Excited-State Distortions Determined from Structured Luminescence of Nitridorhenium(V) Complexes

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The nitridorhenium(V) complexes ReNCi₂(PCy₃)₂ (1), ReNBr₂(PCy₃)₂ (2), ReNCi₂(PPH₃)₂ (3), and ReNBr₂(PPH₃)₂ (4) produce structured emission spectra upon excitation at low temperature. The origin, E₀, occurs at 15 775, 16 375, 15 875, and 16 300 cm⁻¹, respectively. The vibronic peaks are regularly spaced with an average energy separation corresponding to the Re=N stretching frequency. The nitridorhenium stretching frequency ranges from 1095 to 1101 cm⁻¹, as determined by Raman and IR spectroscopy. The excited-state distortions are calculated by fitting the emission spectra. The excited state arises primarily from a dₓₒ (ReN nonbonding) to dₚ (ReN π antibonding) transition. The rhenium—nitrogen bond length in the excited state is 0.08 Å longer than in the ground electronic state, which is consistent with the difference in bond lengths of ReN bonds of bond order 3 and bond order 2.5 as determined from molecular structures.

1. Introduction

Metal—ligand bond length changes in electronic excited states can be determined from analysis of vibronic structure in the electronic spectra.¹⁻² It is of interest to determine how large a bond length change can occur in excited states that weaken the metal—ligand bond. Metal—nitrido complexes that formally contain a triple bond in the ground state may undergo bond weakening in excited states. These complexes are of current interest as possible nitrogen atom transfer agents³⁻¹⁰ and in investigations of nitrogen atom activation.¹¹⁻¹³

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The high prevalence of ReV⁺ª compounds combined with the rich photochemistry of isoelectronic OsV⁺²ª¹⁴⁻¹⁹ and ReV⁺O²⁻⁻²² compounds prompted us to explore the photochemistry of simple nitridorhenium compounds of the formula ReNX₂(PPh₃)₂ (X = Cl, Br; P₃R = PPh₃, PCy₃).

The series of compounds investigated all produce structured emission spectra upon excitation at low temperature. Nitridorhenium(V) compounds are known to luminesce,¹²²⁻²⁶

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and some have been observed to produce vibronic structure.\textsuperscript{12,23,25} The structure has been assigned to the ReN vibration,\textsuperscript{12,23,25} but the excited state has never been analyzed. Detailed assignments of the modes involved in the emitting state will allow for an estimate of the ReN bond length change in the excited state.

Five-coordinate nitridorhenium(V) complexes spatially isolate the ReN along one axis with no ligands in the trans position. These complexes utilize bulky monodentate phosphines (such as triphenylphosphine) or bidentate phosphines to maintain a distorted square pyramid geometry.\textsuperscript{22,26} However, phenyl modes from the phosphines appear in the vibrational spectra in the same range as the ReN stretch, making a conclusive assignment impossible in many cases. A series of compounds were investigated to identify the ligand modes in the ReN vibrational frequency range.

In this paper, we report the synthesis and investigation of four nitridorhenium(V) compounds, ReNX\(_2\)(PR\(_3\))\(_2\) (X = Cl, Br; PR\(_3\) = PPh\(_3\), PCy\(_3\)). We examine the excited state and explain the observed energy trend using a molecular orbital analysis. We assign the frequency of the rhenium–nitrigen (ReN) stretch by comparison of the vibrational spectra. The low-temperature emission spectra are calculated using the time-dependent theory of spectroscopy.\textsuperscript{2,27} An upper limit of the excited-state bond length change is determined from the fitting parameters.

2. Experimental Section

(a) Syntheses and Characterization. All reagents except tricyclohexylphosphine and triphenylphosphine were purchased from Aldrich Chemical Co. Tricyclohexylphosphine (PCy\(_3\)) was purchased from Strem Chemicals, Inc., and triphenylphosphine (PPh\(_3\)) was purchased from Acros Organics. Unless otherwise stated, all chemicals were reagent grade and used without further purification. Benzene and toluene were dried by distillation over calcium hydride. All \(^1\)H, \(^{13}\)C, and \(^{31}\)P NMR spectra were recorded on a Bruker AXR 400 spectrometer. In all cases the solvent was CD\(_2\)Cl\(_2\) and \(^{31}\)P chemical shifts are relative to 85% H\(_3\)PO\(_4\). Elemental analyses were performed in duplicate by Desert Analytics Laboratory, Tucson, AZ.

Complexes 3 and 4 were synthesized according to literature procedures,\textsuperscript{26,29} characterized by \(^1\)H NMR, \(^{31}\)P NMR, and elemental analysis, and found to be of high purity.\textsuperscript{30} Complex 3 was synthesized from the reaction of ReOCl\(_3\)(PPh\(_3\))\(_2\) with phenylhydrazine hydrochloride in ethanol/water solution.\textsuperscript{28} However, attempts to produce complex 4 from 30 mg (0.12 mmol) in dry toluene (25 mL). The solution was refluxed for 16 h. The solvent was removed under vacuum, affording an oil, which was isolated by vacuum filtration and rinsed with hot 95% ethanol (25 mL). The solution was observed to produce an orange-red precipitate. The solution was filtered, and the solid was washed with hot 95% ethanol. The solid was dissolved in diethyl ether, and hot 95% ethanol was added until the pink product precipitated. The product was vacuum-filtered and rinsed with hot 95% ethanol, then dried in air. Yield 38%. \(^1\)H NMR (CD\(_2\)Cl\(_2\)): \(\delta\) 1.22 (m, 18 H), 1.51 (m, 12 H), 1.70 (m, 6 H), 1.82 (m, 12 H), 2.12 (d, 12 H), 2.87 (m, 6 H). \(^{13}\)C NMR (CD\(_2\)Cl\(_2\)): \(\delta\) 26.70 (s), 28.03 (t), 30.13 (s), 32.01 (t). \(^{31}\)P NMR (CD\(_2\)Cl\(_2\)): \(\delta\) 21.31. Anal. Calcd for ReNBr\(_2\)P\(_2\)C\(_36\)H\(_{30}\): C, 48.88; H, 3.42; N, 1.76. Found: C, 49.16; H, 3.41; N, 1.63.

(b) Luminescence Spectroscopy. Emission spectra were acquired from solid samples in capillary tubes at 1 K. An Air Products displ ease closed-cycle helium refrigerator provided low temperature. An Ar ion laser at 514.5 nm wavelength or a Kr ion laser at 351.5 nm wavelength was used for excitation. A Spex 1702 single monochromator equipped with a S1 photomultiplier tube and Stanford Research Systems SR400 photon counter collected and detected the signal. All data were corrected for instrument response.

(c) Vibrational Spectroscopy. Raman spectra were acquired utilizing KCl pellets with a complex-to-salt ratio of 1:5. A Spex 1401 double monochromator collected scattered light at a back-scattering geometry to reduce self-absorption. An RCA C1304 photomultiplier tube connected to a Stanford Research System SR400 photon counter detected the signal. An Ar ion laser at 514.5 nm wavelength was used for preresonance excitation. All infrared spectra were acquired with a Jasco model 420 FTIR spectrometer, using KBr pellets.

3. Results

(a) Emission Spectroscopy. Emission spectra observed at 15 K for complexes 1–4 are shown in Figure 1. The spectrum for complex 1 contains vibronic structure with peaks at 15 775, 14 725, 13 725, and 12 550 ± 100 cm\(^{-1}\).


(30) Characterization for compound 3. \(^1\)H NMR (CD\(_2\)Cl\(_2\)): \(\delta\) 7.44 (m, 18 H), 7.70 (m, 12 H). \(^{31}\)P NMR (CD\(_2\)Cl\(_2\)): \(\delta\) 24.78. Anal. Calcd for ReNCl\(_2\)P\(_2\)C\(_36\)H\(_{30}\): C, 54.34; H, 3.80; N, 1.76. Found: C, 54.20; H, 3.69; N, 1.51. Characterization for compound 4. \(^1\)H NMR (CD\(_2\)Cl\(_2\)): \(\delta\) 7.43 (m, 18 H), 7.80 (m, 12 H). \(^{31}\)P NMR (CD\(_2\)Cl\(_2\)): \(\delta\) 24.20. Anal. Calcd for ReNBr\(_2\)P\(_2\)C\(_36\)H\(_{30}\): C, 48.88; H, 3.42; N, 1.58. Found: C, 49.16; H, 3.41; N, 1.63.
with the maximum intensity at the second peak and an average spacing of $1075 \pm 100 \text{ cm}^{-1}$. The spectrum for complex 2 contains vibronic structure with peaks at 16 375, 15 325, 14 250, and 13 225 $\pm 100 \text{ cm}^{-1}$, with the maximum intensity at the second peak and an average spacing of $1075 \pm 100 \text{ cm}^{-1}$.

Complexes 3 and 4 emit at room temperature as well as at low temperature. Both complexes display vibronic structure at the high-energy side of the spectrum and a broad unresolved band on the low-energy side that changes intensity as the excitation wavelength changes. The spectrum for complex 3 contains vibronic structure with peaks at 15 875 and 14 800 $\pm 100 \text{ cm}^{-1}$ and a spacing of 1075 $\pm 100 \text{ cm}^{-1}$. The spectrum for complex 4 contains vibronic structure with peaks at 16 300 and 15 200 $\pm 100 \text{ cm}^{-1}$ and a spacing of 1100 $\pm 100 \text{ cm}^{-1}$.

(b) **Vibrational Spectroscopy.** All vibrational spectra shown were acquired from solid samples at room temperature. The preresonance Raman spectra in the region between 950 and 1150 cm$^{-1}$ are shown in Figure 2. Multiple peaks appear in the spectra. The Raman spectra of complexes 1 and 2, containing PCy$_3$, have peaks at 1026, 1048, and 1099 $\pm 4 \text{ cm}^{-1}$. The spectra of complexes 3 and 4, containing PPh$_3$, have peaks at 998, 1027, and 1095 $\pm 4 \text{ cm}^{-1}$. The IR spectra for complexes 1–4 all possess one intense peak at 1098 $\pm 3 \text{ cm}^{-1}$. The vibrational frequencies and their assignments are summarized in Table 1.

**4. Discussion**

(a) **Interpretation of Emission Spectra.** The four complexes in this study produce a red emission with vibronic structure upon excitation at low temperature. The first peak in the progression from each of the complexes is within 600
In the literature, \( \text{ReNX}_2(\text{PR}_3)_2 \) with Angular Overlap Model Calculation Results

<table>
<thead>
<tr>
<th>ReNCl_2(PCy_3)_2</th>
<th>ReNB_2(PCy_3)_2</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1098 (1101^a)</td>
<td>1099 (1103^b)</td>
<td>( \nu(\text{ReN}) )</td>
</tr>
<tr>
<td>1048</td>
<td>1046</td>
<td>( \text{PCy}_3, \text{ring} )</td>
</tr>
<tr>
<td>1026</td>
<td>1026</td>
<td>( \text{PCy}_3, \text{ring} )</td>
</tr>
</tbody>
</table>

\(^a\) In units of cm\(^{-1}\). Experimental uncertainty of all frequencies is \( \pm 2 \) cm\(^{-1}\). \(^b\) IR frequency for ReN mode.

The angular overlap model (AOM) for a square pyramid complex of the form M(E)L\(_4\) has been shown by the trans arrangement of the phosphine and halide ligands.

Since typical \( l_\sigma \) values for halides are larger than those for phosphines and the halide ligands are defined as being on the \( x \) axis, the \( d_{\sigma} \) is higher in energy than the \( d_{\pi} \) orbital.

Table 2. Orbital Energy Diagram for ReNX_2(\text{PR}_3)_2 (X = Cl; Br; \text{PR}_3 = \text{PPh}_3, \text{PCy}_3) with Angular Overlap Model Calculation Results

<table>
<thead>
<tr>
<th>Orbitals</th>
<th>Bonding</th>
<th>Atoms Involved</th>
<th>AOM Energies</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{d}_{\sigma} )</td>
<td>( \sigma^* )</td>
<td>( \text{ReN} )</td>
<td>( \varepsilon_{\sigma} + 0.5\varepsilon_{\sigma} + 0.5\varepsilon_{\sigma} )</td>
</tr>
<tr>
<td>( \text{d}_{\sigma,z} )</td>
<td>( \sigma^* )</td>
<td>( \text{ReN} )</td>
<td>( 1.5\varepsilon_{\sigma} + 1.5\varepsilon_{\sigma} )</td>
</tr>
<tr>
<td>( \text{d}_{\pi} )</td>
<td>( \pi^* )</td>
<td>( \text{ReN} )</td>
<td>( \varepsilon_{\pi} + 2\varepsilon_{\pi} )</td>
</tr>
<tr>
<td>( \text{d}_{\pi,z} )</td>
<td>( \pi^* )</td>
<td>( \text{ReN} )</td>
<td>( \varepsilon_{\pi} + 2\varepsilon_{\pi} )</td>
</tr>
<tr>
<td>( \text{d}_{\rho} )</td>
<td>nonbonding</td>
<td></td>
<td>( \varepsilon_{\rho} + 2\varepsilon_{\rho} )</td>
</tr>
</tbody>
</table>

In all four complexes, the metal is in a pentavalent oxidation state with a \( d^2 \) electronic configuration. The \( d_{\sigma} \) orbital is the HOMO, and the \( d_{\pi} \) is the LUMO. The lowest energy transition involves promotion of an electron from the ReN nonbonding \( d_{\sigma} \) to antibonding \( d_{\pi} \) orbital. The occupancy of the antibonding orbital reduces the net bonding between the rhenium and the nitrogen, from a formal bond order of 3 to 2.5. The ReN bond weakens, the bond lengths, and the bond length change in the excited state is expected to be positive.

Although this transition is mainly metal-centered, the character of the LUMO leads to a significant increase in electron density on the nitrogen in the excited state. The nitrogen becomes more nucleophilic. This effect has been observed in another ReN complex; the excited state was found to be more basic than the ground state toward acid protonation.

Explanation of Trends in Energy of the Transition. The AOM calculations predict a change in the transition energy with halide substitution and lack of a significant energy change upon substitution of the phosphine ligands. The change in energy for the \( d_{\sigma} \) to \( d_{\pi} \) transition contains only terms for the ReN and the ReX interactions (neglecting electron repulsion) because the RePR\(_3\) terms cancel out, \( \Delta E = 1\varepsilon_{\text{ReN}} - 2\varepsilon_{\text{ReX}} \). Accordingly, the halide substitution changes the energy of the transition, while the phosphine substitution leaves it unaffected. The results are not substantially changed when the distortion of complex 3 from a square pyramid\(^3\) is included in the AOM analysis. If the reported experimental angles\(^3\) are used, the \( \Delta E \) of the transition changes from \( 1\varepsilon_{\text{ReN}} - 2\varepsilon_{\text{ReX}} \) to \( 1\varepsilon_{\text{ReN}} - 1.54\varepsilon_{\text{ReX}} + 0.13\varepsilon_{\text{RePR}_3} + 0.13\varepsilon_{\text{RePR}_3} \). The small coefficients for the phosphines do not alter the conclusion.

The energy of the \( \varepsilon_{\text{ReN}} \) transition decreases by \( 425-600 \) cm\(^{-1}\) when Cl replaces the Br ligand. This is consistent with Cl as a better \( \pi \) donor than Br.\(^3\) The better \( \pi \) donation destabilizes the filled \( d_{\sigma} \) orbital and decreases the energy of the transition. In contrast, there is only a small change (75-100 cm\(^{-1}\)) in the energy of the transition when the alkylphosphate is substituted by a better \( \pi \)-accepting arylphos-


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phine. This supports the prediction that $\Delta E$ consists mainly of $I_{3\alpha}$ and $2I_{\alpha\gamma}$ terms, which confirms the arrangement of the ligands and the assignment of the HOMO and LUMO.

(c) Assignment of Rhenium–Nitrogen (ReN) Stretching Mode in Raman and IR Spectra. The range of reported nitridorhenium bond stretching frequencies is $1000–1100$ cm$^{-1}$.

However, the assignment of the ReN stretching frequency is complicated by the interference of modes from the other ligands. Only the ReN bond is common to the four complexes under investigation; the other ligands are common to two complexes each, allowing for the identification of their modes. Bulky phosphine groups were selected to isolate the ReN spatially along one axis with no ligand trans to it. The ReN stretch is allowed in both IR and Raman spectroscopy, making both of these spectroscopies useful in determining the mode.

The peaks in the Raman spectra (Figure 2) that are within the literature range of the ReN stretch are listed in Table 1. The peaks at 1025 and 1045 cm$^{-1}$ in the spectra of complexes 1 and 2 are observed in the spectra of the free PCy$_3$ ligand. The remaining peak at 1099 cm$^{-1}$ is assigned as the ReN stretching frequency. This assignment is consistent with another five-coordinate nitridorhenium(V) complex with two 2-(diphenylphosphino)phenolate ligands.

Assignment of the ReN vibration for complexes 3 and 4 is complicated by the appearance of three phenyl modes. These modes at 998, 1027, and 1095 cm$^{-1}$ are assigned as a trigonal ring breathing mode, an in-plane C–H deformation mode, and an X-sensitive mode, respectively. The X-sensitive mode is accidentally degenerate with the ReN mode for complexes 3 and 4. Thus, the broad peak at 1095 cm$^{-1}$ contains overlapping ReN and the X-sensitive phenyl vibrations.

The IR spectra for the four complexes contain many peaks derived from the phosphine ligands. These ligand modes presumably have smaller changes in the dipole moments than the ReN mode. Under this assumption, the ReN stretch should be more pronounced in the IR spectra than the phosphine modes. The strongest band in the IR spectra of complexes 1 and 2 is at 1101 cm$^{-1}$ and is not present in the spectrum of the free PCy$_3$ ligand. It is assigned as the ReN vibration. The spectrum of free PPh$_3$ does contain a band at 1088 cm$^{-1}$, but the most intense band in this region of the spectrum of complexes 3 and 4 occurs at 1098 cm$^{-1}$ and is assigned as the ReN mode. The less intense bands are attributed to the phosphine modes.

(d) Calculation of Excited-State Bond Length Changes.

The ReN bond length change in the excited electronic state, $\Delta$, is determined from the intensities in the vibronic progression in the emission spectrum by using the time-dependent theory of spectroscopy. There are three parameters in addition to $\Delta$ that are required to calculate a spectrum: the electronic origin ($E_0$), the vibrational stretching frequency ($\omega$), and the phenomenological damping ($\Gamma$). The $E_0$ is obtained from the first peak in the progression, the ReN vibrational frequency $\omega$ is obtained from the Raman and IR spectra, and the value $\Gamma$ is obtained from the width of the vibronic bands. The distortion $\Delta$ is varied to obtain a best fit to the experimental spectrum. The emission spectra with calculated spectra overlaid are shown in Figure 3, and the parameters used in the calculations are given in Table 3. The excellence of the fit based on one mode indicates that the ReN mode distortion is the dominant distortion. Normal modes involving the other ligands will also contribute to the spectrum. A slightly better fit can be obtained by including low-frequency metal–ligand modes with small distortions. The inclusion of additional modes will at most decrease the $\Delta$ ReN value by 2% for compounds 1 and 2 and 5% for compounds 3 and 4.

The excited-state ReN bond length change ($\delta$) in Å is calculated using the following equation

$$\delta = \sqrt{\frac{6.023 \times 10^{23}}{m} \frac{h}{2\pi c\omega} \times 10^6 \Delta}$$

where $m$ is the mass of the vibration in molecular mass, $h$ is Planck’s constant in g cm$^2$ s$^{-1}$, $c$ is the speed of light in cm s$^{-1}$, $\omega$ is the frequency of the vibrational mode in cm$^{-1}$, and $\Delta$ is the dimensionless distortion along the normal coordinate.

The dimensionless distortions calculated from fitting the emission spectra range from 1.80 for complex 1 to 2.04 for complex 2. If the normal coordinate is assumed to be for the pure ReN stretch and the normal mass is the mass of the nitrogen atom, the calculated bond length change for the ReN bond ranges from 0.084 for complex 1 to 0.095 Å for complex 2. The changes are summarized in Figure 4. These changes are similar to that found in [OsNX$_4$]$^-$. The values are upper limits because inclusion of other atoms in the normal coordinate will distribute the distortion among other bonds. Additional atoms involved in the normal coordinate would increase the mass involved in the vibration and decrease the bond length change. The ReN bond in the compounds studied is spatially isolated along an axis, limiting the involvement of the perpendicular ligands in the stretching mode and in the mass of the mode. Additional modes in the fitting calculation would reduce the dimensionless distortion of the ReN mode and decrease the bond length change. The maximum error associated with additional modes is 0.002 Å for compounds 1 and 2 and 0.005 Å for 3 and 4.

The ReN bond distance is 1.60 Å in complex 3 in the ground state. Since the transition places an electron in the ReN $π^*$, the bond length change is expected to be positive. Therefore, the ReN bond length is 0.084 Å longer in the

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excited state than in the electronic ground state, or approximately 1.68 Å. Crystallographic determinations of ReN bond lengths report that the difference between the bond lengths when the bond order is 3 and 2.5 is approximately 0.082 Å (bonds of bond order 3 have an average length of 1.633 Å,²⁶,³⁵,⁴⁷,⁴⁸ and bonds between a bond order of 2 and 3 have an average length of 1.715 Å²⁵,⁴⁹,⁵⁰). The good agreement shows that the bond order changes in the excited states are consistent with a reduction from 3 to 2.5.

5. Summary

The five-coordinate nitridorhenium(V) complexes are luminescent, and the spectra contain resolved vibronic structure. Vibrational spectroscopy is used to assign the ReN stretching frequency and to verify that the vibronic progression in the emission is attributable to the ReN stretch. Angular overlap model calculations account for the emission energy changes and are consistent with the assignment of the emission as a dₓᵧ to dᵧz transition. The changes in the ReN bond length in the excited electronic state are about 0.09 Å and are consistent with a decrease in the ReN bond order.

Acknowledgment. We thank Dr. Anna S. Acosta for preliminary measurements on complex 3. Financial support from NSF (Grant CHE-9874857-CAREER to M.M.A.O.; Grant CHE-9816557 to J.I.Z.) is gratefully acknowledged.

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Figure 3. Experimental (grey line) and calculated (black line) emission spectra of (1) ReNCl₂(PCy₃)₂, (2) ReNBr₂(PCy₃)₂, (3) ReNCl₂(PPh₃)₂, and (4) ReNBr₂(PPh₃)₂. The parameters used in the calculation of each spectrum are listed in Table 3.

Table 3. Parameters Used in Calculation of the Emission Spectra

<table>
<thead>
<tr>
<th>parameter</th>
<th>ReNCl₂(PCy₃)₂</th>
<th>ReNBr₂(PCy₃)₂</th>
<th>ReNCl₂(PPh₃)₂</th>
<th>ReNBr₂(PPh₃)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₀ (cm⁻¹)</td>
<td>15 775</td>
<td>16 375</td>
<td>15 875</td>
<td>16 300</td>
</tr>
<tr>
<td>o (cm⁻¹)</td>
<td>290</td>
<td>280</td>
<td>300</td>
<td>240</td>
</tr>
<tr>
<td>Γ (cm⁻¹)</td>
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<td>1097</td>
</tr>
<tr>
<td>Δ</td>
<td>1.80</td>
<td>2.04</td>
<td>1.80</td>
<td>1.80</td>
</tr>
</tbody>
</table>

*From emission spectra. *From vibrational spectra.

Figure 4. Structure of ReNX₂(PR₃)₂ with the calculated ReN bond length changes.

excited state than in the electronic ground state, or approximately 1.68 Å. Crystallographic determinations of ReN bond lengths report that the difference between the bond lengths when the bond order is 3 and 2.5 is approximately 0.082 Å (bonds of bond order 3 have an average length of 1.633 Å,²⁶,³⁵,⁴⁷,⁴⁸ and bonds between a bond order of 2 and 3 have an average length of 1.715 Å²⁵,⁴⁹,⁵⁰). The good agreement shows that the bond order changes in the excited states are consistent with a reduction from 3 to 2.5.

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