Conversions of Ruthenium(III) Alkyl Complexes to Ruthenium(II) through Ru–C<sub>alkyl</sub> Bond Homolysis

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Single-electron oxidation of the Ru(II) complexes TpRu(L)(L′)(R) (L = CO, L′ = NCMe, and R = CH<sub>3</sub> or CH<sub>2</sub>CH<sub>2</sub>Ph; L′ = PMe<sub>3</sub> and R = CH<sub>2</sub>) with AgOTf leads to alkyl elimination reactions that produce TpRu(L)(L′)(OTf) and organic products that likely result from Ru–C<sub>alkyl</sub> bond homolysis. Density functional calculations on TpRu(CO)(NCMe)(Me) and its Ru(III) cation indicate that the Ru–CH<sub>3</sub> homolytic bond dissociation enthalpy is substantially reduced (48.6 to 23.2 kcal/mol) upon oxidation.

Introduction

The reductive elimination of an organic molecule from a transition metal complex is the product-forming step in many catalytic cycles. Several mechanisms exist for the reductive elimination of metal–carbon bonds including direct C–C elimination from a single metal center, C–C elimination from two metal centers, and initial metal–carbon bond homolysis (Scheme 1). For transformations that occur from two metal centers, both intramolecular and intermolecular processes have been reported, with the former pathway being observed more frequently.1–4 Examples of less common intermolecular pathways include C–C elimination from Mn carbonyl complexes, H–H elimination from HCo(CO)<sub>4</sub>, H–H and C–H elimination from osmium carbonyl complexes, elimination of aldehydes from mixtures of alkyl and hydride complexes that possess carbonyl ligands, and the elimination of dienes from metal-vinyl complexes.5–13

The microscopic reverse of reductive elimination, oxidative addition, has also been reported to occur across two metal centers via both intra- and intermolecular reactions.14,15 Metal–carbon bond homolysis can also initiate the elimination of alkyl or aryl groups and results in a formal reduction of the metal center by a single electron.16–19

We have reported that complexes of the type TpRu(CO)(NCMe)(R)(Tp = hydridotris(pyrazolyl)borate; R = Me or aryl) serve as catalyst precursors for the hydroarylation of olefins;20–22 however, in the presence of electron-deficient olefins the Ru(II) complexes initiate radical polymerization reactions.23 Recent reports of intramolecular olefin hydroarylation reactions catalyzed by Ru(III) prompted us to explore single-electron oxidation sequences of the Ru(II) complexes TpRu(L)(L′)(R) (L = CO, L′ = NCMe, and R = Me or CH<sub>2</sub>CH<sub>2</sub>Ph; L′ = PMe<sub>3</sub> and R = Me).24 Herein, we report on the

Scheme 1. Reductive Elimination of Metal–Carbon Bonds

| Reductive Elimination from a Single Metal Center: |
| R<sup>n</sup>–M<sup>III</sup> + 2e<sup>-</sup> ———> M<sup>II</sup> + R + R |

| Reductive Elimination from Two Metal Centers: |
| 2 R<sup>n</sup>–M<sup>III</sup> + 2 e<sup>-</sup> ———> 2 M<sup>II</sup> + R + R |

| Reductive Elimination through Bond Homolysis: |
| R<sup>n</sup>–M<sup>III</sup> + 2 e<sup>-</sup> ———> M<sup>II</sup> + R |

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predilection of the putative Ru(III) systems [TpRu(L)-(L')(R)][OTf] (OTf = trifluoromethanesulfonate) to undergo reductive transformations and return to formal Ru(II) oxidation states through pathways that likely involve Ru–C<Calkyl bond homolysis.

Results

The reaction of TpRu(CO)(NCMe)(Me) with 1 equiv of AgOTf in methylene chloride results in the quantitative formation (by 1H NMR spectroscopy) of TpRu(CO)-(NCMe)(OTf) (1) within 10 min at room temperature (eq 1). Complex 1 is isolated in 60% yield after workup and has been characterized by 1H and 13C NMR spectroscopy, IR spectroscopy (νCO = 1993 cm⁻¹), and elemental analysis. The overall reaction sequence involves a single-electron transfer to form Ag(s) and net loss of a methyl ligand from the putative Ru(III) intermediate [TpRu(CO)(Me)(NCMe)][OTf]. In addition to complex 1, performing the reaction as a CD₂Cl₂ solution in a gastight NMR tube reveals the formation of CH₃D and ethane in a 1:9.4 molar ratio as determined by ¹H NMR spectroscopy. In the ¹H NMR spectrum, a singlet due to production of ethane is observed at 0.9 ppm, while a multiplet (0.15 ppm) is observed due to the presence of CH₃D. In addition, sampling of the headspace from this reaction followed by analysis using mass spectrometry confirms the formation of CH₃D and ethane. The analogous reaction is observed in toluene-d₈ favoring CH₃D over CH₃. In addition, the formation of methane, relative to ethane, is increased for reaction in toluene versus reaction in methylene chloride. In addition, performing the oxidation of TpRu(CO)(Me)(NCMe) in CD₂Cl₂ in the presence of approximately 4 equiv of the radical trap 2,2,6,6-tetramethyl-1-piperidinol (TEMPO) yields TpRu(CO)(OTf)(NCMe) (1) without observation of ethane or methane. Finally, analysis of several reactions of TpRu(CO)(NCMe)(Me) with AgOTf in toluene-d₈ revealed a kinetic isotope effect of 5.9(7) as determined by integration of the resonance due to CH₄ versus CH₃D in the ¹H NMR spectra.

Similar to the Ru(II) methyl complex, the reaction of TpRu(CO)(NCMe)(CH₂CH₂Ph) with AgOTf produces complex 1 and is complete within 5 min at room temperature (eq 2). The reaction also produces ethylbenzene, 1,4-diphenylbutane, and styrene. Although deuterium incorporation into ethylbenzene is a possibility, ¹H NMR spectroscopy does not allow a definitive determination whether deuterium is present. Using GC FID, the molar ratio of 1,4-diphenylbutane:styrene: ethylbenzene was determined to be 4:1:1.3.

To probe the influence of the ancillary ligand set on the oxidation/reduction sequence, we sought to explore the oxidation of a complex of the type TpRuL₄(R). TpRu(PMe₃)₂(Me) (2) is prepared by heating a solution of TpRu(PMe₃)₂Cl with Me₂Mg (Scheme 2), and the oxidation of TpRu(PMe₃)₂(Me) with AgOTf in CD₂Cl₂ produces CH₃D, ethane, and TpRu(PMe₃)₂(OTf) (3). The molar ratio of CH₃D to ethane in solution is approximately 1:10. The combination of complex 2 with AgOTf in toluene-d₈ produces complex 3 as well as CH₃D and ethane in an approximate 1.6:1 molar ratio. The molar ratios of methane and ethane upon oxidation of TpRu(PMe₃)₂(Me) in CD₂Cl₂ or toluene-d₈ are almost identical to those observed for analogous reactions of TpRu(CO)(NCMe)(Me).

Discussion

One possible pathway for the observed Ru(III)/(II) elimination sequences is RuIII–R bond homolysis to generate free radical species, and the formation of CH₃D after the oxidation of TpRu(CO)(NCMe)(Me) or TpRu(PMe₃)₂(Me) in CD₂Cl₂ is consistent with such a pathway. The C–H bond dissociation enthalpy (BDE) of CH₃Cl is approximately 100 kcal/mol, while the C–H BDE of methane is approximately 105 kcal/mol. Thus, the formation of methane from methyl radical and methane chloride is thermodynamically favorable. The formation of methane that results from C–C coupling of two methyl species is apparently in kinetic competition with hydrogen atom abstraction from solvent by methyl radical. Transformations that generate methyl radical should exhibit increased production of methane in solvents with weaker C–H bonds. Indeed, the oxidation of TpRu(CO)(Me)(NCMe) or TpRu(PMe₃)₂(Me) in toluene-d₈ (BDE of benzylic C–H bond approximately 88 kcal/mol) yields increased production of methane relative to ethane compared with reactions in methylene chloride. The nearly identical molar ratios of CH₃D:ethane for the oxidation of either TpRu(CO)(NCMe)(Me) or TpRu(PMe₃)₂(Me) in CD₂Cl₂ or toluene-d₈ suggests that organic products are formed from a common intermediate, and these data are consistent with the formation of methyl radical for both systems. In addition, the sequestration of methyl radical prior to hydrogen atom abstraction upon addition of TEMPO to the reaction of TpRu(CO)(NCMe)(Me) and AgOTf is consistent with the intermediacy of methyl radical. The reaction of TpRu(CO)(NCMe)(Me) with [Cp₂Fe][PF₆] at 80 °C produces a single Ru(II) complex, ferrocene, ethane, and CH₃D.


These results are analogous to the reaction with AgOTf, suggesting that inner-sphere electron transfer upon reaction with AgOTf to produce Ag–R with subsequent Ag–C bond homolysis is an unlikely reaction pathway. Cyclic voltammetry experiments indicate a quasi-reversible oxidation of TpRu(CO)(NCMe)(Me) at 0.95 V (vs NHE). Similar analyses of TpRu(CO)(NCMe)(CH2CH2Ph) and TpRu(PMe3)2(Me) reveal quasi-reversible oxidation waves at E1/2 = 1.02 and 0.25 V, respectively.

The formation of ethylbenzene and styrene in the oxidation of TpRu(CO)(NCMe)(CH2CH2Ph) is also consistent with the generation of alkyl radical. Thus, the formation of ethylbenzene radical can produce 1,4-diphenylbutane through C–C coupling, a 1:1 ratio of styrene and ethylbenzene through intermolecular hydrogen atom transfer, and ethylbenzene through hydrogen atom abstraction from the solvent (Scheme 3).

In support of the experimental studies, B3LYP/SBK(d) calculations were carried out on full models of the methyl radical, neutral TpRuII(CO)(NCMe)(Me), and (TpRuI(CO)(NCMe)) complexes as well as the cationic [TpRuII(CO)(NCMe)(Me)]+ and [TpRuII(CO)(NCMe)]+ complexes to determine Ru–CH3 BDEs. In general, there are no major differences in the geometries of the corresponding neutral and cationic complexes. Interestingly, the calculated RuII–Me and RuIII–Me bond lengths of TpRuII(CO)(NCMe)(Me) and [TpRuII(CO)(NCMe)(Me)]+ were 2.15 and 2.14 Å, respectively. On the basis of available ionic radii in the literature for RuII and RuIII, it is expected that bond lengths involving RuII will be 0.06 Å shorter than similar bonds involving RuIII, yet the calculated ΔRuIII–CH3 bond length is only 0.01 Å, which implies that the RuIII–Me bond is weaker than the RuII–Me bond. This supposition is further supported by the Mulliken bond orbital population (BOP), which yields a value of 0.45 for the RuII–Me bond and 0.36 for the RuIII–Me bond. The DFT-derived BOPs thus suggest that the metal–alkyl bond in the RuIII complex is weaker than that in the corresponding RuII complex.

Calculated Ru–Me homolytic BDEs reveal a substantial decrease of 25.4 kcal/mol upon oxidation from RuII (48.6 kcal/mol) to RuIII (23.2 kcal/mol) (Scheme 4). This decrease in BDE is mirrored by the calculated ionization potentials (IPs) shown in the thermochemical cycle where the difference between the IPs of d6-RuII–Me (6.3 eV) and d6-RuII (5.2 eV) is 1.1 eV, which is 25.4 kcal/mol (Figure 1). Hence, the calculations support the notion that the decrease in Ru–Me BDEs arises from weakening of the Ru–C bond upon oxidation of Ru from +2 to +3 as well as stabilization of the product, i.e., its return to a d6 configuration upon homolytic Ru–C bond scission for the RuIII complex.

Understanding metal–ligand bond energies and the factors that dictate them is crucial to the rational development of synthetic methodologies as well as understanding some biological processes.26–28 In particular, relevant to single-site organometallic catalysts are the BDEs of metal–alkyl bonds. At room temperature, the Ru-alkyl complexes TpRu(CO)(NCMe)(R) (R = Me or CH2CH2Ph) and TpRu(PMe3)(2)Me exhibit no evidence of decomposition after at least one week in solution at room temperature. In contrast, single-electron oxidation to yield the cationic RuIII complexes [TpRu(L)(L')(R)][OTf] results in rapid Ru–R bond homolysis at room temperature. For all three TpRuIII alkyl complexes discussed herein, the formation of organic products and TpRu(L)(L')(OTf) through bond homolysis occurs within at least 5 min at room temperature. This observation places an upper limit on the half-life for the reactions of approximately 1 min. Thus, kobs ≥ 1.1 × 10–2 s–1, which corresponds to ΔG° ≥ 20 kcal/mol at 298 K. Since Ru–C bond homolysis is likely the rate-determining step or precedes the rate-determining step

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\begin{align*}
\text{BDE} & = 23.2 \text{ kcal/mol} \\
\text{d}^6-\text{[RuIII]} & - \text{Me} \\
\text{d}^6-\text{[RuII]} & - \text{Me} \\
\text{IP} & = 6.3 \text{ eV} \\
\text{IP} & = 5.2 \text{ eV} \\
\text{BDE} & = 48.6 \text{ kcal/mol}
\end{align*}
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\[\text{Scheme 4. Computational Studies Indicate Ru–CH}_3\text{ BDEs of 48.6 kcal/mol for RuII and 23.2 kcal/mol for RuIII} \]

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in the conversion of [TpRu(L′)(L′′)(R)][OTf] to TpRu(L′)-
L′′)(OTf), it is anticipated that the BDEs of the Ru–C
bonds will be less than or similar to the magnitude of the
free energy of activation. Therefore, the rapid
conversions from RuIII to RuII indicate that the Ru–C
bonds of the RuIII complexes [TpRu(L)(L′)(R)][OTf] are
likely to be near 20 kcal/mol and represent a series of
relatively weak metal–alkyl bonds. This estimation is
consistent with the calculated Ru–C BDE of 23.2 kcal/ mol
for [TpRu(Me)(NCMe)(Me)][OTf].19 Riordan and Halpern
have reported that porphyrin Fe(III) alkyl BDEs range from 15 to 31 kcal/mol, and related studies have
been performed on Co(III) systems.16,17 The Ru–C BDE
of a RuIV porphyrin bis-ethyl complex has been esti-
mated at 21.7 (1.5) kcal/mol.18 Oxidation of CpRu(PR3)2-
(CO)(Me) systems yields methane and Ru(II) products.30

We have previously reported that the combination of
TpRu(CO)(NCMe)(R) and electron-deficient olefins at
elevated temperatures.23 The apparently
weak RuIII–Calkyl bonds at the Ru(III) oxidation state
of these TpRu systems are consistent with the observa-
tion of radical-initiated polymerization reactions. Thus,
single-electron oxidation of TpRu(CO)(NCMe)(R) by the
electron-deficient olefins, regardless of whether the electron
transfer is thermodynamically favored, would provide
facile access to alkyl radical species and initiate
radical-based olefin polymerization. This result is key
to the development of future generations of hydro-
arylating catalysts, as any substrate that can oxidize
the TpRu(L)(L′)(R) systems would likely lead to decom-
position through Ru–C bond homolysis.

A potential contributing factor to the decrease in
BDEs upon oxidation to Ru(III) is the driving force to
return to a d6 electronic configuration. A comprehensive
study of closely related pseudo-octahedral Cp8Fe(dppe)X
complexes (Cp8 = pentamethylcyclopentadienyl; dppe =
1,2-bis(diphenylphosphino)ethane; X = halide, H, or
Me) BDEs has revealed that oxidation from Fe(II) to
Fe(III) also decreases homolytic BDEs by 9
kcal/mol.20 Thus, for the Ru–Me systems discussed herein, the
calculated change in homolytic BDE upon oxidation from
d0 to d5 is 25.4 kcal/mol, while the change is
approximately 9 kcal/mol for the Cp3Fe(dppe)CH3.31
Thus, decrease in BDEs for metal–ligand bonds may
be general for d0 to d5 oxidations of octahedral or pseudo-
occatahedral complexes.

Experimental Section

General Methods. All procedures were performed under
an atmosphere of dry dinitrogen in a Vacuum Atmospheres
glovebox or using standard Schlenk techniques. The glovebox
atmosphere was maintained by periodic nitrogen purges and
monitored by an oxygen analyzer (O2(g) < 15 ppm for all
reactions). Toluene and hexanes were purified by reflux over
sodium/benzzenepheneketyl followed by distillation under a
dinitrogen atmosphere. Pentane and methane chloride were
refluxed over P2O5, followed by distillation under a dinitrogen
atmosphere. Toluene-d8, CDCl3, and CDC13 were degassed by
three freeze–pump–thaw cycles and stored over 4 A molecular
sieves.1H and 13C NMR measurements were performed on
either a Varian Mercury 300 or a 400 MHz spectrometer and
were referenced against tetramethyilisilane using residual
proton signals (1H NMR) or the 13C resonances of the deuter-
ated solvent (13C NMR). Resonances due to the Tp ligand are
reported by chemical shift and multiplicity only (all coupling
constants are 2 Hz). All 31P NMR spectra were recorded on a
Varian Mercury instrument operating at a frequency of 161
MHz with 85% phosphoric acid (0 ppm) as external standard.
31P NMR spectra were recorded on a Varian Mercury instru-
ment operating at a frequency of 376.5 MHz with CdF6 (163
ppm) as internal standard. Cyclic voltammograms were re-
corded in a standard three-electrode cell from –2.00 V to +2.00
V with a glassy carbon working electrode and tetrabutylam-
nonium hexafluorophosphate as electrolyte. Tetrabutylam-
onium hexafluorophosphate was dried under vacuum at 110 •C
for 48 h prior to use. All potentials are reported versus NHE
(normal hydrogen electrode) using cobaltocenium
hexafluorophosphate as internal standard. Gas chromatogra-
phy was performed on a Hewlett-Packard 5890 GC using
either an HP-5 capillary column (30 m × 0.25 mm with 0.25
μm film thickness) or a J&W Scientific DB-1 capillary column
(30 m × 0.25 mm with 1.00 μm film thickness) equipped with
a PID detector. Chromatograms were produced using Perkin-
Elmer TotalChrom 6.2 software. GC-MS was performed using
a HP GCD system with a 30 m × 0.25 mm HP-5 column with
0.25 μm film thickness. Ethylbenzene, styrene, 1,4-diphenyl-
butane, and decane were obtained from Sigma Aldrich Chemi-
cal Co. and used as received. Methane (99.5%) and ethane
(90%) were received in gas lecture bottles from Airgas, and
Purity Gases and used as received. All IR spectra were
acquired using a Mattson Genesis II FTIR as thin films on
KBr plates or as solutions. The preparation, isolation, and
characterization of TpRu(CO)(NCMe)(Me), TpRu(PMe3)2Cl,
and TpRu(PMe3)2(OTf) have been previously reported.30,31

TpRu(CO)(NCMe)(OTf) (1). TpRu(CO)(NCMe)(Me) (0.314
g, 0.79 mmol) was dissolved in 50 mL of methylene chloride
in a dry Schlenk flask. To this solution was added AgOTf
(0.200 g, 0.78 mmol), and the resulting mixture was stirred
at room temperature for 1 h. Completion of the reaction
occurred within 5 min, as indicated by a shift in vCO from 1919
to 1993 cm–1 in the IR spectra. The solution was filtered
through a plug of Celite. The volatiles were removed from the
filtrate under reduced pressure, and the subsequent residue
was washed with pentane. The resulting pale yellow solid was
dried in vacuo and isolated in 60% yield (0.250 g). IR (KBr):
vCO = 1995 cm–1, vM=H = 2504 cm–1. 1H NMR (CDCl3, δ):
7.79, 7.76, 7.71, 7.67, 7.43 (each 1H, a d, Tp 3 or 5 position),
6.40 (1H, t, Tp 4 position), 6.23 (2H, overlapping t’s,
Tp 4 position), 2.47 (3H, s, Ru–NCCH3). 13C NMR (CDCl3, δ):
199.8 (s, Ru–CO), 145.7, 145.3, 142.0, 137.2, 136.3, 135.3,
(each a s, Tp 3 or 5 position), 124.5 (s, Ru–NCMe), 119.1 (q
due to low signal-to-noise, only the inner lines of the
expected quartet were observed), 19F NMR (CDCl3, δ):
–78.6 (s, Ru–O2SCF2). Anal. Calcd for C13H13–
BF2–N2O2Ru: C, 29.34; H, 2.46; N, 18.42. Found: C, 29.58; H,
2.52; N, 18.33.

TpRu(PMe3)2(Me) (2). TpRu(PMe3)2Cl (0.187 g, 3.7 mmol)
and toluene (~50 mL) were combined in a round-bottom flask
to give a homogeneous yellow solution. To this solution was
added Me2Mg (0.024 g, 4.4 mmol), and the mixture was heated
in reflux for 6 h. The dark yellow solution was passed through
a plug of Celite with a copious amount of diethyl ether to give
a yellow filtrate. The volatiles were removed from the filtrate
under reduced pressure. The white solid that remained was
recrystallized by dissolving in 1 mL of methylene chloride
followed by addition of 10 mL of methanol. The precipitate
was collected by vacuum filtration and dried in vacuo (0.041
g, 23%). 1H NMR (CDCl3, δ): 7.71, 7.60, 7.57, 7.55 (6H total,

4974–4975.

(31) Jayaprakash, K. N.; Conner, D.; Gunnod, T. B. Organometallics
2.2: 2.1 integration, each a d, Tp 3 or 5 position), 6.15, 6.08 (3H total, 1:2 integration, each a t, Tp 4 position), 1.22 (18H, 1:2:2:1 integration, each a d, Tp 3 or 5 position), 10.4, 10.4 (each a s, Tp 4 position), 19.5 (vt, P(CH$_3$)$_3$, $N = 25$ Hz), $-9.6$ (t, Ru–CH$_3$, $J_{1P}$ = 11 Hz). CV (CH$_3$CN, 100 mV/s): $E_{p1/2}$ = 0.25 V (quasi-reversible). Anal. Calcd for C$_9$H$_{13}$BN$_3$P$_2$Ru: C, 39.93; H, 6.49; N, 17.46. Found: C, 40.21; H, 6.48; N, 16.65. 1H and 31P NMR spectra of complex 2 are included in the Supporting Information.

**Oxidation of TpRu(II)(L)(Me) (L = L’ = PMe$_2$ or L = CO and L’ = NCMe).** A sample reaction is given. A screwcap NMR tube was charged with TpRu(CO)(Me(NCMe)) (0.020 g, 0.05 mmol). The solid was dissolved in 0.5 mL of CD$_2$Cl$_2$, and a 1H NMR spectrum was recorded. The NMR tube was purged into a glovebox, and AgOTf (0.013 g, 0.05 mmol) was added. Upon addition of AgOTf, conversion of the colorless homogeneous solution to a honey-colored solution with gray precipitate was observed. A 1H NMR spectrum was recorded after 5 min of reaction time. In addition to resonances due to the production of TpRu(CO)(NCMe)(OTf) (confirmed by resonances at 2.65 ppm), the production of ethylbenzene, styrene, and 1,4-diphenylbutane was determined by 1H NMR spectroscopy. The production of styrene was indicated by a multiplet at 0.15 ppm along with a singlet due to CH$_3$D from four separate reactions revealed a kinetic isotope effect of 5.9(7).

**Computational Methods.** Quantum mechanical calculations were performed using Gaussian98. The calculations employed density functional theory (DFT), in particular the B3LYP hybrid functional. Ruthenium and main group elements were described with the Stevens (CEP-31G) relativistic effective core potentials (ECPs) and valence basis sets (VPBSs). The valence basis sets of main group elements (carbon, nitrogen, oxygen) were augmented with a d polarization function with an exponent of 0.8, and no polarization function was used on the boron. This combination of ECPs and VPBSs, termed SBK(d), has been employed for calculations on a wide selection of transition metal complexes, including Ru-scorpionates. All stationary points for the models investigated were fully optimized to minima (i.e., no imaginary frequencies) without symmetry constraints. Open-shell molecules were calculated within the unrestricted Kohn–Sham formalism. All reported energetics include zero-point and enthalpic corrections calculated using vibrational frequencies determined at the B3LYP/SBK(d) level of theory.

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**Supporting Information Available:** 1H and 31P NMR spectra of complex 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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