Kinetics and Catalysis, Vol. 41, No. 1, 2000, pp. 33–37. Translated from Kinetika i Kataliz, Vol. 41, No. 1, 2000, pp. 40–45.

Structure of Products of H–H and C–H Bond Activation by Ni atom, Ni_2 Cluster, and Ni–Porphyrin Complex of Ni_2 Cluster

V. M. Mamaev, I. P. Gloriozov, D. A. Lemenovskii, and E. V. Zernova

Department of Chemistry, Moscow State University, Vorob'evy gory, Moscow, 119899 Russia

Received July 2, 1998

Abstract—New catalytic systems based on porphyrin complexes of Ni_2 cluster and capable of activating C–H and H–H bonds are proposed. DFT calculations showed that a Ni_2 cluster can coordinate Ni–porphyrin with a considerable gain in energy. The structures of the products of methane and hydrogen activation were discussed.

INTRODUCTION

The design of catalytic cycles for the selective conversion of alkanes is one of the most important chemical problems. The processes of H–H, C–H, and C–C bond activation are considered as the key steps in the mechanisms occurring in these catalytic systems [1–5]. According to experimental data, transition metal complexes in solutions [6–8], metal surfaces [9, 10], or atoms and clusters in the gas phase [11, 12] may efficiently activate these bonds.

In the first case, with an increase in temperature or as a result of photolysis, one of the weakly bound ligands is eliminated from a complex; and a coordinately unsaturated intermediate is formed, which is capable of activating the oxidative addition reactions of hydrogen or alkanes. These reactions occur with an activation barrier. An increase in the electron density on a metal atom favors the occurrence of these reactions, and bimetallic complexes react with hydrogen and alkanes at rates that are substantially larger than those for mononuclear complexes [7].

The dissociative chemisorption of methane on a metal surface requires the overcoming of the activation barrier. Chemisorption can be induced by temperature, which should be increased to ~1000 K [10, 13–16], or by collisions of adsorbed methane with the beam of neutral argon atoms. Collision-induced activation of the C–H bond in methane on the Ni(111) single-crystal surface was reported in [10]. According to experimental data, the metal-cluster region of a metal surface exhibits the highest catalytic activity [17]. In this region, a multicentered bond of the cluster with metal atoms and alkyl fragments can be formed.

In many cases, the processes of H–H and C–H bond activation by transition metal clusters in the gas phase occurs without an activation barrier [18, 19], which is contrasting to the activation by the corresponding atoms [20, 21]. Evidently, clusters and atoms of metals exhibit a higher catalytic activity than complexes of these metals. At the same time, contrary to metal complexes, clusters are unstable in the gas phase; they are formed before the activation process under the powerful irradiation of the metal surface [12]. The instability of atoms and clusters in the gas phase is unfavorable for the preparation of catalytic systems on their basis.

Several recent experimental findings show the possibility for forming stable cluster complexes based on sandwich-like compounds with phenyl ligands [22–24]. In these compounds, coordinately saturated clusters of transition metals form multicentered bonds with carbon atoms of phenyl rings.

In our opinion, a model of a metal-cluster surface may be created on the basis of the macrocyclic molecular structure of metalloporphyrins.

In the preceding paper [25], we showed that Ni and Pd atoms form relatively stable compounds with Ni–porphyrin (NiPn), and the Ni_2–porphyrin complex is capable of activating the H–H bond. In this work, we studied the structures of the products of H–H and C–H bond activation by the Ni atom, Ni_2 cluster, and a complex formed by Ni–porphyrin and Ni_2 cluster bound to carbon atoms of the macrocyclic system:

$$Ni + Ni \longrightarrow Ni\text{–}Ni, \quad (I)$$

$$Ni + H_2 \longrightarrow NiH_2, \quad (II)$$

$$Ni + CH_4 \longrightarrow HNiCH_3, \quad (III)$$

$$Ni_2 + H_2 \longrightarrow Ni_2H_2, \quad (IV)$$

$$Ni_2 + CH_4 \longrightarrow HNi_2CH_3, \quad (V)$$

$$NiPn + Ni \longrightarrow Ni\text{–}NiPn, \quad (VI)$$

$$Ni\text{–}NiPn + H_2 \longrightarrow H_2Ni\text{–}NiPn, \quad (VII)$$

$$NiPn + Ni_2 \longrightarrow NiPnNi_2, \quad (VIII)$$

$$NiPnNi_2 + H_2 \longrightarrow NiPnNi_2H_2, \quad (IX)$$

$$NiPnNi_2 + CH_4 \longrightarrow NiPnHNi_2CH_3. \quad (X)$$

0023-1584/00/4101-0033$25.00 © 2000 MAIK "Nauka/Interperiodica"

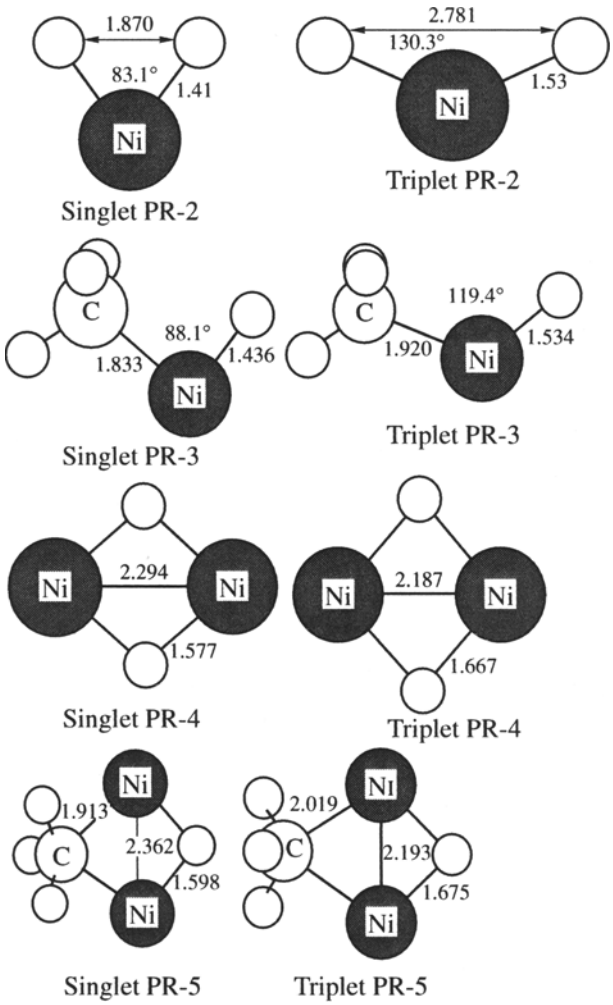

Fig. 1. Structures of the products of reactions (II)–(V) (bond lengths are in Å).

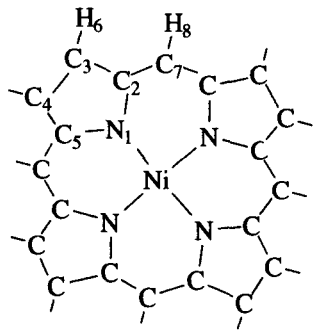

Fig. 2. Enumeration of atoms in a Ni–porphyrin molecule.

CALCULATION METHOD

Calculations were carried out by the density functional method (DFT) that has recently showed a good performance in quantum-chemical studies of metal complexes, particularly metalloporphyrins [25–27]. We used an efficient computer program [28], which has an important advantage that it enables the use of the approximate representation of Coulomb and exchange–correlation energy components by expanding the electron density in the auxiliary basis. This approximation substantially reduces calculation time for large molecular systems (~100 atoms) [28]. In all our calculations, we used the generalized gradient approximation based on first principles [29]. A high efficiency of the computer program allowed us to use large atomic basis sets of contracted Gaussian functions provided by the author of the program. The following basis sets were used: {311/1} for H, {611111/411/11} for C, N, and O, and {711111111111/511111111/5111} for Ni. The auxiliary basis sets were used for the representation of electron density and consisted of the ungrouped Gaussian functions (5*s*1*p*) for H, (10*s*3*p*3*d*1*f*) for C, N, and O, and (18*s*6*p*6*d*5*f*5*g*) for Ni.

RESULTS OF CALCULATION

The geometry of the products of reactions (I)–(X) were carried out with complete optimization. Tables 1–3 and Figs. 1–3 present the geometries and relative energies for the products of reactions (I)–(X). According to our calculations, the singlet product of reaction (II) (PR-2, Fig. 1) is 12.9 kcal/mol more stable than the triplet product. Earlier in [30], the structure of this product was studied by the complete active space SCF (CASSCF) method using contracted CI calculations for several electron states. According to [30], the triplet state of the product was about 6 kcal/mol lower in energy than its singlet state. At the same time, the geometrical parameters found in [30] are in good agreement with our results. In going from the singlet to the triplet state, the length of the Ni–H bond elongated by 0.16 Å (in our case, by 0.12 Å).

The *ab initio* calculations were performed for the product of reaction (III) in a singlet state [31]. The calculated geometrical parameters r(Ni–H) = 1.47 Å, r(Ni–C) = 1.98 Å, and ∠(H–Ni–C) = 94° agree with our results (Fig. 1). The energy of the PR-3 product of reaction (III) depended on the basis used in calculations. Thus, E(PR-3) with respect to separated reactants decreased from 4.3 to –3.3 kcal/mol when going to a larger basis [32]. In our case, the energy of singlet PR-3 was lower than in the triplet state (see Table 1).

We failed to find the data for reaction (IV). The energy of the PR-4 product in the singlet state was found to be 6.6 kcal/mol lower than that in the triplet state.

According to [33], the energy of the singlet product PR-5 of reaction (V) was higher than that for the triplet state, which was equal to 19.6 kcal/mol with respect to the separated reactants (Ni_2 cluster was in the triplet state). However, in the cited work, geometry optimization was not carried out; in the calculations made for the Ni_2CH_4 system, the geometrical parameters were

Table 1. Energies of the products of hydrogen and methane oxidative addition to the Ni atom, Ni_2 cluster, and Ni_2–porphyrin and Ni_3–porphyrin complexes

Reaction	Separated reactants*		Products*		
	structure	energy, kcal/mol	structure	energy, kcal/mol	
				s	tr
(I)	$Ni^s + Ni^s$	70.8	Ni_2 (PR-1)	–33.1	–63.2
	$Ni^{tr} + Ni^{tr}$	0.0			
(II)	$Ni^s + H_2^s$	35.4	NiH_2 (PR-2)	–21.9	–9.0
	$Ni^{tr} + H_2^s$	0.0			
(III)	$Ni^s + CH_4^s$	35.4	$HNiCH_3$ (PR-3)	–14.3	1.1
	$Ni^{tr} + CH_4^s$	0.0			
(IV)	$Ni_2^s + H_2^s$	30.0	Ni_2H_2 (PR-4)	–16.4	–9.8
	$Ni_2^{tr} + H_2^s$	0.0			
(V)	$Ni_2^s + CH_4^s$	30.0	Ni_2CH_4 (PR-5)	–3.2	7.2
	$Ni_2^{tr} + CH_4^s$	0.0			
(VI)	$NiPn^s + Ni^{tr}$	0.0	Ni–NiPn (PR-6)	–30.0	–18.8
(VII)	$Ni–NiPn^s + H_2^s$	0.0	H_2Ni–NiPn (PR-7)	–15.9	–
(VIII)	$Ni_2^{tr} + NiPn^s$	0.0	$NiPnNi_2$ (PR-8)	–32.6	–20.7
(IX)	$NiPnNi_2^s + H_2^s$	0.0	$NiPnNi_2H_2$ (PR-9)	–31.8	–
(X)	$NiPnNi_2^s + CH_4^s$	0.0	$NiPnNi_2CH_4$ (PR-10)	–13.5	–

* "s" denotes a singlet state and "tr" denotes a triplet state.

Table 2. Geometrical parameters of the Ni–porphyrin complex

Parameter*	Calculations [26]	Our calculations	Experimental data [35]**	Parameter*	Calculations [26]	Our calculations	Experimental data [35]**
$r(Ni–N_1)$, Å	1.935	1.967	1.953	$r(N_1–C_2)$, Å	1.377	1.384	1.384
$r(C_2–C_3)$, Å	1.426	1.439	1.439	$r(C_3–C_4)$, Å	1.358	1.362	1.334
$r(C_2–C_7)$, Å	1.370	1.382	1.378	$r(C_3–H_6)$, Å	1.094	1.086	–
$r(C_7–H_8)$, Å	1.097	1.089	–	$\angle\theta(C_2–C_7–H_8)$, degree	118.6	118.3	–
$\angle\theta(Ni–N_1–C_2)$, degree	128.1	127.7	127.6	$\angle\theta(N_1–C_2–C_3)$, degree	111.6	111.1	110.2
$\angle\theta(C_2–C_3–C_4)$, degree	106.5	106.7	107.4	$\angle\theta(N_1–C_2–C_7)$, degree	125.5	125.5	126.3
$\angle\theta(C_2–C_7–C_9)$, degree	122.8	123.5	121.9	$\angle\theta(C_2–C_3–H_6)$, degree	124.0	124.3	–

* Enumeration of atoms is given in Fig. 2.

** Experimental data obtained for Ni–tetramethoxyphenylporphine.

taken from the Pd_2CH_4 system, which reduces the reliability of the results.

Thus, according to our calculations performed for the products of the oxidative addition of hydrogen and methane molecules to the Ni atom and Ni_2 cluster, singlet states possessed the lowest energy. At the same time, the ground states of isolated Ni atoms and Ni_2 clusters are triplet. When the state of products changed from singlet to triplet, the lengths of the Ni–H and Ni–C bonds increased by ~0.1 Å.

Recently, using the CNDO/S^2 [34] and DFT methods, we demonstrated that Ni and Pd atoms can com-

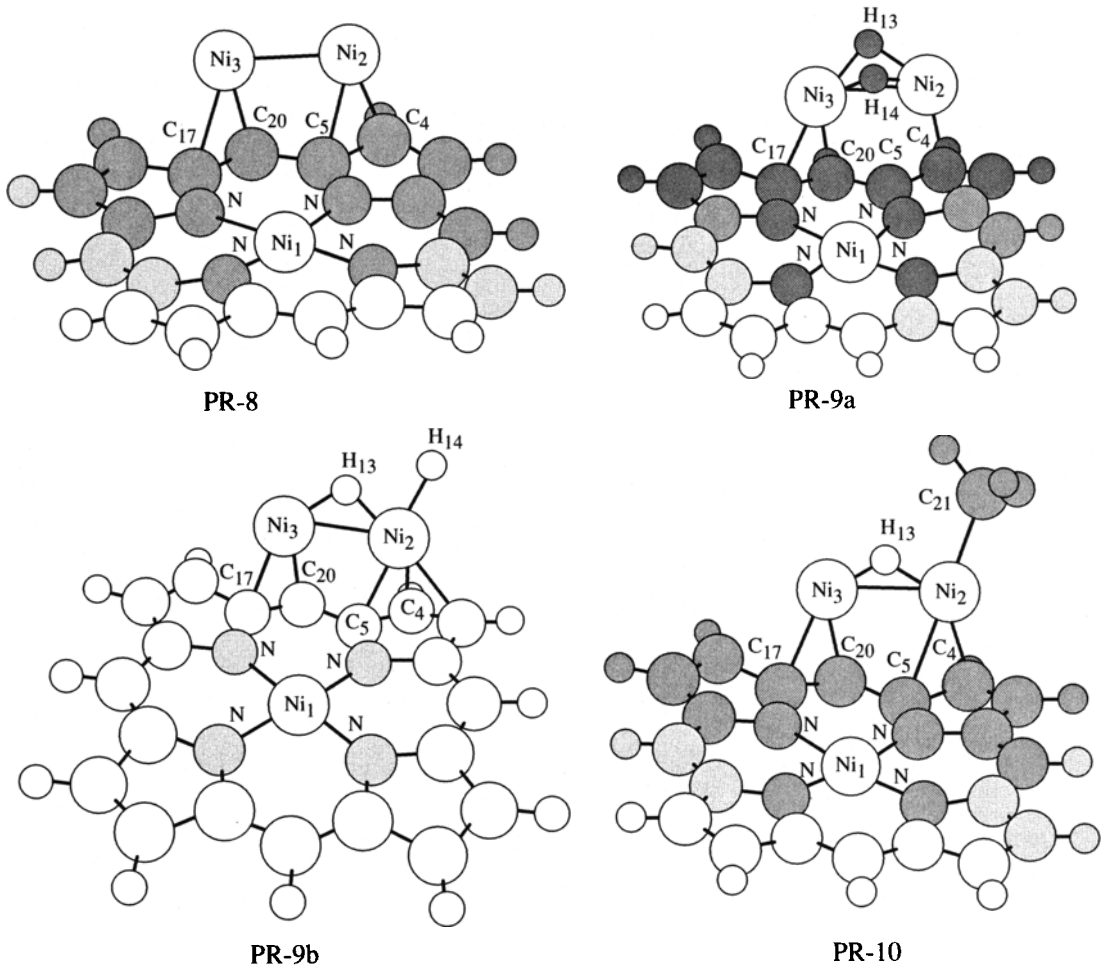

Fig. 3. Enumeration of atoms in the molecules of products of reactions (VIII)–(X).

bine with Ni–porphyrin [25]. It was found that the energy of the triplet state of NiPn is 28.9 kcal/mol higher than the energy of the singlet state. Table 2 presents the calculated geometrical parameters of an Ni–porphyrin molecule (see the enumeration of atoms in NiPn in Fig. 2) and the experimental data obtained in [35]. The calculated parameters agree well with the experimental data and previous calculations [26]. The energy of the Ni atom addition to Ni–porphyrin was 30 kcal/mol (the energy of PR-6 in the singlet state was

Table 3. Geometrical parameters of the products of reactions (VIII)–(X)

Parameter*, Å	PR-8	PR-9a	PR-9b	PR-10
$r(Ni_2–Ni_3)$	2.39	2.35 (2.29)**	2.46	2.44 (2.36)***
$r(Ni_2–C_4)$	1.93	2.00	2.03	2.06
$r(Ni_2–C_5)$	2.03	2.43	2.15	2.26
$r(Ni_3–C_{17})$	2.08	2.17	2.03	2.06
$r(Ni_3–C_{20})$	1.90	2.00	1.95	1.94
$r(Ni_2–H_{13})$	–	1.60 (1.58)**	1.54	1.55 (1.60)***
$r(Ni_2–H_{14})$	–	1.64	1.48	–
$r(Ni_3–H_{13})$	–	1.60	1.67	1.63
$r(Ni_3–H_{14})$	–	1.64	–	–
$r(Ni_2–C_{21})$	–	–	–	1.92 (1.91)***

* Enumeration of atoms is given in Fig. 3.

** The corresponding values for PR-4 (see Fig. 1) are given in brackets.

*** The corresponding values for PR-5 (see Fig. 1) are given in brackets.

11.2 kcal/mol lower than that in the triplet state). The activation of an H–H bond by a Ni atom coordinated to Ni–porphyrin gained less energy than the activation with an isolated Ni atom. According to our calculations, the activation of methane resulted only in the adsorption complex. In this work, we showed that an Ni_2 cluster was also capable of coordinating Ni–porphyrin (PR-8, Fig. 3), and the formation energy of the complex was 32.6 kcal/mol (the energy of its singlet state was 19.9 kcal/mol lower than the energy of the triplet state). The activation of an H–H bond by the PR-8 complex led to the formation of two products (PR-9a and PR-9b) with close energies. As in the case of an Ni_2 cluster, the activation of the C–H bond in reaction (X) (PR-10) yielded a smaller gain in energy. It follows from Fig. 3 and Table 3 that the Ni_2 cluster formed multicentered bonds with the peripheral carbon atoms of NiPn involving one-fourth of a macrocycle. From the symmetry consideration, it might be expected that four Ni_2 clusters may undergo the addition from one side of the metalloporphyrin plane. This allows us to hope that efficient catalytic cycles based on these complexes can be designed for hydrocarbon conversions and other systems.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 96-03-32536, and INTAS-RFBR, project no. 95-0163.

REFERENCES

1. James, R., *Homogeneous Hydrogenation*, New York: Wiley, 1973.
2. Shilov, E., *The Activation of Saturated Hydrocarbons by Transition Metal Complexes*, Dordrecht: Riedel, 1984.
3. Daley, S.P., Utz, A.L., Trautman, T.R., and Ceyer, S.T., *J. Am. Chem. Soc.*, 1994, vol. 116, no. 13, p. 6001.
4. Burke, M.L. and Madix, R.J., *J. Am. Chem. Soc.*, 1991, vol. 113, no. 5, p. 1475.
5. *Homogeneous Transition Metal Catalysed Reactions*, Moser, W.R. and Slocum, D.W., Eds., Washington: American Chemical Society, 1992, vol. 230.
6. Duckett, S.B., Eisenberg, R., and Goldman, A.S., *J. Chem. Soc., Chem. Commun.*, 1993, no. 15, p. 1185.
7. Zhang, X.-X. and Wayland, B.B., *J. Am. Chem. Soc.*, 1994, vol. 116, no. 17, p. 7897.
8. Schultz, R.H., Bengali, A.A., Tauber, M.J., *et al.*, *J. Am. Chem. Soc.*, 1994, vol. 116, no. 16, p. 7269.
9. Johnson, A.D., Daley, S.P., Utz, A.L., and Ceyer, S.T., *Science*, 1992, vol. 257, no. 5067, p. 223.
10. Ceyer, S.T., *Science*, 1990, vol. 249, no. 4965, p. 133.
11. Carroll, J.J., Haug, K.L., Weisshaar, J.C., *et al.*, *J. Phys. Chem.*, 1995, vol. 99, no. 38, p. 13955.
12. Fayet, P., Kaldor, A., and Cox, D.M., *J. Chem. Phys.*, 1990, vol. 92, no. 1, p. 254.
13. Stewart, D.M. and Ehlrich, G., *J. Chem. Phys.*, 1975, vol. 62, no. 12, p. 4672.
14. Winters, H.E., *J. Chem. Phys.*, 1975, vol. 62, no. 6, p. 2454.
15. Winters, H.E., *J. Chem. Phys.*, 1976, vol. 64, no. 9, p. 3495.
16. Rettner, A.C.T., Pflur, H.E., and Auerbach, D.J., *J. Chem. Phys.*, 1986, vol. 84, no. 8, p. 4163.
17. Davis, S.C. and Klabunde, K.J., *Chem. Rev.*, 1982, vol. 82, p. 153.
18. Mamaev, V.M., Gloriozov, I.P., Simonyan, V.V., *et al.*, *Mendeleev Commun.*, 1996, no. 4, p. 146.
19. Mamaev, V.M., Gloriozov, I.P., Simonyan, V.V., *et al.*, *Mendeleev Commun.*, 1997, no. 6, p. 246.
20. Mamaev, V.M., Gloriozov, I.P., Khmara, V.A., *et al.*, *Dokl. Ross. Akad. Nauk*, 1994, vol. 338, no. 1, p. 65.
21. Mamaev, V.M., Gloriozov, I.P., Ishchsenko, S.Ya., *et al.*, *J. Chem. Soc., Faraday Trans.*, 1995, vol. 91, no. 21, p. 3779.
22. Allegra, G., Casagrande, G.T., Immirzi, A., *et al.*, *J. Am. Chem. Soc.*, 1970, vol. 92, no. 2, p. 289.
23. Dupont, J., Pfeffer, M., Rotteveel, M.A., *et al.*, *Organometallics*, 1989, vol. 8, no. 4, p. 1116.
24. Kannan, S., James, A.J., and Sharp, P.R., *J. Am. Chem. Soc.*, 1998, vol. 120, no. 1, p. 215.
25. Mamaev, V.M., Gloriozov, I.P., and Prisyajnyuk, A.V., *Mendeleev Commun.*, 1998, no. 2, p. 53.
26. Matsuzava, N., Ata, M., and Dixon, D.A., *J. Phys. Chem.*, 1995, vol. 99, no. 19, p. 7698.
27. Rovira, C., Kunc, K., Hutter, J., *et al.*, *J. Phys. Chem.*, 1997, vol. 101, no. 47, p. 8914.
28. Laikov, D.N., *Chem. Phys. Lett.*, 1997, vol. 281, nos. 1–3, p. 151.
29. Perdew, J.P., Burke, K., and Ernzerhof, M., *Phys. Rev. Lett.*, 1996, vol. 77, no. 18, p. 3865.
30. Blomberg, M.R.A. and Siegbahn, P.E.M., *J. Chem. Phys.*, 1983, vol. 78, no. 9, p. 5682.
31. Blomberg, M.R.A., Brandemark, U., and Siegbahn, P.E.M., *J. Am. Chem. Soc.*, 1983, vol. 105, no. 17, p. 5557.
32. Blomberg, M.R.A., Siegbahn, P.E.M., Nagashima, U., and Wennerberg, J., *J. Am. Chem. Soc.*, 1991, vol. 13, no. 2, p. 424.
33. Blomberg, M.R.A., Siegbahn, P.E.M., and Svensson, M., *J. Phys. Chem.*, 1992, vol. 96, no. 14, p. 5783.
34. Filatov, M.J., Gritsenko, O.V., and Gidomirov, G.M., *J. Mol. Catal.*, 1989, vol. 54, no. 3, p. 462.
35. Kutzler, F.W., Swepston, P.N., Berkovitch-Yellin, Z., *et al.*, *J. Am. Chem. Soc.*, 1983, vol. 105, no. 10, p. 2996.