

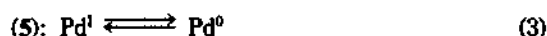
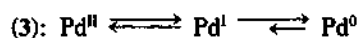
Table 2. Electrochemical Data<sup>a</sup>

| Compound   | Solvent            | Wave 1 <sup>b</sup> |            | $E_{1/2}$ | Wave 2   |
|--|--------------------|---------------------|------------|-----------|----------|
|  |                    | $E_{pa}/V$          | $E_{pc}/V$ |           | $E_{pc}$ |
| Pd(dppm)(N <sub>3</sub> ) <sub>2</sub>                             | CH <sub>3</sub> CN | -0.85               | -0.76      | -0.81     | -1.08    |
|  | DMF                | -0.83               | -0.64      | -0.74     | -1.09    |
| Pd(dppm)Cl <sub>2</sub>  | CH <sub>3</sub> CN | -0.86               | -0.76      | -0.81     | -1.12    |
|  | DMF                | -0.86               | -0.65      | -0.76     | -1.16    |
| Pd <sub>2</sub> (dppm) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub> | CH <sub>3</sub> CN | -0.90               | -0.64      | -0.77     |          |
|  | DMF                | -1.14               | -0.53      | -0.84     |          |
| Pd <sub>2</sub> (dppm) <sub>2</sub> Cl <sub>2</sub>                | CH <sub>3</sub> CN | -0.90               | -0.69      | -0.80     |          |
|  | DMF                | -1.12               | -0.52      | -0.82     |          |

<sup>a</sup>Potentials referred to an Ag/AgCl electrode at a scan rate of 100 mV s<sup>-1</sup> and with 0.1 M TBAP as supporting electrolyte;  $E_{1/2}$  for  $Fc^+/Fc = +0.48$  V. <sup>b</sup> $E_{pc}$  and  $E_{pa}$  are the peak potentials of the reduction and oxidation waves, respectively.

plex from the reaction mixture. Dppm bridged dinuclear type of complexes having halogen ligand are previously well studied.<sup>9b</sup> However, comparable studies including electrochemical property between mononuclear and dinuclear complexes are scarce to our knowledge.

**Electrochemistry.** We have examined the electrochemical behavior of 3-6 complexes having dppm ligand. Cyclic voltammogram of mononuclear Pd(II) complex, Pd(dppm)(N<sub>3</sub>)<sub>2</sub> (3) exhibits a reversible one electron reduction ( $E_{1/2} = -0.81$  V) and an irreversible one-electron reduction ( $E_{1/2} = -1.08$  V) in CH<sub>3</sub>CN (see Figure 1). As can be seen in Figure 1, relative high intensity of complex 3 by irreversible one-electron reduction can be attributed to Pd<sup>I</sup>/Pd<sup>0</sup> reduction accompanied by partial dissociation of azide ligands to give palladium black. In DMF solvent we also observe similar redox features. The potentials corresponding to the features are summarized in Table 2. On the other hand, dinuclear Pd(II) complex, Pd<sub>2</sub>(dppm)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub> (5) shows a reversible one electron reduction ( $E_{1/2} = -0.77$  V) in CH<sub>3</sub>CN. In case of Pd(dppm)Cl<sub>2</sub> and Pd<sub>2</sub>(dppm)<sub>2</sub>Cl<sub>2</sub> under the same conditions we have also observed similar electrochemical behavior. This observation supports that the azido ligand in the palladium and platinum azide complexes has character as pseudohalide.<sup>1b</sup> On the basis of the electrochemical behavior of mononuclear and dinuclear palladium azide complexes we suggest the following process.



In contrast with the above palladium (I, II) azide complexes platinum (I, II) azide complexes display no redox features within various solvent limits which support higher stability than palladium azide complexes. In the present work we described the preparation and some properties of palladium and platinum azide complexes and to the best of our knowledge the comparison between M(I) and M(II) (M = Pd, Pt) azide complexes was unnoted.

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## Ruthenium-catalyzed Partial Oxidation of Alcohols by Paraformaldehyde

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Transition metal-catalyzed oxidations of alcohols have recently attracted considerable interest and various metal compounds and oxidant systems have been reported.<sup>1</sup> Ruthenium complex combined with several oxidants is also effective for the oxidation of alcohols.<sup>2,3</sup> Recently, Bäckvall reported that RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> exhibited a remarkable activity in hydrogen transfer from propan-2-ol to several ketones at reflux condition.<sup>4</sup>

In this Note, we wish to report that primary aliphatic and benzylic alcohols are readily oxidized to the corresponding aldehydes by paraformaldehyde in the presence of a catalytic amount of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>.

**Table 1.** Effect of Amount of Paraformaldehyde on the Oxidation of Benzyl Alcohol to Benzaldehyde<sup>a</sup>

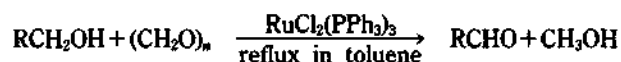
| Mole ratio PhCH <sub>2</sub> OH : HCHO | Yield of benzaldehyde, % <sup>b</sup> |
|--|---------------------------------------|
| 1 : 1                                  | 43                                    |
| 1 : 3                                  | 84                                    |
| 1 : 4                                  | 72                                    |
| 1 : 6                                  | 48                                    |
| 1 : 9                                  | 32                                    |

<sup>a</sup>The reaction was performed on benzyl alcohol (3.0 mmol) with a catalyst (0.05 mmol) in toluene (15 ml) under reflux condition for 7h. <sup>b</sup>Determined by GLC.

**Table 2.** Effect of Some Ruthenium-ligand Catalysts on the Oxidation of Benzyl Alcohol to Benzaldehyde<sup>a</sup>

| Ru-ligand catalyst   | Yield of PhCHO, % <sup>b</sup> |
|--|--------------------------------|
| None   | 0                              |
| RuCl <sub>3</sub> ·3H <sub>2</sub> O                             | Trace                          |
| RuCl <sub>3</sub> ·3H <sub>2</sub> O + 3 eq. PPh <sub>3</sub>    | 75                             |
| RuCl <sub>3</sub> ·3H <sub>2</sub> O + 3 eq. P(OPh) <sub>3</sub> | 18                             |
| RuCl <sub>3</sub> ·3H <sub>2</sub> O + 3 eq. PBu <sub>3</sub>    | 53                             |
| RuCl <sub>3</sub> ·3H <sub>2</sub> O + 3 eq. P(OBu) <sub>3</sub> | 8                              |
| RuCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>3</sub>               | 84(80) <sup>c</sup>            |
| RuH <sub>2</sub> (PPh <sub>3</sub> ) <sub>4</sub>                | 3(41) <sup>d</sup>             |

<sup>a</sup>The reaction was performed on benzyl alcohol (3.0 mmol) and paraformaldehyde (9.0 mmol) in toluene (5 ml) with a substrate to ruthenium ratio of 60 : 1. <sup>b</sup>Determined by GLC. <sup>c</sup>The number in parenthesis indicates isolated yield of benzaldehyde. <sup>d</sup>The number in parenthesis indicates isolated yield of benzyl formate.



In this reaction, paraformaldehyde, widely used as a carbonylating or reducing agent for metal complexes, is used as a hydrogen acceptor. A typical procedure is as follows. A mixture of paraformaldehyde (270 mg, 9.0 mmol), benzyl alcohol (1,360 μl, 3.0 mmol), and RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (48.5 mg, 0.05 mmol) in toluene (15 ml) was refluxed with stirring under N<sub>2</sub> atmosphere for 7 h and benzaldehyde was obtained in 84% GLC yield.

We initially investigated the effectiveness of the amount of paraformaldehyde, and concluded that the use of 3 equiv. of paraformaldehyde gave the highest yield of benzaldehyde, but more than 3 equiv. resulted in lower yields (Table 1). This is probably owing to the formation of inactive ruthenium carbonyl complexes.<sup>5,6</sup>

Among the several types of ruthenium complex catalysts and solvent systems, RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> and toluene gave the best results. Some experimental results are summarized in Table 2 and 3.

Above results reveal that the catalyst precursor has a critical effect on the oxidation reaction. RuCl<sub>3</sub>·3H<sub>2</sub>O with combined 3 equiv. of PPh<sub>3</sub> and RuCl<sub>3</sub>·3H<sub>2</sub>O combined with 3 equiv. of PBu<sub>3</sub> showed fairly good catalytic activities. However RuCl<sub>3</sub>·3H<sub>2</sub>O had no catalytic activity in hydrogen transfer, while

**Table 3.** Effect of Solvents on the Oxidation of Benzyl Alcohol to Benzaldehyde<sup>a</sup>

| Solvent    | Yield of PhCHO, % <sup>b</sup> |
|------------|--------------------------------|
| Benzene    | 59                             |
| Toluene    | 84                             |
| Xylene     | 85                             |
| Mesitylene | 73                             |
| THF        | 40                             |
| Dioxane    | 52                             |

<sup>a</sup>The reaction was performed on benzyl alcohol (3.0 mmol) and paraformaldehyde (9.0 mmol) in solvent (15 ml) with RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (0.05 mmol) under reflux condition for 7h. <sup>b</sup>Determined by GLC.

**Table 4.** Ability of Some Hydrogen Acceptors in RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>-catalyzed Partial Oxidation of Benzyl Alcohol to Benzaldehyde<sup>a</sup>

| Hydrogen acceptor                | Yield of PhCHO, % <sup>b</sup> |
|----------------------------------|--------------------------------|
| (CH <sub>2</sub> O) <sub>n</sub> | 84                             |
| DMF                              | 51                             |
| Cyclohexene                      | 16                             |
| Acetone                          | 42                             |
| Acetaldehyde                     | 36                             |

<sup>a</sup>The reaction was performed on benzyl alcohol (3.0 mmol) and hydrogen acceptor (9.0 mmol) in toluene (15 ml) with RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (0.05 mmol) under reflux condition for 7h. <sup>b</sup>Determined by GLC.

**Table 5.** Oxidation of Some Alcohols to Carbonyl Compounds with RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>/(CH<sub>2</sub>O)<sub>n</sub> Oxidizing System<sup>a</sup>

| Alcohol  | Product   | Yield, % <sup>b</sup> |
|--|---|-----------------------|
| PhCH <sub>2</sub> OH   | PhCHO   | 84(80)                |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>2</sub> OH | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CHO | 62(59)                |
| PhCH=CHCH <sub>2</sub> OH  | PhCH=CHCHO  | 58(58)                |
| PhCH <sub>2</sub> CH <sub>2</sub> OH                               | PhCH <sub>2</sub> CHO                               | 64(60)                |
| (CH <sub>3</sub> ) <sub>2</sub> CHCH(OH)CH <sub>3</sub>            | (CH <sub>3</sub> ) <sub>2</sub> CHCOCH <sub>3</sub> | Trace                 |
| Cl <sub>3</sub> CCH <sub>2</sub> OH                                | Cl <sub>3</sub> CCHO                                | Trace                 |

<sup>a</sup>The reaction was performed on alcohol (3.0 mmol) and paraformaldehyde (9.0 mmol) in toluene (15 ml) with RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (0.05 mmol) under reflux condition for 7h. <sup>b</sup>Determined by GLC. The numbers of parentheses indicate isolated yield.

RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> preferred the oxidative condensation reaction rather than partial oxidation of alcohol, reported by Murahashi group.<sup>5</sup> Table 3 shows that the reaction rate was influenced by boiling point of solvent, because hydrogen acceptor is formaldehyde which is formed from decomposition of paraformaldehyde (163-165°C). We examined the ability of some hydrogen acceptors and the results are shown in Table 4. Among them, paraformaldehyde showed the highest acceptability of hydrogen.

Several alcohols were oxidized by RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> and some results are listed in Table 5. Primary, benzylic and allylic alcohols were oxidized to the corresponding aldehydes in

good yields, and secondary alcohols were not affected to this oxidation system. The advantage of this new oxidizing agent lies in its simplicity and avoidance of the reactive oxidants.

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### Overtone Transition Intensities for NH by *Ab Initio* Effective Valence Shell Hamiltonian

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Recently the effective valence shell Hamiltonian method ( $H^e$ ) has been extended to calculate one-electron molecular properties as well as valence state energies. The  $H^e$  method is an *ab initio* multireference state perturbation formalism for treating electron correlations, and is based on the quasi-degenerate many-body perturbation theory (QDMBPT). In the  $H^e$  method, the effective operators act only in the space spanned by the set of valence orbitals, and the effective operators are defined in terms of perturbation sums over a complete set of complementary core and excited orbitals. In energy calculations,  $H^e$  is the effective operator of Hamiltonian ( $H$ ), which has been applied to a number of atomic and molecular systems where the computations of valence state energies show that the method provides an accurate description of the electronic structure.<sup>1-10</sup>

As for molecular properties, an operator  $A$ , which represents a molecular property is transformed to the effective valence shell operator  $A^e$ . And the diagonal and off-diagonal matrix elements of a given  $A^e$  can be obtained simultaneously for all valence states of a molecule and its ions. The dipole moment and transition dipole moment functions of CH and OH have been calculated using  $A^e$ .<sup>11-15</sup> Also the dipole and transition moments of SiH, PH and SH at each molecule's equilibrium internuclear distance have been reported.<sup>16</sup> As another test case for understanding  $A^e$ , we have calculated

the dipole moment functions of NH and NH<sup>+</sup>.<sup>17</sup> NH in particular has been previously studied theoretically and experimentally.<sup>18-38</sup>

Now we calculate the overtone vibrational transition intensities of various electronic states of NH using the dipole moment functions computed with  $A^e$  method. This provides a more stringent test of the quality of the  $H^e$  effective valence wavefunction than that given by potential energy curves alone. The accuracy of dipole moment function much depends on the accuracy of the electronic wavefunction. And to study the vibrational transition, we, of course, have to calculate vibrational wavefunction which depends on the whole profile of potential energy curve. Therefore, the calculation of overtone intensities is very meaningful to assess the quality of the new  $A^e$  method.

The brief summary of the effective valence shell Hamiltonian formalism is as follows. The molecular electronic Hamiltonian  $H$  can be divided into a zeroth order part  $H_0$  and a perturbation  $V$ , *i.e.*,  $H=H_0+V$ . The full many-electron Hilbert space can be divided into a primary space with projector  $P$  and its orthogonal complement with projector  $Q=1-P$ , where the  $P$  space is supposedly taken to contain a set of many-electron basis functions which are quasidegenerate with respect to the zeroth order Hamiltonian  $H_0$ . Our choice for  $P$  takes it to span the valence space of all distinct configuration state functions involving a filled core and the remaining electrons distributed among the valence orbitals. Hence, the  $Q$  space contains all basis functions with at least one core hole and/or one occupied excited orbital.

QDMBPT transforms the full Schrödinger equation

$$H\Psi_\Lambda = E_\Lambda\Psi_\Lambda \quad (1)$$

into the  $P$  space effective valence shell Schrödinger equation,

$$H^e\Psi_\Lambda^e = E_\Lambda\Psi_\Lambda^e \quad (2)$$

for the projection  $\Psi_\Lambda^e = P\Psi_\Lambda$  where the  $E_\Lambda$  are the exact eigenvalues of (1). Note that the energies  $E_\Lambda$  in (1) and (2) are identical. QDMBPT gives, in the second order approximation,

$$H^e = PHP + (1/2) \sum_{\lambda'} \{P(\lambda)VQ(E_\Lambda - H_0)^{-1}QVP(\lambda') + h.c.\} \quad (3)$$

where *h.c.* designates the Hermitian conjugate of the preceding term and  $P(\lambda)$  designates the projector onto the valence space basis function  $|\lambda\rangle$ . The detailed expressions for (3) are given elsewhere.<sup>8,9</sup> As described in (2), the  $\Lambda$  indicates a valence state. Therefore the state energy for the valence state  $\Lambda$  is  $E_\Lambda = \langle\Psi_\Lambda^e|H^e|\Psi_\Lambda^e\rangle$ .

From the characteristics of  $H^e$ , by one computation, we determine  $E_\Lambda$  for all the valence states of NH. When the calculation is repeated for various internuclear distances, we finally determine the potential energy curves for valence state  $\Lambda$ , *i.e.*,  $v_\Lambda(R)$  and effective electronic wavefunction  $\Psi_\Lambda^e$ .

Now consider an operator  $A$  whose diagonal matrix elements between the normalized full space  $\Psi_\Lambda$  we desire. The matrix elements may be transformed into the matrix elements of an effective valence shell operator  $A^e$  between the orthonormal valence space eigenfunctions  $\Psi_\Lambda^e$ ,

$$\langle\Psi_\Lambda|A|\Psi_\Lambda\rangle = \langle\Psi_\Lambda^e|A^e|\Psi_\Lambda^e\rangle. \quad (4)$$