

The platinum-olefin binding energy in series of $(\text{PH}_3)_2\text{Pt}(\text{olefin})$ complexes - a theoretical study

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Abstract Theoretical investigation of Pt(0)-olefin organometallic complexes containing tertiary phosphine ligands was focused on the strength of platinum-olefin electronic interaction. DFT theoretical study of electronic effects in a substantial number of ethylene derivatives was evaluated in terms of the Pt-olefin binding energy using MP2 correlation theory. Organometallics bearing coordinated olefins with general formula $(\text{R}^1\text{R}^2\text{C}=\text{CR}^3\text{R}^4)\text{Pt}(\text{PH}_3)_2$ [R=various substituents] had been selected, including olefins containing both electron-donor substituents as well as electron-withdrawing groups. The stability of the corresponding complexes increases with a strengthening electron-withdrawal ability of the olefin substituents.

Keywords Binding energy · DFT · Molecular modeling · Platinum complexes

Introduction

The electronic and geometric structure of platinum zerovalent complexes has become well known after the formulation of the Dewar-Chat-Duncanson theory [1, 2] of metal-olefin

bonding (metal=Ni, Pd, Pt) in these coordination compounds of transition metals. The nature and the strength of a metal-olefin bond, similar to species adsorbed on a metal-surface, keep inspiring chemists to carry on the research of synthesis and characterization of such compounds. In the case of platinum(0) complexes, several attempts to compare the stability of olefinic complexes have been published. This included their assortment by the decomposition point [3], by calorimetric measurements concerning the enthalpy of decomposition or the reaction enthalpy of olefin exchange [4, 5] throughout the experimental studies. Also calculations on the Pt(0)-olefin binding energy [6–14] and C=C bond order decrease on the theoretical basis have appeared.

Experimental studies showed that complexes of olefins bearing electron donors are rather unstable. Olefin electronic properties thus had the determining influence on the stability of the final co-ordination compound. Another important criterion is the bulkiness of the olefin substituents (referred to as the structure effects), i.e., the more substituents are present on the C=C bond and the bulkier they are, the less stable is the resulting complex.

Several groups of olefins that undergo the coordination forming the platinum(0) complexes are known so far. These substances were studied experimentally and/or theoretically, namely: strained olefins [9–14], fullerenes [15–18], carboxylic acid derivatives [3, 19, 20], α,β -unsaturated ketones and aldehydes [21], vinyltrimethylsilane [22] etc. An interesting feature is the strong coordination to fullerenes, which are usually believed to contain C-C bonds with more or less aromatic character. The stabilization energy upon coordination has been found much larger than for the case of ethylene.

Quantitative results achieved by the above-mentioned empirical methods [3–5] have only partially been confirmed

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by appropriate theoretical calculations [e.g., 6–18]. Lengthening of C=C bond lengths and changes in bond angles were not sufficient results since they are strongly affected by sterical hindering of the phosphine ligands used in a particular study. Although detailed studies were performed on the basis of CDA (charge decomposition analysis by Frenking, [6–8]) scheme used to evaluate the bonding and anti-bonding terms in to the entire Pt-olefin bonding scheme, no deliberate attempt to scan the strength of metal-olefin interaction in a larger series of olefin molecules had been described in the literature.

Our aim in the presented study is to utilize the results of the coordination-compound stability as they elucidate the properties of structurally similar species present on transition metal surfaces, which have the key impact in heterogeneously catalyzed reactions. Surface-coordinated olefins play an important role in catalytic hydrogenation and oxidation processes. We have selected this comparison due to the complexity of metal cluster / slab description in the *ab initio* (first-principles) calculations of metal-metal bonding and expected these results to be more easily interpreted.

Methods

Gaussian 03W package [23] was used throughout all calculations. The comparison of model chemistries used for computations on this kind of compounds had already been performed earlier [6–8], nevertheless none of the tested models showed sufficient agreement with the real structures and energies at the same time. The structures had always showed more or less some discrepancy with X-ray crystallographic data (the angle between P-Pt-P and C-Pt-C planes) and experimental binding energy values (measured by dissociation calorimetry), which could not be fully overcome by using more precise parameterizations. Therefore, we have decided to use the DFT level of theory with B3LYP hybrid functional of Lee, Yang and Parr [24] for optimizations and moderate-demanding MP2 electron correlation method for energies.

The 6-31G(d) basis set was used for light elements (H, C, N, O, F, P, S, Cl) and LanL2DZ basis set for platinum, accompanied by LanL2 effective core potential, as implemented in the original code Gaussian 03W package.

Throughout all computations, a simplification of triphenylphosphine PPh₃ ligand to simple phosphine PH₃ ligand was applied (Fig. 1). This treatment led to enormous saving of computational time by reducing the number of atoms in the molecule by 60 and thus decreasing the number of basis functions by 552 to 106 in the case of (PH₃)₂Pt(CH₂=CH₂). This simplification, used already previously, e.g., by Yates [4, 5], is the most decisive step in this study. It contracts the

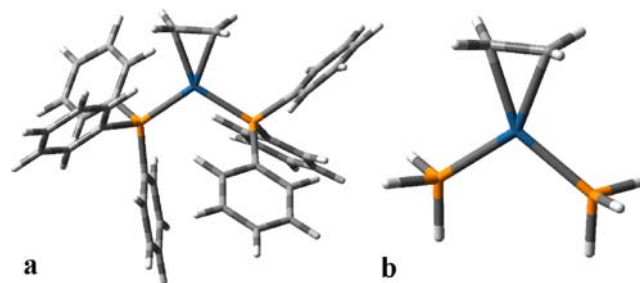


Fig. 1 Representation of typical structures of (olefin)Pt(PPh₃)₂ (a) and (olefin)Pt(PH₃)₂ (b)

sterical hindering of bulky phenyl radicals to only a few atoms, thus affecting the strength of Pt-C interaction. However, for reasons of comparison in a group of complexes bearing different olefins, this works well when one takes the relative numbers of energy or geometry into account.

Use of calculations with more layers at different level of theory is in this case within Gaussian 03W code not applicable, since pseudopotentials and generated basis sets have to be set up at the same time.

Although values on different levels of theory for a reduced system were computed, the same trends in stability of the according complexes were observed. Therefore, there was no need to use larger basis sets (basis set “II”, triple-zeta quality for platinum or higher). A more detailed description of the molecular structure and properties would require usage of the highest order available electron correlation methods with large basis sets, providing PPh₃ would be simplified to PH₃ [6–8].

Geometry optimization and vibrational analysis

Both full geometry optimizations and vibration calculations were performed using B3LYP/LanL2DZ:6-31G(d) in vacuum. The initial estimates of the compound optimal geometries were set up using the geometry of the non-coordinated olefins, with respect to the significant “bending away” effect of the substituent groups from C=C bond plane. According to X-Ray structural analyses, the five atoms P₂-Pt-C₂ formed a slightly distorted plane, which was set up to 0 degrees at the start of the calculation, instead of the perpendicular geometry [15–18]. No degrees of freedom were constrained in any calculation. No constraints on the molecular symmetry were applied.

The final optimized structures were tested by vibrational frequency calculation to be true energy minima. The evaluation of vibrational modes was also utilized as a key factor for comparison of stability of the complexes. The C=C stretching mode wavenumbers in free / coordinated olefins were scaled by an appropriate factor of 0.9613 (for B3LYP/6-31G(d)) and summarized in the results section.

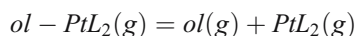
Single point energy and binding energy evaluation

Energies were calculated using MP2/LanL2DZ:6-31G(d). The platinum-olefin binding energy in the studied systems was considered to be the difference between the single-point energies of (olefin + Pt(PH₃)₂) and the coordinated olefin:

$$E_B = [E(ol) + E(PtL_2)] - E(ol - PtL_2)$$

$$[ol = olefin; L = PH_3, PPh_3]$$

The fact that all the above-mentioned species were calculated in their equilibrium geometries is an important feature. The binding energy calculated in this way was equivalent to the dissociation energy of the Pt-olefin bond in the decomposition reaction as follows:



Considerable angular distortion of olefin and PtL₂ moieties, as they appear in the complex, represent in fact the significant energy terms of the resulting binding energy, as presented by Nunzi [25], who called the re-organization energies “snapping energies”. In our study, the snapping energies were not evaluated here, since they do not refer to the strength of the coordination itself.

Furthermore, Yates [6–14] described that the sum of corrections (ZPVE + thermal correction, BSSE) did not play the dominant role (since these almost cancel) in comparison to the other terms and thus could be neglected in the calculation.

Results

Several series of olefin structures were taken into account. The studied groups are discussed separately below. Coordinated ethylene was described more thoroughly to introduce a consistency with previous experimental and calculated data.

In general, the C=C double bonds, coordinated to zerovalent platinum, showed an increase of the bond lengths compared to non-coordinated species. Remarkable bending of double bond substituents out of C=C double bond plane was found. The above facts confirmed that olefins undergo immense structural and electronic changes. Depending on a particular olefin, the distortion of dihedral angle between P-Pt-P and C-Pt-C planes in the organometallic compound significantly varies.

The olefin moiety of the complexes was attached to platinum(0) via two σ(Pt-C) bonds, the olefins coordinated to platinum in η²-fashion. No free rotation of the

coordinated olefin appears in the studied series, in contrast to the proven rotation of ethylene in platinum(II) derivatives such as Zeise’s salt K[Cl₃Pt(CH₂=CH₂)] [4].

Separated computational examination unequivocally demonstrated that continuum solvation (implicit solvation via PCM method, dielectric constant of dichloromethane) had negligible effects on optimal geometries, energies, vibrational frequencies and NMR magnetic shielding tensors. For this reason no solvation model was used any further.

Table 1 shows an overall evaluation of energetic and structural results of calculations. The energetics of Pt-olefin electron-overlap interaction was evaluated by values of the binding energy *EB*. The decrease in the vibrational wave-number of C=C stretching mode upon coordination is denoted as Δ*ν*. Elongation of the C=C bonds upon coordination, Δ*R*, is the impact of a primary effect of metal-olefin coordination strength. The pyramidalisation δ is given as an average angle of R¹-C=C-R³ and R²-C=C-R⁴ dihedrals, thus it is applicable also for asymmetrical olefins, unlike in previous papers [6–8, 26], where the pyramidalisation angle is given only for R₂C=CR₂, i.e., olefins forming complexes with C_{2v} symmetry.

Ethylene complexes

Ethylene (ethene) was selected as the reference compound for further comparisons. The results for ethylene are hereinafter discussed more thoroughly as to ensure a consistency with the previous studies.

Yates [6–8] performed extensive calculations on the basis set consistency and obtained the binding energy of 111.9 kJ mol⁻¹ in (PH₃)₂Pt(CH₂=CH₂) at MP2/6-31G(d):LANL2DZ level, however, interestingly much lower values for the system containing PPh₃ ligands. Nunzi et al. [25] calculated the “bond dissociation energy”, corrected on basis set superposition error (BSSE) as 102 kJ mol⁻¹ at LDA-DFT level of theory using mixed ζ-quality STO basis sets. It was mentioned, however, that the experimental values [26, 27] for (PPh₃)₂Pt(CH₂=CH₂) of Mortimer (152 ± 18 kJ mol⁻¹, gas-phase) and Kirkham et al. (11.6 ± 1.6 kJ mol⁻¹) seemed to be by far over- and underestimated.

In our study, the binding energy of Pt-ethylene bonds in a fully optimized complex (PH₃)₂Pt(CH₂=CH₂) (Fig. 2), was calculated as 116.8 kJ mol⁻¹ at MP2/6-31G(d):LANL2DZ level of theory. The small discrepancy from the results of Yates [6–8] comes from a slightly different basis set used for the optimization.

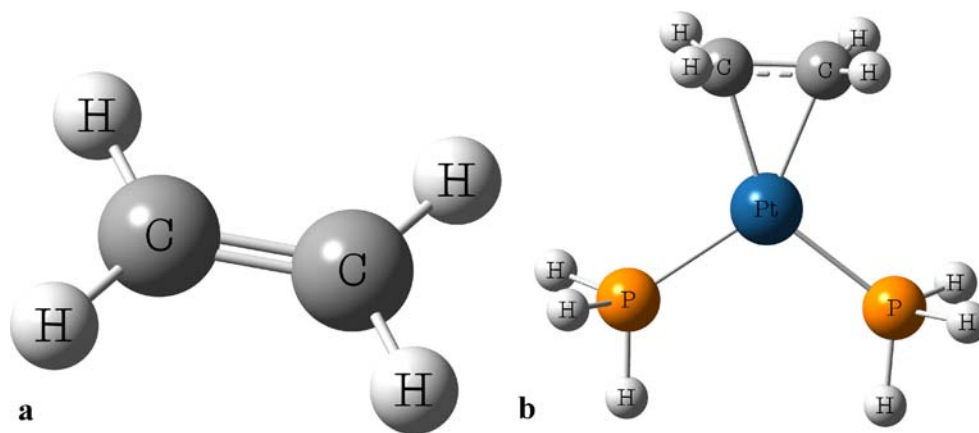
The binding energy for a fully optimized model of (PPh₃)₂Pt(CH₂=CH₂) was herein evaluated only at B3LYP/6-31G(d):LANL2DZ level, giving a value of only 9.9 kJ mol⁻¹ (in comparison to 51.9 kJ mol⁻¹ for the PH₃ analogue).

Table 1 Binding energies in (olefin)PtL₂ complexes

Compound / group	E _B [kJ mol ⁻¹]	Δν [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 ^b	125.8	404.41 ^g	0.0795 ^g	–
Unsaturated Alcohols				
(prop-2-en-1-ol)Pt(PH ₃) ₂	107.6	513.64	0.0944	30.52
(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
Cyanoethylenes				
(methacrylonitrile)Pt(PH ₃) ₂	127.2	369.05	0.1038	32.36
(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
Compounds containing ?-carbonyl group(s)				
(but-1-en-3-on)Pt(PH ₃) ₂	132.0	466.08	0.0922	27.24
(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
Halogen containing compounds				
(tetrachloroethylene)Pt(PH ₃) ₂	101.1	433.82	0.1303	53.49
(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
Strained olefins				
(3-methylcyclopropene)Pt(PH ₃) ₂	153.7	414.73	0.1236	–
(1,2-dimethylcyclopropene)Pt(PH ₃) ₂	144.9	377.94	0.1175	–
(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	–
Various compounds				
(vinyltrimethylsilane)Pt(PH ₃) ₂ ^c	128.3	463.25	0.0938	29.35
(<i>Z</i> -1,2-bis(phenylsulfinyl)ethene)Pt(PH ₃) ₂ ^d	118.5	332.58	0.1140	39.20
(carbonyl disulfide)Pt(PH ₃) ₂ ^e	74.8	341.57 ^h	0.1291 ^h	–
(dioxigen)Pt(PH ₃) ₂ ^f	194.3	637.49 ⁱ	0.1849 ⁱ	–

^a Coordination via C=C double bond;^b Coordination via C≡C triple bond, vibrational shift for C≡C stretch;^{c,d,e,f} Syntheses of complexes see Refs. [9, 12, 13], and [16] respectively;^g Vibrational shift of the C≡C stretch and elongation of the C≡C triple bond;^h Vibrational shift of the C=S stretch and elongation of the C=S bond;ⁱ Vibrational shift of the O=O stretch normal mode and elongation of the O=O bond.

Fig. 2 Molecular structures of ethylene (**a**) and (ethylene)Pt(PH₃)₂ (**b**)



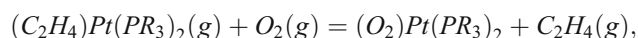
Concerning the geometrical parameters, the C=C bond in (PH₃)₂Pt(CH₂=CH₂) is elongated from 1.331 (free) to 1.425 (coordinated) by 0.094 Å. For the PPh₃ analogue, the coordinated value was 1.430 Å, which was nearer to 1.434 Å measured in the experiment [28].

In the complex (PH₃)₂Pt(CH₂=CH₂), having C_{2v} symmetry, both Pt-P bonds are 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). Mean experimental value is 2.268 Å.

The σ-Pt-C bonds in (PH₃)₂Pt(CH₂=CH₂) are 2.157 Å long. Concerning the PPh₃ analogue, the bondlength of 2.153 Å (mean value of 2.168 and 2.138 Å) had been calculated. Both of these achieved results were overestimated in comparison to 2.112 Å (average) found in experiment [28].

We would also like to demonstrate the similarity of Pt(0)-olefin organometallics to olefins coordinated on metal surfaces. In our study, the perpendicular 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, similar values had been found. Furthermore, although calculated at different levels of theory, the bond dissociation energies 116.8 kJ mol⁻¹ in the case of organometallic compound (MP2 value, this study) and 106.1 kJ mol⁻¹ in the case of C₂H₄ on p(2×2)-Pt(111) (GGA-DFT calculation, [29]), are comparable for these systems.

Furthermore, the energetics of an overall reaction of molecular oxygen with platinum(0) complex has been studied. It is known [30–32] that ethylene in (C₂H₄)Pt(PR₃)₂ undergoes a replacement by dioxygen to form (O₂)Pt(PR₃)₂. The reaction occurs favorably when (C₂H₄)Pt(PR₃)₂ exposed to air atmosphere. The reaction enthalpy calculated for R=H,



leads to the value of $\Delta H_r^{298} = -77.4 \text{ kJ mol}^{-1}$, i.e., a moderate number for exothermic reaction.

Propadiene, Butadiene and Vinylacetylene

Although these hydrocarbon species contain only alkenic or alkynic substituents on the multiple bond to be coordinated, the calculation shows they possess sufficient stability upon coordination. This may lead to a statement, that residues like CH=CH₂ (vinyl) or C≡CH (ethynyl) were in our case moderately-strong electron acceptors. Furthermore, breaking the conjugation of multiple bonds is an energy demanding process at the expense of dissociation energy.

Varying bond strengths were observed for vinylacetylene (but-1-ene-3-yne). In this compound, unlike in buta-1,3-diene or propadiene, either double or triple bond may coordinate to platinum(0) central atom with various bond strength. As described in previous calculations and experiments, triple bond coordination is preferred. Such was also confirmed while observing an easy substitution reaction of olefinic complexes with substrates containing acetylenic function. This was perhaps caused by stronger electron-acceptor contribution of the triple bond, providing the C=C double bond acts as a substituent.

A strong coordination of allene (propadiene) to Pt(0) is associated with a high bond dissociation energy and a low decrease of the wavenumber of C=C stretch (~ 275 cm⁻¹) of the coordinated double bond.

Unsaturated alcohols

The unsaturated alcohols bearing the -OH function in α- or β-position to the C=C bond show less stabilization in the coordinated state than ethylene. This is caused by particular donor / acceptor properties of these compounds, hydroxy group acting rather as electron donor. The decrease in C=C stretch wavenumbers was similar to the one calculated for ethylene complex.

The hydroxyl-group attached in β -position to the C=C bond gave less stable coordination compounds. The dissociation energies for complexes of hex-1-en-3-ol and allyl alcohol (prop-2-en-1-ol) were slightly lower than for ethylene, assuming that they are rather unstable. However, the synthesis of the semi-stable allyl alcohol complex in solution was described [8], although this was only detected by NMR for a short time. This, however, presumes the possibility to synthesize its analogues.

Although energetically low stable, the complex of hept-1-en-4-ol showed a substantial decrease of the C=C stretch wavenumber. The structure effects of sterical hindrance (bulkiness) of the methyl groups in 2-methylbut-3-en-2-ol did not seem to have a tangible impact in this kind of coordination compounds. To the contrary, it looks even slightly more stable than allyl alcohol complex.

Cyanoethylenes

Table 1 conspicuously shows a clear growing stability trend along the increasing elevating number of cyano groups on the ethylene double bond. The sterical hindering of the double bond is outweighed by a strong electron withdrawal of the nitrile groups, which induces a lowering of HOMO orbital level in cyanoethylenes toward platinum unoccupied orbitals (see Fig. 3). Previous charge decomposition analysis (CDA) [25] studies particularly showed that platinum-olefin back-bonding plays an important role in the bonding scheme in studied molecules.

It could be assumed that the electron-rich methyl group in methacrylonitrile has a destabilizing effect on the resulting complex, when compared to acrylonitrile. In 1,2-dicyanoethylenes, the *E*-isomer (fumaric acid dinitrile) was slightly more stable ($\Delta E=1.3 \text{ kJ mol}^{-1}$) than the *Z*-isomer (maleic acid dinitrile).

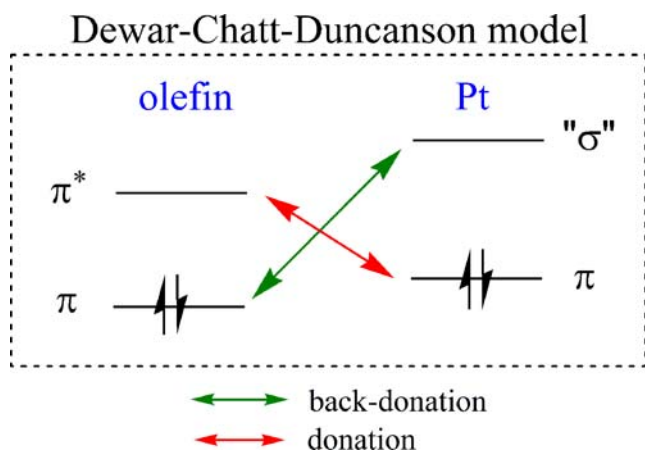


Fig. 3 The principle of electronic exchange in the Dewar-Chatt-Duncanson model

Compounds containing α -carbonyl group(s)

In ester function of acrylic acid derivatives, the alkyl chain length has a negligible effect on the electron-acceptor properties of the carbonyl group. Therefore, the strength of the adjacent Pt-C bond is not weakened either. Similar trend appears within fumaric acid esters - diethyl esters are just slightly less stable than dimethyl esters.

Furthermore, the role of breaking the conjugation in α,β -unsaturated compounds must also be considered. Simple ketones, e.g., but-1-en-3-one form relatively stable complexes. This is even more evident in the simplest unsaturated aldehyde - acrylic aldehyde (prop-2-en-1-al), which maintains even a higher stability (i.e., higher dissociation energy). Other derivatives of acrylic acid (amide, methylester) show a moderate stability (125.4 and 122.1 kJ mol^{-1} , respectively). Maleic acid anhydride appears to have the highest dissociation energy (154.1 kJ mol^{-1}), due to the strong electron withdrawal of π -electrons of the C=C bond and a low sterical stress, since no bulky substituents are present.

Halogen containing compounds

Halogenated hydrocarbons present a good example for an overview of donor/acceptor electronic contributions to the C=C double bond in olefins. Thus, e.g., 3-chlorobut-1-ene gave a moderately stable complex, which was remarkable due to high pyramidalization (33.7 degrees).

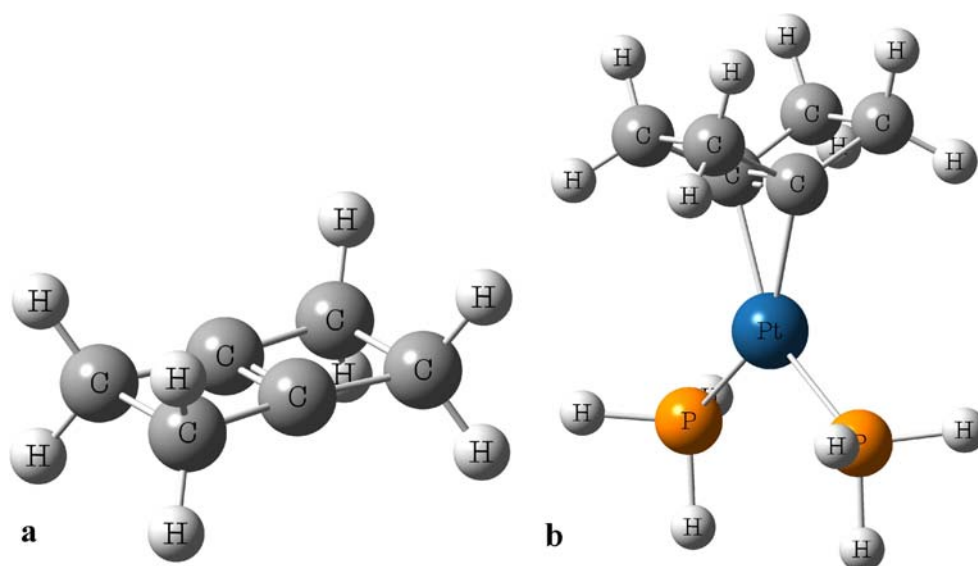
Perfluorinated ethylenes, if coordinated to bis(triphenylphosphine)platinum, show a much higher stability than perchlorinated analogues, which is probably caused by geometric hindering of chlorine atoms. Furthermore, carbon-halogen bonds are much more apparently elongated after coordination in C_2F_4 than in C_2Cl_4 , perhaps owing to a decreased conjugation of fluorine atoms with C=C bond. In addition, trifluoromethyl groups in *E*- $\text{CF}_3\text{CF}=\text{CFCF}_3$ tend to stabilize the coordination compound far more than direct fluoro-substitution in C_2F_4 , resulting in one of the highest dissociation energy observed for the Pt-C₂ bonding (165.2 kJ mol^{-1}). The presence of halogen atoms in α -position with respect to the C=C double bond seems to invoke high stability of the resulting organometallic compounds.

Strained olefins

The C=C bond in strained olefins exhibited a high stabilization, as the sp^2 -carbon atoms became truly sp^3 -hybridised. The treated compounds were selected according to literature [5] describing their successful synthesis and spectroscopic characterization.

All of the complexes of the selected strained olefins showed large binding energies. The evaluation of pyramidal-

Fig. 4 Molecular structures of bicyclo[2.2.0]hex-3(5)-ene (**a**) and its Pt(PH₃)₂ complex (**b**)



ization of substituents produced inadequately large numbers, after we have defined this magnitude for acyclic substitution on the C=C double bond. However, once coordinated, the distortion of substituents from the original position was very large in this series of complexes. Figure 4 depicts one of the examples: bicyclo[2.2.0]hex-3(5)-ene complex.

Various compounds

Several compounds of interest (described by experiments in literature), containing several kinds of double bonds in their structure, were calculated to explore their stability in the coordinated state.

One example of organosilicium compounds, vinyltrimethylsilane CH₂=CH-Si(CH₃)₃ [22], gave moderate values for E_B as well as the other properties evaluated, leading to an assumption that silicon atoms had in some respects a very similar electronic behavior as carbon.

A compromising situation occurred for *rac*-Z-1,2-bis(phenylsulfinyl)ethene [33], since the binding energy for coordination of the species calculated here (*R,R*-isomer) was lower than that for ethylene. However the complex had been synthesized from (PPh₃)₂Pt(CH₂=CH₂) by the olefin exchange. It may be necessary to calculate a weighted average of binding energies of all enantiomers in order to estimate the behavior of the racemic mixture.

Furthermore, although experiments showed that carbon disulfide (CS₂) adduct was formed in solution of the olefin complex very rapidly, the calculated binding energy was surprisingly very low. This may have been caused by a solvent-stabilization effect in carbon disulfide solution, as the adduct enhanced the formation of induced dipoles in a near environment of the molecule. The formation of dimeric polynuclear complexes could be excluded by X-Ray analyses [34].

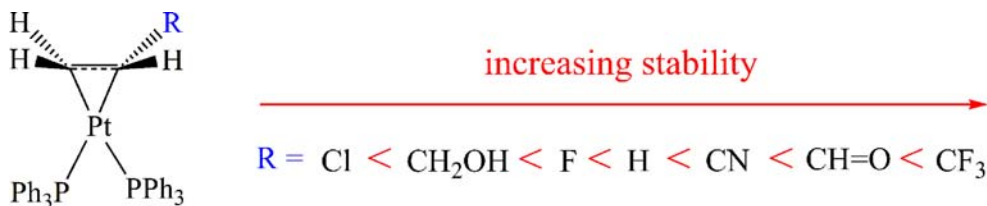
It is noteworthy that dioxygen adduct (O₂)Pt(PH₃)₂, was irreversibly formed whenever olefin complexes reacted with molecular oxygen, producing by far the highest calculated stable complex, as the oxidation state of central metal atom formally becomes Pt(II) [30–32].

Discussion

Structure properties and energy relations in a group of Pt(0) coordination compounds were investigated theoretically at DFT and MP2 levels of theory. The achieved trends confirmed the experimental results obtained by means of various physical measurement methods.

The general trend in stability depended basically on the olefin part. For single substituted olefin species CH₂=CHR (Fig. 5), we may summarize this as follows:

Fig. 5 Representation of (CH₂=CHR)Pt(PPh₃)₂ and the stability chart



Extremely high estimated stability of dioxygen complex, together with the estimated energy change value for its formation, explains why the studied compounds tend to add oxygen readily under air atmosphere.

From an experimental point of view, one can assume that compounds with platinum-olefin binding energy higher than that of ethylene complex, may be synthesized by a simple olefin exchange. There are however several different synthetic methods (based on reductive coupling or equilibrium PR_3 ligand-exchange), which can feasibly carry out the formation of less stable olefin complexes.

Some compounds taken to computation surprisingly showed lower stability than the referent ethylene complex, although they have already been prepared from this substance. This phenomenon is probably caused, in theoretical calculations, by neglecting the sterical demands of the olefin moiety, or even the generally well-working $\text{PPh}_3 \rightarrow \text{PH}_3$ approximation.

This work presents innovative endeavors to compare the complex stability using the binding energy, in association with a decrease of the $\text{C}=\text{C}$ stretching mode vibrational frequency, elongation of the $\text{C}=\text{C}$ (or another coordinated) bonds and evaluation of an averaged pyramidalization on the coordinated carbons.

Further calculations shall include adjustments for the changes in bond orders in these compounds and thus prove the effect of breaking the electron conjugation in olefins via coordination to platinum. Successful synthesis of the selected compounds may be considered as confirming the theoretical results and proposing an appropriate quantitative “*structure-stability*” relationship.

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