

# A Theoretical Study on the Reactivity of Nucleophiles Coordinated to Palladium

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**Abstract:** Ab initio calculations using an effective core potential (ECP) have been performed on complexes Pd(Nu)<sub>2</sub> with Nu<sup>-</sup> = CH<sub>3</sub><sup>-</sup>, H<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, CN<sup>-</sup>, <sup>-</sup>CH(CHO)<sub>2</sub>, OOH<sup>-</sup>, OCH<sub>3</sub><sup>-</sup>, and OH<sup>-</sup>. An analysis of the reactivity of the coordinated nucleophiles was carried out on the basis of the bond strength and the energy of the Pd-Nu bond orbital.

We recently reported a theoretical model for the reactivity of coordinated nucleophiles in ( $\pi$ -olefin)palladium complexes.<sup>2</sup> The ability of the nucleophiles to undergo a cis migration to the coordinated olefin was correlated with the orbital energy of the metal-nucleophile bond. With use of a perturbation theory approach<sup>2,3</sup> only the nucleophiles with a high-energy metal-nucleophile bond orbital were predicted to undergo a migration, in accordance with experimental data. The calculations (ab initio-ECP) were performed on complexes *trans*-Pd(H<sub>2</sub>O)(Nu)<sub>2</sub> (ethene), and four simple nucleophiles were investigated. Further studies showed that the energy of the Pd-Nu bond orbital in *trans*-Pd(H<sub>2</sub>O)(Nu)<sub>2</sub>(ethene) correlates very well with the energy of the Pd-Nu bond orbital in Pd(Nu)<sub>2</sub> complexes.<sup>4</sup> In order to gain further insight into the reactivity of coordinated nucleophiles, we have studied a range of Pd(Nu)<sub>2</sub> complexes. The results reported here show a good agreement with experimental results for cis migration to olefins. The results can also be used for predicting related frontier orbital controlled processes involving reaction of the Pd-Nu bond.

## Details of Calculations

The calculations were performed at the Hartree-Fock level of approximation with an effective core potential (ECP) description of the noble gas cores of the heavier elements. In some cases additional calculations were performed with use of the complete active space SCF (CASSCF)<sup>5</sup> method which includes the most important correlation effects. The basis sets used in all calculations were of double- $\zeta$  quality or better.

The ECP methods used for the lighter elements were essentially that of Bonifacic and Huzinaga<sup>6</sup> and that of Wahlgren,<sup>7</sup> while for the heavier elements Br and Pd the frozen orbital ECP method of Pettersson, Wahlgren, and Gropen<sup>8</sup> was used. Orbital energies, atomic excitation energies (including ionization potentials), and electron affinities are in general obtained to within 0.1 eV of those of the corresponding all-electron calculation. Bond lengths and bond angles are normally reproduced to within 0.02 au and 0.3°, respectively, of a comparable all-electron calculation.

The ECP method is based on the frozen core approximation and consists of replacing the core by an effective potential to give the same interaction with the valence orbitals. The resulting savings in the computational effort are of the order of 60% in the integral evaluation step, in the type of calculations performed here. This makes larger molecules available to a higher-level theoretical treatment.

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(4) By using Nu = CH<sub>3</sub><sup>-</sup>, H<sup>-</sup>, F<sup>-</sup>, and OH<sup>-</sup> it was found that the energy of the unsymmetrical Pd-Nu bond orbital of the two complexes correlates well, being systematically between 1.1 and 1.5 eV lower for the Pd(Nu)<sub>2</sub> complexes compared to the Pd(OH<sub>2</sub>)Nu<sub>2</sub>(ethene) complexes (cf. Table III).

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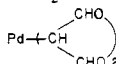
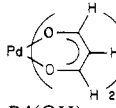
**Table I.** ECP Parameters and Valence Basis Sets for C, N, and Br

A. ECP Parameters <sup>a</sup>			
	atom		
	C	N	BR
Z <sup>eff</sup>	4.0	5.0	25.0
B <sub>1s</sub>	11.5	20.0	500.0
B <sub>2s</sub>			70.0
B <sub>2p</sub>			65.0
A <sub>1</sub>	0.356996	0.234153	0.9274
A <sub>2</sub>	0.309560	0.271910	0.15391
A <sub>3</sub>	0.058175	0.024796	0.0919
$\alpha_1$	237.89167	235.235516	7730.513
$\alpha_2$	20.09236	23.55097	150.0654
$\alpha_3$	3.815735	3.564666	10.4472
C <sub>1</sub>	0.856501		
$\beta_1$	492.667602		
state <sup>b</sup>	3p	4s	2p
basis <sup>c</sup>	ref 11	ref 11	ref 12
B. Valence Basis Sets and Contractions			
C		N	
exponent	coeff	exponent	coeff
s	2s	s	2s
26.07067	-0.087298	36.46476	-0.102282
4.61666	-0.213833	6.528058	-0.238549
0.524194	0.514984	0.764993	0.504506
0.163484	1.0	0.234424	1.0
p	2p	p	2p
4.18286	0.111693	5.95461	0.118880
0.851563	0.466226	1.23293	0.474376
0.199206	1.0	0.286752	1.0
Br			
exponent	coefficient	coefficient	
s	CGTO-1	CGTO-2	CGTO-3
355.7519	-0.170167	-0.020054	
21.94133	0.653236	0.197044	
7.85584	0.248315	0.069321	
4.412	-0.759298	-0.330206	
1.862	-0.605858	-0.500572	
0.5455	-0.026746	0.529350	
0.1902			1.0
p	CGTO-1	CGTO-2	CGTO-3
183.5897	-0.096213	0.017150	
44.6924	-0.295676	0.059033	
4.70329	0.724382	-0.273221	
1.595	0.353762	-0.068021	
0.4918	-0.003319	0.557199	
0.1507			1.0
d	CGTO		
11.86524	0.553400		
2.526681	0.646979		

<sup>a</sup> For definition of ECP parameters see ref 8. <sup>b</sup> Atomic state used in the parametrization. <sup>c</sup> Original basis set.

For the first row elements, C, N, O, and F, the 1s orbital was replaced by an ECP and the basis set reduced to a valence basis.

**Table II.** Calculated Pd–Nu Bond Distance, Bond Strength, and Bond Orbital Energy

entry	complex	calcd bond distance (Å)	exptl bond distance (Å)	force constant (eV/Å <sup>2</sup> )	energy of Nu > Pd–Nu orbital (eV) <sup>a</sup>
1	Pd(CH <sub>3</sub> ) <sub>2</sub>	2.17	2.02–2.16 <sup>b</sup>	27.6	–7.97
2	PdH <sub>2</sub>	1.66		30.6	–9.07
3		2.14	2.10 <sup>c</sup>	32.9	–10.05
4	PdBr <sub>2</sub>	2.49	2.54 <sup>d</sup>	27.8	–10.99
5	Pd(OOH) <sub>2</sub>	1.94 <sup>e</sup>			–12.02
6	PdCl <sub>2</sub>	2.39	2.44 <sup>f</sup>	25.4	–12.17
7	Pd(CN) <sub>2</sub>	2.06	1.98–2.04 <sup>g</sup>	33.7	–12.73
8	Pd(OCH <sub>3</sub> ) <sub>2</sub>	1.94		57.1	–14.53
9	PdF <sub>2</sub>	1.92	1.96 <sup>h</sup>	58.4	–14.97
10		2.06 <sup>i</sup>	2.06 <sup>i</sup>		–15.52
11	Pd(OH) <sub>2</sub>	1.94		63.4	–16.12

<sup>a</sup>In entry 10 the energy refers to the orbital shown in Figure 1. <sup>b</sup>From ref 13. <sup>c</sup>From ref 14. <sup>d</sup>From ref 15. <sup>e</sup>Not optimized. <sup>f</sup>From ref 16. <sup>g</sup>From ref 17. <sup>h</sup>From ref 18. <sup>i</sup>The experimental value was used without optimizing the bond distance. <sup>j</sup>From ref 19.

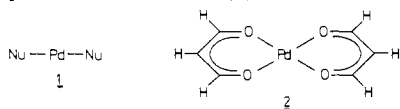
The ECP parameters and basis set for carbon were those given by Wahlgren<sup>7</sup> except for Pd(CH<sub>3</sub>)<sub>2</sub> where a different description was used with four s and three p functions contracted to two s and two p. The ECP parameters and basis set are given in Table I. The main difference between these two descriptions is that the latter retains the valence orbital nodal structure while the former is nodeless. This, however, had a negligible effect on the results and thus the smaller (primitive) basis set of Wahlgren<sup>7</sup> was used in the larger calculations. For N, O, and F the basis sets used were four s, three p contracted to two s, and two p and in addition a diffuse p exponent was added for oxygen (0.082) and fluorine (0.104). The parameters for O and F have been presented elsewhere<sup>2</sup> while those for N are given in Table I.

The description of Cl is that used in ref 9 with one diffuse p function (0.058) added, giving a total of four s and four p functions contracted to one s and two p including the nodes in both the 3s and 3p orbitals in the contractions.

In the case of Br the 1s, 2s, 2p orbitals were replaced by an ECP while the 3s, 3p, 3d orbitals were expanded in the smaller valence basis and kept frozen in the calculations as part of the atomic description. The parameters and basis set for Br are included in Table I. The ECP description of Pd is that of ref 8 with the 1s, 2s, 2p, 3s, 3p orbitals replaced by an ECP and the 4s, 4p, and 3d orbitals expanded in the contracted valence basis (4s4p4d) and kept frozen in the calculations. The basis set for hydrogen, finally, was in all cases the Huzinaga<sup>10</sup> 4s basis contracted to 2s.

## Results and Discussion

SCF calculations were carried out on the Pd(Nu)<sub>2</sub> complexes for the nucleophiles shown in Table II. For all complexes where the nucleophiles coordinate with one center, the two nucleophilic centers and palladium are linear (1). For the malonaldehyde



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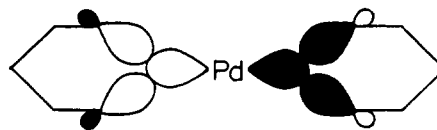
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**Table III.** Correlation between Pd–Nu Bond Orbital Energies for Pd(Nu)<sub>2</sub> and Pd(OH<sub>2</sub>)(Nu)<sub>2</sub>(ethene) Complexes

ligand	energy of Pd–Nu bond orbital <sup>a</sup> (eV)		diff
	Pd(Nu) <sub>2</sub>	<i>trans</i> -Pd(H <sub>2</sub> O)(Nu) <sub>2</sub> (ethene)	
CH <sub>3</sub> <sup>-</sup>	–8.0	–6.9	1.1
H <sup>-</sup>	–9.1	–7.6	1.5
F <sup>-</sup>	–15.0	–13.5	1.5
OH <sup>-</sup>	–16.1	–14.8	1.3

<sup>a</sup>Refers to the unsymmetrical bond orbital. <sup>b</sup>Taken from ref 2.

**Figure 1.**

anion complex in which the oxygens are coordinated to palladium, the square-planar structure 2 was utilized.<sup>20</sup> For each of the molecules investigated, except for the *O,O*-bonded malonaldehyde complex 2 and the peroxide complex, the Pd–Nu bond length was optimized with three points at a 0.05-Å separation around the minimum. This also provided a value of the force constant of the Pd–Nu bond from the parabolic fit. The calculated bond distances agree well with experimental values (Table II).

The energies of the antisymmetric Pd–Nu bond orbital are given in Table II for all the complexes. These energies show a good correlation between the corresponding Pd–Nu bond orbital energies of *trans*-Pd(H<sub>2</sub>O)(Nu)<sub>2</sub>(ethene) for Nu<sup>-</sup> = CH<sub>3</sub><sup>-</sup>, H<sup>-</sup>, F<sup>-</sup>, and OH<sup>-</sup> (Table III). The former energies are systematically 1.1–1.5 eV lower than the latter. For complex 2 the Pd–Nu bond orbital energy given in Table II is for the b<sub>1u</sub> orbital indicated in Figure 1. This orbital is the one highest in energy (–15.5 eV) of the orbitals involving Pd–O bonding. The completely symmetric Pd–O bond orbital (a<sub>g</sub>) is much lower in energy (–21.2 eV). Of the two remaining combinations the b<sub>2g</sub> orbital (–18.8 eV) is also bonding, whereas the b<sub>3u</sub> orbital (–18.3 eV) is nonbonding.

As can be seen from Table II the Pd–Nu bond orbitals in Pd(CH<sub>3</sub>)<sub>2</sub> and PdH<sub>2</sub> are higher than –9.1 eV in energy, whereas the corresponding orbitals in Pd(OCH<sub>3</sub>)<sub>2</sub>, PdF<sub>2</sub>, 2, the Pd(OH)<sub>2</sub> are below –14.5 eV. The former complexes (high-energy Pd–Nu bond orbital) are predicted to undergo facile frontier-controlled migration, while the latter class of complexes (low-energy Pd–Nu bond orbital) would not undergo such reactions.<sup>2</sup> In agreement with experimental results this is the observed reactivity in cis migration to olefins and reductive elimination. Thus, coordinated hydride and methyl readily undergo migration reactions in both cis migration to olefins<sup>21,22</sup> and reductive eliminations.<sup>23,24</sup> On

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