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Binding of Ethylene to Anionic, Neutral, and Cationic Nickel(II), Palladium(II), and Platinum(II) *cis/trans* Chloride Ammonia Complexes. A Theoretical Study

Staffan Strömberg,* Mats Svensson,* and Krister Zetterberg

Department of Chemistry, Organic Chemistry, Royal Institute of Technology,
SE-100 44 Stockholm, Sweden

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Calculations using the hybrid density functional method B3LYP have been performed on square-planar, group X metal complexes of the type $(C_2H_4)MCl_x(NH_3)_{3-x}$ (M = Ni(II), Pd(II), or Pt(II); $x = 1$, 2, or 3). Generally, the ability to coordinate ethylene is in the expected order Pt > Pd > Ni. In line with the abundance of reported anionic, neutral, and cationic alkene complexes of Pt, the bonds between Pt and ethylene are strong and rather independent of the charge on the complexes, and bond energies range from 33.9 to 46.1 kcal/mol. For Ni, the situation is different. The never-observed anionic $(C_2H_4)NiCl_3^-$ coordinates ethylene weakly (6.1 kcal/mol), whereas the still not observed cationic $(C_2H_4)NiCl(NH_3)_2^+$ shows a reasonably strong intrinsic coordination (25.2 kcal/mol). A significant degree of π-back-donation is observed for all three metals, the order being Pt > Pd > Ni. However, for each metal, the π-back-donation is independent of charge. In all cases where comparisons are possible, Cl^- exerts a stronger *trans* influence on ethylene than NH_3.

Introduction

The bond between olefins and group X transition metals has a central role in the field of organometallic chemistry, and a large body of research related to this subject has been completed over the years.[1] In several catalytic cycles, such as the olefin polymerization,[2] hydrogenation,[3] and hydroformylation,[4] π-alkene complexes are present as key intermediates. An accurate knowledge of the nature of the alkene−metal bond is essential for understanding the mechanisms behind a large number of transition metals catalysts involving an alkene−metal interaction.[5] Despite the great interest in the nature of the alkene−metal bond, there exist very few reports on the actual bond strength and the nature of the bond between transition metals and alkenes. Due to the frequent instability of alkene−metal interactions, such figures have been difficult to measure.[6] In particular, systematic experimental data for all three metals of a triad are scarce, as the ability to prepare similar model complexes with different metal centers is limited. However, new accurate and computationally relatively inexpensive quantum chemical methods allow studies of larger and more realistic systems, thereby providing us with the missing tool for a direct systematic comparison between the bond strengths of different but well-defined alkene−metal complexes. A general advantage of a theoretical approach over an experimental one is the possibility in the theory to systematically change, for example, the electronic and steric effects of ligands without inducing practical problems related to laboratory work. Previously, only theoretical studies at a lower level[7] have been reported in which a well-defined set of alkene−metal(II) complexes has been compared. Recently, alkene−metal(0) complexes have been studied theoretically by Ziegler et al. using a gradient-corrected density functional method.[8]

We have calculated the π-complexation energy between ethylene and five different, well-defined metal complexes of three different metals in the nickel triad: Ni, Pd, and Pt. The ligands apart from ethylene are Cl^- and NH_3 in different combinations. The coordination number of the metal is always kept as four. These complexes are labeled $(C_2H_4)MCl_x(NH_3)_{3-x}$ (M = Ni(II), Pd(II), or and Pt(II); $x = 1$, 2, or 3). All complexes are d^8 and are assumed to be square-planar. Both the *cis* and *trans* isomers have been studied. In this study, we present theoretically obtained data that provide us with the answers to some of the observations left unexplained

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in previous studies. An example is whether an alkene binds more strongly to a cationic metal center than to a neutral center. The influence of the charge in cationic metal(II) complexes on the π-bonding has been discussed in an experimental study.[9] Our calculations introduce a possibility to compare how the π-bond is affected by the charge of the metal complex and by different types of ligands. In addition, the amount of olefin activation upon coordination to the metal center can be estimated. This is important for possible later steps, such as nucleophilic attack or migratory insertion.

Computational Details

The calculated complexation energy of ethylene, in this study, is defined as the difference in the electronic energy between the alkene−metal complex and the sum of the 14-electron metal complex and free ethylene in the gas phase. In a previous study on a similar alkene−metal(II) complex, the zero-point energy effect was calculated to be 2.6 kcal/mol.[10] This correction is included in our relative energies.

Geometries and energies of all intermediates are calculated using the gradient-corrected hybrid density functional method B3LYP.[11] This popular and computationally relatively inexpensive method has been shown to predict reliable geometries and energetics.[12] In the geometry optimizations, we used a basis set of double-ζ valence quality, labeled BSI, and in these B3LYP/BSI structures, the final energetics were calculated using a triple-ζ valence quality basis set with one polarization function added on all atoms. This basis set is referred to as BSII in this study.

BSI includes a double-ζ valence basis set, {5s5p*n*d}/[3s3p2d] (n(Ni) = 5, n(Pd) = 4, and n(Pt) = 3), for Ni, Pd, and Pt, replacing the core electrons with an electron core potential (ECP) developed by Hay and Wadt.[13] For Ni, Pd, ant Pt, 18 valence electrons are explicitly described, and the ECP includes relativistic effects for Pd and Pt. For nonmetal atoms, the double-ζ basis sets of Huzinaga and Dunning were assigned.[14] BSII was only used to recalculate the binding energies of ethylene at the B3LYP/BSI optimized geometries. For the metal atoms, the same primitive basis as in BSI were used, but the valence s, p, and d regions had a triple-ζ valence contraction and, in addition, one f-function[15] was added. All other atoms were described by the 6-311G(d,p) basis set.[16] In fact, the binding energy of ethylene was not very sensitive to the choice of basis set. The difference between the B3LYP/BSI- and B3LYP/BSII-calculated ethylene binding energies never exceeded 1.6 kcal/mol. All calculations were done using the Gaussian 94 package.[17]

Table 1. Ethylene Complexation Energies (kcal/mol) at the B3LYP/BSII Level

	Ni	Pd	Pt
MCl$_3^-$	6.1	19.0	33.9
c-MCl$_2$(NH$_3$)	12.9	22.0	34.5
t-MCl$_2$(NH$_3$)	20.8	29.7	41.8
t-MCl(NH$_3$)$_2^+$	23.4	27.4	40.3
c-MCl(NH$_3$)$_2^+$	25.2	34.0	46.1

Results

The first and maybe most obvious effect seen in the ethylene−metal binding energies presented in Table 1 is that the Pt−ethylene complexes are more stable than those containing Ni or Pd. This trend is most apparent for the MCl$_3^-$ complexes, where the binding energy of the ethylene−Pt bond is 28 kcal/mol stronger than that of the Ni analogue. A clear trend in the binding energies of the olefin, Ni < Pd < Pt, is present for all combinations of different ligands and charges for these M(II) complexes. Platinum generally binds ethylene 12−15 kcal/mol more strongly than the corresponding Pd systems. For the Ni complexes, the binding energies are another 4−13 kcal/mol smaller. This difference in binding energies might be one of the reasons why a multitude of square-planar Pt(II) complexes are reported, whereas the corresponding Pd complexes appear less frequently.[18] To the best of our knowledge, the same type of Ni complexes have not been reported.

Ziegler et al. have reported another trend,[8b] using density functional methods, with the Pd−alkene bond as the weakest and the Ni−alkene bond as the strongest of the three metals in the nickel triad. In ref 8b, the V-liked bond strength trend of the ethylene−metal(0) complexes is rationalized by comparing the atomic energy levels of Ni, Pd, and Pt atoms. However, this does not explain the trend for the M(II) complexes. If the metal is in a high oxidation state, there are fewer electrons in the valence shell compared with the neutral atom. With this in mind, a correlation between our observed trend, increased binding energy down the triad, and the *cationic* energy levels seems more suit-

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Table 2. Ethylene C−C[a] Bonds (Å), Optimized at the B3LYP/BSI Level

	Ni	Pd	Pt
MCl_3^-	1.38	1.40	1.42
c-$MCl_2(NH_3)$	1.38	1.39	1.42
t-$MCl_2(NH_3)$	1.38	1.39	1.41
t-$MCl(NH_3)_2^+$	1.38	1.39	1.41
c-$MCl(NH_3)_2^+$	1.38	1.39	1.41

[a] In free ethylene, 1.35 Å.

Table 3. Ethylene "CH_2-Tilt" Angle,[a] Optimized at the B3LYP/BSI Level

	Ni	Pd	Pt
MCl_3^-	6.8	9.4	15.8
c-$MCl_2(NH_3)$	8.4	10.7	16.6
t-$MCl_2(NH_3)$	6.8	9.2	13.8
c-$MCl(NH_3)_2^+$	8.9	10.8	14.8
t-$MCl(NH_3)_2^+$	8.6	11.5	16.9

[a] This angle is defined as the *difference* in the angle between the midpoint of the hydrogens on one carbon and the two carbons in ethylene from free ethylene.

able. In fact, our trend correlates with the energy levels of Ni^+, Pd^+, and Pt^+. The less stable 5d-orbital of Pt^+ is more prone to donate electrons than the more stable 4d-orbital of Pd^+. The even more stable 3d-orbital of Ni^+ is even more reluctant to donate its electrons.

As can be seen from Table 2, the elongation of the C−C double bond in the coordinated ethylene increases down the nickel triad, irrespective of the types of ligands. For the Ni complexes, the C−C double bond is 1.38 Å, and for the Pd analogues, the bond is slightly more elongated, 1.40 Å, and even more so, 1.42 Å for the Pt species. This geometry effect is correlated with the amount of back-donation from the metal center into the π*-orbital on ethylene.[19] In the study by Ziegler et al. on the ethylene−M(0) complexes, the C−C double bond varies less, 1.41−1.42 Å, between the different metals.[8b] The tilt angle, presented in Table 3, i.e., the angle by which the sp^2 hybridization is perturbed from 0° in free ethylene, correlates with the elongation of the C−C double bond and can be seen as another indication of π-back-donation from the metal. It varies from around 7 to 9° for Ni and up to 14−17° for Pt.

An interesting and somewhat surprising trend is that the increased stability of the π-complexes with the positive charge on the metal (see Table 1) is not correlated with the amount of π-back-donation. The π-back-donation can be estimated from the amount of elongation of the C−C double bond, and since the variation in the bond length for the different complexes with the same metal center is very small, as can be seen from Table 2, we conclude that this donation is not strongly influenced by the charge on the metal complex. Furthermore, the varying amount of π-back-donation observed for Ni, Pd, and Pt rationalizes the trends in the binding energies of ethylene seen for different metals.

Table 4. Total Charge of the Coordinated Ethylene[a]

	Ni	Pd	Pt
MCl_3^-	+0.20	+0.16	+0.04
c-$MCl_2(NH_3)$	+0.26	+0.22	+0.14
t-$MCl_2(NH_3)$	+0.36	+0.32	+0.24
t-$MCl(NH_3)_2^+$	+0.36	+0.32	+0.28
c-$MCl(NH_3)_2^+$	+0.40	+0.38	+0.36

[a] Mulliken charges calculated at the B3LYP/BSII level.

Although the ethylene−metal bonds are stronger for the cationic complexes, resulting in more stable complexes compared with the neutral or the anionic complexes of the same metal, we find that the carbon atoms on the coordinated ethylene are more positive (see Table 4) and should, therefore, be more susceptible to nucleophilic attack.[20] In addition, if an alkyl group would be present on the metal center, migratory insertion should be more facile in these cases. In fact, fast migratory insertions on Ni and Pd species are most common for cationic systems.[21] The reason why migratory insertion is less probable for Pt complexes is related not only to a large kinetic barrier but also to the fact that the insertion reaction is endothermic. This is discussed comprehensively in a separate paper based on similar calculations by our group.[22]

Excluding the differences in the *trans* influence by looking at the cases where a Cl^- is *trans* to the coordinating ethylene, a clear trend of increased stability of the metal−olefin bond with positive charge on the metal complex is seen for all three metals, but it is most pronounced for Ni. This effect has to be associated with the interaction in the σ-system, that is, the donation from ethylene into an empty orbital of the metal, since large differences in the π-back-donation are not present, illustrated by the stability of the C−C double bond length with the type of metal. The electrostatic part of the interaction between the coordinating ethylene and the metal obviously increases with the total charge of the complex.

As can be clearly seen from Table 1, the complexation energy is strongly dependent on the type of ligand positioned *trans* to the coordinating site of ethylene. For the neutral $(C_2H_4)MCl_2(NH_3)$ complexes, the olefin binding energy differs by 7.9 kcal/mol for Ni in favor of the isomer, where NH_3 coordinates *trans* to ethylene. For the Pd and Pt complexes, the differences are 7.7 and 7.3 kcal/mol, respectively. A similar but somewhat smaller effect is present for the cationic (C_2H_4)MCl-

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(19) The C−C double bond length coordinated to the metal center could be influenced by the σ-donation to the metal center as well. However, when considering the the C−C bond length of alkenes in d^0-metal complexes, in which no π-back-donation can be present, both experimentally and theoretically determined C−C bond lengths are almost unchanged upon coordination by σ-donation to d^0-metal centers. (a) Horton, A. D.; Orpen, G. A. *Organometallics* **1992**, *11*, 8. (b) Wu, Z.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 5867. (c) Woo, T. K.; Fan, L.; Ziegler, T. *Organometallics* **1994**, *13*, 2252. (d) Yoshida, T.; Koga, N.; Morokuma, K. *Organometallics* **1995**, *14*, 746. (e) Fan, L.; Harrison, D.; Woo, T. K.; Ziegler, T. *Organometallics* **1995**, *14*, 2018. (f) See also discussion in the following: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; p 39.

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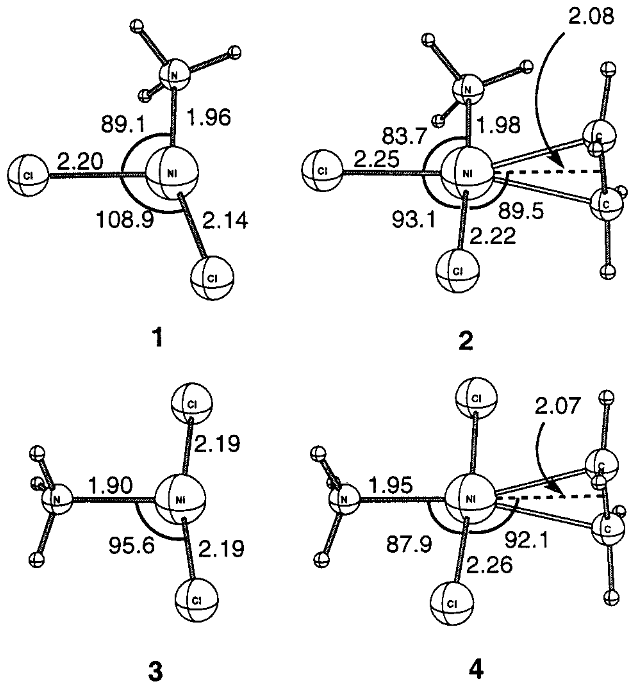

Figure 1. B3LYP/BSI-optimized structures of the $NiCl_2$-NH_3 and $(C_2H_4)NiCl_2NH_3$ isomers.

$(NH_3)_2$ complexes. The origin of this effect is the stronger *trans* influence of the Cl^- compared to that of NH_3.[23] The two ligands with strong *trans* influence, ethylene and Cl^-, interfere with each other's bonding if positioned *trans* to each other. One could expect part of the energy differences above to originate from the fact that the *cis* chloride ethylene complexes are destabilized by the increased repulsion between the chlorides. However, as exemplified by the neutral Ni complexes, only a small part, as discussed below, of the 8 kcal/mol difference in the binding energy between the *cis* and *trans* $(C_2H_4)NiCl_2(NH_3)^+$ systems is due to the structural changes of the ligand surrounding the metal.

As shown in Figure 1, the naked isomer with *cis* Cl^- groups **1** has a bending angle of 108.9°, which is quite different from that in the corresponding π-complex **2** of 93.1°, because the coordinating ethylene forces the chlorides together. On the other hand, for the isomer in which the chloride ions are positioned *trans* to each other, the structural differences between the reactant **3** and the olefin complex **4** are smaller. By calculating the binding energy relative to reactants in the geometry of the π-complexes without the coordinated ethylene, the difference in the complexation energy for the *cis* and *trans* isomers is reduced from 8 to 6 kcal/mol. Therefore, the larger binding energy observed for the isomers with the Cl^- positioned *trans* to ethylene originates from electronical effects, that is, a *trans* influence. Finally, we can also conclude that the *trans* influence is not sensitive to the type of metal, which means that it does not depend on the amount of π-back-donation.

Conclusions

(1) Bond strengths for the square-planar, group X ethylene complexes are found to be Ni(II) < Pd(II) < Pt(II).

(2) Positive charge on the metal increases the strength of the ethylene−metal interaction, the most for Ni.

(3) The π-back-donation does not depend on the charge of the metal center.

(4) The amount of π-back-donation is found to be in the order of Ni < Pd < Pt for the ethylene complexes.

(5) A notable *trans* influence is found for the complexes. If Cl^- is positioned *trans* to ethylene, the ethylene−metal bond is weaker than for the corresponding *cis* complexes.

(6) Ethylene coordinated to a Ni, Pd, or Pt metal center is positively charged, independently of the total charge on the complex. As expected, the carbon atoms coordinated to a cationic complex are found to be more positively charged than they are in neutral and anionic analogues and are, therefore, believed to be better electrophiles.

It must be emphasized that the figures calculated are gas phase figures and show *intrinsic* thermodynamic properties. In solution, we will observe values that could differ more or less from those of the calculations. However, the *tendencies* seen from calculations seem to be reliable also in solution. In all, the results of the calculations are commonly in nice accordance with trends accepted but rarely verified in the alkene chemistry of the group X transition metals.

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