

different from that of the most strain-free cyclooctane (twist-chair-chair).

As shown in Figure 2, one of the hydrogen atoms bonded to C(9) is located near the axial coordination site with the Ni...H[C(9)] distance of 2.31 (6) Å. A number of strained bond lengths and angles are noted not only within the eight-membered ring but also in the trien ring moiety (see Table VI).

**trans-[NiCl<sub>2</sub>(N<sub>4</sub>9)] (3).** As is seen in Figures 3 and 6a, this complex has a crystallographic twofold axis through the Ni, the midpoint of the C(6)-C(6') bond in the nine-membered ring, and the midpoint of the C(1)-C(1') bond in the central five-membered ring. Three five-membered rings associated with the trien moiety adopt a stable gauche conformation. The structure of the nine-membered ring is very similar to that of cyclononane in the most strain-free, twist-boat-chair conformation<sup>22</sup> (see Figure 6b). The nine-membered ring has the corner carbon atoms (C(5), C(5')) as seen in large cycloalkanes (see Figure 6a). The structural parameters about the Ni are indicative of a large amount of strain in the complex. Bite angles of the three five-membered rings are narrowed to 80.39 (4) - 80.81 (5)°, while that of the nine-membered ring is opened out to 119.14 (4)°. The Ni-N(2) distance associated with the nine-membered ring is lengthened to 2.236 (1) Å, while the Ni-N(1) distance associated with only five-membered rings is within the normal range (2.086 (1) Å).

Deviations of the four nitrogen atoms from the N<sub>4</sub> best plane (Table VIII) show that the square-planar array of the nitrogens about the Ni is more planar than that of the N<sub>4</sub>7 analogue. The dihedral angle between the Ni-N(1)-N(1') and Ni-N(2)-N(2') planes is 8.6°. A large angle distortion is noted at the Ni-N(2)-C(4) angle (123.88 (7)°) within the nine-membered ring. Angle strain of carbon atoms within the nine-membered ring is not so significant (112.6 (1)-113.6 (1)°).

In crystal structures of cyclononane derivatives, strong transannular hydrogen-hydrogen interactions have been noted.<sup>23,24</sup> Likewise, close hydrogen-hydrogen contacts are

(22) Anet, F. A. L.; Wagner, J. J. *J. Am. Chem. Soc.* 1971, 93, 5226.

observed in the nine-membered chelate ring: H[C(6)]...H[N(2)], 2.31 (3) Å; H[C(6)]...H[C(4')], 2.22 (3) Å. They are depicted as dashed lines in Figure 6a.

The Ni-Cl distance of 2.426 (1) Å is significantly shorter than those in *trans*-[NiCl<sub>2</sub>(N<sub>4</sub>7)] (1).

**Correlation between the Ni-Cl and Ni-N Distances—An Electronically Controlled Cis Effect.** The Ni-Cl distances of complexes 1 and 3 are 2.548 (8) (average) and 2.426 (1) Å, respectively, and are significantly different from each other. It seems that the Ni-Cl distance becomes longer as the mean Ni-N distance decreases (see Table V and VII). The spatial orientation of the macrocyclic ligand in these complexes indicates no obvious intramolecular steric interaction against chloride ion coordination. The nature of this phenomenon must be electronic in origin. Busch et al. reported a correlation, which they called a cis effect, between ligand field parameters *Dq<sup>z</sup>* (axial) and *Dq<sup>xy</sup>* (in plane) in the electronic spectra of *trans*-diacido(tetraaza macrocycle)nickel(II) complexes: the *Dq<sup>z</sup>* value decreases linearly as the *Dq<sup>xy</sup>* value increases.<sup>25</sup> The correlation observed for the Ni-Cl and Ni-N distances should be of the same nature as the cis effect. A similar trend is observed for the Ni-Cl (2.492 Å) and Ni-N (2.058 (8) Å) distances of *trans*-dichloro(1,4,8,11-tetraazacyclotetradecane)nickel(II).<sup>18</sup>

It is most reasonable to consider the correlation found for Ni-Cl and Ni-N distance of *trans*-dichloro(tetraaza macrocycle)nickel(II) complexes to be a result of the electronically controlled cis effect.

Registry No. 1, 84194-09-2; 2, 84194-12-7; 3, 84194-18-3.

**Supplementary Material Available:** Tables of hydrogen atomic coordinates and structure factors and stereoscopic views of the crystal structures of complexes 1-3 (50 pages). Ordering information is given on any current masthead page.

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## Rhodium Nitro Complexes as Oxygen-Transfer Agents: Oxidation of Olefins

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In acetonitrile, dicationic rhodium nitrosyl complexes [(bpy)(CH<sub>3</sub>CN)<sub>3</sub>RhNO]<sup>2+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>2</sub> (5) and [(CH<sub>3</sub>CN)<sub>4</sub>RhNO]<sup>2+</sup>(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> (9) are oxidized by molecular oxygen to the corresponding nitro complexes 7 and 10. Complex 7 oxidizes ethylene or terminal olefins to acetaldehyde or alkanones only in the presence of (PhCN)<sub>2</sub>PdCl<sub>2</sub> (an olefin activator). In nitromethane, the acetonitrile ligand in complex 10 is displaced by olefins and an oxygen atom from the nitro ligand in 10 is transferred to the coordinated olefin in the absence of a cocatalyst with the formation of acetaldehyde from ethylene and 2-alkanones from terminal olefins. In contrast to the dicationic complexes, the neutral complex (CH<sub>3</sub>CN)<sub>2</sub>Rh(NO)Cl<sub>2</sub> (13) does not form the corresponding nitro complex when exposed to molecular oxygen. A plausible explanation is offered for this seemingly contradictory behavior of the dicationic and the corresponding neutral rhodium nitrosyl complexes.

### Introduction

In previous reports, we described the roles played by py(saloph)CoNO<sub>2</sub> (1) and py(TPP)CoNO<sub>2</sub> (2) (Table I) in the selective oxidation of organic substrates.<sup>1</sup> For a bimetallic

system consisting of the above coordinatively saturated nitro complexes as oxygen-transfer agents and palladium(II) species as olefin activators, we have demonstrated the oxidation of ethylene to acetaldehyde and higher terminal olefins to 2-alkanones.<sup>1b,d</sup> The most important extension of this system was recently achieved by the replacement of palladium(II) by thallium(III). In this modified bimetallic system, the oxidation of olefins leads to epoxides rather than ketones.<sup>2</sup> Olefins are

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Table I. Metal Nitrosyl and Nitro Complexes

py(saloph)CoNO<sub>2</sub> (1)  
 py(TPP)CoNO<sub>2</sub> (2)  
 (CH<sub>3</sub>CN)<sub>2</sub>Pd(NO<sub>2</sub>)Cl (3)  
 [(bpy)(1,5-COD)Rh]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (4)  
 [(bpy)(CH<sub>3</sub>CN)<sub>3</sub>RhNO]<sup>2+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>2</sub> (5)  
 [(bpy)(CO)<sub>2</sub>Rh]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (6)  
 [(bpy)(CH<sub>3</sub>CN)<sub>2</sub>RhNO]<sup>2+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>2</sub> (7)  
 [(CH<sub>3</sub>CN)<sub>4</sub>RhNO]<sup>2+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>2</sub> (8)  
 [(CH<sub>3</sub>CN)<sub>4</sub>RhNO]<sup>2+</sup>(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> (9)  
 [(CH<sub>3</sub>CN)<sub>4</sub>RhNO]<sup>2+</sup>(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> (10)  
 [Rh(NO)Cl<sub>2</sub>]<sub>2</sub> (11)  
 [Rh(NO)<sub>2</sub>Cl]<sub>2</sub> (12)  
 (CH<sub>3</sub>CN)<sub>2</sub>Rh(NO)Cl (13)  
 (Ph<sub>3</sub>P)<sub>2</sub>Rh(NO)Cl<sub>2</sub> (14)  
 (OEP)RhNO (15)

also oxidized by (CH<sub>3</sub>CN)<sub>2</sub>Pd(NO<sub>2</sub>)Cl (3). This palladium complex fulfills the functions of oxygen transfer agent and olefin activator.<sup>3</sup> Ketones<sup>3a</sup> are the principal products, except in a few special cases such as with cyclic olefins, in which epoxides<sup>3b,c</sup> are also formed. These systems have the potential to be developed into a long-sought catalytic system for the direct epoxidation of olefins by molecular oxygen. They represent an important departure from the known methods for propylene and higher olefin epoxidation and underscore the need for continuing research in this area. The extension of this chemistry to include rhodium nitro complexes is discussed in this report.

## Results and Discussion

**1. Choice of Ligands.** The function of the metal nitrosyl complex is to split molecular oxygen and form 2 mol of a nitro complex—the oxidant in this system. Therefore, only complexes containing nonoxidizable ligands can be employed. This fact severely limits the choice of ligands.<sup>4</sup> The ligands have a profound effect on (a) the ability of the resulting nitrosyl complex to activate olefins, (b) the geometry of the resulting complex, which in turn is reflected in the ability of the nitrosyl ligand to interact with molecular oxygen, and (c) the preferential oxidation of the nitrosyl ligand to the desired nitro ligand (M–NO<sub>2</sub>) rather than to the inactive nitrito (M–ONO) or nitrate (M–ONO<sub>2</sub>) ligands. Thus, on interaction with molecular oxygen, certain nitrosyl complexes that dissociate the nitrosyl ligands (e.g., Co(DH)<sub>2</sub>NO, DH = dimethylglyoximate monoanionic ligand) yield nitrate complexes.<sup>5</sup> In contrast, tetradentate<sup>6</sup> (e.g., Schiff bases, porphyrins) and certain bidentate<sup>6,7</sup> (e.g., *N,N*-dialkyldithiocarbamate) ligands tend to form square-pyramidal complexes with axial, bent nitrosyls which usually are easily oxidized by molecular oxygen to the desired nitro ligands.<sup>1,6</sup> For this reason Schiff base and

porphyrin complexes have played a dominant role in the bimetallic systems.<sup>1,2</sup> However, these complexes are coordinatively saturated and therefore unacceptable for the demonstration of a monometallic system. These considerations narrowed the choice of ligands to a precious few; from these, nitriles are prominent as potentially labile ligands replaceable by unsubstituted olefins.

**2. Dicationic Complexes.** Initially, our efforts centered on the preparation of cationic complexes containing a bipyridine ligand and at least one nitrogen- or oxygen-based monodentate ligand. It was hoped that the bipyridine ligand would stabilize the nitrosyl complex and that the monodentate ligands would be replaceable by olefins. Both the nitrosyl ligand and a  $\pi$ -coordinated olefin would thus be assembled on one metal and form the basis for a monometallic oxygen-transfer system. The reaction of [(1,5-COD)(bpy)Rh]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (4) with 1 equiv of NOPF<sub>6</sub> in acetonitrile yields a pale green solid, which, when dry, is stable in air. This solid, obtained in high yield, exhibits a strong nitrosyl band at 1660 cm<sup>-1</sup>, a band at 830 cm<sup>-1</sup> corresponding to the PF<sub>6</sub><sup>-</sup> anion, and bands typical of the bipyridine and acetonitrile ligands. On the basis of IR and elemental analysis, the compound can be formulated as [(bpy)(CH<sub>3</sub>CN)<sub>3</sub>Rh(NO)]<sup>2+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>2</sub> (5). The same complex can be prepared from [(bpy)(CO)<sub>2</sub>Rh]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (6) and NOPF<sub>6</sub> in acetonitrile. Any attempt to prepare (bipyridine)-nitrosylrhodium(III) complexes by the interaction of complex 4 with NOPF<sub>6</sub> in noncoordinating (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, etc.) or slightly coordinating (THF, CH<sub>3</sub>OH, acetone) solvents resulted in brown oils from which no complex containing a nitrosyl ligand could be isolated. Thus, all attempts to prepare bipyridine nitrosyl complexes with monodentate ligands other than acetonitrile have failed.

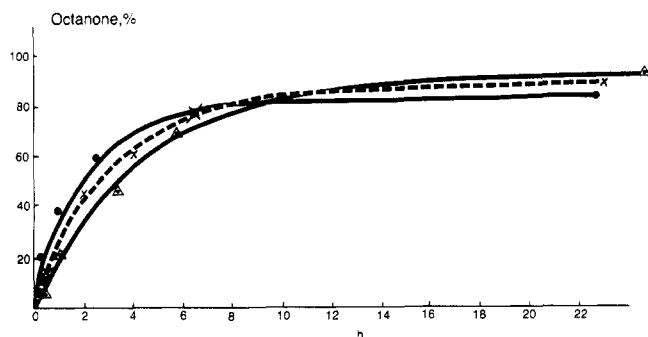
Complex 5, when dissolved in acetonitrile, interacts with molecular oxygen at room temperature and atmospheric pressure. The nitrosyl band at 1658 cm<sup>-1</sup> decreases, and a set of new bands characteristic of the nitro ligand grows in. However, the strong diagnostic band of the nitro ligand at ~830 cm<sup>-1</sup> is not detectable due to its overlap with a very strong and broad P–F band of the anion. The resulting nitro complex [(bpy)(CH<sub>3</sub>CN)<sub>2</sub>RhNO]<sup>2+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>2</sub> (7) can be isolated in high yield.

In acetonitrile, complex 7 does not oxidize olefins even at elevated temperatures. This complex exhibits extremely low solubilities in other organic solvents such as chlorinated hydrocarbons or even slightly polar solvents such as tetrahydrofuran, acetone, and nitromethane. Independent experiments demonstrated that the acetonitrile ligands in complexes 5 or 7 cannot be displaced by olefins or even by strongly coordinating dienes, e.g., 1,5-hexadiene and 1,5-cyclooctadiene. Further support for the above statement comes from the fact that the addition of (PhCN)<sub>2</sub>PdCl<sub>2</sub> to a solution of complex 7 leads to the expected oxidation of ethylene to acetaldehyde and of terminal olefins to alkanones with concomitant formation of the nitrosyl complex 5. No epoxide formation has been observed. Thus, complex 7 behaves analogously to the coordinatively saturated complexes 1 and 2 reported earlier.<sup>1</sup>

Replacement of the bipyridine ligand in complex 5 by monodentate ligands possessing no  $\pi$ -bonding capabilities may lead to a more labile system. Therefore, the complexes [(CH<sub>3</sub>CN)<sub>4</sub>RhNO]<sup>2+</sup>(PF<sub>6</sub><sup>-</sup>)<sub>2</sub> (8) and [(CH<sub>3</sub>CN)<sub>4</sub>RhNO]<sup>2+</sup>(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> (9) previously reported by Connelly and co-workers<sup>8,9</sup> were examined. These complexes are soluble in most polar, coordinating solvents, e.g., acetonitrile, acetone, tetrahydrofuran, and dimethyl sulfoxide. However, the oxidation of

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 (4) Examples of possibly suitable ligands are ammonia, tertiary amines, nitriles, amides, pyridine, bipyridine, pyridine-2-carboxylic acid, *N,N*-dialkyldithiocarbamates, pyridine-2,6-dicarboxylic acid, porphyrins, phthalocyanines, etc.  
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 (9) Connelly, N. G.; Draggett, P. T.; Green, M.; Kuc, T. A. *J. Chem. Soc., Dalton Trans.* **1977**, 70.

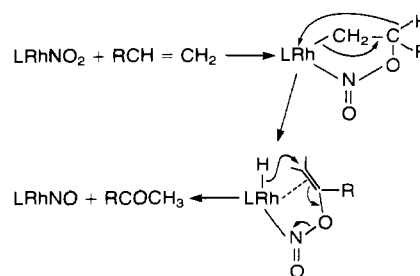


**Figure 1.** Comparison of the reactivity of octene with **9** and **10**: (●) **9** under 344 kPa (50 psi) of O<sub>2</sub>; (X) **10** under 344 kPa (50 psi) of O<sub>2</sub>; (Δ) **10** under 206 kPa (30 psi) of Ar. The oxidation was run in nitromethane at 60 °C; the percentage of octanone is relative to the amount of **9** or **10** used.

complex **9** to the corresponding nitro complex [(CH<sub>3</sub>CN)<sub>4</sub>RhNO<sub>2</sub>]<sup>2+</sup>(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> (**10**) proceeds to completion only in acetonitrile. In solvents other than acetonitrile, e.g., nitromethane, the oxidation is extremely slow or does not proceed at all.

Oxidation of olefins by complex **10** is hindered by problems similar to those encountered with complex **7**. In acetonitrile, complex **10** does not interact with olefins. When the nitro complex **10** is first prepared in acetonitrile, concentrated, and then reacted with olefins in dry nitromethane, the oxidation of ethylene to acetaldehyde and 1-octene to 2-octanone (see Experimental Section) is observed. This reaction, carried out under argon, is relatively slow, yielding approximately 80% of 2-octanone from 1-octene at 60 °C in approximately 10 h. The maximum yield of 2-octanone (~90%) is observed in approximately 20 h (Figure 1). Exactly the same reaction profile is obtained when the oxidation is carried out with either the nitrosyl complex **9** or nitro complex **10** under pressure of oxygen (345 kPa, 50 psi) (Figure 1). At the end of these reactions, the isolated nitrosyl complex contains only small amounts of acetonitrile apparently due to displacement of the coordinated acetonitrile in complex **9** by the solvent, nitromethane. These findings can be explained only if it is assumed that (1) in the cationic rhodium nitrosyl and nitro complexes, the coordinated acetonitrile can be displaced by olefins in solvents of coordinating ability lesser than that of acetonitrile and (2) complex **9**, in the presence of a small amount of acetonitrile, can be oxidized by molecular oxygen to complex **10** while the corresponding nitrosyl complex, in which the acetonitrile ligands are to a very great extent replaced by nitromethane, is inert to molecular oxygen. The latter statement is confirmed by an independent experiment. When complex **9** is first heated to 60 °C in nitromethane under argon and oxygen is then introduced, no nitro complex is formed and the recovered nitrosyl complex is practically free of acetonitrile. This should be contrasted with the above described oxidation of 1-octene in nitromethane containing complex **9**, a small amount of acetonitrile, and molecular oxygen (introduced before the heating was started). The results (Figure 1) clearly show that the nitro complexes **10** had to be formed rapidly at the beginning of the reaction, suggesting that the oxidation of complex **9** to complex **10** is faster than the ligand exchange. Introduction of greater amounts of acetonitrile into the nitromethane solutions, in the hope of increasing the rate of nitrosyl complex reoxidation, stopped the olefin oxidation. Evidently, in the monometallic system based on the dicationic rhodium complexes, the two basic steps, oxidation of the nitrosyl to the nitro complex and oxygen transfer from the nitro ligand to an olefin, require solvents of different coordinating abilities. This requirement prevents the conversion of the above described oxidations into a catalytic system.<sup>10</sup> A probable

**Scheme I**



mechanism of olefin oxidation by **10** is outlined in Scheme I. An analogous mechanism was offered earlier for the oxidation of olefins by bis(acetonitrile)chloronitropalladium(II).<sup>3</sup>

The cationic character of complex **7** or **10** precludes the detection of epoxides. This is supported by the following observations. Oxidation of norbornene (bicyclo[2.2.1]-2-heptene) either by the bimetallic system, consisting of the nitro complex **7** and (PhCN)<sub>2</sub>PdCl<sub>2</sub>, or by the monometallic system represented by the cationic complex **10** leads only to a low yield of norcamphor rather than the expected *exo*-2,3-epoxynorbornane. The expectation that *exo*-2,3-epoxynorbornane will be formed is supported by the previously reported<sup>3b</sup> epoxidation of norbornene by palladium nitro complex **3** and by the finding that even the cobalt-based bimetallic system **2** + (CH<sub>3</sub>CN)<sub>2</sub>PdCl<sub>2</sub> follows the same reaction pathway (see the Experimental Section).

Cationic rhodium complexes such as **5**, **7**, **9**, or **10** cause either isomerization of epoxides to ketones<sup>12</sup> or rapid degradation of epoxides presumably to form oligomers. This may be demonstrated by the finding that *exo*-2,3-epoxynorbornane or 1,2-epoxyoctane, when reacted with complex **9** in dry and degassed nitromethane at 60 °C, is completely consumed in 5 min with concomitant formation of only minor quantities of norcamphor or 2-octanone, respectively. Thus, the intermediacy of 1,2-epoxyoctane in the oxidation of 1-octene to 2-octanone by the nitro complexes **7** and **10** cannot be ascertained.

Decomposition of *exo*-2,3-epoxynorbornane has also been observed in the cobalt-based bimetallic system, although at a much slower rate. This decomposition is apparently responsible for reaching only a moderate yield of *exo*-2,3-epoxynorbornane (~75%). In this case, presumably the palladium cocatalyst is responsible for the observed loss of epoxide.

In the presence of complex **9** or **10**, conjugated dienes such as 1,3-butadiene and 2,3-dimethylbutadiene undergo polymerization. The polymerization is so fast that no oxidation could be observed. The enormous tendency of complex **9** or **10** to catalyze the polymerization is directly related to the dicationic character of the complexes as revealed by the recent report that dicationic palladium complexes such as [(CH<sub>3</sub>CN)<sub>4</sub>Pd]<sup>2+</sup>(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> or [(CH<sub>3</sub>CN)(Ph<sub>3</sub>P)<sub>3</sub>Pd]<sup>2+</sup>(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> are effective catalysts for the cationic polymerization of olefins at room temperature.<sup>11</sup> These observations prompted us to examine neutral rhodium nitrosyl complexes.

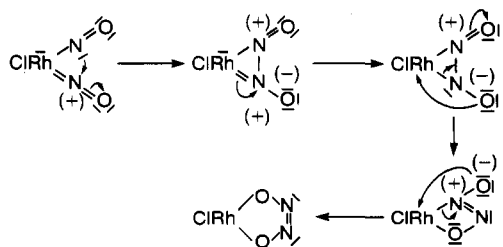
**3. Neutral Complexes.** There are two possible entries into a series of neutral rhodium nitro complexes containing labile and nonoxidizable ligands. These are based on the complexes [Rh(NO)Cl<sub>2</sub>]<sub>2</sub> (**11**) and [Rh(NO)<sub>2</sub>Cl]<sub>2</sub> (**12**).

Complex **11**, formed by the interaction of excess nitrosyl chloride with the (1,5-cyclooctadiene)chlororhodium(I) dimer

(10) Under an oxygen atmosphere more than 1 mol of ketones/mol of rhodium is formed. However, the complex is always recovered from the reaction mixture as a nitrosyl species, suggesting that in nitromethane the rate-determining step is the formation of the nitro complex.

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(12) Milstein, D.; Buchman, O. *Tetrahedron Lett.* **1974**, 2257; *J. Org. Chem.* **1977**, *42*, 2299.

Scheme II<sup>a</sup>

<sup>a</sup> Tetrahydrofuran and other ligands are omitted for clarity.

in dichloromethane, readily loses nitric oxide when exposed to air.<sup>13</sup> However, it forms stable complexes in the presence of phosphines and arsines. On the basis of the behavior of the dicationic complex **9**, it was assumed that stable complexes may be formed by solvation of the dimer **11** by strongly coordinating solvents such as acetonitrile or tetrahydrofuran. Indeed, dimer **11** slowly dissolves in acetonitrile and forms a stable green solid, which exhibits nitrile bands ( $\nu_{\text{C}\equiv\text{N}} = 2290$  and  $2320 \text{ cm}^{-1}$ ) and a nitrosyl band ( $\nu_{\text{NO}} = 1630 \text{ cm}^{-1}$ ), very close to the nitrosyl band of the known  $\text{L}_2\text{Rh}(\text{NO})\text{Cl}_2$  complexes with  $\text{L} = \text{Ph}_3\text{P}$  and  $\text{Ph}_3\text{As}$ .<sup>13</sup> Thus, the complex isolated from acetonitrile can be formulated as  $(\text{CH}_3\text{CN})_2\text{Rh}(\text{NO})\text{Cl}_2$  (**13**). This was very encouraging since  $(\text{Ph}_3\text{P})_2\text{Rh}(\text{NO})\text{Cl}_2$  (**14**) ( $\nu_{\text{NO}} = 1632 \text{ cm}^{-1}$ ) has been shown to possess a bent nitrosyl with a  $\text{Rh}-\text{N}-\text{O}$  angle of  $124.8^\circ$  and a square-pyramidal geometry with the nitrosyl in the apical position.<sup>14</sup> The same geometry is expected for  $(\text{OEP})\text{RhNO}$  (**15**) ( $\text{OEP} = \text{octaethylporphyrinato ligand}$ ,  $\nu_{\text{NO}} = 1630 \text{ cm}^{-1}$ ), which can be oxidized by molecular oxygen to the corresponding nitro complex.<sup>6c</sup> The rhodium complexes **13–15** are isoelectronic with  $(\text{TPP})\text{CoNO}$  (**2**) ( $\nu_{\text{NO}} = 1690 \text{ cm}^{-1}$ ), which can also be oxidized<sup>1</sup> to the corresponding nitro complex and is known to possess the same geometry as complex **14** or **15**.<sup>15</sup> To our surprise, the neutral complex **13** shows no tendency for interaction with molecular oxygen even at elevated pressure (345 kPa, 50 psi) in either coordinating (e.g., acetonitrile) or non-coordinating (e.g., dichloromethane) solvents. These facts strongly underscore the inability of  $\nu_{\text{NO}}$  to serve as a diagnostic tool for the prediction of the bonding and chemistry of nitrosyl ligands.

Dimer **12**, after dissolution in polar coordinating solvents (e.g., THF), exhibits two bands in the nitrosyl region ( $\nu_{\text{NO}} = 1630$  and  $1715 \text{ cm}^{-1}$ ), which may indicate the presence of both a bent and a linear nitrosyl. Only in THF at room temperature and under pressure of 50 psi of  $\text{O}_2$  can the dimer **12** be very slowly oxidized to a nitro complex, which has not been isolated in a pure form. This may be due to a side reaction that prevails at a higher temperature. Thus, on heating, the IR spectrum of an oxygen-free solution of **12** in THF or acetonitrile gradually loses nitrosyl bands and new bands at 930, 1025, and  $1120 \text{ cm}^{-1}$  grow in. These bands are reminiscent of hyponitrite complexes, which all exhibit bands in the same regions. The formation of transition-metal hyponitrite complexes has been reported previously in the reaction of nitric oxides with low-valent metal complexes such as platinum(0),<sup>16</sup> cobalt(II),<sup>17</sup> and molybdenum(II),<sup>18</sup> and such a complex has also been

postulated as an intermediate in the reduction of  $(\text{Et}_3\text{P})_2\text{Pt}(\text{NO})(\text{NO}_2)$  by carbon monoxide.<sup>16b,c</sup>

A plausible mechanism for the assumed rearrangement of the dinitrosyl complexes to the hyponitrite isomers is presented in Scheme II.<sup>19</sup>

The proposed mechanism requires the presence of both a linear and a bent nitrosyl and a change in the formal valency of the metal from rhodium(I) in the dinitrosyl complex to rhodium(III) in the hyponitrite species. Metal dinitrosyl complexes may be divided into two broad categories. One category contains complexes with two linear nitrosyls exhibiting no tendency toward hyponitrite formation or oxidation by molecular oxygen. The second category contains complexes having one linear and one bent nitrosyl, which can potentially be oxidized by molecular oxygen or rearranged into a hyponitrite complex. There are two examples where the presence of both bent and linear nitrosyl ligands has been established by a single-crystal X-ray structure; they are  $[(\text{Ph}_3\text{P})_2\text{Ru}(\text{NO})_2\text{Cl}]^+\text{PF}_6^-$  and  $[(\text{Ph}_3\text{P})_2\text{Os}(\text{NO})_2]^+\text{PF}_6^-$ .<sup>20</sup> Both complexes possess square-pyramidal geometry with the linear nitrosyl in the basal plane and the bent nitrosyl in the apical position. Dinitrosyl complexes containing two bent nitrosyl ligands have not been crystallographically characterized as of this time. Thus, the problem of hyponitrite formation will most likely prevent the use of dinitrosyl complexes as catalysts for olefin oxidation by molecular oxygen.

**4. Comparison of Dicationic and Neutral Rhodium Nitrosyl Complexes.** In nonpolar or very slightly coordinating solvents, cationic and neutral complexes are inert toward oxygen. In acetonitrile, however, the cationic complexes undergo oxidation while neutral complexes remain inactive. The opposite is expected if only the electron density on the central metal atom is taken into consideration. A plausible explanation for this seemingly contradictory observation can be found in the relative ability of neutral and cationic complexes to coordinate acetonitrile. In the case of the cationic pentacoordinate complexes, strongly coordinating solvents may convert the originally trigonal-pyramidal complex containing an equatorial linear nitrosyl to a hexacoordinate, octahedral complex containing an axial, bent nitrosyl. This assumption is nicely corroborated by the observation that the hexacoordinate dicationic complex **5** exhibits a lower  $\nu_{\text{NO}}$  ( $1658 \text{ cm}^{-1}$ ) than the pentacoordinate dicationic complex **9** ( $1760 \text{ cm}^{-1}$ ). Only the bent nitrosyl in the octahedral complex can be oxidized by molecular oxygen. The central metal in the neutral pentacoordinate complexes is not electron deficient, and accordingly it exhibits a very low tendency to coordinate even relatively basic ligands such as acetonitrile. In solution, the neutral complexes retain a trigonal-bipyramidal geometry with an equatorial, linear, and therefore nonoxidizable nitrosyl. This is supported by the finding that in the cobalt triad hexacoordinate dicationic complexes possess a bent nitrosyl.<sup>21</sup> A few examples have also been reported in which trigonal-bipyramidal complexes with a linear nitrosyl were converted into octahedral complexes with a bent nitrosyl.<sup>6d,22</sup> However, in these cases anionic, rather than neutral, ligands were added and the dicationic complexes were converted to monocationic species. This work represents the first example where this structural change caused by neutral ligands is reflected in the

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chemistry of the nitrosyl ligand.

Porphyrin-based complexes represent the only known neutral rhodium species exhibiting an apical and therefore oxidizable nitrosyl. They are, however, coordinatively saturated and require activation of olefins by cocatalysts.<sup>23</sup>

## Experimental Section

**1. General Procedures.** All reactions were run under an atmosphere of argon unless stated otherwise. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. Gas-liquid chromatographic (GLC) analyses were performed on a Hewlett-Packard Model 5880 and Model 5830A equipped with a 2.48 m (8 ft) × 3.2 mm (1/8 in.) Porapak QS column for analysis of oxidation products of ethylene and propylene and with a 1.83 m (5 ft) × 3.2 mm (1/8 in.) 5% Carbowax on Supelcoport for analysis of oxidation products of 1-octene. The temperature was programmed in the range of 75–220 °C at a rate of 30 °C/min. GC-MS data were recorded on a Finnigan Model 3300; <sup>1</sup>H NMR spectra were recorded on a Varian Model T-60 spectrometer.

**2. Organic Materials.** Acetonitrile, dimethyl sulfoxide (Me<sub>2</sub>SO), chloroform, and dichloromethane were dried over activated molecular sieves. Acetonitrile and Me<sub>2</sub>SO were subsequently treated with CaH<sub>2</sub> and vacuum distilled before use. Nitromethane was first dried over CaCl<sub>2</sub> and then distilled. Ethylene and propylene were dried by passage over activated molecular sieves. 1-Octene, purchased from Aldrich, was dried with LiAlH<sub>4</sub> and vacuum distilled. Norbornene (bicyclo[2.2.1]-2-heptene), norcamphor (2-norbornanone), and *exo*-2,3-epoxynorbornane were used as received from Aldrich. Nitrosyl hexafluorophosphate and tetrafluoroborate were purchased from Alfa-Ventron and used as received.

**3. Complexes.** (PhCN)<sub>2</sub>PdCl<sub>2</sub>,<sup>24</sup> [(bpy)(CO)<sub>2</sub>Rh]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (6), [(CH<sub>3</sub>CN)<sub>4</sub>RhNO]<sup>2+</sup>(BF<sub>4</sub>)<sub>2</sub><sup>-</sup> (9), [Rh(NO)Cl<sub>2</sub>]<sup>+</sup> (11), and [Rh(NO)<sub>2</sub>Cl]<sub>2</sub><sup>2+</sup> (12) were prepared according to published procedures. All complexes were synthesized with exclusion of air and moisture unless stated otherwise.

[(bpy)(CH<sub>3</sub>CN)<sub>3</sub>RhNO]<sup>2+</sup>(PF<sub>6</sub>)<sub>2</sub> (5). An excess of 2,2'-bipyridine (4.47 g, 28.2 mmol) was added to a solution of [(1,5-COD)RhCl]<sub>2</sub> (4.7 g, 19.0 mmol) in methanol (200 mL). The resulting solution was stirred for 3 h at room temperature. Addition of an excess of ammonium hexafluorophosphate (4.0 g, 24.5 mmol) yielded [(bpy)(1,5-COD)Rh]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (4) in the form of a red precipitate (9.5 g, 18.47 mmol, 97%), which was filtered and dried under an inert atmosphere. Anal. Calcd for C<sub>18</sub>H<sub>22</sub>F<sub>6</sub>N<sub>2</sub>PRh: C, 42.20; H, 3.93; N, 5.47. Found: C, 41.85; H, 3.97; N, 5.47.

The above cationic complex (1.0 g, 1.94 mmol) was dissolved in acetonitrile (20 mL), and the resulting solution was cooled to 0 °C. Addition of nitrosyl hexafluorophosphate (NOPF<sub>6</sub>, 96% purity, 0.37 g, 2.02 mmol) resulted in a green solution, which was stirred at room temperature for 50 min. Addition of diethyl ether (50 mL) resulted in a green oil, which slowly crystallized. The crystals of 5 (1.28 g, 97%) were filtered, washed with diethyl ether, and dried under vacuum. Anal. Calcd for C<sub>16</sub>H<sub>17</sub>F<sub>12</sub>N<sub>6</sub>OP<sub>2</sub>Rh: C, 27.36; H, 2.44; N, 11.97. Found: C, 27.57; H, 2.61; N, 11.49. The IR spectrum in Nujol showed a nitrosyl band at 1658 cm<sup>-1</sup> and nitrile bands at 2290, 2300, and 2320 cm<sup>-1</sup>. The same complex is prepared by the reaction of [(bpy)(CO)<sub>2</sub>Rh]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (6) with nitrosyl hexafluorophosphate in acetonitrile.

**Formation of (CH<sub>3</sub>CN)<sub>2</sub>(NO)RhCl<sub>2</sub> (13).** On a vacuum line, dry and degassed acetonitrile (10 mL) was transferred to a flask containing [Rh(NO)Cl<sub>2</sub>]<sub>2</sub> (11) (0.11 g). Within 15 min, complex 11 dissolved, forming a deep red solution. The following day, the excess acetonitrile was evaporated, leaving behind a green solid. The IR spectrum (KBr pellet) exhibits one NO band at 1630 cm<sup>-1</sup> (shifted from the two bands of 11 at 1670 and 1770 cm<sup>-1</sup>) and nitrile bands at 2290 and 2320 cm<sup>-1</sup>.

## 4. Oxidation of Nitrosyl Complexes by Molecular Oxygen.

[(bpy)(CH<sub>3</sub>CN)<sub>2</sub>RhNO]<sup>2+</sup>(PF<sub>6</sub>)<sub>2</sub> (7). Oxygen was bubbled through a solution of 5 (0.49 g) in acetonitrile (20 mL) at room temperature for 24 h. When diethyl ether was added to the solution, a green oil was formed, which slowly solidified. The pale green solid (0.448 g) was filtered off, washed with diethyl ether, and dried under vacuum. Anal. Calcd for C<sub>14</sub>H<sub>14</sub>F<sub>12</sub>N<sub>5</sub>O<sub>2</sub>P<sub>2</sub>Rh: C, 24.83; H, 2.08; N, 10.34. Found: C, 25.76; H, 2.55; N, 10.28. The IR spectrum (Nujol) showed no band in the nitrosyl region (1658 cm<sup>-1</sup>), nitro bands at 1280, 1330, and 1375 cm<sup>-1</sup>, and two CN bands at 2310 and 2330 cm<sup>-1</sup>. The region for the characteristic nitro band at approximately 800 cm<sup>-1</sup> is obscured by the broad P-F band of the anion. The number of acetonitrile ligands retained by the complex may be dependent on the conditions used for drying.

[(CH<sub>3</sub>CN)<sub>4</sub>RhNO]<sup>2+</sup>(BF<sub>4</sub>)<sub>2</sub> (10). A. A solution of complex 9 (0.2 g) in acetonitrile (20 mL) was placed into a Fisher-Porter tube and pressurized with oxygen to 275 kPa (40 psi). After 24 h of stirring at room temperature, the solvent was evaporated under vacuum, leaving behind a quantitative yield of complex 10 as a yellow hygroscopic solid. Anal. Calcd for C<sub>8</sub>H<sub>12</sub>B<sub>2</sub>F<sub>8</sub>N<sub>5</sub>O<sub>2</sub>Rh: C, 19.74; H, 2.49; N, 14.39. Found: C, 20.85; H, 2.78; N, 14.09. The IR spectrum (KBr pellet) shows new bands at 815, 1270, 1313, and 1380 cm<sup>-1</sup> typical for the nitro ligand, no band in the nitrosyl region (1758 cm<sup>-1</sup>) of the initial nitrosyl complex,<sup>9</sup> and two nitrile bands at 2310 and 2340 cm<sup>-1</sup>.

B. In a Fisher-Porter tube complex 9 (0.076 g) was dissolved in dry and degassed nitromethane. The solution was heated to 60 °C for 2 h. After it cooled to room temperature, the system was pressurized with oxygen to 414 kPa (60 psi) and the heating was resumed. The extent of oxidation was followed by IR spectroscopy. Even after 24 h, only approximately 50% of 9 had been oxidized to the nitro complex 10. In acetonitrile, 50% complex 9 was oxidized during the short time needed to record the IR spectrum.

**Oxidation of [Rh(NO)<sub>2</sub>Cl]<sub>2</sub> (12) in Coordinating Solvents.** A solution of complex 12 (0.3 g) in tetrahydrofuran (20 mL) was placed into a Fisher-Porter tube that was pressurized to 344 kPa (50 psi) with oxygen. After 66 h of stirring at room temperature, the system was vented. The solvent was removed under vacuum, leaving behind a dark brown solid (~0.3 g). The IR spectrum reveals a substantial decrease in the intensity of the nitrosyl bands at 1630 and 1715 cm<sup>-1</sup> and the appearance of new bands at 868, 1268, and 1360 cm<sup>-1</sup> characteristic of a nitro ligand.

**Oxidation of Olefins by Rhodium Nitro Complexes. Ethylene. A.** A degassed mixture of complex 7 (0.058 g, 0.082 mmol), *n*-octane (0.1 g, internal GC standard), (PhCN)<sub>2</sub>PdCl<sub>2</sub> (0.060 g, 0.15 mmol), and acetonitrile (10 mL) was saturated with ethylene, stoppered with a serum cap, and heated to 70 °C. In 2.5 h, a quantitative yield (0.085 mmol) of acetaldehyde was formed as determined by GC. When (PhCN)<sub>2</sub>PdCl<sub>2</sub> was omitted, no acetaldehyde was formed even after 22 h at 70 °C.

B. A degassed solution of complex 10 (0.0719 g, 0.148 mmol), *n*-octane (0.1 g), and nitromethane (6 mL) was placed into a Fisher-Porter tube, pressurized to 138 kPa (20 psi) with ethylene, and heated to 60 °C. After 16 h, a quantitative yield of acetaldehyde (0.15 mmol) was present in the reaction mixture.

**1-Octene. A.** Complex 7 (0.1018 g, 0.155 mmol), (PhCN)<sub>2</sub>PdCl<sub>2</sub> (0.1053 g, 0.275 mmol), 1-octene (1 mL), and *n*-undecane (0.1 g, internal GC standard) were dissolved in dry and degassed acetonitrile (7 mL). After 24 h of heating at 70 °C under an argon atmosphere, the following products were present (GC): 2-octanone (0.093 mmol), 3-octanone (0.047 mmol), and 4-octanone (0.029 mmol).

B. A solution of complex 10 (0.0376 g, 0.077 mmol), 1-octene (1 mL), and *n*-undecane (0.1 g) in dry and degassed nitromethane (6 mL) was pressurized with argon to 220 kPa (32 psi) and heated at 60 °C. After 16 h, 0.050 mmol of the expected 2-octanone was formed.

**Rates of 1-Octene Oxidation.** Three Fisher-Porter tubes were charged with nitromethane (6 mL), 1-octene (1 mL), and biphenyl (0.050 g, GC internal standard). Into the first tube was added complex 10 (0.059 g, 0.122 mmol), and the system was pressurized to 344 kPa (50 psi) with oxygen. The second tube was charged with the nitrosyl complex 9 (0.054 g, 0.114 mmol) and pressurized to 344 kPa (50 psi) with oxygen. The third tube was charged with the nitro complex 10 (0.0419 g, 0.086 mmol), degassed, and pressurized to 206 kPa (30 psi) with argon. The tubes were heated at 60 °C. Samples were taken periodically and analyzed by GC. The results are summarized in Figure 1.

**Norbornene. A. Oxidation by Complex 2 in the Presence of (CH<sub>3</sub>CN)<sub>2</sub>PdCl<sub>2</sub>.** Norbornene (0.1825 g, 1.94 mmol) and dodecane

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(0.0665 g) were dissolved in 1,2-dichloroethane (20 mL), and the solution was purged with argon for 45 min. The solution was transferred with use of a cannula into an argon-filled flask containing complex **2** (0.1618 g, 0.203 mmol) and  $(\text{CH}_3\text{CN})_2\text{PdCl}_2$  (0.1569 g, 0.665 mmol). The solution was stirred, and samples were removed periodically for GC analysis. The yield of *exo*-2,3-epoxynorbornane reached 74% after 10 min and then declined (23% after 6.5 h). A small amount of norcamphor (~10%) also formed. In addition, a product appeared concomitant with the decrease in epoxide. GC-MS showed this to have a molecular weight of 204, in agreement with the formula  $\text{C}_{14}\text{H}_{20}\text{O}$  (norbornene + epoxynorbornane).

**B. Oxidation by 10.** A solution of norbornene (0.211 g, 2.24 mmol) in nitromethane (8 mL) was purged with argon for 30 min. Complex **10** (0.144 g, 0.296 mmol) was added and the flask sealed with a rubber septum. The flask was immersed in a hot oil bath (65 °C), the contents were stirred, and samples were removed periodically for GC analysis. A peak with a retention time corresponding to that of norcamphor rapidly grew in. After approximately 28 h, biphenyl (0.254 g) was added as an internal standard. Analysis showed a 23% yield of norcamphor, and GC-MS confirmed the identification of the ketone.

**C. Oxidation by 7 in the Presence of  $(\text{PhCN})_2\text{PdCl}_2$ .** A solution of norbornene (0.073 g, 0.775 mmol) in acetonitrile (8 mL) was purged with argon for 30 min.  $(\text{PhCN})_2\text{PdCl}_2$  (0.1062 g, 0.277 mmol) and complex **7** (0.0603 g, 0.085 mmol) were added. The flask was sealed with a rubber septum and immersed in a hot oil bath (70 °C). After ~4.5 h, biphenyl (0.0069 g) was added. Periodic GC analysis showed

the production of norcamphor with the yield reaching 20% after 1 day.

A solution of *exo*-2,3-epoxynorbornane (0.002 g) in  $\text{CH}_3\text{CN}$  (2 mL) was added. GC analysis after 25 min showed that all the epoxide had reacted.

**Reaction of Complex 9 with Epoxides. A. *exo*-2,3-Epoxynorbornane.** A solution of *exo*-2,3-epoxynorbornane (0.0122 g, 0.11 mmol) in nitromethane (5 mL) was purged with argon for 45 min. Complex **9** (0.0869 g, 0.18 mmol) was added, and the flask was sealed with a rubber septum. The flask was immersed in a hot oil bath (65 °C), and samples were removed periodically for GC analysis. The reaction was complete in approximately 5 min. The peak corresponding to the epoxide had disappeared, and a small peak corresponding to a low yield of norcamphor had grown in.

**B. 1,2-Epoxyoctane.** Nitromethane (5 mL) was purged with argon for 45 min. 1,2-Epoxyoctane (15  $\mu\text{L}$ ) was added, followed by complex **8** (0.0733 g). The flask was sealed with a septum and immersed in a hot oil bath (60 °C). GC analysis after 5 min revealed the complete disappearance of the epoxide and the production of a low yield of 2-octanone.

**Registry No.** 1, 69377-51-1; 2, 75778-52-8; 3, 77933-52-9; 4, 37726-78-6; 5, 84642-19-3; 6, 82411-90-3; 7, 84623-37-0; 8, 53738-55-9; 9, 62793-29-7; 10, 84623-39-2; 11, 84623-40-5; 12, 40770-06-7; 13, 84623-41-6; 14, 40231-80-9; 15, 77944-62-8; ethylene, 74-85-1; 1-octene, 111-66-0; norbornene, 498-66-8.

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## Synthesis of Some $d^0$ Organoimido Complexes of the Early Transition Metals

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A series of  $d^0$  *tert*-alkylimido complexes has been prepared for the group 5-7 transition metals. The complexes have the general formula  $\text{M}(\text{NR})_n\text{X}_{4-n}$  where X is a monoanionic ligand and R is a tertiary alkyl group. Complexes where M = Nb, Ta, or W were prepared by in situ deprotonation of *tert*-alkylamido ligands. Complexes where M = V, Cr, Mo, or Re were prepared by treatment of the metal oxide or oxychloride with the corresponding *tert*-alkyl(trimethylsilyl)amine. Ligand exchange and insertion reactions gave access to a range of X ligands; examples include complexes with OR,  $\text{OSiR}_3$ , NHR,  $\text{NR}_2$ ,  $\text{S}_2\text{CNR}_2$ ,  $\text{CH}_3$ , Cl, and Br substituents.

### Introduction

Transition-metal imido (NH and NR) complexes are currently the focus of increasing research activity. Recently, the reactions of imido complexes have been studied as mechanistic models for important industrial processes including the Haber ammonia synthesis,<sup>1</sup> the reduction of nitriles,<sup>2</sup> and the ammoxidation of propylene.<sup>3</sup> Related species have been prepared as models for the intermediates in various enzymatic transformations.<sup>4,5</sup> Organoimido ligands have been increasingly utilized as ancillary ligands in organometallic chemistry,<sup>6</sup> and

recent theoretical studies<sup>7</sup> suggest that imido ligands may prove uniquely effective in promoting catalytic olefin metathesis.

Recently we have reported several structural studies<sup>8</sup> on imido derivatives of the early transition metals. The novel imido complexes were generally obtained in high yield and have a number of potentially useful properties including re-

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