [400.1 MHz, d^8-THF] (δ/ppm): 0.78 (d, 6.8 Hz, CH_3(*i*Pr), 6H); 1.84 (s, CH_3(cymene), 3 H); 2.41 (sept, 6.8 Hz, CH(*i*Pr), 1 H); 3.52 (dd, J_1 = 1.6 Hz, J_2 = 8.8 Hz, PC(H_2)P, 2 H); 5.18 (d, 6.4 Hz, CH(cymene), 2 H); 5.34 (d, 5.2 Hz, CH(cymene), 2 H).

(Cym)Ru(η^2-dppm). $^{31}P\{^1H\}$ NMR [162.0 MHz, C_6D_6] (δ/ppm): –11.67 (s). ^{1}H NMR [400.1 MHz, C_6D_6] (δ/ppm): 0.98 (d, 6.8 Hz, CH_3(*i*Pr), 6 H); 1.85 (s, CH_3(cymene), 3 H); 2.25 (sept, 6.8 Hz, CH(*i*Pr), 1 H); 4.15 (t, 11.2 Hz, PC(H_2)P, 2 H); 5.19 (d, 5.6 Hz, CH(cymene), 2 H); 5.22 (d, 5.6 Hz, CH(cymene), 2 H). $^{31}P\{^1H\}$ NMR [162.0 MHz, d^8-THF] (δ/ppm): –12.22 (s). ^{1}H NMR [400.1 MHz, C_6D_6] (δ/ppm): 0.98 (d, 6.8 Hz, CH_3(*i*Pr), 6 H); 1.85 (s, CH_3(cymene), 3 H); 2.25 (sept, 6.8 Hz, CH(*i*Pr), 1 H); 4.15 (t, 11.2 Hz, PC(H_2)P, 2 H); 5.19 (d, 5.6 Hz, CH(cymene), 2 H). ^{1}H NMR [400.1 MHz, d^8-THF] (δ/ppm): 0.91 (d, 6.8 Hz, CH_3(*i*Pr), 6 H); CH_3(cymene) not observed, apparently obscured by other stronger signals in the spectrum; 2.21 (sept, 6.8 Hz, CH(*i*Pr), 1 H); 4.11 (t, 11.2 Hz, PC(H_2)P, 2 H); 5.17 (d, 6.0 Hz, CH(cymene), 2 H); 5.20 (d, 5.6 Hz, CH(cymene), 2 H).

***trans*-$Cl_2Ru(dppm)_2$.** $^{31}P\{^1H\}$ NMR [162.0 MHz, C_6D_6] (δ/ppm): 6.29 (s). ^{1}H NMR [400.1 MHz, C_6D_6] (δ/ppm): 4.94 (t, 4.2 Hz, PC(H_2)P, 2 H).

Reaction of (Cym)$RuCl_2$ with dppm. To 10 mg [(Cym)$RuCl_2$]$_2$ (16.3 μmol) dissolved in 0.5 mL C_6D_6, was added 13.0 mg (32.6 μmol) of dppm. Species (Cym)$RuCl_2(\eta^1$-dppm) (see spectra above) started to form within 10 min and gradually precipitated out after 12 h and was separated and characterized. This product slowly converts, with liberation of free cymene, to [$RuCl_2(\eta^2$-dppm)]$_2$, established to be a dimer by its inequivalent dppm CH_2 protons in a square pyramidal structure; this shows that the dangling arm of dppm in (Cym)$RuCl_2(\eta^1$-dppm) is competitive for binding to Ru, and thus ultimately displaces the leaving group cymene. This conversion from (Cym)$RuCl_2(\eta^1$-dppm) to (Cl_2Ru(dppm))$_2$ and free cymene is much faster in THF than in benzene.

(Cl_2Ru(dppm))$_2$. $^{31}P\{^1H\}$ NMR [162.0 MHz, C_6D_6] (δ/ppm): –6.46 (s). $^{31}P\{^1H\}$ NMR [162.0 MHz, d^8-THF] (δ/ppm): –6.80 (s). ^{1}H NMR [400.1 MHz, C_6D_6] (δ/ppm): 4.93 (br t, 4.0 Hz, PC(H_2)P). ^{1}H NMR [400.1 MHz, d^8-THF] (δ/ppm): 5.07 (br t, 4.0 Hz, PC(H_2)P).

Reaction of (Cym)$RuCl_2(\eta^1$-dppm) with Zn powder

To a THF solution of (Cym)$RuCl_2(\eta^1$-dppm) was added Zn powder (10 fold excess). Two products, (Cym)Ru(η^2-dppm) (see spectra above) and (Cym)Ru(η^1-$ZnCl_4$)(η^2-dppm), were observed to form with equimolar ratio in the early time (3 h of vigorous agitation).

(Cym)Ru(η^1-$ZnCl_4$)(η^2-dppm). $^{31}P\{^1H\}$ NMR [162.0 MHz, d^8-THF] (δ/ppm): 3.95 (s). ^{1}H NMR [400.1 MHz, d^8-THF] (δ/ppm): 0.99 (d, 6.8 Hz, CH_3(*i*Pr), 6H); 1.42 (s, CH_3(cymene), 3 H); 2.83 (sept, 6.8 Hz, CH(*i*Pr), 1 H); 4.60 (dt, $J_{H\text{-}H'}$ = 15.6 Hz, $J_{H\text{-}PP'}$ = 12.8 Hz, PC(H_A)P, 1 H); 5.44 (dt, $J_{H\text{-}H'}$ = 15.2 Hz, $J_{H\text{-}PP'}$ = 10.4 Hz, PC(H_B)P, 1 H); 6.50 (d, 6.4 Hz, CH(cymene), 2 H); 6.54 (d, 6.0 Hz, CH(cymene), 2 H).

Reaction of (Cym)$RuCl_2(\eta^1$-dppm) with anhydrous $ZnCl_2$. To a THF solution of (Cym)$RuCl_2(\eta^1$-dppm) and (Cl_2Ru(dppm))$_2$, which was synthesized (as above) from ($CymRuCl_2$)$_2$ (10 mg, 16.3 μmol) and dppm (13 mg, 32.6 μmol), was added anhydrous $ZnCl_2$ (4.5 mg, 33 μmol). (Cl_2Rudppm)$_2$ remained unchanged, but (Cym)$RuCl_2(\eta^1$-dppm) was converted to a new species **X**. Although many of the chemical shifts duplicated those of (Cym)Ru(η^1-$ZnCl_4$)(η^2-dppm) above, curiously, **X** showed a singlet resonance for all four cymene ring protons in THF. If **X** was vacuum dried (5 h), then washed with pentane, then Et_2O, to remove any free cymene, **X** was insoluble in C_6D_6 (by lack of color and absence of detectable ^{1}H and ^{31}P NMR signals); **X** is thus probably a salt in THF. Completely dissolving this solid residue in CD_2Cl_2, chosen to break the accidental degeneracy, reveals the existence of one single species **X′**, without the presence of any (Cl_2Ru(dppm))$_2$. **X′** showed two nondegenerate cymene ring chemical shifts in CD_2Cl_2. We conclude that both **X** and **X′** are (Cym)Ru(η^1-$ZnCl_4$)(η^2-dppm), with only small solvent-induced spectroscopic differences.

X. $^{31}P\{^1H\}$ NMR [162.0 MHz, d^8-THF] (δ/ppm): 3.82 (s). ^{1}H NMR [400.1 MHz, d^8-THF] (δ/ppm): 0.98 (d, 6.8 Hz, CH_3(*i*Pr), 6 H); 1.37 (s, CH_3(cymene), 3 H); 2.34 (sept, 6.8 Hz, CH(*i*Pr), 1 H); 4.57 (dt, $J_{H\text{-}H'}$ = 14.8 Hz, $J_{H\text{-}PP'}$ = 13.2 Hz, PC(H_A)P, 1 H); 5.45 (dt, $J_{H\text{-}H'}$ = 15.2 Hz, $J_{H\text{-}PP'}$ = 10.4 Hz, PC(H_B)P, 1 H); 6.48 (s, CH(cymene), 4 H).

X′. $^{31}P\{^1H\}$ NMR [162.0 MHz, CD_2Cl_2] (δ/ppm): 3.56 (s). ^{1}H NMR [400.1 MHz, CD_2Cl_2] (δ/ppm): 1.09 (d, 7.2 Hz, CH_3(*i*Pr), 6 H); 1.50 (s, CH_3(cymene), 3 H); 2.48 (sept, 7.2 Hz, CH(*i*Pr), 1 H); 4.56 (dt, $J_{H\text{-}H'}$ = 15.2 Hz, $J_{H\text{-}PP'}$ = 12.8 Hz, PC(H_A)P, 1 H); 4.96 (dt, $J_{H\text{-}H'}$ = 15.2 Hz, $J_{H\text{-}PP'}$ = 10.0 Hz, PC(H_B)P, 1 H); 6.12 (d, 6.4 Hz, CH(cymene), 2 H); 6.20 (d, 6.0 Hz, CH(cymene), 2 H). ^{31}P decoupling studies confirmed that the CH_2 multiplicity was due to P at 3.56 ppm.

Ru(terpy)$_2^{2+}$·2Cl$^-$: reaction of [RuCl(*p*-cymene)]$_2$ with 2,2′:6′,6″ terpyridine (terpy). To 5 mg [RuCl(*p*-cymene)]$_2$ (9.2 μmol) dissolved in C_6D_6, was added 4.3 mg (18.4 μmol) of terpy, which is a 2 : 1 ligand to dimer ratio. The blood red reaction mixture was

heated to 50 °C for 72 h and then cooled to room temperature and the resultant deep brown precipitate (46% isolated yield) was separated and redissolved in DMSO-d^6 and the ^{1}H NMR obtained. ^{1}H NMR (300 MHz, DMSO-d^6) (see ESI†) (δ/ppm): 9.13 (m, 2 H, $J_{H-H} = 4.5$ Hz), 8.86 (m, 2 H, $J_{H-H} = 4.4$ Hz), 8.55 (m, 1 H), 8.05 (m, 2 H), 7.42 (m, 2 H), 7.33 (m, 2 H). ESI-MS (CH_2Cl_2): obs. m/z 284.06 (Ru(terpy)$_2^{2+}$) and 568.09 (Ru(terpy)$_2^{+}$).

Ru(tri-^{t}butylterpy)$_2^{2+}$·2Cl$^-$: reaction of [RuCl(*p*-cymene)]$_2$ with 4,4′,4″-tri-tert-butyl-2,2′:6′,6″ terpyridine (tri-^{t}butylterpy). To 3.8 mg [RuCl(*p*-cymene)]$_2$ (7.0 μmol) dissolved in C_6D_6, was added 5.5 mg (13.8 μmol) of tri-^{t}butylterpy, which is a 2 : 1 ligand to dimer ratio. The blood red reaction mixture was then heated to 90 °C for 72 h, then cooled to room temperature and the resultant bright orange precipitate (48% isolated yield) was separated and redissolved in CD_2Cl_2 and the ^{1}H NMR recorded. ^{1}H NMR (400 MHz, CD_2Cl_2) (see ESI†) (δ/ppm): 9.18 (s, 2 H), 8.88 (s, 2 H), 7.35 (s, 2 H), 7.14 (m, 2 H, $J_{H-H} = 7.8$ Hz), 1.83 (s, 9 H), 1.37 (s, 18 H). ESI-MS (THF): obs. m/z 453.72 (Ru(tri-^{t}butylterpy)$_2^{2+}$).

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