Synthesis, Spectroscopic Investigation, and Theoretical Study of the Ruthenium Diazide Complex [Ru(tpy)(PPh₃)(N₃)₂]

Won K. Seoka, Sun B. Yima, Heung N. Leea, and Thomas M. Klapötkeb

a Department of Chemistry, Dongguk University, 26 Pil-Dong, Chung-Ku, Seoul 100-715, Korea
b Department of Chemistry, University of Munich (LMU), Butenandtstr. 5-13 (D), D-81377, Munich, Germany

Reprint requests to Prof. Dr. T. M. Klapötke. E-mail: tmk@cup.uni-muenchen.de

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Ruthenium, Diazide, ZINDO/1 Calculations

The reaction of [Ru(tpy)(PPh₃)(Cl)₂] (tpy = 2,2':6',2"-terpyridine) with sodium azide in acetone/water afforded [Ru(tpy)(PPh₃)(N₃)₂]. The new Ru-diazide complex was fully characterized by elemental analysis, IR, Raman, and multinuclear NMR spectroscopy. The structures, energies and vibrational frequencies of the ruthenium diazide isomers, cis- and trans- [Ru(tpy)(PMe₃)(N₃)₂] (Me=CH₃), were calculated at the semi-empirical ZINDO/1 level of theory.

1. Introduction

The six-electron reduction of nitrite to ammonia catalyzed by the nitrite reductase enzyme is an important step in the overall reduction of nitrate to ammonia in green plants [1]. Attempts to model the active site of the enzyme via a synthetically accessible way have been reported by many research groups [2]. Certain features of the reactivity have been reported: Ru-NO₂⁺ is reduced to Ru-N₃⁺ quantitatively or Ru-NH₃²⁺ is rapidly and quantitatively oxidized to give Ru-NO₂⁺ [3]. The related complexes with various nitrogen-containing ligands have been known as models of intermediates in the multiple electron transfer of nitrogen fixation chemistry. It is well known that the metal complex containing the nitride ligand is a precursor in the nitrite reduction reaction. From the point of coordination chemistry, the strong trans effect of the nitride ligand plays an important role in determining stereochemistry and, presumably, substitution rates [4].

The metal nitride complex containing a metal-nitrogen triple bond can be formed through chemical activation and photolysis of the metal azide complex [5]. Like NCS and NCO, the azide anion is often used as a ligand and its geometry can be linear or non-linear. Recent results on preparation and structural characterization of metal azides [6, 7] and diazides [8] prompt us to report the synthesis and spectroscopic investigation of the ruthenium diazide complex. The semi-empirical calculations of theoretical models of ruthenium diazide isomers, cis- and trans- [Ru(tpy)(PMe₃)(N₃)₂] (Me=CH₃), were performed at the ZINDO/1 level of theory using the VSTO-3G* basis set.

2. Results and Discussion

The preparations of six-coordinate ruthenium and osmium complexes have been reported by many research groups [9]. The syntheses reported here represent an alternative procedure for obtaining similar complexes. The mono-chloro complex [Ru(tpy)(PPh₃)(Cl)₂](PF₆) (tpy = 2,2':6',2"-terpyridine) prepared by the reaction of the free ligand PPh₃ with [Ru(tpy)(PPh₃)Cl₂] was useful in obtaining ligand PPh₃ with [Ru(tpy)(PPh₃)Cl₂] was useful in obtaining the mono-azide complex [Ru(tpy)(PPh₃)(N₃)Cl](PF₆) [6, 9, 10]. We found that the ruthenium diazide complex was obtained by the reaction of [Ru(tpy)(PPh₃)(Cl)₂](PF₆) with excess NaN₃ albeit in low yield. However, the reaction of trans-[Ru(tpy)(PPh₃)(Cl)₂] with 2.6 molar equivalent of NaN₃ in acetone/water solution provided the desired product with higher yield (eq. (1)).

2.1. Spectroscopy

The new diazide complex of ruthenium was characterized by elemental analysis and spectroscopic methods. A broad MLCT band at $\lambda_{\text{max}} = 550$ nm was observed in the UV-vis spectrum. The most intense and characteristic absorption peaks for the asymmetric in plane and out of plane diazide stretching modes were found at 2032 and 2014 cm$^{-1}$ in the FT-IR spectrum.

The Raman spectrum of the ruthenium diazide complex shown in Fig. 1 displays the characteristic symmetric azide stretching mode as a very strong peak at 1329 cm$^{-1}$.

The characterization of the complex was corroborated with the use of proton, nitrogen, and phosphorus NMR spectroscopy. The $^1$H-NMR spectrum (Fig. 2) showed well resolved peaks in the region between 7.5 and 8.9 ppm for the tpy ligand ring and between 6.9 and 7.3 ppm for the aromatic protons of the PPh$_3$ ligand rings.

It should be noted that the chemical shift of one of the 6 or 6'' protons of the tpy ligand in complexes of the type [(tpy)(PPh$_3$)$_2$Ru$^{II}$-L]$^{7/2+}$ is affected by the nature of the Ligand L and is usually observed far downfield as a doublet of doublets [6]. This observation can be explained by the molecular structure, which shows that both 6 and 6'' protons of the tpy ligand ring are out of the ring currents of the tpy and PPh$_3$ rings. We observed that the chemical shift of these particular protons in the [Ru(tpy)(PPh$_3$)$_2$- (N$_3$)]$^+$ complex are slightly shifted from 8.73 to 8.80 ppm in the [Ru(tpy)(PPh$_3$)(N$_3$)$_2$] complex. Because most of the protons for the tpy ligand are effectively shielded by in plane phenyl groups in the PPh$_3$ ring systems, they are observed in a region upfield from that proton presumably located in a deshielding region. The $^1$H NMR data suggest the trans geometry. The $^{31}$P NMR spectrum of
Table 1. Semi-empirically calculated structural parameters and total energies for trans-[Ru(tpy)(PMe₃)(N₃)₂] (1a) and cis-[Ru(tpy)(PMe₃)(N₃)₂] (1b) obtained using ZINDO/1 with a VSTO-3G* basis set.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E$ [kcal/mol]</th>
<th>NIMAX (N3, asym) [cm⁻¹] (Int.)</th>
<th>$d$(Ru-Nₐ) [Å]</th>
<th>$d$(Na-Nₖ) [Å]</th>
<th>$d$(Nb-Nₐ) [Å]</th>
<th>$\angle$(NaNbNₖ°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>-15317</td>
<td>0</td>
<td>2.094(6) ip</td>
<td>1.24</td>
<td>1.19</td>
<td>174.7</td>
</tr>
<tr>
<td>1b</td>
<td>-15306</td>
<td>0</td>
<td>2.090(10) ip</td>
<td>1.24</td>
<td>1.19</td>
<td>173.8</td>
</tr>
<tr>
<td>Exp.</td>
<td></td>
<td></td>
<td>2.074(6) oop</td>
<td>1.24</td>
<td>1.18</td>
<td>170.2</td>
</tr>
</tbody>
</table>

*a* trans-position with respect to the PMe₃ group; 
*b* cis-position with respect to the PMe₃ group; 
*c* [(tpy)Ru(PPh₃)(N₃)₂]; 
*d* scaled with the empirical factor of 0.62.

The complex shows a singlet resonance at 32.3 ppm for the coordinated PPh₃ group, which suggests a trans complex [6, 11]. It is shifted to slightly lower field than that of ruthenium mono-azide molecule [Ru(tpy)(PPh₃)(N₃)]⁺ (26.5 ppm).

$^{14}$N NMR spectroscopy was also used to characterize the prepared diazide complex. From earlier $^{14}$N NMR data for coordinated azides [12, 13], individually well resolved resonances of Na, Nb, and Nc (connectivity: Ru-Nₐ-Nₖ-Nₖ) have been assigned in the $^{14}$N NMR spectrum of the complex. Each resonance at -337, -136, and -225 ppm corresponds to azide coordinated to Ru in the [Ru(tpy)(PPh₃)₂(N₃)]⁺ complex [6]. Although the three N atoms of the tpy ligand system in the [Ru(tpy)(PPh₃)₂(N₃)₂] complex could not be observed, the three nitrogen chemical shifts for the diazide ligands coordinated to the ruthenium atom in the complex were obtained at -335, -132, -278 ppm. It should be noted that the relative line widths in the $^{14}$N NMR spectra for the Ru-azide complex are related to the local symmetry around the nitrogen atom [14 - 16].

### 2.2. Semi-empirical calculations

The structure and total energy of the cis and trans isomers of the ruthenium diazide complex containing PMe₃ instead of PPh₃ were calculated at the semi-empirical ZINDO/1 level of theory. These cis- and trans- [(tpy)Ru(PMMe₃)(N₃)₂] molecules have been used instead of the corresponding [(tpy)Ru(PPh₃)(N₃)₂] complexes, because the trimethylphosphine ligand is electronically similar and closely related to the triphenylphosphine ligand. Reducing the number of parameters can also save cpu time.

The isomers are very close in their total energy with the trans form being thermodynamically slightly favored over the cis isomer [$\Delta E$(cis-trans) = 11 kcal mol⁻¹], as is shown in Table 1.
3. Experimental

RuCl₃, 2,2':6',2''-terpyridine(tpy), NaN₃, and NH₄PF₆ were purchased from Aldrich Chemical Co. and used without further purification. Triphenylphosphine ( Aldrich Chemical Co.) was recrystallized twice from (99.9 atom% D), and dichloromethane-di (99.6% D) (Aldrich Chemical Co.) was used as received. Acetonitrile was used after passing through a Nanopure™ (Barnstead) water system.

Routine UV-visible spectra were recorded on a Hewlett-Packard 8452A Diode array spectrophotometer. FT-IR spectra were obtained on a Bomen MB 100 FT-IR spectrophotometer either on nujol mulls or in solutions using NaCl plates. All ¹H and ³¹P NMR data were obtained with a Varian Gemini-200 FT-NMR spectrometer using (CD₃)₂SO as solvent at 25 °C. The chemical shift parameters are presented in parts per million (δ) downfield from internal reference tetramethylsilane (TMS) while the ³¹P chemical shifts were referenced to external 85% H₃PO₄.

The ¹⁴N NMR spectrum was recorded in a 10 mm NMR tube using CD₂Cl₂ as solvent at −20 °C using a Brucker SY 200 spectrometer operating at −14.462 MHz and was referenced to external CH₃NO₂ in CD₂Cl₂ solution. The Raman spectrum was obtained on a Perkin Elmer System R 2000 at 25 °C. Elemental analyses were performed by the analytical laboratory at Basic Science Institute of Korea using a Carlo Erba EA1180.

3.1. Preparation of [Ru(tpy)(PPh₃)(N₃)]₂

First method: Previously prepared [Ru(tpy)(PPh₃)Cl₂] (100 mg, 0.15 mmol) [9c] and NaN₃ (25 mg, 0.39 mmol) dissolved in 10 ml of acetonitrile and 1 ml of distilled water were heated under reflux under a stream of Ar for 2 h. During this period, a precipitate developed under a deep purple solution. The hot reaction mixture was cooled down in the refrigerator to r.t. overnight. The precipitate was filtered off in air and washed with cold acetonitrile and water. The deep purple-colored product was vacuum-dried. Yield: 61 mg (60%).

Second method: The same procedure as for the preparation of [Ru(tpy)(PPh₃)Cl₂(N₃)]PF₆ was applied [6], except using 0.10 mmol of [Ru(tpy)(PPh₃)Cl₂](PF₆) and 0.43 mmol of sodium azide. Yield: 20 mg (30%).


IR (cm⁻¹): 3054 (w), 2032 (vs), 2014 (vs), 1600 (m), 1482 (m), 1452 (s), 1386 (s), 1280 (w), 1094 (w), 771 (s), 747 (m), 700 (s), 527 (s), 516 (s), 500 (m). - Raman (1064 nm, 200 mW, 500 scans, cm⁻¹, (Int)): 3060 (4), 2040 (1), 1596 (12), 1484 (3), 1463 (5), 1329 (17), 1280 (5), 1178 (4), 1038 (8), 1007 (12), 725 (2), 646 (4) 526 (4). - ¹H NMR (δ (multiplicity)): 8.80 (d), 8.26 (d), 8.13 (d), 7.91 (t), 7.69 (t), 7.57 (t), 7.32 - 6.88 (m). - ³¹P NMR (δ): 32.3. ¹⁴N NMR (δ): −335, −132, −278.

3.2. Semi-empirical calculations

All semi-empirical calculations were performed with the program package HyperChem (version 4.0 and 5.0) at the ZINDO/I level of theory using a VSTO-3G* basis set [20, 21]. The ZINDO/I is a variation of INDO extended to transition metals, which is equivalent to the most recent version of the INDO/I method that differs from the original by using constant orbital exponents. The model that is within the unrestricted Hartree-Fock formalism is characterized by inclusion of one-center exchange terms as well as an accurate description of integrals involving 3d atomic orbitals.

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