1544 *Inorg. Chem.* **1990**, *29*, 1544-1549

Contribution from the Département de chimie, Université de Montréal, C.P. 6128, Succursale A,
Montréal, Québec H3C 3J7, Canada, and Ecole Nationale Supérieure de Chimie,
8 rue de l'Ecole Normale, F-34075 Montpellier Cedex, France

Bis(phosphine)nickelacyclopentane: An Investigation by Local Spin Density Theory

Andrea Peluso,[†,‡] Dennis R. Salahub,*[,‡] and Annick Goursot*[,§]

Received December 28, 1988

We present here for the first time a self-consistent (local spin density) calculation of the electronic structure of a four-coordinated nickelacyclopentane complex (bis(phosphine)nickelacyclopentane). Three low-lying electronic configurations appear to be important for the chemistry of the complex, namely two ^1A singlets with square-planar and tetrahedral structures and a ^3B tetrahedral state, which might be responsible for a low-spin-high-spin equilibrium. Implications for the complex degradation pattern have been discussed in terms of these three states. The possibility of a square-planar-tetrahedral interconversion has been analyzed and its possible importance in the decomposition pathway discussed.

Introduction

Metallacycles are of current interest in modern organometallic chemistry. In fact members of this class of compounds have been observed as intermediates in a number of transition-metal-catalyzed reactions,[1-4] particularly cycloaddition of olefins and isomerization of strained carbocyclic rings. In many cases, they have been prepared as stable compounds that easily decompose, forming a large variety of organic products, including cycloalkanes, alkanes, and olefins. Actually, the reaction products depend both on the number of ligands coordinated to the metal atom and on their chemical nature, as well as on the metal involved in the complex.[1-8]

Metallacyclopentanes are among the most studied metallacycles; stable compounds of platinum,[5] palladium,[6] titanium,[7] and nickel[8] have been prepared and the products of thermal decomposition analyzed and identified. Among all of them, the (triphenylphosphine)nickelacyclopentane complexes appear to be very interesting, since they decompose in three different ways, illustrating many of the degradation features of the whole class.

In a series of communications, Grubbs and co-workers have reported that the complex can undergo a reductive elimination, leading to cyclobutane, a β-hybride elimination from which 1-butene is formed, or, finally, a C-C bond cleavage reaction, leading to two ethylene molecules. The relative composition of the reaction products depends strongly on the concentration of triphenylphosphine in solution. On the basis of this observation, they suggested that tri-, tetra-, and pentacoordinated complexes can be involved in a chemical equilibrium, the concentration of each species depending on the concentration of phosphine added.

For each complex, there is a dominant, though not exclusive, reaction channel as shown in Scheme I.

In an extensive theoretical study, Hoffmann and co-workers explored the relationships between geometry, coordination number, and degradation pathways of the three nickelacyclopentane complexes.[9] Using correlation diagrams,[10] they showed that reductive elimination of cyclobutane from a square-planar four-coordinated complex is symmetry-allowed, whereas formation of ethylene can take place from a distorted tetrahedral structure formed in going from the penta- to the tetracoordinated complex. Grubbs' rationalization of the whole degradation pattern has then been confirmed.

Although this work provided considerable insight, it was based on the extended Hückel (EH) method[11] (corrected for two-body repulsion[12]) and therefore could not address questions requiring evaluation of the total energies. Therefore, several relative energies of equilibrium states, as well as the barriers for interconversion, which are the most important parameters in describing a reaction pathway, had to be based on estimates. Furthermore, when the ligand-metal interactions are small, the HOMO-LUMO separation may also be small, and the activation energy for "allowed" and "forbidden" reactions may also be small, several reactions with similar activation energies but different symmetry requirements will compete.

Scheme I

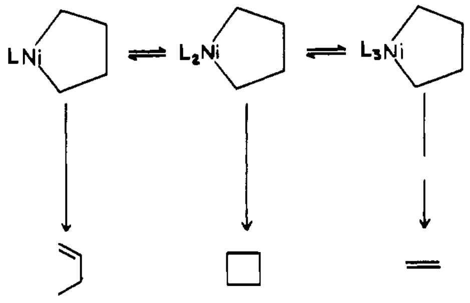

Table I. Model Potential Parameters for Ni^{16+} and P^{5+}

Ni^{16+} exponent	Ni^{16+} coeff	P^{5+} exponent	P^{5+} coeff
533.830	-1.336	86.90	-4.177
76.594	-3.079	84.44	-2.221
24.380	-6.161	1.773	-3.484
3.492	-1.270	1.249	-0.117
1.049	-0.153		

It is worthwhile therefore to undertake a more accurate evaluation of the relevant potential energy surfaces. Generating the "complete" surfaces for all relevant reactions is beyond the capabilities of presently available tools; however, we thought it interesting to use local spin-density functional theory to study a bis(phosphine) model of the bis(triphenylphosphine)nickel complex, which provides several key elements in understanding the overall degradation patterns.

[†] Permanent address: ENICHEM, Gruppo di ricerca sui material fotoaltrusi, via Medici del Vascello 26 A, 20100 Milano, Italy.

[‡] Université de Montréal.

[§] Ecole Nationale Supérieure de Chimie.

(1) Acton, N.; Roth, R. J.; Katz, T. J.; Franck, J. K.; Maier, C. A.; Paul, I. C. *J. Am. Chem. Soc.* **1972**, *94*, 5446.

(2) Casser, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515.

(3) Doyle, M. J.; McMeeking, J.; Binger, P. *J. Chem. Soc., Chem. Commun.* **1976**, 376.

(4) Grubbs, R. H.; Miyashita, A. *J. Organomet. Chem.* **1978**, *161*, 371; *J. Am. Chem. Soc.* **1978**, *100*, 7416, 7418.

(5) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4451; **1976**, *98*, 6521. Young, G. B.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978**, *100*, 5808.

(6) Diversi, P.; Ingrosso, G.; Lucherini, A. *J. Chem. Soc., Chem. Commun.* **1978**, 735.

(7) McDermott, J. X.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 947. McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529.

(8) (a) Grubbs, R. H.; Miyashita, A.; Liu, M. M.; Burk, P. L. *J. Am. Chem. Soc.* **1977**, *99*, 3863. (b) Grubbs, R. H.; Miyashita, A.; Liu, M. M.; Burk, P. L. *J. Am. Chem. Soc.* **1978**, *100*, 2418. (c) Grubbs, R. H.; Miyashita, A. *J. Am. Soc.* **1978**, *100*, 1300, 7416, 7418.

(9) McKinney, R. J.; Thorn, D. L.; Hoffmann, R.; Stockis, A. *J. Am. Chem. Soc.* **1981**, *103*, 2595.

(10) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

(11) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1963**, *36*, 2179, 3489; **1962**, *37*, 2872. Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(12) Anderson, A. B. *J. Chem. Phys.* **1975**, *62*, 1187.

0020-1669/90/1329-1544$02.50/0 © 1990 American Chemical Society

Table II. Atomic Core Orbital Basis Sets and Energies

Ni^{16+}

α	1s	2s	3s
1.083	-0.0067	0.0271	0.9377
3.891	0.0135	-0.2167	0.2545
13.970	-0.0232	-0.9260	-0.7124
50.156	0.2371	-0.0707	0.0544
180.068	0.5892	0.3036	0.1110
646.479	0.2437	0.0770	0.0329
2320.977	0.0882	0.0298	0.0105
ϵ	595.352	70.191	7.511

	α	2p
	8.737	0.3738
	28.213	0.5678
	91.106	0.1982
	294.200	0.0481
ϵ		61.308

P^{5+}

α	1s	2s
1.648	0.0458	-0.6898
5.956	0.0577	-0.5037
21.531	0.4201	0.2646
77.831	0.5115	0.1777
281.340	0.1538	0.0471
1016.976	0.0544	0.0145
ϵ	152.086	12.625

	α	2p
	1.470	0.348
	5.260	0.579
	18.823	0.238
	67.362	0.054
ϵ		9.119

Table III. Valence Basis Sets for Nickel and Phosphorus Atoms

	Ni		P	
	α	*c*	α	*c*
*n*s	255.00	-0.033	71.891	-0.0833
	13.22	0.151	27.211	0.406
	1.41	-0.420	8.298	0.242
	0.109	1.00	0.304	1.00
	0.038	1.00	0.107	1.00
*n*p	41.53	-0.328	27.33	0.038
	2.264	0.750	5.36	0.182
	0.693	0.307	0.337	1.00
	0.135	1.00	0.090	1.00
*n*d	26.87	0.080	0.340	1.00
	7.30	0.291		
	2.22	0.473		
	0.59	1.00		
	0.104	1.00		

Method and Computational Details

The computations were performed using the linear combinations of Gaussian-type orbitals-model core potential-Local Spin-Density (LCGTO-MCP-LSD) approach, which has been extensively described elsewhere.[13,14] The VWN potential was used.[15] For carbon and hydrogen atoms, all-electron basis sets were employed, whereas for nickel and phosphorus, only valence electrons were treated explicitly, core electrons being replaced by a model potential.[16] For the nickel atom, 16 electrons were included in the valence shell in order to treat explicitly the 3p-3d interactions. For phosphorus, only the five 3s and 3p electrons were included in the valence shell. Model potentials for both atoms have been optimized by following the usual procedure.[13-17] The pattern of the orbital basis set used in the computations is (521/41/1), (311/211/1*), (311/31/311), and (5) for carbon, phosphorus, nickel, and hydrogen respectively. As usual, the numbers in parentheses represent the primitive GTOs within each contraction, slashes separate contractions with different angular momentum, and the star indicates a polarization function.

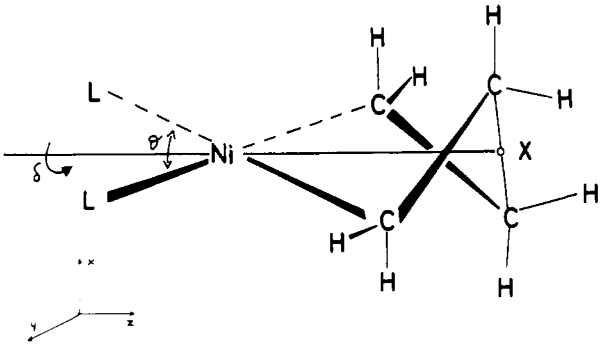

Figure 1. Structure of bis(phosphine)nickelacyclopentane.

All parameters concerning basis sets, model potentials, and auxiliary basis sets, necessary to fit the density and exchange-correlation potential, are given in Tables I-IV. The quality of the basis set and model potential has been tested in molecular calculations. For P_2 we obtain R_e = 1.87 Å (1.89 Å experimental (see ref 18) and 1.808 Å for an STO-3G calculation and 1.949 Å for a 44-31G calculation[18]), ω_e = 786 cm^{-1} (780 cm^{-1} experimental). For PH_3, our calculations yield a bond length of 1.41 Å (1.41 Å experimental, 1.378 Å (STO-3G), 1.438 Å (44-31G) and an angle of 94.0° (93.4° experimental, 95.01° (STO-3G), 95.52° (44-31G). The accurate geometries and spectroscopic constants as well as the negligible influence of the basis-set superposition error (BSSE) are indicative of the high quality of the basis set and model potential. The only remark to be made concerns the importance of adding a d function to the phosphorus orbital basis set; without this function, the computed bond distance in the P_2 molecule goes up to 1.95 Å.

In the same way, the model potential of the nickel atom has been tested on Ni_2 and NiH diatomics. The interpretation of the results and comparisons with experiments are not as straightforward as for P_2 and PH_3, because of the large number of low-lying states, and go beyond the purpose of this paper. The results will be presented elsewhere.[19a] The same parameters have recently been used in a study[19b,c] of carbon atom chemisorption on nickel clusters with highly satisfactory results for the geometry and vibrational frequency.

Results and Discussion

1. The Square-Planar Tetracoordinate Complex. No experimental data concerning the structure of the four-coordinate Ni complex are available in the literature. We therefore began our study by computing the equilibrium geometry. Because of the large size of the molecule and also the fact that our computer programs do not yet allow an automatic optimization of the geometry, we could not perform a full geometry optimization and we had to limit the number of degrees of freedom to be optimized. Following McKinney et al.,[9] we kept the bond distances and valence angles for the carbon skeleton frozen at their standard values (r_{CC} = 1.54 Å, r_{CH} = 1.10 Å, $\alpha_{CCC} = \alpha_{HCH}$ = 109.47°).

We used our optimized parameters for the phosphine groups, which, in the computations, replace the triphenylphosphine groups of the real system. In the end, 4 degrees of freedom have been optimized, namely the Ni-P and Ni-C bond distances, the valence angle between the two phosphine groups, and the dihedral angle between the plane containing the nickel and the two phosphorus atoms and that containing the nickel and the two carbons nearest to it (see Figure 1).

Although the number of degrees of freedom has been drastically reduced, the problem of finding the optimum geometry remains a challenge, especially because of the presence of the nickel atom.

---

(13) Andzelm, J.; Radzio, E.; Salahub, D. R. *J. Chem. Phys.* **1985**, *83*, 4573; *J. Comput. Chem.* **1985**, *6*, 520.

(14) Salahub, D. R. *Adv. Chem. Phys.* **1987**, *69*, 447. Salahub, D. R. In *Applied Quantum Chemistry*; Smith, V. H., Jr., Schaefer, H. F., III, Morokuma, K., Eds.; Reidel, Dordrecht, The Netherlands, 1986; p 185.

(15) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(16) Sakai, Y.; Huzinaga, S. *J. Chem. Phys.* **1982**, *76*, 2537, 2552.

(17) Huzinaga, S., Andzelm, J., Klobukowski, M., Radzio-Andzelm, E., Sakai, Y., Tatewaki, H. *Gaussian Basis Sets for Molecular Calculations*; Elsevier, New York, 1984.

(18) Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976**, *64*, 5142.

(19) (a) Fournier, R. Ph.D. Thesis, Université de Montrēal, 1989. (b) Fournier, R.; Andzelm, J.; Goursot, A.; Russo, N.; Salahub, D. R. submitted for publication in *J. Chem. Phys.* (c) Chiarello, G.; Andzelm, J.; Fournier, R.; Russo, N.; Salahub, D. R. *Surf. Sci. Lett.* **1988**, *202*, L621.

Table IV. Auxiliary Basis Set for the Fit of Charge Density and Exchange Correlation Potential

Ni	charge density							
	s functions	160.0	42.0	11.0	3.0	0.820	0.220	0.060
	p functions	4.80	1.40	0.30				
	d functions	11.0	3.60	0.720	0.25			
Ni	exchange corr							
	s functions	146	41.0	12.0	3.30	0.90	0.26	0.04
	p functions	2.20	0.5	0.11				
	d functions	4.60	0.79	0.10				
P	charge density							
	s functions	143.78	5.44	1.66	0.608	0.213		
	p functions	1.66	0.608	0.214				
	d functions	1.66	0.608	0.214				
P	exchange corr							
	s functions	47.92	1.81	0.55	0.202	0.071		
	p functions	0.55	0.203	0.071				
	d functions	0.55	0.203	0.071				

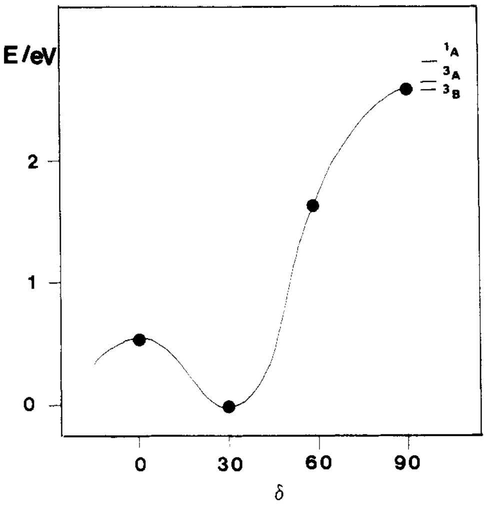

Figure 2. Energy of bis(phosphine)nickelacyclopentane vs the PNiP-C-NiC dihedral angle, δ (see Figure 1 for definition), for θ (the PNiP bond angle) equal to 93°, in the ^{1}A ($17a^2$, $15b^2$) configuration. The ^{3}B (17a, 16b) and ^{3}A (15b, 16b) states are shown for comparison (see text).

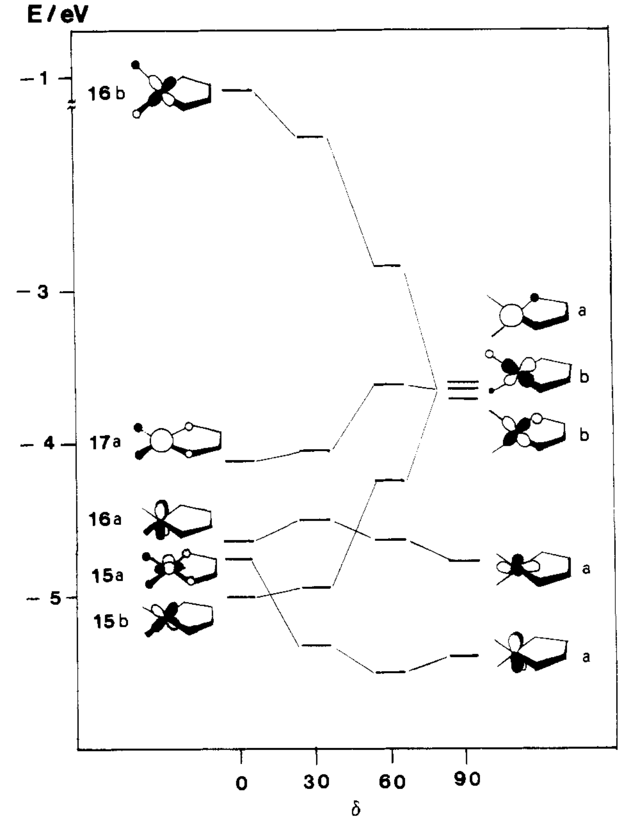

Figure 3. Orbital energies of bis(phosphine)nickelacyclopentane as a function of the PNiP-CNiC dihedral angle, δ, for θ (the PNiP bond angle) equal to 90°.

In fact, apart from the usual difficulties that arise in dealing with transition-metal atoms, the d levels of the nickel are tremendously sensitive to the geometry of the whole complex, so several stable geometries with different electronic configurations may exist. An example of this peculiar behavior of the nickel atom is in the very easy equilibrium between a low-spin square-planar and a high-spin, tetrahedral-like structure shown by many d^8 nickel complexes.[20-23]

In the light of the EH results of McKinney et al.,[9] we start from a conformation with dihedral angle equal to zero and we optimize the Ni-P and Ni-C bond distances. In this step the valence angle between the two phosphine groups is kept constant, being fixed around 90° degrees for steric reasons. The results of this first optimization compare reasonably with the X-ray values for related compounds.[24,25] We find the Ni-C and Ni-P bond distances to be 2.02 and 2.1 Å, respectively, with respect to the values 1.96 and 2.18 Å obtained by X-ray analysis for the $(C_3H_4)Ni[P(Ph)_3]_2C_2H_4$ complex.

In a second step, with the optimized bond distances kept fixed, we allow the two phosphine groups to rotate out of plane until the tetrahedral structure has been reached. C_2 symmetry is retained throughout. In Figure 2, we show the potential energy for this *rigid* rotation with $\theta = 93°$ and the electronic configuration of the square-planar ground state (^{1}A ($17a^2$, $15b^2$)). For $\delta = 90°$, the energies of two other low-lying states (^{3}B (17a, 16b) and ^{3}A (15b, 16b)) are also shown and illustrate the changes of configuration discussed further below. The orbital correlation diagram is sketched in Figure 3. The minimum energy corresponds to a distorted square-planar configuration, the optimum dihedral angle being about 30°. This is not a completely novel picture since some degree of distortion from planarity has been found in analogous compounds too. The complex cited previously, for instance, has a crystal structure in which the distortion from planarity is about 10°. However, in this case a sort of C-C bridge, which joins the two phosphine groups, prevents the angle from opening, which should be important in lowering the energy of a distorted structure. Therefore, the equilibrium configuration obtained by the optimization of the dihedral angle seems to us not unreasonable and besides suggests that the whole region between square planar and tetrahedral conformations has to be analyzed more deeply.

Before coming to this point, we briefly analyze the nature of electronic interactions between ligands and the central atom. A

---

(20) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley-Interscience: New York 1988.

(21) Holm, R. H. *Acc. Chem. Res.* **1969**, *2*, 307. Gerlach, D. H.; Holm, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 3457.

(22) McGarvey, J. J.; Wilson, J. *J. Am. Chem. Soc.* **1975**, *97*, 2531.

(23) Lohr, L. L., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 1093. (b) Lohr, L. L.; Grimmelmann, E. K. *J. Am. Soc.* **1978**, *100*, 1100.

(24) Jolly, P. W.; Kruger, C.; Salz, R.; Sakutowsky, J. C. *J. Organomet. Chem.* **1979**, *165*, C39.

(25) Fereday, R. J.; Hathaway, B. J.; Dudley, R. J. *J. Chem. Soc. A* **1970**, 571; Sacconi, L.; Bertini, I.; Mani, F. *Inorg. Chem.* **1967**, *6*, 262.

Table V. Main Character of the Upper Valence MOs of $(PH_3)_2Ni(C_4H_8)$ at $\delta = 0°$ and Rigidly Rotated to $\delta = 90°$[a]

level	$\delta = 0$	$\delta = 90°$
16b	a(d_{yz} – C,P)	a(d_{yz} – C)
17a	b(s,d_{yz} – C) a(d_y2 – C) b(d_y2 – P) a(s,d_z2 – P)	b(s,d_x2 – C) a(s,d_x2 – P)
16a	nb(d_{xy})	a(d_z2 – C)
15a	b(d_y2 – C) a(d_y2 – P)	nb(d_{xy})
15b	nb(d_{xz})	a(d_{xz} – P)
14a	a(d_z2 – C) b(d_z2 – C)	b(d_y2 – C)
14b	b(d_{yz} – C) a(d_{yz} – P)	b(d_{yz} –C)

[a] See Figure 1 for definition of angles and axes. The letter b signifies a bonding interaction between the orbitals or lobes indicated, the letter a an antibonding interaction, and nb a nonbonding orbital.

helpful tool in doing that is provided by Mulliken population analysis, even though this method is sometimes questionable, especially when diffuse and polarization functions are included in the basis set. For the sake of simplicity, we only give a general outline for a few of the highest occupied and the first unoccupied MOs in Figure 3. The main character of the levels at $\delta = 0$ and $\delta = 190$ is given in Table V. The most important remarks are as follows:

The square-planar complex appears to belong to the class of "classical complexes" (see e.g. ref 30 and 31), the strongest interactions being between orbitals of "σ" symmetry. The HOMO level (17a) is an example of this behavior.

We do not find any clear evidence of "π" interactions, which often in such complexes appear to be the driving force in the stabilization of the square-planar configuration with respect to the tetrahedral one.[29]

Finally, it is interesting to observe the rapid decrease in energy of the 15a level (Figure 3), which is probably responsible for the distorted structure of the square-planar form. This level is mainly due to the overlap of the metal $d_{y^2-z^2}$ orbital, with a small contribution from the d_{xy} orbitals, with the s–p_z orbitals of the carbon and phosphorus atoms. The interaction is bonding as concerns Ni–C and antibonding for Ni–P. When the phosphine groups are rotated 30° out of the plane, the antibonding character of this level decreases and is nearly balanced by the bonding overlap between the s–p_z orbitals of the phosphorus with d_{xy} of the metal atom. Further increasing δ leads to a strong destablization of the 17a and especially the 15b orbital, as antibonding Ni–P interactions increase.

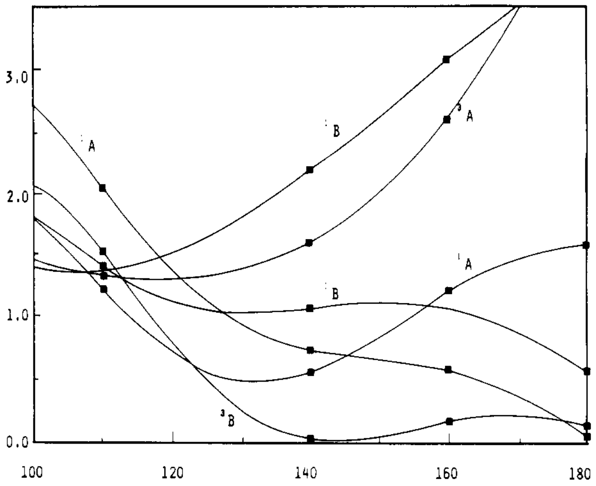

Figure 4. Energy of bis(phosphine)nickelacyclopentane vs θ (the PNiP bond angle) for various states, for $\delta = 90°$.

2. The Tetrahedral Complex. The energy difference between the square-planar form and the tetrahedral one is of the order of 65 kcal/mol in favor of the former, when only a rigid change of the dihedral angle is allowed. This value might suggest that the tetrahedral form is a high-energy conformer and therefore would not play any role in the chemistry of the complex, as is the case for other nickel complexes such as the trialkylphosphine class.[26] However, there is much evidence, both experimental and theoretical, that would suggest that a deeper analysis is required. First of all, it seems now well established that the arylphosphines always favor tetrahedral geometry, whereas replacement of aryl with alkyl groups stabilizes the planar form.[27,28] Also, the stabilization of the square-planar compound has been interpreted as being due to π NiP interactions.[29] The presence of the phenyl groups reduces this interaction by reducing the π-acceptor capacity of the phosphorus atom.[27]

In our study, we have found only slight evidence for the presence of NiP π interactions. Therefore, if this were really the leading reason for the stability of the planar form, we are in a case where square-planar and tetrahedral conformers might both exist in equilibrium. We have therefore searched for a more stable minimum in the tetrahedral-like conformation.

Now the situation is much more complicated than for the square-planar form. For the latter the HOMO–LUMO separation is about 3 eV, whereas, for the tetrahedral form, three levels are very near each other, within a range of 0.2 eV, and only four electrons are to be placed in them. (For the energy level scheme, refer to Figure 3.) From such a structure, nine different electronic configurations can arise, six singlets and three triplets; the energy of each state can strongly depend on the value of the PNiP valence angle.[9] We have therefore computed the potential energy profile for the variation of the angle θ (Figure 1), keeping fixed the bond distances at the optimized values of the square-planar form. Results are shown in Figure 4 for the six lowest states, two triplets and four singlets.

The lowest state is a ^{3}B with configuration ($15b^2$, $17a^1$, $16b^1$), which shows a broad minimum around $\theta = 140°$. ^{1}A, which corresponds to the square-planar ground state ($17a^2$, $15b^2$), is stabilized by angle opening too, having a minimum for $\theta \approx 130°$, but as already shown by McKinney et al.,[9] another ^{1}A state with configuration ($16a^2$, $16b^2$) becomes the more stable singlet for $\theta = 180°$. The ^{3}B and the latter ^{1}A states are further stabilized by shortening the Ni–C distances. This distance has been optimized roughly (a three-point computation) only for the electronic configuration of interest. The results are only slightly different from those presented in Figure 4. The potential energy profiles for the triplet state has a minimum for $\theta = 160°$. The minimum of the ^{1}A state is also shifted toward a smaller value of θ, 170°, and in fact, it becomes the lowest in energy, its energy being lower than that of the ^{3}B configuration for θ values in the region 160–180°. The other ^{1}A singlet remains practically unchanged.

However, some caution is needed since a full optimization of Ni–P and Ni–C bond distances for each value of θ has not been performed. Therefore, in the discussion of the degradation pathway, we think it to be more appropriate to use those results

---

(26) Vanquickenborne, L. G.; Ceulemans, A.; Beyens, D.; McGarvey, J. J. *J. Phys. Chem.* **1982**, *86*, 494.

(27) Que, L., Jr.; Pignolet, L. H. *Inorg. Chem.* **1973**, *12*, 156.

(28) Browing, M. C.; Mellor, J. R.; Morgan, D. J.; Pratt, S. A. J.; Sutton, L. E.; Venanzi, L. M. *J. Chem. Soc.* **1962**, 693. Stone, P. J.; Dori, Z. *Inorg. Chim. Acta* **1971**, *5*, 434. Shupack, S. I. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2418. Hayter, R. G.; Huniec, F. S. *Inorg. Chem.* **1965**, *4*, 1701.

(29) Pignolet, L. H.; Horrocks, D. W., Jr.; Holm, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 1855.

(30) Veillard, A.; Demuynck, J. In *Modern Theoretical Chemistry*; Schafer, H. F., Ed.; Plenum Press: New York, 1977; Vol. 4.

(31) Mingos, D. M. P. *Adv. Organomet. Chem.* **1977**, *15*, 1.

(32) Akermark, B.; Ljungqvist, A. *J. Organomet. Chem.* **1979**, *182*, 59.

for which these distances were kept fixed, keeping in mind that changes in the bond distances will likely only provoke changes of a few kilocalories per mole in the relative energies and slightly shift the minimum positions. Those changes might be important if one is seeking the absolute minimum and its geometry, but, in our opinion, are not so crucial in the qualitative discussion of the degradation pathway of the complex.

The final scheme can be summarized as follows:

state	electr config	nuclear structure	relative energy, eV
^{1}A	$(17a)^2(15b)^2$	quasiplanar $\delta = 30°$ $\theta = 90°$	0.0
^{1}A	$(17a)^2(15b)^2$	tetrahedral $\delta = 90°$ $\theta = 140°$	1.5
^{1}A	$(16a)^2(16b)^2$	tetrahedral $\delta = 90°$ $\theta = 180°$	1.0
^{3}B	$(17a)^1(16b)^1$	tetrahedral $\delta = 90°$ $\theta = 140°$	0.98

We will return to these energies in the discussion of the degradation pathway.

The orbital scheme for the tetrahedral configuration ($\delta = 90°$, $\theta = 110°$) is shown in Figure 3. As already mentioned, three levels lie very near each other in energy: 15b, 16b, and 17a. The 16b level is roughly due to an antibonding interaction between the d_{yz} orbital of the nickel with the p_y and p_z orbitals of the carbon (*yz* being the C–Ni–C plane (Figure 1)). This level should not be influenced too much by the P–Ni–P angle opening. On the contrary, the 15b level, roughly due to the antibonding interaction of the nickel d_{xz} orbital with the s–p orbitals of the phosphorous atoms, will be strongly stabilized by angle opening and is therefore responsible for the structure of the lowest tetrahedral states, ^{1}A and ^{3}B, in both of which it is doubly occupied. The last level, 17a, is mainly the 4s orbital of the nickel with minor contribution of d_{x^2}, d_{y^2}, and d_{z^2}. Owing to its roughly spherical symmetry, it should be essentially unchanged by P–Ni–P angle opening.

3. Degradation Pathway and the Singlet–Triplet Equilibrium. Our results fully confirm the general orbital-filling and symmetry arguments already suggested as a basis for the discussion of the degradation pathway.[8,9] Simple symmetry correlation rules indicate that the square-planar singlet, with configuration $(17a)^2(15b)^2$, which we found to be the most stable, leads to reductive elimination with formation of cyclobutane.

As concerns the production of ethylene, Grubbs[8c] suggested that it is more reasonable to assume that the tris complex loses a phosphine group prior to carbon–carbon bond cleavage. The intermediate species formed cannot be the square-planar form, since it degrades only into cyclobutane,[8c] and therefore could be the large angle tetrahedral complex, already predicted by EH, which we find to be among the most stable tetrahedral conformers.

However, in our opinion, at least two questions remain open. First of all, in our calculations, we have replaced the triphenylphosphine groups of the Grubbs experimental work with the more simple phosphine, electronically similar but certainly not sterically appropriate. Therefore, it must be taken in to consideration the chance that steric hindrance might favor a tetrahedral configuration.[27,28] Is it then possible that both ethylene and cyclobutane are formed from the tetrahedral conformation?

As clearly pointed out by McKinney et al., both cyclobutane and ethylene formation require that an electron pair be transferred to the metal atom; in the case of cyclobutane formation, the electron pair must be transferred into an orbital of b symmetry of the metal fragment, whereas ethylene formation requires that an orbital of a symmetry be empty. Our computations confirm that both cyclobutane and ethylene might be formed from a tetrahedral precursor: cyclobutane from the ^{1}A state with configuration $(17a)^2(15b)^2$ and ethylene from the other ^{1}A state, $(16a)^2(16b)^2$, the latter being more stable than the former by about 0.5 eV.

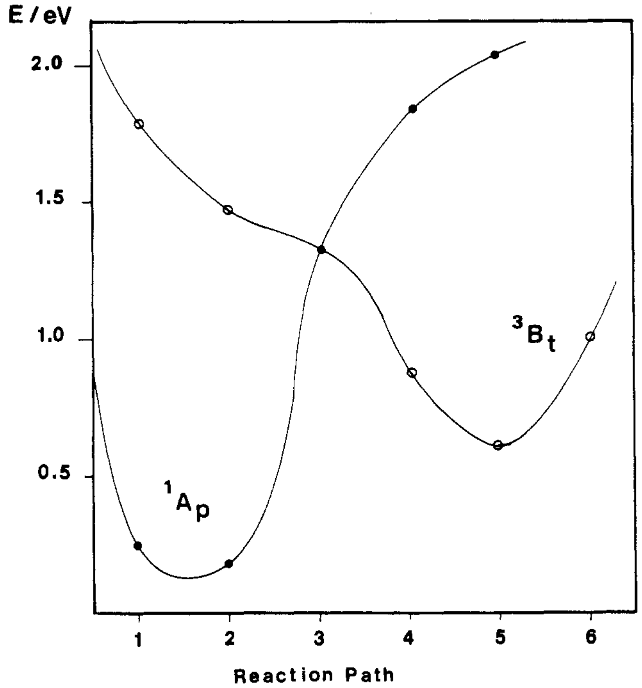

Figure 5. Energy of bis(phosphine)nickelacyclopentane along the "reaction path" described in the text.

If we admit that steric hindrance of the real system will raise the relative energy of the square-planar complex by, e.g., 10–20 kcal/mol, then the question is the following: Is the tetrahedral structure formed from the pentacoordinate complex, as suggested by McKinney et al.,[9] or can a direct isomerization take place? This problem is to some extent related to the well-known puzzle of the low-spin-singlet–high-spin-triplet interconversion in d^8 nickel complexes, which is often surprisingly rapid, considering that it involves both changes in spin multiplicity and a significant change in geometry. In a simple application of Woodward–Hoffmann arguments, Eaton[33] suggested that the process is fast simply because it is symmetry-allowed. In a more detailed analysis, Whitesides[34] showed that the process is not allowed, since the ground state of the square-planar form cannot correlate with the ground state of the tetrahedral form, the same conclusion as in Holm's studies.[35] More recently, Lohr has tried to explain the fast kinetics of equilibration assuming that interconversion proceeds by a "twisting motion" without breaking any bond.[23] He computed the potential energy surface for both singlet and triplet by using a crystal field model. The barriers for interconversion are always quite high, not less than 45 kcal/mol, whereas experiments would suggest values around 10 kcal/mol.[23b]

We therefore thought it of interest to verify whether the square-planar–tetrahedral isomerization might not occur via a concerted motion, without passing through the pentacoordinated complex. We have tried to compute a rough "minimum interconversion path" joining the two conformers. The problem is now very delicate since we have learned that the total energies of different electronic configurations are very sensitive to geometrical parameters with the exception perhaps of the Ni–P bond distance. Owing to the fact that we cannot perform a full optimization of the geometry, we had to limit our search for the minimum interconversion path to a few points for the dihedral angle in the range 30–70 degrees. The energy profile is shown in Figure 5, which displays the energy curves of ^1A_P and ^3B_T as a function of the three optimized parameters (r_{Ni-X}, δ, θ). Each set of these values gives one point of the so-called "reaction path". If one starts from the first point ($r_{Ni-X} = 2.65$ Å, $\delta = 30°$, $\theta = 90°$), it turns out that, after δ is increased to 45°, the opening of θ up to 120°

---

(33) Eaton, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 4272.
(34) Whitesides, T. H. *J. Am. Chem. Soc.* **1969**, *91*, 2396.
(35) Holm, R. H. *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975.

lowers the energy of ${}^1A_P$ to almost the same as at the equilibrium point at $\delta = 30°$ (point 2). Then, if θ is kept at 120° and the phosphine groups are turned 60° out of the CNiC plane, intersystem crossing takes place. When the Ni–C distance is decreased to 2.55 Å, the energy of the ${}^3B$ state is similar to the energy of the ${}^1A$ state (point 3). The next step is to increase δ to 90°. This value being kept constant, Ni–C is decreased to 2.50 Å and θ opened to 140° (point 4) and then to 160°, where the energy of the triplet reaches its minimum (point 5). The next point describes $\delta = 180°$, all other parameters being constant. (The value of the barrier to interconversion is $\approx$25 kcal/mol.) This is, of course, only a rough path and a more concerted motion might lower the barrier considerably. Although it is still quite large, we believe that this raises the possibility that an isomerization, perhaps solvent controlled, may take place, especially if steric effects are also taken into consideration. In fact, the experimental results[8] are not inconsistent with a possible interconversion between the planar and tetrahedral forms. Indeed, they show that cyclobutane, generated from square-planar forms, is the major product of thermal decomposition of various $(R_3P)_2NiC_4H_8$ complexes, in toluene, at 9 °C. However, it must be kept in mind that (i) the routes of decomposition vary with varying R (methyl, phenyl, cyclohexyl, or a chelating system), (ii) there is always a small amount (6–15%) of ethylene in the gaseous products, with the exception of the rigid planar compound where $(R_3P)_2$ is a bidentate system, (iii) the thermal decomposition is particularly susceptible to the nature of the solvent (6% ethylene in toluene, 16% in acetonitrile, and 72% in pyridine, for R = phenyl), and (iv) photochemical decomposition always yields an increased amount of ethylene. More experimental data and calculations are necessary to clarify this aspect further. At a minimum, the result underlines the necessity, for this type of process, of including motions more complex than the simple "rigid" displacements that first come to mind.

Concluding Remarks

The orbital diagrams and, in fact, the energetics, resulting from our local density functional calculations, are to a large extent consistent with the EH analysis of ref 9. The sole point where we would propose a possible alternative has to do with the facility of interconversion of the square-planar and tetrahedral forms of $(PH_3)_2NiC_4H_8$. We believe it may be possible to find a pathway of lower energy than usually assumed, which does not involve breaking Ni–P bonds. This could then lead to the possibility of forming (some) ethylene, in addition to cyclobutane, without necessitating the decomposition of a tris(triphenylphosphine) complex. A more detailed computational verification, in a reasonable manner, will require the use of analytical gradient techniques, which are currently under development.[36]

Acknowledgment. We are grateful to the NSERC (Canada), to the Fonds FCAR (Quebec), and to the France–Québec exchange program for financial support and to the Centre de Calcul de l'Université de Montréal and NSERC's Supercomputing Access program for computational resources. Help with the manuscript from René Fournier, Alain Rochefort, and Alain St-Amant is much appreciated.

---

(36) Fournier, R.; Andzelm, J.; Salahub, D. R. *J. Chem. Phys.* **1990**, *90*, 6371.

Contribution from the Departamento de Química,
Universidade de Coimbra, 3049 Coimbra, Portugal

Electron Transfer from Halide Ions to UO_2^{2+} Excited-State Ions in Aqueous Solution: Formation and Decay of Dihalide Radical Anions

Hugh D. Burrows

Received August 15, 1989

The decay of the excited uranyl ion in water in the presence of Cl^-, Br^-, I^-, and SCN^- is studied by laser flash kinetic spectrophotometry. The four anions all quench $^*UO_2^{2+}$ by a bimolecular process suggested to involve electron or charge transfer. Steady-state luminescence studies suggest that there is also some static contribution to the quenching. For Br^-, I^-, and SCN^-, radical anions, $X_2^{\bullet-}$, are observed. However, kinetic studies indicate that these are not formed directly from $^*UO_2^{2+}$ but probably come by bimolecular reaction of an intermediate uranium(V)/radical pair with the corresponding halide ion. The extinction coefficient for the $^*UO_2^{2+}$ absorption is reported, and by use of this and transient absorbance data radical-anion yields are obtained and found to depend linearly upon the halide anion concentration. The variation of the yield in the series I^-, SCN^-, and Br^- is interpreted in terms of the effect of overall free energy change on back-electron-transfer in the uranium(V)/radical pair. With the chloride system no significant yield of radical anion was observed. The decay of $X_2^{\bullet-}$ was found to be unaffected by the presence of uranyl ion, supporting the previously suggested mechanism for radical-anion decay in these systems.

The excited uranyl ion, $^*UO_2^{2+}$, is a powerful oxidant, with an estimated standard electrode potential of $E° = +2.5–2.7$ V.[1-3] It has long been known[4-7] that the halide ions, with the exception of F^-, and other polarizable anions such as SCN^- are effective quenchers of the green luminescence of the uranyl ion, and this effect has found application in eliminating interferences from luminescence in Raman spectral studies on this species. A number of studies on the quenching process have been reported using both dynamic and steady-state luminescence quenching,[8-10] and the general consensus is that the dominant mechanism involves an electron-transfer reaction from the halide to excited uranyl ion.[6,8-10] However, only with the uranyl iodide system is any permanent change observed on photolysis.[11,12] In all of these systems, except

---

(1) Burrows, H. D.; Formosinho, S. J.; Miguel, M. G. M.; Pinto Coelho, F. *Mem. Acad. Cienc., Lisboa* **1976**, *19*, 185.
(2) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.
(3) Jørgensen, C. K.; Reisfeld, R. *Struct. Bonding (Berlin)* **1982**, *50*, 121.
(4) Perrin, F. *C. R. Hebd. Seances Acad. Sci.* **1926**, *182*, 929.
(5) Volmar, Y. *Arch. Phys. Biol.* **1928**, *6*, 61.
(6) Weiss, J. *Trans. Faraday Soc.* **1938**, *34*, 451.
(7) Sill, C. W.; Peterson, H. E. *Ind. Eng. Chem., Anal. Ed.* **1947**, *19*, 646.
(8) Matsushima, R.; Fujimori, H.; Sakuraba, S. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 1702.
(9) Yokoyama, Y.; Moriyasu, M.; Ikeda, S. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1329.
(10) Romanovskaya, G. I.; Atabekyan, L. S.; Chibisov, A. K. *Theor. Exp. Chem. (Engl. Transl.)* **1981**, *17*, 221.
(11) Rabinowitch, E.; Belford, R. L. *Spectroscopy and Photochemistry of Uranyl Compounds*; Macmillan: New York, 1964.
(12) Wan, J. K. S.; Schuck, E. A.; Foote, J. K.; Pitts, J. W. *Can. J. Chem.* **1964**, *42*, 2029.

0020-1669/90/1329-1549$02.50/0