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

## Jan-E. Bäckvall.\*<sup>1a</sup> Eva E. Björkman.<sup>1a</sup> Lars Pettersson,<sup>1b</sup> and Per Siegbahn\*<sup>1b</sup>

Contribution from the Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden, and the Institute of Theoretical Physics, University of Stockholm, S-113 46 Stockholm, Sweden. Received April 3, 1985

Abstract: Ab initio calculations using an effective core potential (ECP) have been performed on complexes  $Pd(Nu)_2$  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>, 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  $trans-Pd(H_2O)(Nu)_2$  (ethene) correlates very well with the energy of the Pd-Nu bond orbital in  $Pd(Nu)_2$  complexes.<sup>4</sup> In order to gain further insight into the reactivity of coordinated nucleophiles, we have studied a range of  $Pd(Nu)_2$  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.

Table I.	ECP	Parameters	and	Valence	Basis	Sets	for	С,	Ν,	and	Br
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A. ECP Parameters<sup>a</sup>

	atom			
	С	N	BR	
$Z^{\rm eff}$	4.0	5.0	25.0	
B <sub>1s</sub>	11.5	20.0	500.0	
$B_{2s}$			70.0	
$B_{2p}$			65.0	
$A_1^{-1}$	0.356996	0.234153	0.9274	
$A_2$	0.309560	0.271910	0.15391	
$A_3$	0.058175	0.024796	0.0919	
$\alpha_1$	237.89167	235.235516	7730.513	
$\alpha_2$	20.09236	23.55097	150.0654	
α3	3.815735	3.564666	10.4472	
$C_1$	0.856501			
$\beta_1$	492.667602			
state <sup>b</sup>	<sup>3</sup> P	4S	<sup>2</sup> P	
basis <sup>c</sup>	ref 11	ref 11	ref 12	

В.	Valence	Basis	Sets	and	Contractio	'n
В.	Valence	Basis	Sets	and	Contractio	J

	С	1	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
р	2p	р	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
	B	r	
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
р	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
đ	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. '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.

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Chem. Soc. 1968, 90, 2. (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 II.	Calculated Pd-Nu	Bond Distance,	Bond Strength, and	Bond Orbital Energy
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entry	complex	calcd bond distance (Å)	exptl bond distance (Å)	force constant $(eV/Å^2)$	energy of Nu⇔ Pd ● Nu orbital (eV)ª
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	$Pd(OOH)_2$	1.94 <sup>e</sup>			-12.02
6	PdČl <sub>2</sub>	2.39	2.44 <sup>f</sup>	25.4	-12.17
7	$Pd(CN)_2$	2.06	1.98-2.048	33.7	-12.73
8	$Pd(OCH_3)_2$	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		-15.52
	Pd(OH) <sub>2</sub>	1.94	h=	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.

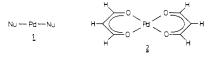
The ECP parameters and basis set for carbon were those given by Wahlgren<sup>7</sup> except for  $Pd(CH_3)_2$  where a different description was used with four s and three p functions contracted to two s and two p. The ECP parameters and basis set are given in Table I. The main difference between these 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  $Pd(Nu)_2$  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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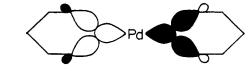
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Table III. Correlation between Pd-Nu Bond Orbital Energies for  $Pd(Nu)_2$  and  $Pd(OH_2)(Nu)_2$  (ethene) Complexes

	energy of Pd-Nu bond orbital <sup>a</sup> (eV)				
ligand	$Pd(Nu)_2$	$trans-Pd(H_2O)(Nu_2)$ (ethene)	diff		
CH <sub>3</sub> -	-8.0	-6.9	1.1		
H-	-9.1	-7.6	1.5		
F-	-15.0	-13.5	1.5		
OH-	-16.1	-14.8	1.3		
		11 1 11 h h = 1 0 0			





#### 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  $b_{1u}$  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  $(a_g)$  is much lower in energy (-21.2 eV). Of the two remaining combinations the  $b_{2g}$  orbital (-18.8 eV) is also bonding, whereas the  $b_{3u}$  orbital (-18.3 eV) is nonbonding.

As can be seen from Table II the Pd-Nu bond orbitals in  $Pd(CH_3)_2$  and  $PdH_2$  are higher than -9.1 eV in energy, whereas the corresponding orbitals in  $Pd(OCH_3)_2$ ,  $PdF_2$ , 2, the  $Pd(OH)_2$ 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 reactons.<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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<sup>94.673.</sup> 

 
 Table IV. Correlation between Force Constants, Orbital Energies, and CASSCF Occupation Numbers for [L-Pd-L] Complexes

ligand	force constant <sup><i>a</i></sup> $(eV/Å^2)$	orbital energy <sup>a</sup> (eV)	CASSCF occ no.
CH <sub>3</sub> -	27.6	-7.97	1.925
F~ ́	58.4	-14.97	1.965
OH-	63.4	-16.12	1.981

<sup>a</sup> From SCF calculations (cf. Table II).

the other hand, there are no reported examples of either cis migration to olefins<sup>25</sup> or reductive eliminations for coordinated methoxide,  $\beta$ -diketonate, hydroxide, or fluoride.

The complexes in entries 3-7 (Table I) have a Pd-Nu bond orbital energy ranging from -10.1 to -12.7 eV. The reactivity of these coordinated nucleophiles in migration reactions is more difficult to predict. It is interesting to note that the calculated force constant parallells the energy of the Pd-Nu bond orbital. Thus, for the complexes predicted to undergo migration the force constant is  $27-31 \text{ eV}/\text{Å}^2$ , and for those predicted not to react in migration reactions the force constant is  $57-63 \text{ eV}/\text{Å}^2$ . The values of the force constants suggest that the complexes in entries 1-7would be able to undergo migration reactions, whereas complexes in entries 8-11 would not. Interestingly, peroxide complex 3 oxidizes olefins to ketones (eq 1),<sup>26</sup> and it was suggested that the reaction takes place via a cis migration of the peroxide from palladium to coordinated olefin, followed by decomposition to ketone. No stereochemical evidence was provided, but in view

$$R \sim CF_3COOPHOO-t-Bu \rightarrow R \sim CF_3COOPHO-1-Bu$$
 (1)  
 $R=n-C_2H_3 = 3 = 98\%$ 

of the fact that peracids cleave alkyl-platinum<sup>27a</sup> and allyl-pal-

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(25) (a) Methoxypalladation of the conjugated diene 2-methylene-6,6dimethylbicyclo[3.1.1]hept-3-ene has recently been reported to occur cis.<sup>15b</sup> This is a special strained diene and methoxypalladation of 1,3-cyclohexadiene, which is less strained, occurs trans.<sup>15c</sup> (b) Hosokawa, T.; Imada, Y.; Murahashi, S. I. *Tetrahedron Lett.* **1982**, *23*, 3373. (c) Bäckvall, J. E.; Nordberg, R. E.; Björkman, E. E.; Moberg, C. J. Chem. Soc., Chem. Commun. **1980**, 943.

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ladium<sup>27b</sup> bonds with retention of configuration at carbon, such a mechanism is quite likely. Also, reductive elimination of alkylpalladium cyanides to alkylcyanides with retention of configuration at carbon has been reported.<sup>28</sup>

The calculations suggest that migration of monodentate carbon coordinated  $\beta$ -diketonates is possible, whereas migration of bidentate O,O-coordinated  $\beta$ -diketonates is unlikely. The reason why only trans attack and no cis migration by these stabilized carbon nucleophiles has been observed in the addition of olefins<sup>29</sup> could be that the bidentate O,O-coordinated form is favored when they coordinate.<sup>30</sup>

In this and our earlier studies the ability of a coordinated nucleophile to undergo a migration reaction has been correlated with the bond strength between the nucleophile and the metal. The simplest way to get a measure of the bond strength has been to use the corresponding orbital energy and the harmonic force constant. A third measure of the bond strength is obtained from CASSCF<sup>5</sup> calculations. If the bonds are included in the active space it is expected that the bonding orbital of a strong bond will have a high occupation number. For this reason CASSCF calculations were performed with CH3-, F-, and OH- as ligands and the resulting occupation numbers are shown in Table IV together with the corresponding SCF force constants and orbital energies. As can be seen from Table IV there is a nearly perfect linear correlation between all these measures of the bond strengths for these three ligands, which gives some confidence to the use of any one of them in the present context.

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(30) Rearrangement of bidentate O,O-coordinated  $\beta$ -dicarbonyl palladium complexes to the corresponding monodentate C-coordinated form requires the addition of strongly coordinating ligands such as pyridine, triphenylphosphine, or dimethylamine: see ref 14 and 20 and references cited therein.

# Cation Binding Effect on Hydrogen Bonding

### Harold Basch,<sup>†</sup> M. Krauss,\* and W. J. Stevens

Contribution from the Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland 20899. Received January 22, 1985

Abstract: Cation binding effects on nearby H bonds are studied for the imidazole dimer. The binding of the cations,  $H^+$ ,  $Na^+$ ,  $Zn(OH)^+$ , and  $Zn^{2+}$ , is found to have a significant effect on both the H bond energy and the equilibrium internuclear separation of the H bond. The net stabilization energy ranges from 8.0 kcal for  $Na^+$  to 28.0 kcal for  $Zn^{2+}$ . The polarization of the dimer is also appropriate to increase the binding of another imidazole. Proton transfer is also studied for the dimer itself and the cation perturbed dimer. Double wells are found in all cases in the energy curve for proton transfer with a fixed N-N' distance between the imidazole monomers. With the exception of  $Zn^{2+}$  a substantial barrier is calculated for the proton transfer reaction. Compact effective potentials (CEP) were used in the calculations. Comparisons of the orbital energies and gradient optimized geometry of the CEP calculation for imidazole with a GTO 4-31G all-electron calculation are quite satisfactory.

#### I. Introduction

Metal cation binding to biomolecules is often an essential element in their function. In addition to the ion-multipole contribution to the intermolecule binding one of the consequences of the cation binding is the polarization of the attached ligands which strengthens the H bond. Rode has already noted that these polarization effects can alter the donor-acceptor interaction in hydrogen-bonded systems, influence the binding energies, and substantially alter the equilibrium geometry of the H bond.<sup>1-4</sup>

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