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Organometallics: Exploration Tool for Surface Phenomena in Heterogeneous Catalysis

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Abstract

Homogeneous and heterogeneous catalyses have sufficient common features that are based on the same molecular phenomena, thus permitting them and their benefits to be directed to the same objective. Moreover, conditions that apply to one of them can yield benefits to the other. In this chapter, the progress of combining these advantages is demonstrated on a particular topic of testing a suitable structural model from the field of organometallic compounds, whose structure resembles complexes adsorbed on the surface of heterogeneous catalysts. The adsorbed complexes represent key structures in the conversion of reactants to products, while their demanding structural characterization is one of the main persistent topics of heterogeneously catalyzed reactions. These include compounds procuring a precious mechanistic interpretation of such complex concepts as the catalytic activity and selectivity. The knowledge of the structure of an adsorbed complex leads to a better understanding of the complex surface processes and more precisely defined heterogeneous catalysts. The understanding of processes on the molecular level allows discussing the structure-activity. Analogies and differences between molecular (homogeneous catalysis) and surface (heterogeneous catalysis) chemistry are addressed in this review. The work demonstrates that these two fields are complementary, presenting a large potential for the development of novel and superior catalysts when the advantages of both sub-disciplines are combined.

Keywords: catalysis, molecular modeling, hydrogenation, molecular structure effect, platinum

1. Introduction

Traditionally, the area of catalysis has been divided into three fields: heterogeneous, homogeneous, and enzymatic catalyses. While heterogeneous catalysis has offered a great advantage

in terms of the process design, the separation of products from a catalyst and its regeneration, it has usually suffered from a lack of understanding of the so-called “active site.” This fact has plausibly impeded the rational development of these systems. On the contrary, homogeneous catalysis can be designed in a more rational way as its properties are easily tuned via ligand designs, providing a substantial comprehension of elementary steps. Nevertheless, these processes have often required undertaking many technical advances to be competitive to heterogeneous catalysts. From the industrial point of view, this led in the final practice to the preference of heterogeneous from homogeneous catalysis. However, the development of enhanced heterogeneous catalysts has been hindered typically owing to their content of numerous variable active sites and their low concentration. Homogeneous catalysts, on the contrary, have been well-defined systems that could be easily characterized and studied. Comparative studies of homogeneous and heterogeneous catalyses, providing a successful implementation of appropriate homogeneous models with molecular modeling, can yield a new insight into the complex of processes accompanying heterogeneous catalysis. In order to perceive the involved complex molecular events, it is also essential to construct a clear-cut active site, test its catalytic performance, and assess the relationship between its structure and activity. Finally, the acquired picture can be utilized to design a new generation of catalysts applicable “as in homogeneous catalysis.”

Typically, the determining characteristic of heterogeneous catalysis lays in the structural composition of its active sites and molecular structures, in the case of a metal catalyst and the reactant, respectively [1, 2]. In other words, the chemical and physical properties of the surface of the active sites and the molecule entering the reaction generate a generous number of parameters decisive for the catalytic mechanism. In order to predict the catalytic behavior, geometric and electronic structural properties have been traditionally studied [2], particularly based on “Theory of Electronic Effects” [2, 3]. The core of this study consists in the active site (catalyst side)-reaction center (substrate side) whose behavior is determined by their interdependent electronic properties, with each component either donating or accepting electrons. Orbitals of both of the reaction players are thus directed by relatively strongly dependent interactions of their affinity and repelling forces. Last but not the least, geometric degree of freedom may have decisive impact on the surface complex (active site-reactant interaction) [2, 4]. However, the above list of parameters is not complete as other potentially significant aspects could contribute to the problem: thermodynamics, reaction conditions, and hydrogen-catalytic surface interaction [5].

Electronic effects and spatial geometry are reckoned to play the most prominent role in heterogeneously catalyzed processes. Catalytic properties, related particularly to the metal behavior, are listed below by their descending importance [2, 6–11]:

1. Form and constitution of metal particles.
2. Metallic surface organization as well as other components (as in surface alloys).
3. Surface complexes.
4. Substrate effects (strong metal-support interaction (SMSI), hydrogen spillover, and surface area).

5. Metallic presence in support pores.

The record of metals having been successfully applied to heterogeneously catalyzed reactions would be considerably extensive. Additionally, no general treatment modifying their properties (electronics, morphology, etc.) to a desired performance in individual reactions is available. As a result, the selection criteria obviously depend on rather empirical decisions.

Transition metals represent an extraordinary group of elements finding a widespread utilization in the applied heterogeneous catalysis. From the point of view of the band theory [12], all of them contain positively charged ions having shells with partially occupied *d*-bands, in which electrons freely fluctuate. Predictably, these form bonds with adjacent atoms using *dsp* orbitals with inerratic *d*-function. As a result, the structure of the metal surface is nonuniform, which is further pronounced [12] by depositing the metal particles on an internal surface of a suitable high surface area support (active carbon, zeolites, etc.). Catalytic particles are rarely uniform as evidently determined by their X-ray diffraction diagrams. Elemental metal crystallites are composed of crystallographic planes diverse in their surface coordination and architecture. There is a direct implication [6, 13] of this phenomenon in a variable degree of saturation of coordination sites on the metal surface. As a consequence, a different catalytic behavior is macroscopically observed [6, 14, 15].

Current methods of molecular modeling offer a wide array of applications even to heterogeneous catalysis. However, it is still necessary to significantly simplify the studied systems in comparison with the reality. Although modeling requires many compromises, its use allows obtaining very interesting results, which provide information on the mechanism of catalytic reactions on the surface. Owing to the development of computer technology, computer modeling and simulation have been increasingly recognized as important tools for the study and development of catalytic systems. These tools have the potential to penetrate into the reaction mechanisms, can predict properties of catalysts not yet synthesized, and provide information obtained by various computational techniques, which together with experimental results procure a comprehensive picture of the system. Nevertheless, it is always essential to maintain a proficient collaboration of computational chemists with researchers. In addition, in order to validate the new modeling techniques, theoretical results must be sufficiently confirmed experimentally. Therefore, it is advisable to have a comparison of various experiments, such as kinetic studies of reaction rates, thermodynamic information on adsorption, and spectroscopic data on the level of molecular structure. The double-feedback technique (dual-feedback mode) seems to be the “most prolific” strategy for the utilization of modeling in catalytic research where experiments are employed to confirm the results of modeling and the modeling is used to explicate the experimental results, to design new experiments, and perhaps in the future also to replace experiments with theoretical screening of different catalysts and reaction conditions.

One option to simplify the heterogeneously catalyzed reactions for the application of molecular modeling is finding a suitable model, which first needs to be designed, then mathematically and experimentally tested and if its quality is proved, the method is validated and the limits of its applicability are determined. In the case of heterogeneous platinum catalysts designated for hydrogenation reactions, well-structurally defined compounds of (ole-

fin)Pt(PPh₃)₂ seems to offer a suitable model of adsorbed surface complexes as the key structures in the transformation of a reactant to products. These compounds are platinum organometallic compounds containing coordinated olefins, which in a sense resemble the morphology of the metal surface and chemisorptions occurring on it. Although these covalent compounds cannot catalyze homogeneous hydrogenation, such as the rhodium analog Rh(PPh₃)₃Cl, their structure very well approximates the adsorbed state on heterogeneous platinum catalysts. The model of organometallic compounds (olefin)Pt(PPh₃)₂ represents an attractive alternative for the application to molecular modeling in heterogeneous catalysis. By comparing values with a similar significance (adsorption *vs.* dissociation energy) or the differences in geometric data, very good qualitative (corresponding order of stabilities) and even quantitative (correlating E_{ads} and E_{diss}) correlations can be achieved.

2. Model of adsorbed complex: (olefin)Pt(PPh₃)₂ complex

The compounds of the type (olefin)Pt(PPh₃)₂ belong to a group of intensively studied substances. One of the reasons for their study are the binding ratios in these molecules. These compounds, are characterized by their structure, which is noticeably similar to the adsorbed state of olefins on the catalyst surface based on transition metals (di- σ -adsorbed complex). The adsorbed complex, as the key structure of a heterogeneously catalyzed reaction, and its problematic structural characterization in comparison to the characterization of (olefin)Pt(PPh₃)₂ complexes, is the reason why the described group of substances has been gaining much interest of “catalytic chemist” despite the fact that the mentioned complexes do not exhibit the catalytic activity in of a homogeneous hydrogenation catalyst. The concept of the similarity of these compounds with the adsorbed di- σ -complexes was initiated from the following experimental observations:

- The organization of alkenes has significantly altered when coordinated with platinum(0). Unsaturated carbonic atoms, diverging from the plane of the double bond near the platinum atom, cause a deviation identical to the decrease in strength and extending the carbonic double bond.
- The olefin double bond in platinum(0) complexes diverges in a minor angle from the triangular plane arranged by platinum, midpoints of the olefinic double bond and the remaining two ligands.
- The platinum(0)-olefin bond appeared firm in the complexes.
- Proton nuclear magnetic resonance (¹H NMR) spectrum of platinum(0)-olefin complexes revealed that during coordination of olefin, the starting sp^2 hybridization of the carbon atom was near the sp^3 hybridization, which could be interpreted as a result of the production of three-membered ring (cyclopropane type) (**Figure 1**).

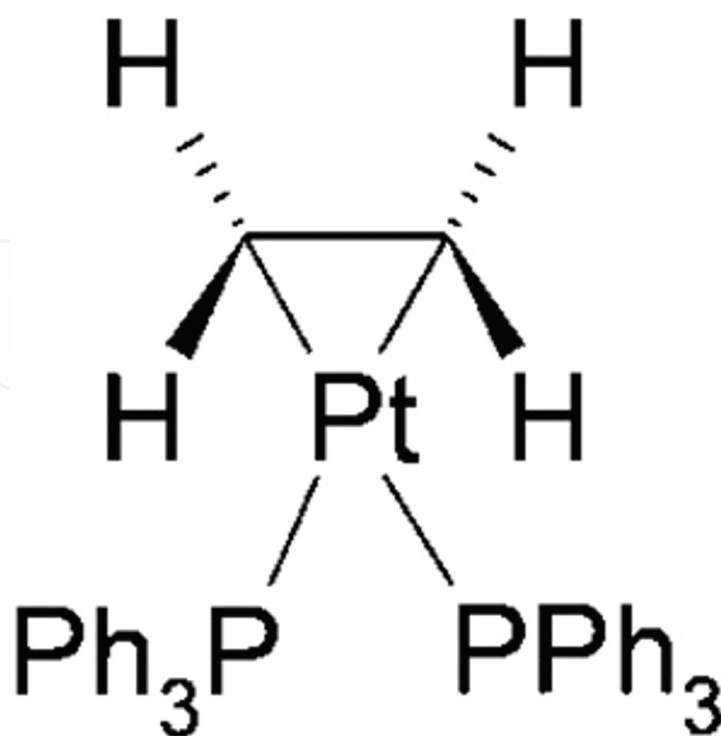


Figure 1. Three-membered ring (cyclopropane type) formed by coordination of alkene to Pt(0).

The bonding mode in Pt(0)-olefin complexes has usually been explained by means of a modified Dewar-Chatt-Duncanson approach, which assumed two simultaneous and partly mutually dependent interactions of the orbitals of the metal and alkenes, namely donation and back donation (**Figure 2**). The significance of donation can be sufficiently described using the classical donation of $\pi_{C=C}$ alkene electrons to vacant d -orbitals of platinum(0). The back donation has been perceived as the interaction of occupied orbitals of platinum (in the band theory of solids, these were the bands laying below the Fermi energy level) with $\pi_{C=C}^*$ olefin orbital. The reverse donation has a significant impact on the stability of the complex.

The lower is the electron density on C=C double bond (causing a stronger withdrawal of electrons), the lower is the level of $\pi_{C=C}^*$ orbital and thus a lower energy difference between $\pi_{C=C}^*$ alkene orbital and the occupied d -orbitals of Pt. As a result, a stronger interaction occurs between $\pi_{C=C}^*$ and occupied Pt (d) orbitals, which constructs a stronger bond of Pt-alkene. If a common alkene is described as ethylene-bearing electron-acceptor substituents, then the substituents have the tendency to stabilize the complex by shifting highest occupied molecular orbital/lowest unoccupied molecular orbital ((HOMO)/LUMO) energy levels in alkene toward the planes of Pt(PPh₃)₂. To the contrary, the groups increasing their electron density destabilize the complex to such an extent that the process of preparation could be rendered impossible. **Figure 3** shows the general order of stability in the group of ethylene derivatives bearing typical smaller substituents.

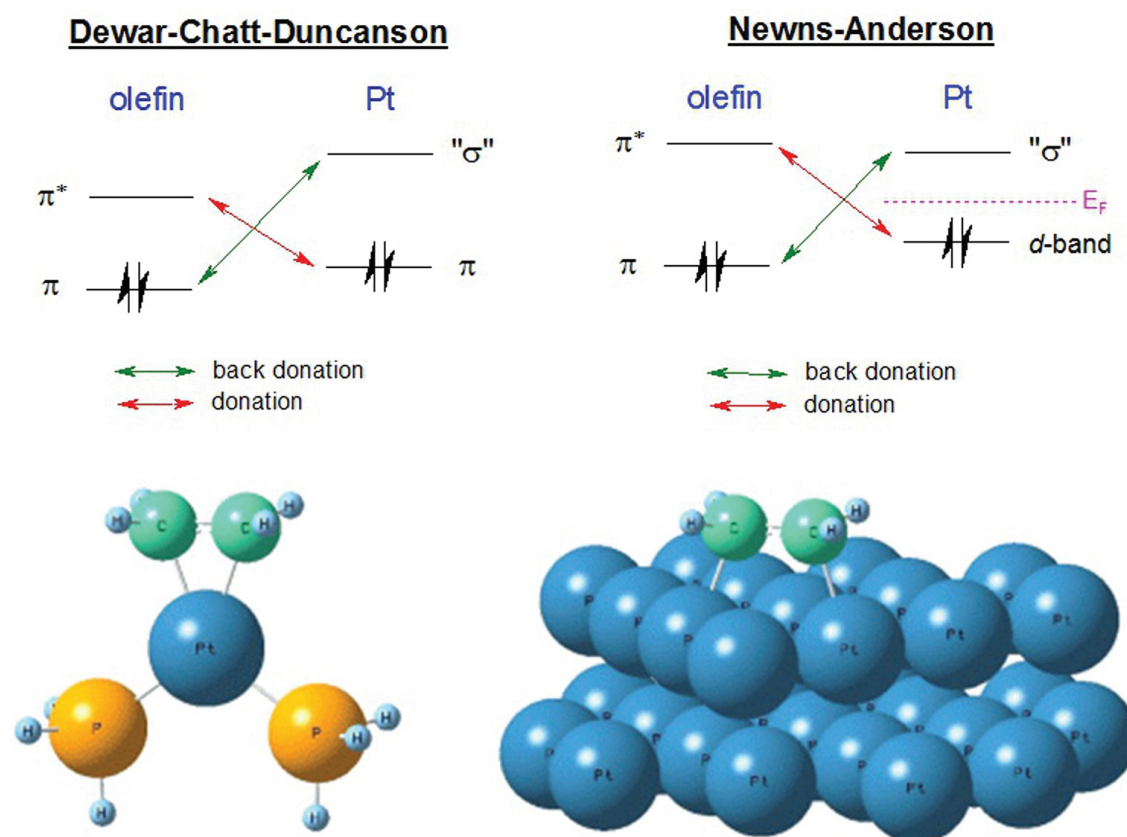


Figure 2. Orbital description of the bonds in the olefin-metal models: (1) Dewar-Chatt-Duncanson model derived for organometallic compounds; (2) Newns-Anderson model derived for surface complex substrate-catalyst.

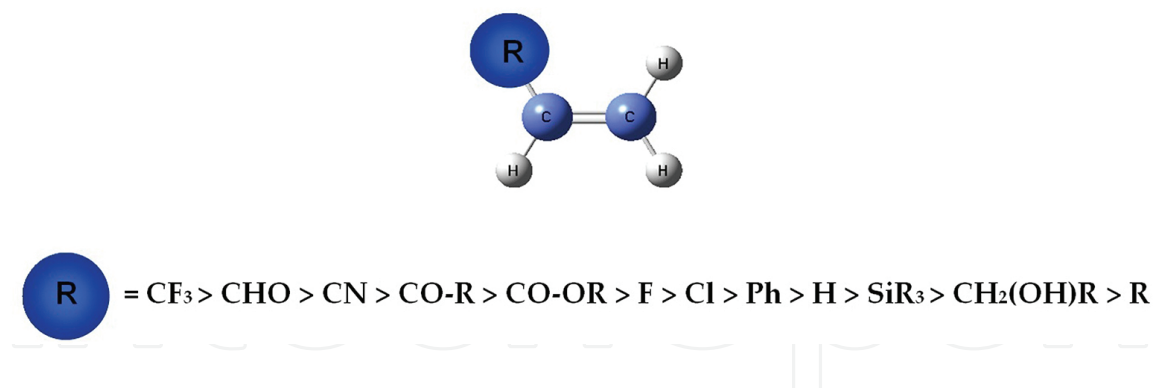


Figure 3. General order of coordinated olefins stability.

3. Synthetic procedures of (olefin)Pt(PPh₃)₂ complex

The literature has described a number of synthetic methods [11, 17] that led to the production of complexes of the type (olefin)Pt(PPh₃)₂. There are few basic procedures for the synthesis of these organometals. The usual starting substance is either chloride of bis(triphenylphos-

phine)platinum(II), ethylene-*bis*(triphenylphosphine)platinum(0), tris(triphenylphosphine)platinum, or tetrakis(triphenylphosphine) platinum. In particular, the following reactions are involved: the reduction reaction of Pt(II)-complexes (e.g., chloride of bis(triphenylphosphine)platinum) and the exchange of alkenic ligands in Pt(0)-coordination compounds, such as $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$. The majority of such synthesized complexes, however, exhibited a very low stability (**Figure 4**).

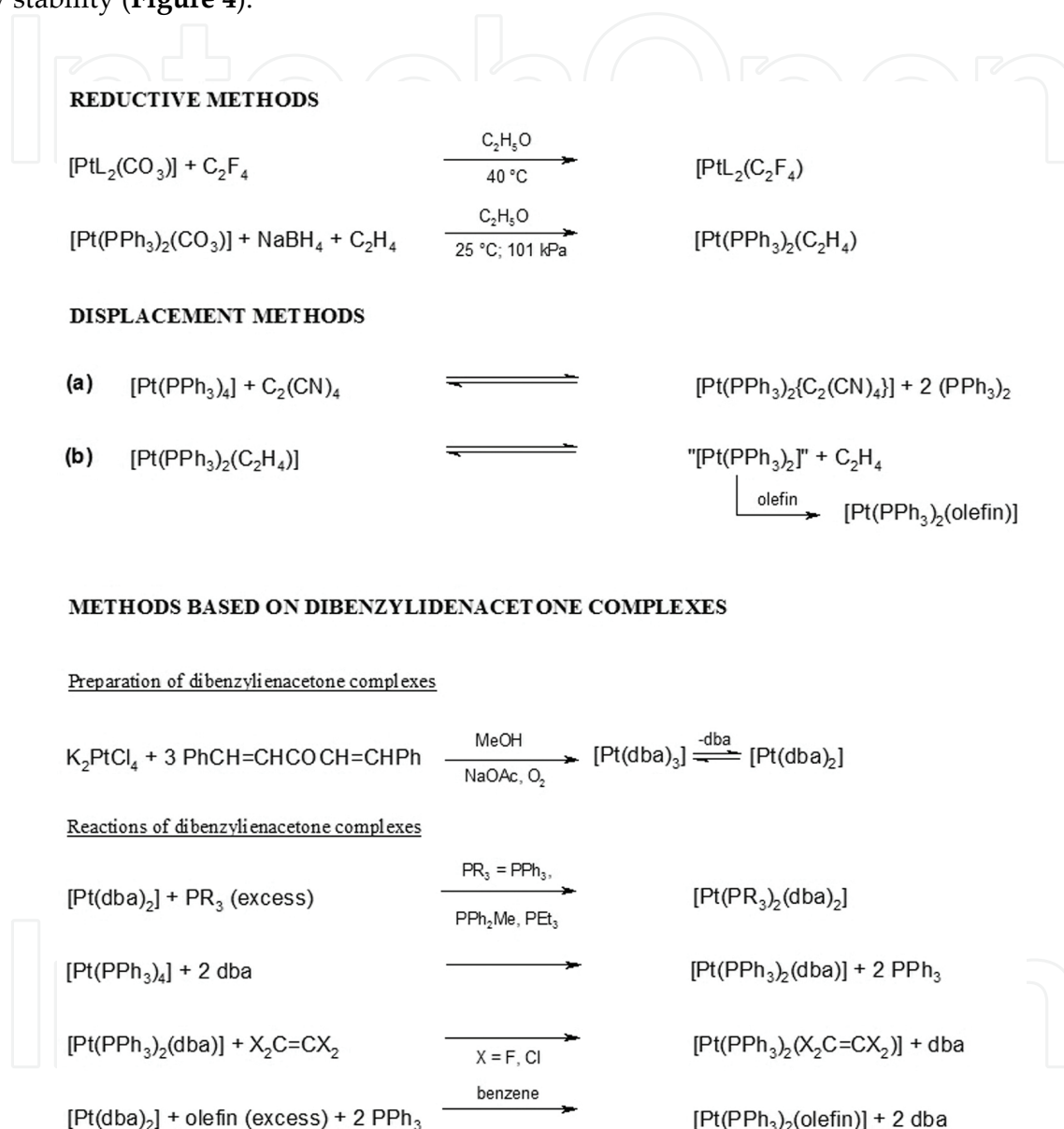


Figure 4. A scheme of preparation methods of (olefin) $\text{Pt}(\text{PPh}_3)_2$ complexes.

A series of model complexes of (olefin) $\text{Pt}(\text{PPh}_3)_2$ type were prepared. The preparation procedure consisted in reductive reactions of Pt (II)-complexes (*cis*-dichloro-*bis*(triphenylphosphane) platinum(II)), alternatively in the exchange of olefinic ligands in Pt-(0)-coordination compounds η -ethylene-*bis*(triphenylphosphane) platinum(0)). The syntheses were carried out in the absence of atmospheric oxygen and moisture, using the so-called Schlenk techniques

(Figure 5). In Figure 6, the ligands of the synthetically prepared complexes of the type (olefin)Pt(PPh₃) are depicted, and clearly imply that the prepared complexes could be characterized as substituted ethylene with electron-accepting substituents, which tend to stabilize the produced complex by shifting the energy levels of HOMO/LUMO in olefin toward the levels of Pt(PPh₃)₂. By contrast, the groups increasing the electron density in this place destabilize the complex to such a degree that its preparation is not possible. The example could be complexes (alkenic alcohol)Pt(PPh₃) that have never been spectroscopically proven in the reaction mixtures. The reason could be sought in a low stability of these complexes probably caused by a hydroxyl group present in molecules of an alkenic ligand, which by increasing the electron density on C=C bond destabilizes the potentially produced complex. Figure 6 captured the theoretically calculated stability order of the group of ethylene derivatives bearing typical smaller substituents, showing a good correlation with the stability of the prepared complexes, which were experimentally verified by NMR “*in situ*” competitive experiments.

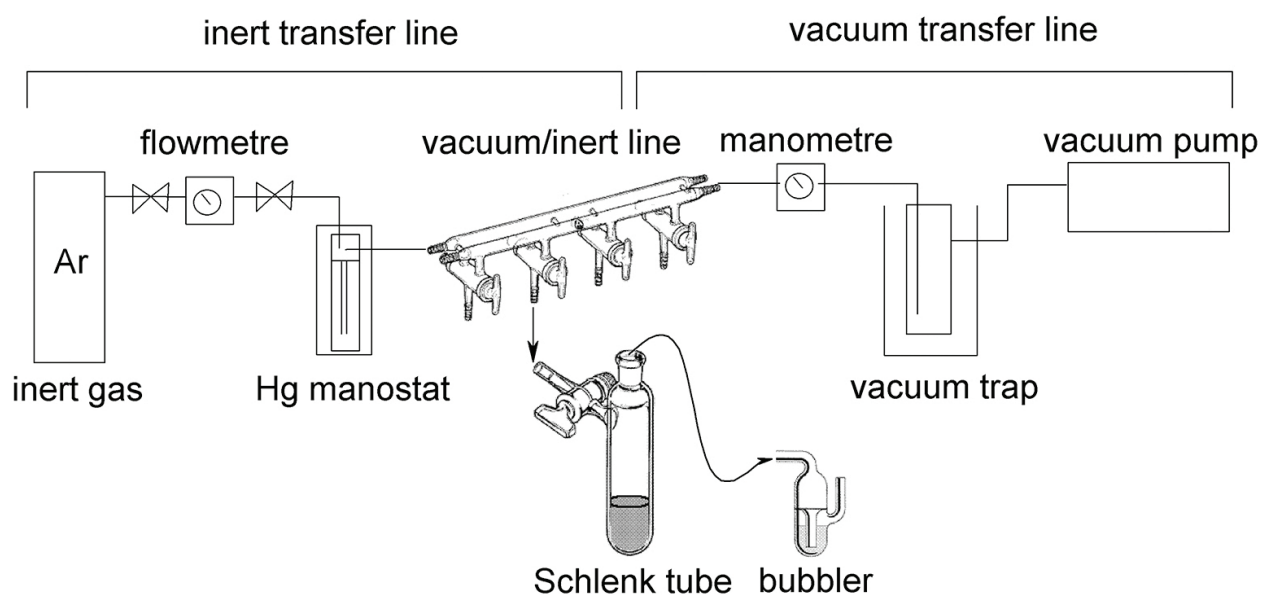


Figure 5. The apparatus used for the synthesis of (olefin)Pt(0)-(PPh₃)₂ complexes.

NMR spectroscopy is one of the most important techniques for the study of substances in a solution. It may therefore be somewhat surprising to combine NMR in the liquid phase with heterogeneous catalysis, but this connection is possible and the results obtained by NMR liquid phase can be used for the interpretation of phenomena related to heterogeneous catalysis. However, it is necessary to find a suitable system by which the interaction of active site-reaction center can be approximated, and which also satisfies the condition of NMR experiments in liquid phase. If this condition is met, it is possible to monitor what is happening at the atomic level, thereby obtaining valuable information for heterogeneous catalysis.

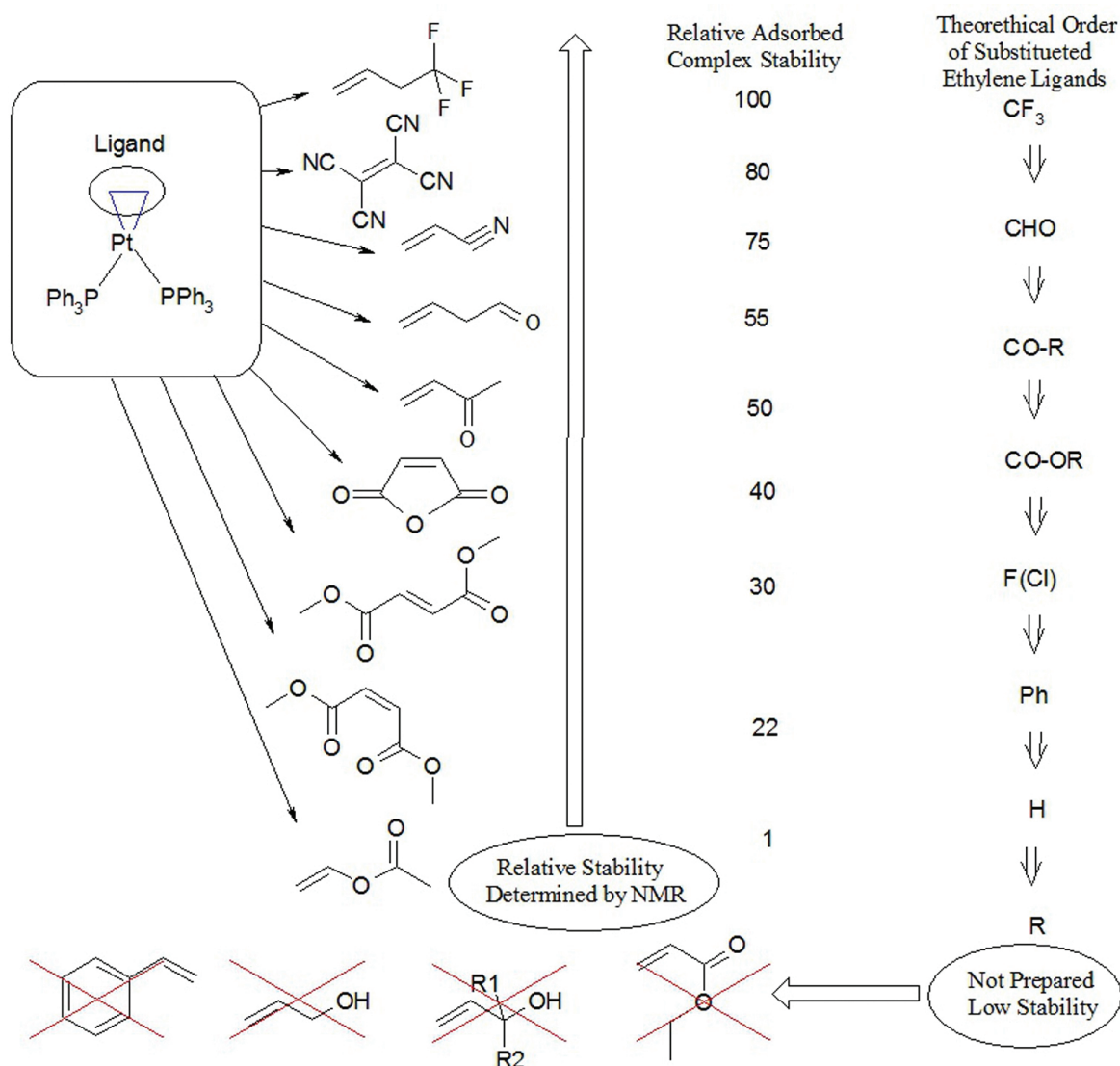


Figure 6. Synthetically prepared complexes of (olefin)Pt(PPh₃) type and their relative stability determined by NMR “*in situ*” experiments.

The developed NMR “*in situ*” method of competitive production of model (olefin)Pt(PPh₃) complexes is a significant progress toward assessing the stability of adsorbed complexes, particularly allowing to express the relative stability of a complex to be produced. The homogeneous complex of ethylene *bis*(triphenylphosphine)platinum(0) was used as the suitable model for studying the interaction of active site-reaction center, which was capable of forming coordination compounds with ligands of the CC double bond. As mentioned above, ethylene coordinated to platinum could be exchanged for other unsaturated substrates. To test this concept, experiments with esters of fumaric acid and maleic were primarily conducted, that is, with dimethyl fumarate and diethyl maleate. Using these substrates, the influence of *cis/trans* isomerism on the CC multiple bond was studied. Both substrates were able to displace ethylene from the complex and form a stable complex with platinum, which was manifested by a splitting of the previous singlet signal of olefinic (Figure 7).

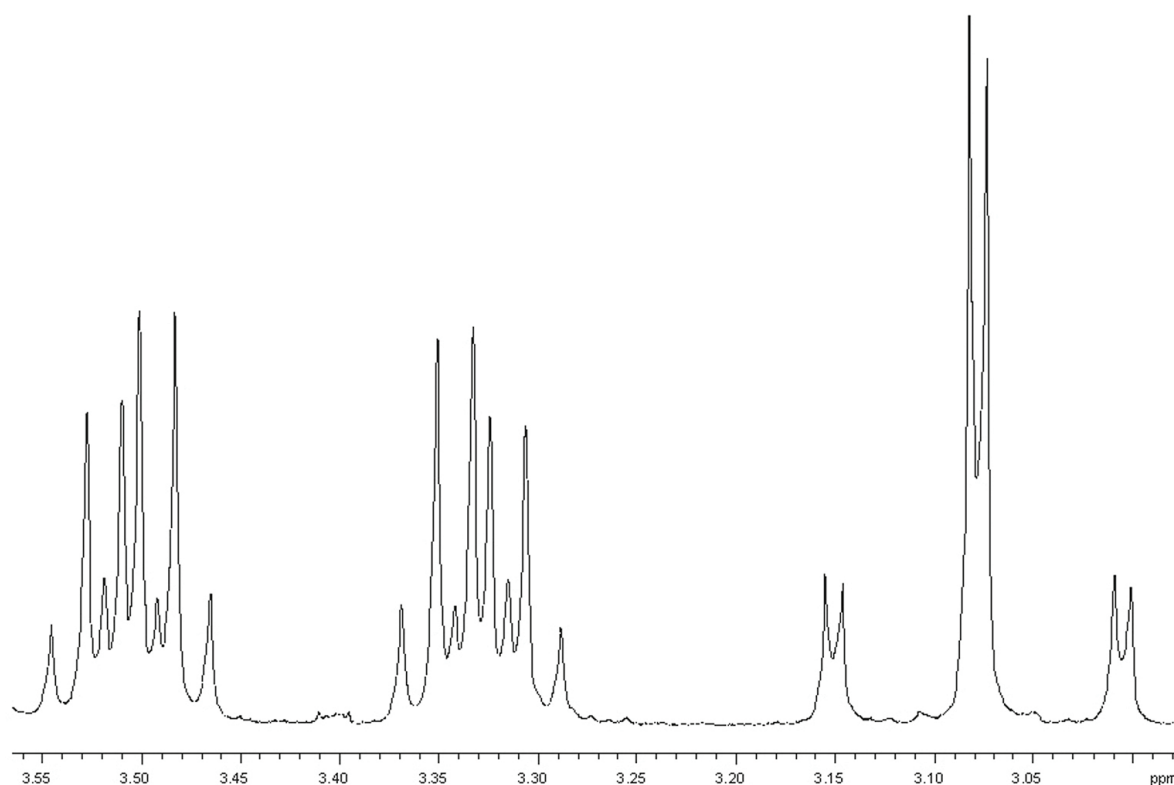


Figure 7. Fragment of ^1H NMR spectra of diethyl maleate bis(triphenylphosphine)platinum(0) complex.

Wherever the equimolar mixture of both ligands was added to the solution of ethylene bis(triphenylphosphine)platinum(0), the formation of the equimolar quantities of both complexes of esters with platinum was prevented, but a complex with dimethyl fumarate was preferentially produced. It could be assumed that the resulting ratio reflected the different adsorption properties of both ligands. In order to verify that it was the case of a behavior resulting from an inter-displacement of ligands, an experiment was conducted, in which first the complex with diethyl maleate was prepared and subsequently dimethyl fumarate added. Even under these circumstances, the ligand (diethyl maleate) displacement took place as well as the stabilizing of a ratio corresponding to the situation of a simultaneous addition of both ligands (**Figure 8**). This method has a certain limit related to a small dynamic range of NMR measurements, and thus it is necessary to compare substrates as described above with near adsorptivities. On the other hand it implies that even minor changes in the absorptivity of substrate molecules can be registered using this procedure. In a series of synthesized complexes of (olefin) $\text{Pt}(\text{PPh}_3)_2$, the complexes with a near stability have always been selected, and NMR “*in situ*” competitive measurements performed. Based on them, a relative stability of the prepared complexes was determined. As shown below, this sequence very well correlated with calculated bonding energies of the listed complexes.

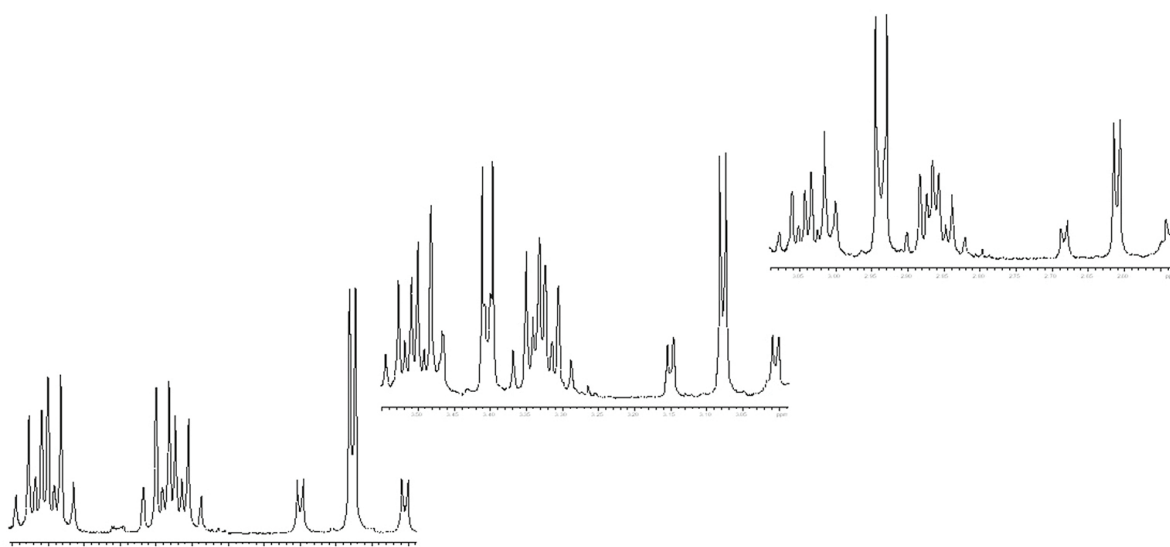


Figure 8. Selected ^1H NMR spectra in the course of competitive displacement of ligands (diethyl maleate and dimethyl fumarate).

4. Theoretical study of complexes of $(\text{olefin})\text{Pt}(\text{PPh}_3)_2$

The purpose of these studies was to find a calculable correlation relationship between the structure and the stability of the complexes of the type $(\text{olefin})\text{Pt}(\text{PPh}_3)_2$. The stability comparison was carried out by numerous available computational methods, that is, using both structural parameters (changes in the binding length and angles after coordination), then the quantification of the bond orders in alkene subunits, and finally the estimation of the binding energy between an alkene and $\text{Pt}(\text{PPh}_3)_2$. It was soon discovered and experimentally confirmed that the chemical nature of the bond metal-alkene is rather nearer the description of cyclopropane ring (see above) than the potential π -bond. These models assume that within the formalism of valence bonds, the compound $\text{Pt}(\text{PPh}_3)_2$ -alkene can be considered as a derivative of platinum(II) rather than platinum(0), providing the change in hybridization of carbon atoms from sp^2 to sp^3 . Many computational approaches to compounds of the type $[(\text{olefin})\text{Pt}(\text{PPh}_3)_2]$ require to tackle one important parameter, that is, a structural simplification leading to a significant reduction in the computing time, which is carried out on the assumption that phenyl groups are simply regarded as hydrogens, and in particular triphenylphosphine groups are regarded as phosphines. This simplification reduces the number of atoms in the calculation by 60 and even more significantly reduces the number of basic functions, which leads to a major acceleration of the computation. It is known that this simplification does not affect the structural and energetic results, although the steric hindrance on the platinum atom is relatively substantially altered.

The results of molecular modeling in the given group of substances were generally confirmed by the experimentally observed geometry of molecules, while any potential discrepancies have been notably dependent on the parameterization. Moreover, some aspects based on the

theoretical approach allowed evaluating also such quantities as the reduction of values in the order of C-C bond, the binding energy of Pt-olefin, and other parameters. The contributions of donation and reversed donation to the bond platinum-olefin were also addressed on the theoretical basis of the orbital interaction method CDA (*charge decomposition analysis*). As a result, it was demonstrated that the π -reversed donation (Pt to LUMO olefin) was the main binding contribution and thus affected the strength of Pt-C bonds much stronger than the donation (**Figure 2**). In the presented study, a considerable attention has been devoted to quantum-mechanical calculations on a group of $(PPh_3)_2Pt(olefin)$ complexes, which were sufficiently reliably approximated by complexes with the structure $(PH_3)_2Pt(olefin)$, **Figure 9**. This approximation led to a marked simplification of calculations; the number of atoms in resolved molecules was thus reduced by 60 and the number of base functions by 552 to 106 bases (while it is known that the computational requirements of chemical structures increase with the number of atoms in a molecule approximately exponentially). In the search of a suitable parameterization for calculating the structure, the convergence of binding energies in molecules was preferred from their geometrical properties (bond lengths of Pt-C and Pt-P and the angles of P-Pt-P and C-Pt-C). For the geometrical optimization, the method of B3LYP (functional density functional theory (DFT) hybrid) was selected with the base 6-31G(d) for the lighter elements (Cl, P, S, O, N, F, C, and H) and the base LanL2DZ with the pseudopotential (ECP, *effective core potential*) LanL2 for Pt based on the study of *Frison and Grützmacher* [16], who utilized only a slightly larger "Basis Set II." To quantify the total energy of molecules, MP2 method was selected as a compromise solution for a better interpreting ability, and simultaneously for only medium requirements on the computing time. For the calculations of Hessian (estimation of infrared (IR) spectra), the same parameterization was used as for the geometrical optimization, that is, B3LYP/6-31G(d):LanL2DZ. The binding energy of olefin-platinum bonds in the molecules of $(olefin)Pt(PH_3)_2$, where the olefin was $R^1R^2C=CR^3R^4$ and bound by two σ -bonds with both carbons to platinum, has been interpreted as the dissociation energy of these bonds, that is, the enthalpy of decomposition reaction of an organometallic complex. Numerically, the binding energy is thus equal to the difference between the energies of a complex splitting (olefin and $(PH_3)_2$), and the complex $(olefin)Pt(PH_3)_2$, the final and the initial state, respectively:

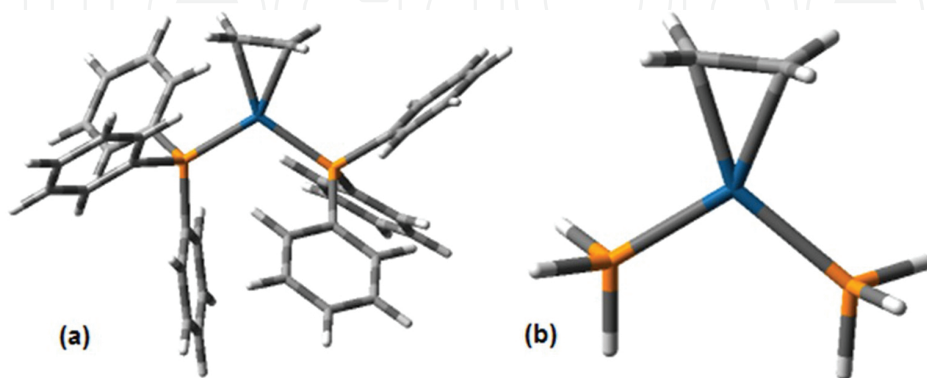


Figure 9. Molecular structure of $(PPh_3)_2Pt(CH_2=CH_2)$ (a) and $(PH_3)_2Pt(CH_2=CH_2)$ (b).

$$E_B = E[\text{Pt}(\text{PH}_3)_2] + E[\text{olefin}] - E[(\text{olefin})\text{Pt}(\text{PH}_3)_2]. \quad (1)$$

During the calculations, the binding energy of Pt-olefin bonds was enumerated. Therefore, it had primarily been necessary to carry out geometrical optimization on both free planar olefins $\text{R}^1\text{R}^2\text{C}=\text{CR}^3\text{R}^4$ and then to evaluate their geometric properties. In olefins with a more complicated conformational behavior (e.g., unsaturated alcohols), a random inspection of the conformation space was performed related especially to those degrees of freedom where a free rotation around CC bonds occurred only with a low barrier (**Figure 10**). then the equilibrium geometry of olefins was introduced to the models of organometallic compounds $(\text{PH}_3)_2\text{Pt}(\text{R}^1\text{R}^2\text{C}=\text{CR}^3\text{R}^4)$, and these models were optimized without any restrictions on any degrees of freedom. The fragment $(\text{H}_3\text{P})\text{-Pt-(PH}_3)$ assumed the optimal geometry in the linear arrangement. The structure of the fragment $(\text{Ph}_3\text{P})\text{-Pt-(PPh}_3)$ was calculated as well, in which the linear structure of P-Pt-P has been analogically identified. These structures have been considered to be metastable. Although their observations have been reported, no credible spectroscopic evidence was provided. IR spectra have been estimated and optimized for different models of olefins and their complexes. The algorithm of molecular modeling of the complex $(\text{olefin})\text{Pt(PPh}_3)_2$ is summarized in **Figure 11**.

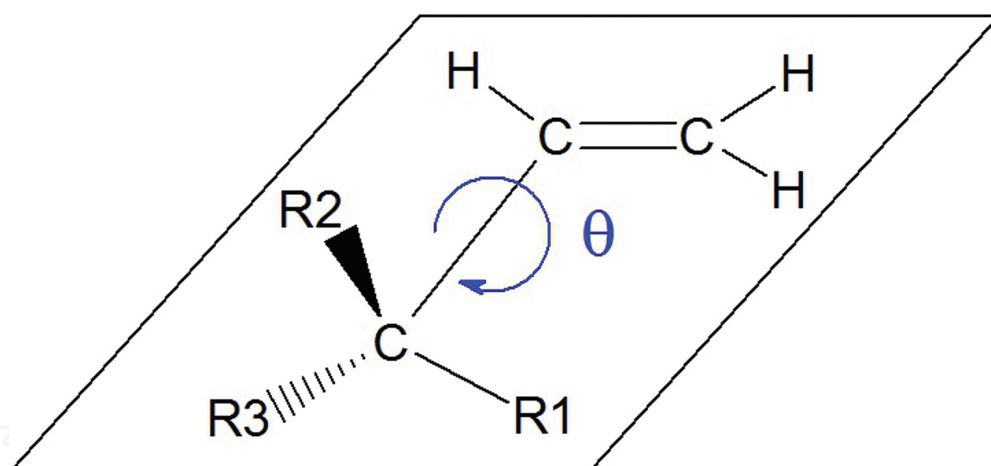


Figure 10. Alkene $\text{CH}_2=\text{CH-CR}^1\text{R}^2\text{R}^3$ with allowed rotation around C-C bond.

4.1. Structure-based effects

As a general rule, the double bonds of carbons associated with platinum(0) manifested their extension compared to the other functional groups. This has also been supported by the determined significant alterations in the constitutional and electronic properties of the olefins. The angle between P-Pt-P and C-Pt-C markedly differs among various organometallic substances due to dissimilar properties of each olefin. Platinum(0) was bound with the olefin functional groups via two $\sigma(\text{Pt-C})$ bonds. Among the listed olefins, all were arranged in η^v -

fashion to platinum with no free rotation, to the contrary of rotations described in the case of ethylene in platinum(II) derivatives such as Zeise's salt $K[Cl_3Pt(CH_2=CH_2)]$.

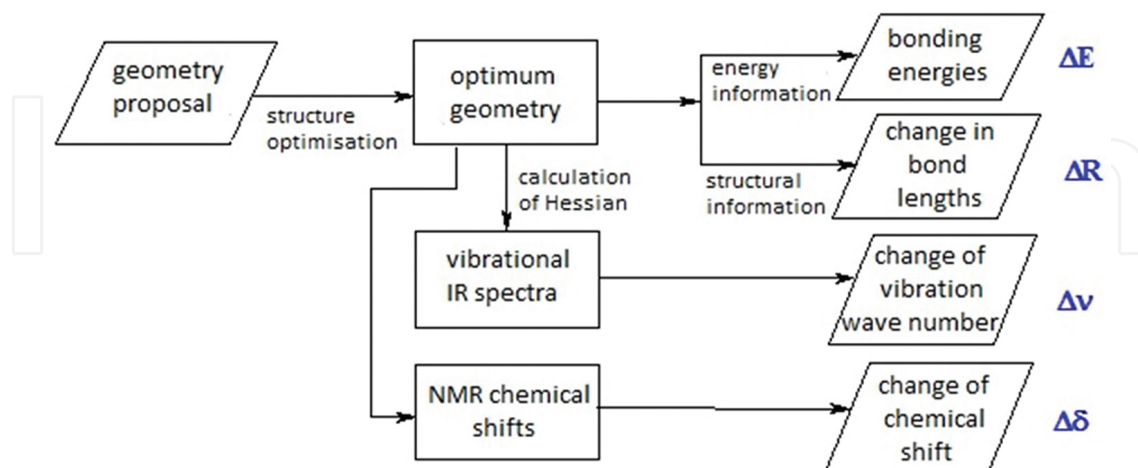


Figure 11. Flowchart of utilization of methods of molecular modeling in the group of “species” $(PH_3)_2Pt(R^1R^2C=CR^3R^4)$, $(H_3P)-Pt-(PH_3)$ and $R^1R^2C=CR^3R^4$.

The implicit solvation method has not been applied any further, as the continuum solvation had negligible effects, the parameters as the vibrational frequencies, optimal geometries, energies, and NMR magnetic-shielding tensors, etc., as proven by a separated computation (pulse-code modulation (PCM) method, dielectric constant of dichloromethane). **Table 1** shows the global assessment of energetic and structural outcomes resulted from the final computations. The values of binding energy EB were applied as to assess the thermodynamic properties of Pt-olefin electron-overlap interaction: $\Delta\nu$ indicates the change in the vibrational wave number of C=C-stretching/contracting mode following the complex production, whereas ΔR is the extension primarily generated by the strength of metal-olefin complex. The pyramidalization δ was determined as an average angle of $R1-C=C-R3$ and $R2-C=C-R4$ dihedrals; thus, it has been applicable also to asymmetrical olefins, to the contrary of the previous papers [4, 14], where the pyramidalization angle was determined merely for $R_2C=CR_2$, that is, olefins shaping complexes in C_{2v} symmetry.

In order to make comparison and consistency with the previous studies, a reference compound was selected, that is, ethylene, whose results are further discussed in detail. Yates [19] carried out broad computations related to the consistency and attained the binding energy of 111.9 kJ/mol in $(PH_3)_2Pt(CH_2=CH_2)$ at MP2/6-31G(d):LANL2DZ level, however, remarkably lower quantities for the arrangements containing PPh_3 ligands. Nunzi et al. [16] determined the “bond dissociation energy,” amended with BSSE (basis set superposition error), as 102 kJ/mol at local density approximation (LDA)-DFT level of theory using mixed ζ -quality Slater-type orbital (STO) basis sets. Nevertheless, the published experimental values [17] for $(PPh_3)_2Pt(CH_2=CH_2)$ of Mortimer (152 ± 18 kJ/mol, gas-phase) and Kirkham et al. (11.6 ± 1.6 kJ/mol) appeared to be relatively inaccurate.

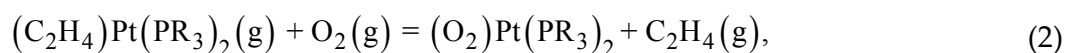
Group/compound		E_B [kJ/mol]	Δv [cm ⁻¹]	ΔR [Å]	δ [°]
Ethylene complex	(ethylene)Pt(PH ₃) ₂	116.8	508.41	0.0943	28.84
	(ethylene)Pt(PH ₃) ₂	–	–	0.0989	30.81
Propadiene, Butadiene and Vinylacetylene	(propadiene)Pt(PH ₃) ₂	136.5	245.47	0.1087	–
	(buta-1,3-diene)Pt(PH ₃) ₂	115.5	507.70	0.0906	28.61
	(vinylacetylene)Pt(PH ₃) ₂ ^a	121.2	476.83	0.0973	29.87
	(vinylacetylene)Pt(PH ₃) ₂ ^a	125.8	404.41 ^s	0.0795 ^s	–
	(prop-2-en-1-ol)Pt(PH ₃) ₂	107.6	513.64	0.0944	30.52
Unsaturated Alcohols	(2-methylbut-3-en-2-ol)Pt(PH ₃) ₂	110.9	503.45	0.0971	32.01
	(hex-1-en-3-ol)Pt(PH ₃) ₂	114.8	506.43	0.0925	29.90
	(hept-1-en-4-ol)Pt(PH ₃) ₂	98.9	501.68	0.0965	29.93
	(methacrylonitrile)Pt(PH ₃) ₂	127.2	369.05	0.1038	32.36
Cyanoethylenes	(acrylonitrile)Pt(PH ₃) ₂	131.2	491.22	0.1039	31.20
	(<i>E</i> -1,2-dicyanoethylene)Pt(PH ₃) ₂	149.3	488.76	0.1112	32.58
	(<i>Z</i> -1,2-dicyanoethylene)Pt(PH ₃) ₂	148.0	479.93	0.1104	31.11
	(tricyanoethylene)Pt(PH ₃) ₂	166.8	377.86	0.1176	32.24
	(tetracyanoethylene)Pt(PH ₃) ₂	181.1	317.12	0.1229	31.29
	(but-1-en-3-on)Pt(PH ₃) ₂	132.0	466.08	0.0922	27.24
Compounds containing α -carbonyl group(s)	(methyl acrylate)Pt(PH ₃) ₂	122.1	485.95	0.0949	28.46
	(maleic anhydride)Pt(PH ₃) ₂	154.1	279.99	0.1011	32.24
	(acrylic aldehyde)Pt(PH ₃) ₂	136.9	467.88	0.0906	25.93
	(cinnamic aldehyde)Pt(PH ₃) ₂	121.0	438.84	0.0879	27.32
	(acryl amide)Pt(PH ₃) ₂	125.4	482.82	0.0955	28.71
	(diethyl fumarate)Pt(PH ₃) ₂	121.4	494.10	0.0944	27.42
	(tetrachloroethylene)Pt(PH ₃) ₂	101.1	433.82	0.1303	53.49
Halogen containing compounds	(tetrafluoroethylene)Pt(PH ₃) ₂	110.1	444.84	0.1254	45.02
	(octafluoro- <i>E</i> -but-2-ene)Pt(PH ₃) ₂	145.4	359.36	0.1224	42.07
	(<i>E</i> -1,1,1,4,4,4-hexafluorobut-2-ene)Pt(PH ₃) ₂	165.2	555.34	0.1134	35.14
	(3-chlorobut-1-ene)Pt(PH ₃) ₂	120.0	521.20	0.1042	33.70
	(3-methylcyclopropene)Pt(PH ₃) ₂	153.7	414.73	0.1236	–
Strained olefins	(1,2-dimethylcyclopropene)Pt(PH ₃) ₂	144.9	377.94	0.1175	–

Group/compound	E_B [kJ/mol]	Δv [cm ⁻¹]	ΔR [Å]	δ [°]	
Various compounds	(bicyclo[2.2.0]hex-3(5)-ene)Pt(PH ₃) ₂	165.3	461.09	0.1248	–
	(bicyclo[4.2.1]non-1(8)-ene)Pt(PH ₃) ₂	145.8	261.94	0.0992	–
	(vinyltrimethylsilane)Pt(PH ₃) ₂ ^c	128.3	463.25	0.0938	29.35
	(Z-1,2-bis(phenylsulfonyl)ethylene)Pt(PH ₃) ₂ ^d	118.5	332.58	0.1140	39.20
	(carbon disulfide)Pt(PH ₃) ₂ ^e	74.8	341.57 ^h	0.1291 ^h	–
	(dioxygen)Pt(PH ₃) ₂ ^f	194.3	637.49 ⁱ	0.1849 ⁱ	–

^aCoordination via C=C double bond; ^bCoordination via C≡C triple bond, vibrational shift for C≡C stretch; ^c–^fSyntheses of complexes, see Refs. [9, 12, 13, 16], respectively; ^gVibrational shift of the C≡C stretch and elongation of the C≡C bond; ^hVibrational shift of the C=S stretch and elongation of the C=S bond; ⁱVibrational shift of the O=O stretch normal mode and elongation of the O=O bond.

Table 1. The calculated parameters of coordination compounds of type (PH₃)₂Pt (olefin).

In our study, for a completely optimized complex (PH₃)₂Pt(CH₂=CH₂) (**Figure 12**), the binding energy of Pt-ethylene bonds was calculated as 116.8 kJ/mol at MP2/6-31G(d):LANL2DZ level of theory. The relatively minor discrepancy from the outcomes of Yates [15] could have been produced by our experimental setup, which has underwent a minor optimization. The binding energy for our entirely optimized model of (PPh₃)₂Pt(CH₂=CH₂) was determined at B3LYP/6-31G(d):LANL2DZ level, yielding a value of only 9.9 kJ/mol (in comparison to 51.9 kJ/mol for the PH₃ analog). Regarding the geometrical parameters, the C=C bond in (PH₃)₂Pt(CH₂=CH₂) stretched from 1.331 (free) to 1.425 (coordinated) by 0.094 Å. For the PPh₃ analog, the coordinated value was 1.430 Å, which was nearer to 1.434 Å as measured in the experiment. In the complex (PH₃)₂Pt(CH₂=CH₂), having C_{2v} symmetry, both Pt-P bonds were of the same length 2.157 Å, while in (PPh₃)₂Pt(CH₂=CH₂) [C_s symmetry], two different Pt-P bond lengths were calculated (2.356 and 2.366 Å). The mean experimental value was 2.268 Å. The σ-Pt-C bonds in (PH₃)₂Pt(CH₂=CH₂) were 2.157 Å long. Regarding the PPh₃ analog, the bond length was calculated 2.153 Å (mean value of 2.168 and 2.138 Å). Both of these achieved results were overestimated in comparison to 2.112 Å (average) as determined by the experiment [18]. The next aim was to determine the similarity of Pt(0)-olefin organometallics from olefins coordinated on metal surfaces. In our study, the vertical distance of platinum and C=C bond in (PH₃)₂Pt(CH₂=CH₂) was 2.036 Å, while for ethylene adsorbed in di-σ-bridge position on the Pt(111) surface, comparable values were obtained. Moreover, regardless of the calculations performed at different theory levels, the bond dissociation energies were 116.8 kJ/mol in the case of organometallic compounds (MP2 value, this study) and 106.1 kJ/mol in the case of C₂H₄ on p(2x2)-Pt(111) (generalized gradient approximation (GGA)-DFT calculation, [15]). Thus, the values were comparable within these arrangements. Additionally, the thermodynamics of the complete reaction of molecular oxygen with platinum(0) complex has been examined. It has been recognized that ethylene in the complex of (C₂H₄)Pt(PR₃)₂ is substituted by dioxygen producing (O₂)Pt(PR₃)₂. This reaction proceeded well, providing the exposure of (C₂H₄)Pt(PR₃)₂ to the ambient air. Having substituted **H** for **R**, the reaction enthalpy was determined according to the following schema:



finally obtaining the value of $\Delta H_r^{298} = -77.4 \text{ kJ/mol}$, a relatively average figure for an exothermic reaction.

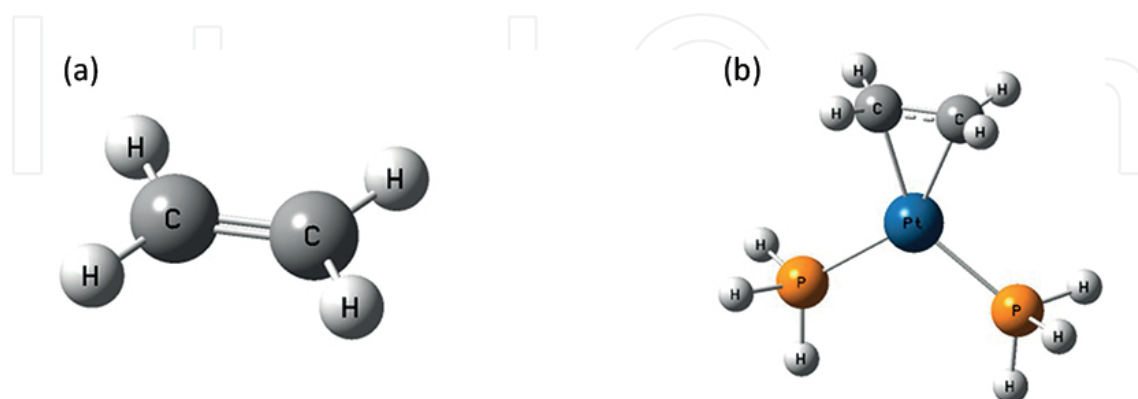


Figure 12. Molecular structure of ethylene (a, left) and (ethylene)Pt(PH₃)₂ (b, right).

4.1.1. Propadiene, butadiene, and vinylacetylene

Even though these hydrocarbon groups contain only alkenic or alkynic functions on the subject multiple bond, the computation disclosed that they retain enough strength upon coordination. It can be deduced that the functions $\text{CH}=\text{CH}_2$ (vinyl) and $\text{C}\equiv\text{CH}$ (ethynyl) apparently favored accepting electrons. Moreover, interrupting the conjugation of multiple bonds is an energy-requiring procedure which has an inversely proportional effect on the dissociation energy. Different bond strengths were recorded for vinylacetylene (but-1-ene-3-yne). Compared to buta-1,3-diene or propadiene, either double or triple bond coordinated to the platinum(0) core atom with different bond strengths. As described in preceding computations and assessments, the triple bond arrangement was the ultimately favored constitution. This observation has been also substantiated during the examining of a relatively well-proceeding substitution reaction of olefinic complexes with substances bearing acetylenic group. It could have been initiated by the triple bond, a stronger electron-acceptor versus the $\text{C}=\text{C}$ double bond acting as the substituent. Allene (propadiene) formed robust bonds to Pt(0), accompanied by a high-bond dissociation energy, and only a subtle wave number drop of $\text{C}=\text{C}$ stretch ($\sim 275 \text{ cm}^{-1}$) of the bound double bond.

4.1.2. Unsaturated alcohols

Unsaturated alcohols with $-\text{OH}$ group in α - or β -position to the double bond manifested a lower stability in the complex than ethylene. Apparently, the electron donor-acceptor characteristics associated with the hydroxy group in the complexes are rather shifted toward the electron donor. The decline in $\text{C}=\text{C}$ stretch wave numbers was comparable to the one determined for the ethylene complex. The hydroxyl group bound in α - position to the $\text{C}=\text{C}$ bond yielded complexes with a lower stability. Other alcoholic complexes, such as hex-1-en-3-

ol and allyl alcohol (prop-2-en-1-ol) gave slightly lower values of dissociation energy than for ethylene, suggesting their relative instability. Furthermore, allyl alcohol complexes were described to have been synthesized [19], yet verified only preliminarily by NMR. Nevertheless, this discovery indicates the potential for the production of alike derivatives. Having mentioned the minimal stability of the complex of hept-1-en-4-ol, a substantial decrease of the C=C stretch wave number was determined as well. The methyl groups in 2-methylbut-3-en-2-ol did not appear to have a noticeable impact on the complexes mainly owing to their pronounced sterical hindering (bulkiness) taking rather an aloof effect. On the other hand, they displayed a slightly higher stability compared to allyl alcohol complexes.

4.1.3. Cyanoethylenes

Table 1 depicts the tendency that can be read as the higher the amount of cyano groups on ethylene, the higher the stability of the complexes. Nitrile groups, strongly attracting electrons, supersede the double bond effect of sterical hindrance, and cause the energy level of HOMO orbitals in cyanoethylenes to be decreased in direction to the vacant orbitals of platinum. Previous studies of charge decomposition analysis predominantly indicated that π -back donation largely contributed to the final production of the platinum-olefin complex. The methyl group in methacrylonitrile, abundant with electrons, apparently caused the final complex to be less stable than the complex coordinated with acrylonitrile. Regarding 1,2-dicyanoethylenes, *E*-isomer (fumaric acid dinitrile) compared to *Z*-isomer (maleic acid dinitrile) displayed a relatively higher stability ($\Delta E = 1.3$ kJ/mol).

4.1.4. Compounds containing α -carbonyl group(s)

The length of an alkyl group in ester products of acrylic acid had a significant impact on the electron-acceptor role of the carbonyl group. Hence, the adjoining Pt-C bond was relatively strong and unaffected. Fumaric acid esters displayed an analogous drift, that is, diethyl esters were observed to have their stability only marginally lower compared to dimethyl esters. Moreover, it is prudent to take into account any disruption of conjugated bonds in α,β -unsaturated compounds. Plain ketones, for example, but-1-en-3-one, produce complexes with a reasonably high stability. The simplest unsaturated aldehydes are a palpable example, for example, acrylic aldehyde (prop-2-en-1-al), which retains even a higher stability (i.e., higher dissociation energy). Other products of acrylic acid (amide, methylester) were demonstrated to have an average stability (125.4 and 122.1 kJ/mol, respectively). The highest dissociation energy (154.1 kJ/mol) was found in maleic acid anhydride owing to an intense π -electrons attraction by the C=C bond and only a minor sterical constraints due to the absence of any massive substituents.

4.1.5. Halogen containing compounds

Halogenated hydrocarbons present a useful model for the review of donor/acceptor electronic impacts on the C=C double bond in olefins. For example, 3-chlorobut-1-ene produced a reasonably rigid complex, which was noteworthy given its high pyramidalization (33.7°). Perfluorinated ethylenes, when bond to bis(triphenylphosphine)platinum, yielded a consid-

erably elevated stability compared to perchlorinated products, probably owing to a geometric hindrance of chlorine atoms. Furthermore, carbon-halogen bonds are evidently more stretched after the coordination in C_2F_4 than in C_2Cl_4 , feasible due to a reduced conjugation of fluorine atoms with $C=C$ bond. Moreover, trifluoromethyl groups in $E-CF_3CF=CFCF_3$ incline to coordinate to a greater stability compared to the products of direct fluoro-substitution in C_2F_4 , which led to obtaining a dissociation energy among the highest observed for the $Pt-C_2$ bonding (165.2 kJ/mol). Halogen atoms located in a position influencing the $C=C$ double bond plausibly contribute to producing relatively stable organometallic complexes.

4.1.6. Strained olefins

The $C=C$ bond in strained olefins coordinated to extraordinarily highly stable complexes, as the sp^2 -carbon atoms apparently well- sp^3 -hybridized. The modified compounds were nominated based on available information found in the literature illustrating their feasible preparation and analytical detection. The complexes of each selected strained olefins revealed high-binding energies. Pyramidalization of substituents was assessed; however, unsatisfactorily high figures were obtained. Subsequently, this extent was determined for acyclic substitution on the $C=C$ double bond. Nevertheless, once the complex settled down, the deformation of substituents from the previous position was exceptionally significant within this group of complexes. **Figure 13** illustrates one of the instances: bicyclo[2.2.0]hex-3(5)-ene complex.

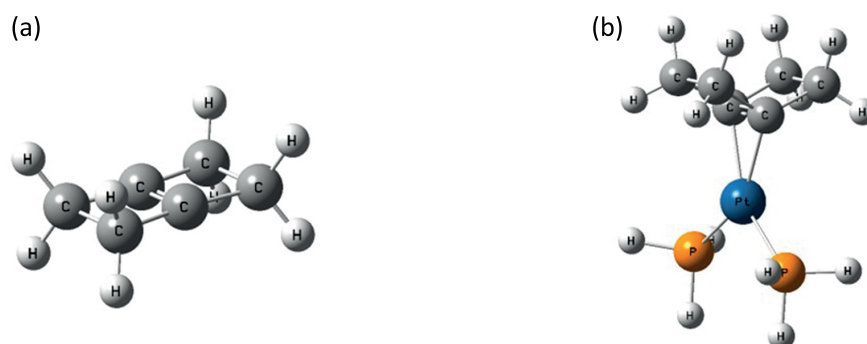


Figure 13. Bicyclo[2.2.0]hex-3(5)-ene free form (a, left) and complex (b, right).

4.1.7. Various compounds

Selected compounds (further elaborated in various publications) contained different types of double bonds in their structure and their stability in the coordinated state was calculated. For example, in the case of organosilicon compounds, particularly vinyltrimethylsilane, $CH_2=CH-Si(CH_3)_3$ delivered average quantities for E_B and further features assessed, inferring that the electronic properties of silicon atoms induced comparable effects as carbon. On the other hand, *rac-Z*-1,2-bis(phenylsulfonyl)ethane [15], yielded surprising data as the obtained binding energy for the coordination of the computed products of (*R,R*-isomer) was minor compared to ethylene. Nonetheless, the complex was prepared from $(PPh_3)_2Pt(CH_2=CH_2)$ by substituting the subject olefins. In order to assess the impact of the racemates, it is advisable to figure out

the average of binding energies of all enantiomers. The previous tests revealed that carbon disulfide (CS_2) adduct was in a solution of the olefin complex produced with a swift reaction rate, while the calculated binding energy was unexpectedly minimal. The cause could have been the solvent-stabilization effect in a carbon disulfide solution, since adduct supported the induction of dipoles in a near vicinity of the molecule. The preparation of dimeric polynuclear complexes could be dismissed by means of X-ray analyses [20]. Following the reaction of olefin complexes with molecular oxygen, dioxygen adduct $(\text{O}_2)\text{Pt}(\text{PH}_3)_2$ was noticeably produced without a reversible option, yielding by far a complex with the maximum computed stability value as the core metallic atom and its oxidation state assumed the form of Pt(II) [21].

5. Conclusion

Molecular modeling in heterogeneous catalysis is a very effective tool for investigating phenomena on the atomic level. As a key factor, an appropriate model for the approximation of the system under study appears to be the determination. The model then opens up new possibilities for predicting the behavior of molecules in particular reaction type. In the present work, models for heterogeneously catalyzed hydrogenations on platinum catalysts were designed which were tested and found limits of their applicability. The proposed approach to the study of molecular structure effects represents another step toward the development of an appropriate procedure for theoretical design of catalysts “tailored” to investigate not only the process but mainly the interaction-reaction center (substrate)—active site (catalyst).

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