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Upright or In-Plane Conformational Preference: Dilemma of η^2-Coordinated C=C Double Bond in $PtX_2(CO)(\eta^2\text{-ene})$ (X = H, Cl, or C_6F_5) Complexes

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In the present work we employ hybrid density functional calculations (at the B3P86 level) in conjunction with natural bond orbitals (NBOs) and charge decomposition analysis (CDA) to unravel the origin of the in-plane or upright conformational preference of η^2-coordinated C=C double bonds in a series of square-planar d^8 metal complexes formulated as *cis*-$[PtX_2(CO)(L)]$ (X = H, Cl, C_6F_5; L = unsaturated hydrocarbon). We find that both the nucleophilicity of the unsaturated hydrocarbon ligands and the electrophilicity of the *cis*-$[PtX_2(CO)]$ electrophilic fragment play a key role in fine-tuning the conformational preference of the coordinated C=C double bond of the unsaturated hydrocarbon ligands. For the complexes of *cis*-$[PtX_2(CO)]$ electrophiles of low electrophilicity (ω values in the range 1.883−4.486 eV) both geometric arrangements (in-plane and upright) correspond to minima on the potential energy surfaces (PES). The two orientations differing slightly in energy are competitive, and therefore it is a dilemma that leads to the coexistence of both conformers in equilibrium in solutions of the unsaturated hydrocarbon complexes of the *cis*-$[PtX_2(CO)]$ electrophiles of low electrophility. In contrast, in the complexes of the *cis*-$[PtX_2(CO)]$ electrophiles with high electrophilicity ($\omega > 7.0$ eV) only one of the orientations could be located as a minimum in the PES, that of the upright orientation of the C=C double bond, except for the complexes of the perfluoroethene, norbornene, 7,7-dimethylnorbornene, and bicyclo[2.2.2]oct-2-ene ligands. Finally, the behavior of the unsaturated hydrocarbon complexes of the *cis*-$[PtX_2(CO)]$ electrophiles of intermediate electrophilicity (ω values in the range 5.0−7.0 eV) is intermediate between those of the *cis*-$[PtX_2(CO)]$ electrophiles with low and high electrophilicity. In this case it is the nucleophilicity of the unsaturated hydrocarbon ligands in conjunction with steric effects that modulates the conformational preference of the unsaturated hydrocarbon. Generally, the high nucleophilicity of unsaturated hydrocarbon ligands in conjunction with high electrophilicity of platinum-containing fragments favors exclusively the upright orientation.

Introduction

The binding of unsaturated hydrocarbons to transition metals (TM) is a topic of paramount importance in organometallic chemistry for various reasons.[1,2] π-Complexes of platinum are experimentally well-known and appear very often as key intermediates in a variety of Pt-catalyzed reactions.[3–5] In particular, alkene complexes were actually the first example of transition metal compounds for which Dewar, Chatt, and Duncanson (DCD) suggested the synergistic ligand → TM σ-donation and ligand ↔ TM π-back-donation.[6,7] Two main classes of π-olefin molecular complexes of platinum are known experimentally, with the metal having either the 0 or +2 oxidation state. Prototype examples of the two classes are the $[(Ph_3P)_2Pt(C_2H_4)]$ complex[8,9] and the so-called Zeise's salt,[10] $K[Cl_3Pt(C_2H_4)]$. The bonding, rotational barriers, and conformational preferences in olefin-ML_{2-5} complexes have comprehensibly been discussed in the seminal paper by Roald Hoffmann et al.[11] about three decades ago. In square-planar ethylene-ML_3 complexes, X-ray structures consistently show the olefin oriented in or near the upright geometry. It was argued that the main factor that determines the equilibrium orientation of the olefin in these complexes is steric and not electronic. The authors devised strategies to lower the barrier or reverse the conformational preference in these complexes, which could be accomplished by changing the electronic or steric properties of the ligands on the metal or the alkene. Borden and co-workers[12–14] have exploited the ability of PtL_2 (L = Ph_3P, for example) fragments to stabilize strained olefins upon

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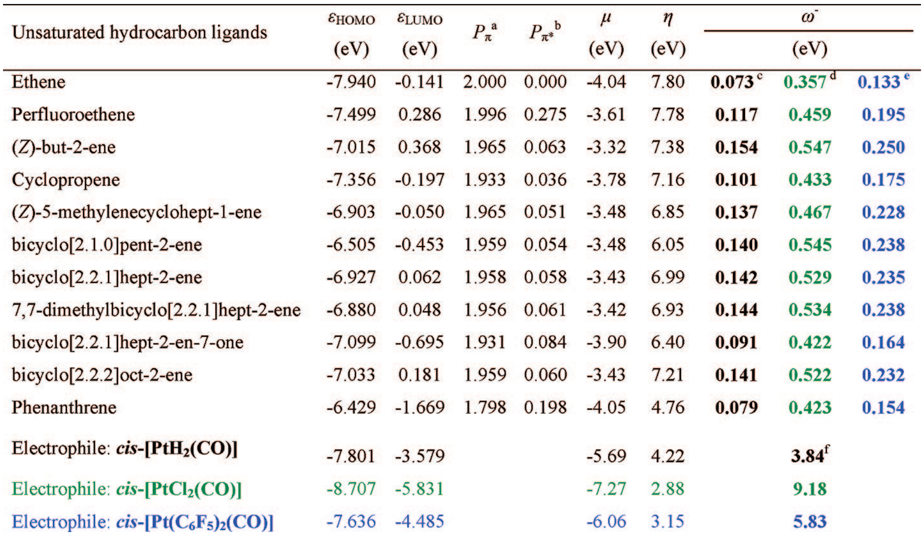
Table 1. Selected Electronic Parameters of Unsaturated Hydrocarbon Ligands Coordinated with the *cis*-[$PtH_2(CO)$], *cis*-[$PtCl_2(CO)$], and *cis*-[$Pt(C_6F_5)_2(CO)$] Electrophilic Metal Containing Fragments Computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) Level



Unsaturated hydrocarbon ligands	ε_{HOMO} (eV)	ε_{LUMO} (eV)	P_π[a]	P_{π^*}[b]	μ (eV)	η (eV)	ω^- (eV)		
Ethene	-7.940	-0.141	2.000	0.000	-4.04	7.80	**0.073**[c]	**0.357**[d]	**0.133**[e]
Perfluoroethene	-7.499	0.286	1.996	0.275	-3.61	7.78	**0.117**	**0.459**	**0.195**
(*Z*)-but-2-ene	-7.015	0.368	1.965	0.063	-3.32	7.38	**0.154**	**0.547**	**0.250**
Cyclopropene	-7.356	-0.197	1.933	0.036	-3.78	7.16	**0.101**	**0.433**	**0.175**
(*Z*)-5-methylenecyclohept-1-ene	-6.903	-0.050	1.965	0.051	-3.48	6.85	**0.137**	**0.467**	**0.228**
bicyclo[2.1.0]pent-2-ene	-6.505	-0.453	1.959	0.054	-3.48	6.05	**0.140**	**0.545**	**0.238**
bicyclo[2.2.1]hept-2-ene	-6.927	0.062	1.958	0.058	-3.43	6.99	**0.142**	**0.529**	**0.235**
7,7-dimethylbicyclo[2.2.1]hept-2-ene	-6.880	0.048	1.956	0.061	-3.42	6.93	**0.144**	**0.534**	**0.238**
bicyclo[2.2.1]hept-2-en-7-one	-7.099	-0.695	1.931	0.084	-3.90	6.40	**0.091**	**0.422**	**0.164**
bicyclo[2.2.2]oct-2-ene	-7.033	0.181	1.959	0.060	-3.43	7.21	**0.141**	**0.522**	**0.232**
Phenanthrene	-6.429	-1.669	1.798	0.198	-4.05	4.76	**0.079**	**0.423**	**0.154**
Electrophile: ***cis*-[$PtH_2(CO)$]**	-7.801	-3.579			-5.69	4.22		**3.84**[f]	
Electrophile: ***cis*-[$PtCl_2(CO)$]**	-8.707	-5.831			-7.27	2.88		**9.18**	
Electrophile: ***cis*-[$Pt(C_6F_5)_2(CO)$]**	-7.636	-4.485			-6.06	3.15		**5.83**	

[a] P_π is the electron population of the π-MOs. [b] P_{π^*} is the electron population of the π^* MOs. [c] Nucleophilicity index ω^- values relative to *cis*-[$PtH_2(CO)$] electrophile. [d] Nucleophilicity index ω^- values relative to *cis*-[$PtCl_2(CO)$] electrophile. [e] Nucleophilicity index ω^- values relative to *cis*-[$Pt(C_6F_5)_2(CO)$] electrophile. [f] Electrophilicity index ω values of the *cis*-[$PtH_2(CO)$], *cis*-[$PtCl_2(CO)$], and *cis*-[$Pt(C_6F_5)_2(CO)$] electrophiles given as $\omega = \mu^2/2\eta$.

formation of the complex. They compared, in particular, the barrier to rotation and the dissociation energy of an unconstrained ethene to those of a highly pyramidalized alkene and found that pyramidalization increases both the binding energy to a large extent, by 21.3 kcal/mol, and the rotational barrier by only 5−6 kcal/mol. These features result from the lowering of the π^*-MO of the olefinic double bond, which includes, in turn, an increase of back-donation from the d_π orbital of Pt. The nature of the metal−alkene bond in platinum complexes of strained olefins has recently been exploited by Frenking et al.[15] using DFT and high-level *ab initio* molecular orbital methods. They concluded that the π^*-MO's eigenvalue and the olefin strain energy of the free olefin appear to be good qualitative predictors of the likely strength of the Pt−olefin interaction and may be used to design strongly bound complexes. Very recently, Sakaki et al.[16] systematically evaluated the binding energies of d^{10}, d^8, and d^6 transition-metal complexes with various π-conjugate systems using the MP2 to MP4, CCSD(T), and DFT methods. It was found that the π-back-donation is stronger than the σ-donation in the Pt(0) complexes, they are comparable in the Pt(II) complexes, and only σ-donation participates in the coordinate bond of the Pt(IV) complexes.

On the other hand, alkenes and carbon monoxide in combination are used in organic syntheses of industrial relevance promoted by transition metals, such as hydroformylation and related reactions and CO/olefin copolymerization. The competitive coordination of CO and olefins to a Pt(II) metal center has extensively been investigated, and a series of $PtX_2(CO)(olefin)$ (X = Cl, Br) complexes have been isolated and structurally characterized.[17] More recently, Forniés et al.[18] observed that the square-planar *cis*-[$Pt(C_6F_5)_2(CO)(thf)$] complex easily undergoes substitution processes of the weakly coordinated tetrahydrofuran (thf) molecule by a number of ligands, yielding coordination derivatives of the electrophilic [$Pt(C_6F_5)_2(CO)$] single-site metal fragment. This metal-containing fragment has proved to enable unusual coordination patterns with unsaturated hydrocarbons (alkenes and arenes). Upon reaction of the *cis*-[$Pt(C_6F_5)_2(CO)(thf)$] complex with ethene, norbornene, or phenanthrene the *cis*-[$Pt(C_6F_5)_2(CO)(L)$] (L = ethylene, norbornene, and phenanthrene) complexes are formed, which have been isolated and structurally characterized by X-ray diffraction methods. An important difference in the geometric arrangement of the C═C double bond with respect to the metal coordination plane has been observed. In both the ethene and phenanthrene derivatives the η^2-coordinated C═C double bond adopts the upright orientation, which is the usually observed orientation in olefins π-coordinated to square-planar d^8 metal centers. In contrast the C═C double bond of norbornene in *cis*-[$Pt(C_6F_5)_2(CO)(\eta^2$-norbornene)] is, in turn, almost coordinated in the coordination plane (in-plane orientation). In-plane coordination has been suggested as a key step in insertion processes of alkenes into M−alkyl or M−CO bonds including polymerization reactions. To unravel the origin of the in-plane or upright conformational preference of η^2-coordinated C═C double bonds in square-planar d^8 metal complexes, the structural, energetic, and electronic properties of a series of *cis*-[$PtX_2(CO)(L)$] (X = H, Cl, C_6F_5; L = ethene, perfluoroethene, (*Z*)-but-2-ene, cyclopropene, (*Z*)-5-methylenecyclohept-1-ene, bicyclo[2.1.0]pent-2-ene, bicyclo[2.2.1]hept-2-ene (norbornene), 7,7-dimethylbicyclo[2.2.1]hept-2-ene (7,7-dimethylnorbornene), bicyclo[2.2.1]hept-2-en-7-one, bicyclo[2.2.2]oct-2-ene, and phenanthrene) complexes are thoroughly investigated using electronic structure calculation techniques, and the results are reported herein. Both the ancillary X and the olefin L ligands were selected on the basis of their different electronic and steric properties.

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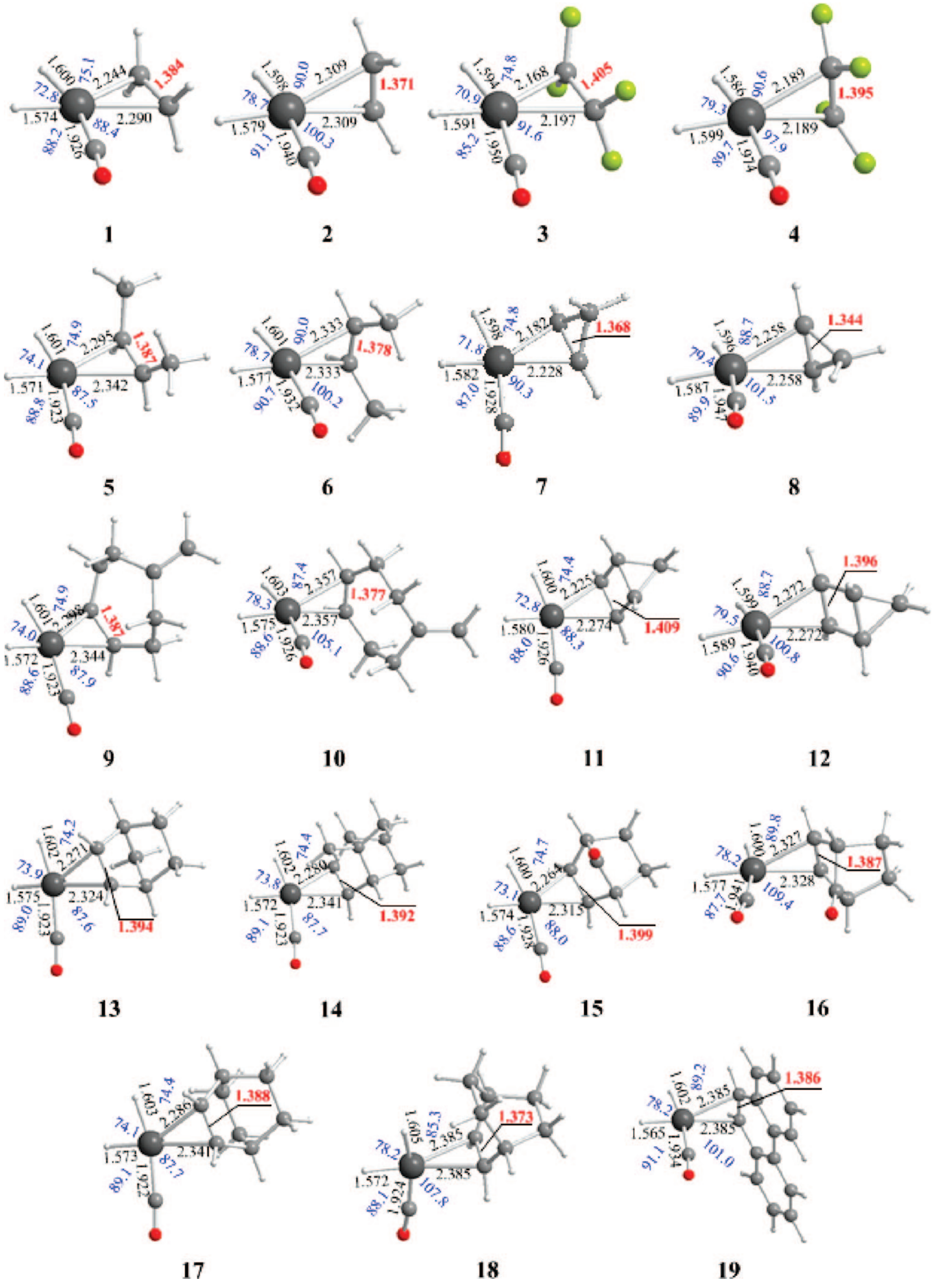

Figure 1. Equilibrium geometries (bond lengths in Å, angles in degrees) of the *cis*-[$PtH_2(CO)(\eta^2$-ene)] complexes computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) level of theory.

Theoretical Methods

All theoretical calculations were carried out by the GAUSSIAN03 program suite.[19] The geometry optimization of the investigated structures was performed in the gas phase at the B3P86 level[20,21] of density functional theory, using the basis set comprised of the quasi-relativistic Stuttgart−Dresden effective small core potential[22] for the Pt atom and a standard all-electron Pople-type basis set with polarization functions 6-31G(d,p)[23] for all remaining nonmetal atoms (E) of the *cis*-[PtX_2(CO)(L)] (X = H, Cl, or C_6F_5) complexes. This computational scheme is abbreviated as B3P86/SDD(Pt)∪6-31G(d,p)(E). Full geometry optimization was performed for each structure using Schlegel's analytical gradient method,[24] and the attainment of the energy minimum was verified by calculating the vibrational frequencies that result in the absence of imaginary eigenvalues. The stationary points found on the potential energy surfaces as a result of the geometry optimizations of the complexes have been tested to represent energy minima rather than saddle points via frequency analysis. All bond lengths and bond

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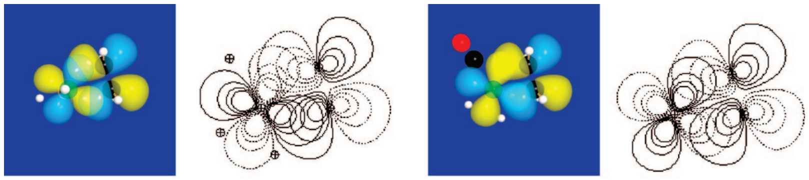
Table 2. Selected Electronic Parameters of the *cis*-[$PtH_2(CO)(\eta^2$-ene)] Complexes Computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) Level

Complex	E_{rel}[a]	E_{int}[b]	q_{Pt}	q_{olefin}	P_{π}	ΔP_{π}	P_{π^*}	ΔP_{π^*}	$\Delta E(2)$[c]
cis-[$PtH_2(CO)(\eta^2$-Ethene$\parallel$)], **1**	0.0	**-40.18**	0.18	-0.05	1.769	**0.231**	0.269	**0.269**	33.66
cis-[$PtH_2(CO)(\eta^2$-Ethene$\perp$)], **2**	3.5[d]	**-32.21**	0.20	0.04	1.783	**0.217**	0.165	**0.165**	31.91
cis-[$PtH_2(CO)(\eta^2$-perfluoroethene$\parallel$)], **3**	0.3	**-50.11**	0.17	-0.13	1.721	**0.275**	0.523	**0.248**	52.01
cis-[$PtH_2(CO)(\eta^2$-perfluoroethene$\perp$)], **4**	0.0	**-41.82**	0.19	-0.03	1.732	**0.264**	0.449	**0.174**	62.35
cis-[$PtH_2(CO)(\eta^2$-(*Z*)-but-2-ene$\parallel$)], **5**	0.0	**-37.40**	0.17	-0.01	1.762	**0.203**	0.263	**0.200**	27.78
cis-[$PtH_2(CO)(\eta^2$-(*Z*)-but-2-ene$\perp$)], **6**	0.2	**-32.83**	0.19	0.06	1.771	**0.194**	0.196	**0.133**	26.74
cis-[$PtH_2(CO)(\eta^2$-cyclopropene$\parallel$)], **7**	0.0	**-47.93**	0.20	-0.12	1.712	**0.221**	0.356	**0.320**	39.91
cis-[$PtH_2(CO)(\eta^2$-cyclopropene$\perp$)], **8**	4.5[e]	**-34.82**	0.23	0.01	1.744	**0.189**	0.199	**0.163**	35.87
cis-[$PtH_2(CO)(\eta^2$-(*Z*)-5-methylenecyclohept-1-ene$\parallel$)], **9**	0.0	**-38.79**	0.17	-0.01	1.759	**0.206**	0.267	**0.216**	27.43
cis-[$PtH_2(CO)(\eta^2$-(*Z*)-5-methylenecyclohept-1-ene$\perp$)], **10**	3.9	**-32.40**	0.19	0.08	1.773	**0.192**	0.193	**0.142**	24.54
cis-[$PtH_2(CO)(\eta^2$-bicyclo[2.1.0]pent-2-ene$\parallel$)], **11**	0.0	**-44.99**	0.20	-0.08	1.729	**0.230**	0.348	**0.294**	36.59
cis-[$PtH_2(CO)(\eta^2$-bicyclo[2.1.0]pent-2-ene$\perp$)], **12**	2.3	**-38.10**	0.23	0.02	1.746	**0.213**	0.247	**0.193**	36.98
cis-[$PtH_2(CO)(\eta^2$-Norbornene$\parallel$)], **13**	0.0	**-40.68**	0.18	-0.03	1.745	**0.213**	0.299	**0.241**	30.86
cis-[$PtH_2(CO)(\eta^2$-7,7-dimethyl-norbornene$\parallel$)], **14**	0.0	**-38.42**	0.18	-0.04	1.755	**0.201**	0.300	**0.239**	28.89
cis-[$PtH_2(CO)(\eta^2$-bicyclo[2.2.1]hept-2-en-7-one$\parallel$)], **15**	0.0	**-38.84**	0.19	-0.07	1.748	**0.183**	0.324	**0.240**	32.58
cis-[$PtH_2(CO)(\eta^2$-bicyclo[2.2.1]hept-2-en-7-one$\perp$)], **16**	3.0	**-32.38**	0.20	0.03	1.770	**0.161**	0.234	**0.150**	29.14
cis-[$PtH_2(CO)(\eta^2$-bicyclo[2.2.2]oct-2-ene$\parallel$)], **17**	0.0	**-38.10**	0.17	-0.02	1.754	**0.205**	0.285	**0.225**	28.42
cis-[$PtH_2(CO)(\eta^2$-bicyclo[2.2.2]oct-2-ene$\perp$)], **18**	5.2	**-30.26**	0.19	0.07	1.787	**0.172**	0.180	**0.120**	21.62
cis-[$PtH_2(CO)(\eta^2$-Phenanthrene$\perp$)], **19**	0.0	**-25.97**	0.18	0.04	1.716	**0.082**	0.304	**0.106**	21.50

[a] Relative electronic energy (in kcal/mol). [b] Interaction energy (in kcal/mol) between the *cis*-[$PtH_2(CO)$] and olefin fragments. [c] Second-order stabilization energy for the [$n(Pt) \rightarrow \pi^*(C{=}C)$] donor−acceptor interaction. [d] Transition state ($vi_i = -23.2\ cm^{-1}$). [e] Transition state ($vi_i = -44.6\ cm^{-1}$).

Scheme 1. Representative 3D Isosurface View and Contour Plot for the $n(Pt) \rightarrow \pi^*(C{=}C)$ Interactions in the Upright (a) and the in-Plane (b) Orientations of the Coordinated C═C Double Bond of Ethene in the *cis*-[$PtH_2(CO)(\eta^2$-ethene)] Complex Computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) Level of Theory[a]



$\Delta E(2)[n(Pt) \rightarrow \pi^*(C{=}C)] = \mathbf{31.91}$ kcal/mol

(a)

$\Delta E(2)[n(Pt) \rightarrow \pi^*(C{=}C)] = \mathbf{33.66}$ kcal/mol

(b)

[a] The outer contour setting is 0.0316 with 0.05 intervals for the four outermost lines in the contour plot.

angles were optimized to better than 0.001 Å and 0.1°, respectively. The computed electronic energies were corrected to constant pressure and 298 K, for zero-point-energy (ZPE) differences. The wave functions were analyzed by natural bond orbital analyses, involving natural atomic orbital (NAO) populations and natural bond orbitals (NBO).[25] Percentage compositions of molecular orbitals and charge decomposition analysis (CDA) of Frenking and co-workers[26,27] were performed as implemented in the AOMix program.[28–30]

Results and Discussion

π-Nucleophility Index of the Unsaturated Hydrocarbon Ligands. Before discussing the electronic structure of the *cis*-[$PtX_2(CO)(L)$] (X = H, Cl, C_6F_5; L = unsaturated hydrocarbon ligand) complexes we evaluated first the π-nucleophility index of the unsaturated hydrocarbon ligands with respect to the *cis*-[$PtX_2(CO)$] (X = H, Cl, C_6F_5) electrophiles. This is given by the relation[31]

$$\omega^- = \frac{1}{2}\frac{(\mu_A - \mu_B)^2}{(\eta_A + \eta_B)^2}\eta_A \qquad (1)$$

where μ_A and μ_B are the chemical potentials of the nucleophile and electrophile, respectively, given as $\mu = (\varepsilon_{HOMO} + \varepsilon_{LUMO})/$

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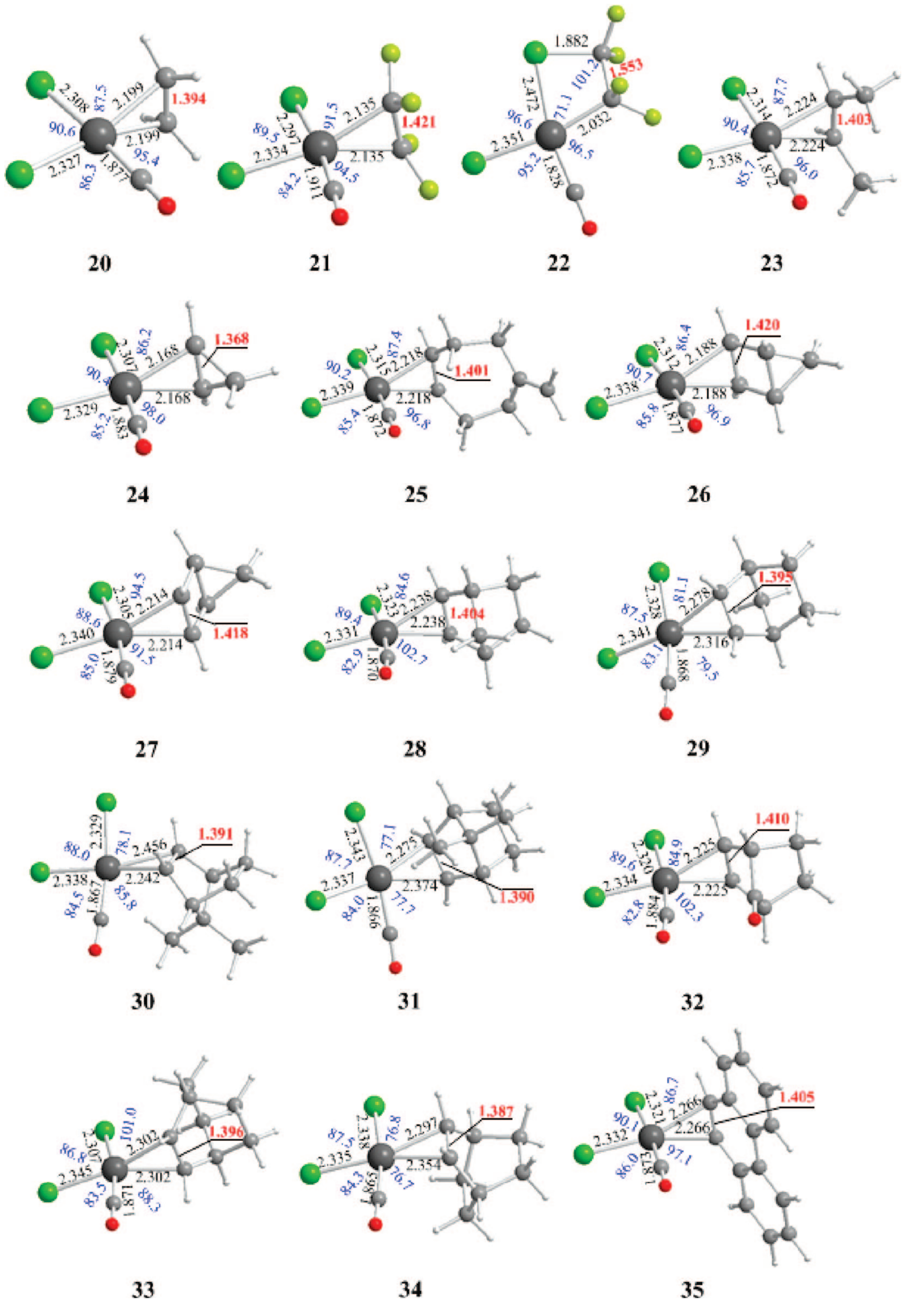

Figure 2. Equilibrium geometries (bond lengths in Å, angles in deg) of the *cis*-[PtCl$_2$(CO)(η^2-ene)] complexes computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) (E = nonmetal element) level of theory.

2, and η_A and η_B are the respective hardnesses given as $\eta = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$. Physically, μ corresponds to the capacity of a system to donate electron density, and the electron transfer between interacting systems flows from high to low μ. η measures the resistance to charge redistribution.[32–34] The nucleophilicity index depends on the electrophilic system and, therefore, is a relative and not an absolute index. Table 1 shows the electronic properties for the unsaturated hydrocarbons used as ligands L in the *cis*-[PtX$_2$(CO)(L)] complexes and the *cis*-

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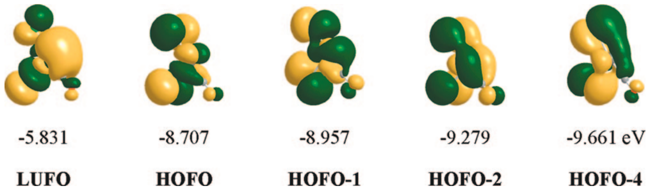
Table 3. Selected Electronic Parameters of the *cis*-[PtCl$_2$(CO)(η^2-ene)] Complexes Computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) Level

Complex	E_{rel}[a]	E_{int}[b]	q_{Pt}	q_{olefin}	P_π	ΔP_π	P_{π^*}	ΔP_{π^*}	$\Delta E(2)$[c]
cis-[PtCl$_2$(CO)(η^2-Ethene⊥)], **20**	0.0	**-52.36**	0.58	0.13	-	-	-	-	-
cis-[PtCl$_2$(CO)(η^2-perfluoroethene⊥)], **21**	5.7	**-61.13**	0.56	0.10	-	-	-	-	-
cis-[PtCl$_2$(CO)(η^1-chlorotetrafluoroethyl)], **22**	0.0	**-127.85**	0.44	-0.13	-	-	-	-	
cis-[PtCl$_2$(CO)(η^2-(*Z*)-but-2-ene⊥)], **23**	0.0	**-54.91**	0.58	0.18	-	-	-	-	-
cis-[PtCl$_2$(CO)(η^2-cyclopropene⊥)], **24**	0.0	**-56.26**	0.60	0.10	-	-	-	-	-
cis-[PtCl$_2$(CO)(η^2-(*Z*)-5-methylenecyclohept-1-ene⊥)], **25**	0.0	**-55.95**	0.59	0.16	-	-	-	-	-
cis-[PtCl$_2$(CO)(η^2-bicyclo[2.1.0]pent-2-ene⊥*syn*)], **26**	0.0	**-60.66**	0.60	0.14	-	-	-	-	-
cis-[PtCl$_2$(CO)(η^2-bicyclo[2.1.0]pent-2-ene⊥*anti*)], **27**	4.0	**-58.00**	0.59	0.15	-	-	-	-	-
cis-[PtCl$_2$(CO)(η^2-Norbornene⊥)], **28**	0.0	**-56.14**	0.59	0.18	-	-	-	-	-
cis-[PtCl$_2$(CO)(η^2-Norbornene//)], **29**	4.7	**-50.50**	0.55	0.18	1.607	**0.351**	0.256	**0.198**	22.20
cis-[PtCl$_2$(CO)(η^2-7,7-dimethyl-norbornene//)], **30**	1.0	**-46.41**	0.56	0.19	1.626	**0.330**	0.232	**0.171**	15.70
cis-[PtCl$_2$(CO)(η^2-7,7-dimethyl-norbornene‖)], **31**	0.0	**-46.55**	0.55	0.19	1.622	**0.334**	0.243	**0.182**	20.63
cis-[PtCl$_2$(CO)(η^2-bicyclo[2.2.1]hept-2-en-7-one⊥)], **32**	0.0	**-54.26**	0.58	0.13	-	-	-	-	-
cis-[PtCl$_2$(CO)(η^2-bicyclo[2.2.2]oct-2-ene⊥)], **33**	3.8	**-49.84**	0.58	0.17	1.616	**0.343**	0.271	**0.211**	27.79
cis-[PtCl$_2$(CO)(η^2-bicyclo[2.2.2]oct-2-ene‖)], **34**	0.0	**-47.06**	0.53	0.20	1.619	**0.340**	0.227	**0.167**	21.58
cis-[PtCl$_2$(CO)(η^2-Phenanthrene⊥)], **35**	0.0	**-45.99**	0.58	0.17	1.567	**0.231**	0.356	**0.158**	28.93

[a] Relative electronic energy (in kcal/mol). [b] Interaction energy (in kcal/mol) between the *cis*-[PtCl$_2$(CO)] and olefin fragments. [c] Second-order stabilization energy for the n(Pt)→π^*(C═C) donor−acceptor interaction.

Scheme 2. MOs of the *cis*-PtCl$_2$(CO) Fragment Responsible for the Stereoelectronic Interactions with the Occupied π-MOs of the Coordinated C═C Double Bond in the *cis*-[PtCl$_2$(CO)(η^2-ene)] Complexes



[PtX$_2$(CO)] (X = H, Cl, C$_6$F$_5$) electrophiles computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) level of theory.

Perusal of Table 1 reveals that the nucleophilicity index values of the unsaturated hydrocarbon ligands is proportional to the electrophilicity index of the respective electrophile. The estimated electrophilicity index values of the *cis*-[PtH$_2$(CO)], *cis*-[PtCl$_2$(CO)], and *cis*-[Pt(C$_6$F$_5$)$_2$(CO)] electrophiles are 3.84, 9.18, and 5.83 eV, respectively, at the B3P86/SDD(Pt)∪6-31G(d,p)(E) level. The estimated nucleophilicity index values of the unsaturated hydrocarbon ligands relative to the *cis*-[PtH$_2$(CO)], *cis*-[PtCl$_2$(CO)], and *cis*-[Pt(C$_6$F$_5$)$_2$(CO)] electrophiles were found in the range 0.073−0.154, 0.357−0.547, and 0.133−0.250 eV, respectively. According to the estimated nucleophility index ω^- (*Z*)-but-2-ene is the stronger nucleophile independently of the electrophile to which it is coordinated, and therefore the nucleophilic reactivity of the double bond of (*Z*)-but-2-ene toward electrophilic addition is kinetically more favored.

On the other hand, the ethene ligand is the weaker nucleophile, while perfluoroethene exhibits an intermediate nucleophilicity between those of the (*Z*)-but-2-ene and ethene ligands. The (*Z*)-5-methylenecyclohept-1-ene, bicyclo[2.1.0]pent-2-ene, 7,7-dimethylbicyclo[2.2.1]hept-2-ene, and bicyclo[2.2.2]oct-2-ene ligands are also strong nucleophiles with nucleophilicity indices comparable to those of the stronger (*Z*)-but-2-ene nucleophiles. Finally, cyclopropene, bicyclo[2.2.1]hept-2-en-7-one and phenanthrene ligands have lower nucleophilicity indices. In general the nucleophilicity of the unsaturated hydrocarbon ligands follows the trend *(Z)-but-2-ene > 7,7-dimethylbicyclo-[2.2.1]hept-2-ene > bicyclo[2.2.1]hept-2-ene ≈ bicyclo[2.2.2]oct-2-ene ≈ bicyclo[2.1.0]pent-2-ene > (Z)-5-methylenecyclohept-1-ene > perfluoroethene > cyclopropene > bicyclo[2.2.1]hept-2-en-7-one > phenanthrene ≈ ethene.*

Electronic Properties and Conformational Preferences of the *cis*-[PtH$_2$(CO)(η^2-ene)] Complexes. We will discuss first the geometric and electronic structures of the *cis*-[PtH$_2$(CO)(η^2-ene)] complexes formed upon coordination of the unsaturated hydrocarbon ligands with the less electrophilic (ω = 3.84 eV) and less crowded *cis*-[PtH$_2$(CO)] fragment. We calculated the possible equilibrium geometries of the *cis*-[PtH$_2$(CO)(η^2-ene)] complexes at the B3P86/SDD(Pt)∪6-31G(d,p)(E) level starting from geometries involving either in-plane or upright η^2-coordination of the C═C double bond. The calculated equilibrium geometries of the *cis*-[PtH$_2$(CO)(η^2-ene)] complexes along with selected structural parameters are shown in Figure 1. Selected electronic parameters of the *cis*-[PtH$_2$(CO)(η^2-ene)] complexes have been collected in Table 2.

For all unsaturated hydrocarbon complexes, except norbornene, **13**, 7,7-dimethylnorbornene, **14**, and phenanthrene, **19**, complexes, both geometric arrangements correspond to minima on the potential energy surfaces (PES). For the norbornene, **13**, and 7,7-dimethylnorbornene, **14**, complexes only the equilibrium geometry with the in-plane orientation of the coordinated C═C double bond was located on the PES independently of the starting point geometry. In contrast, for the phenanthrene complex **19**, only the equilibrium geometry with the upright orientation of the coordinated C═C double bond was located on the PES independently of the starting point geometry.

It is interesting to notice that in all cyclo- and bicycloalkene complexes the in-plane orientation of the η^2-coordinated C═C double bond corresponds to the global minimum, whereas the upright orientation corresponds to local minimum at 0.2−5.2

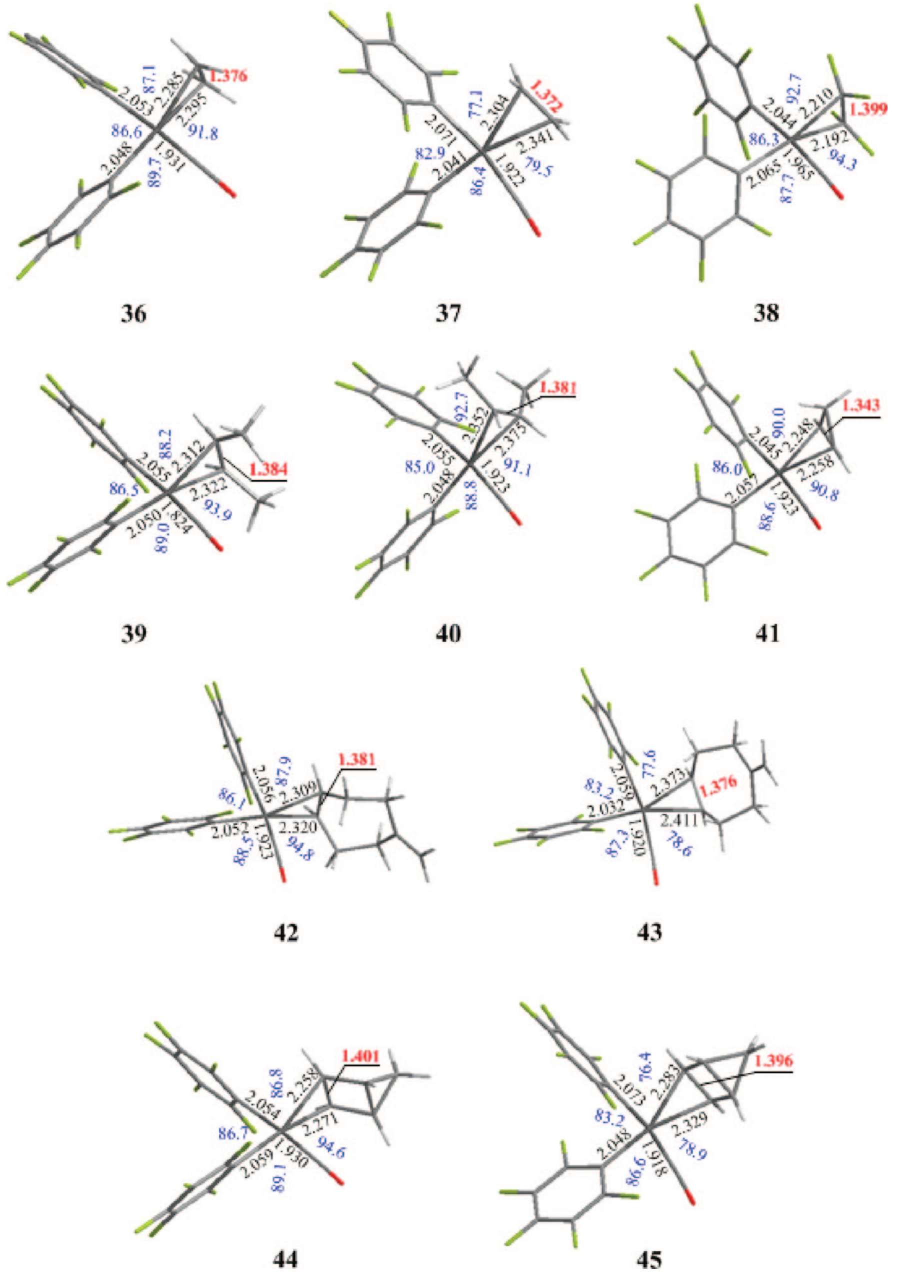


Figure 3. Equilibrium geometries (bond lengths in Å, angles in deg) of the *cis*-[Pt(C_6F_5)$_2$(CO)(η^2-ene)] complexes computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) level of theory.

kcal/mol higher in energy at the B3P86/SDD(Pt)∪6-31G(d,p)(E) level. Noteworthy is that the *cis*-[PtH$_2$(CO)(η^2-ethene⊥)], **2**, and *cis*-[PtH$_2$(CO)(η^2-cyclopropene⊥)], **8**, complexes of the ethene and cyclopropene weak π-nucleophiles correspond to saddle points on the PES with imaginary frequencies at −23.2 and −44.6 cm^{-1}, respectively. These structures constitute the transition states for the rotation about the Pt−(η^2-ene) axis; the rotational barrier is predicted to be 3.5 and 5.2 kcal/mol, respectively. The upright conformation of the perfluoroethene complex corresponds to the global minimum, while the in-plane conformation is a local minimum only 0.3 kcal/mol higher in energy. Finally, (*Z*)-but-2-ene (the stronger π-nucleophile) prefers equally both conformations, the in-plane and upright orientations differing only by 0.2 kcal/mol. In general terms, the unsaturated hydrocarbon ligands with the higher π-nucleophilicity index (strong nucleophiles), exhibiting strong σ-donor and weak π-acceptor capacities, slightly prefer the in-plane orientation of the η^2-coordinated C═C double bond upon coordination with the relatively weak *cis*-[PtH$_2$(CO)] electrophile, while those with the lower π-nucleophilicity index (weak nucleophiles), exhibiting weak σ-donor and strong π-acceptor capacities, slightly prefer the upright orientation. On the other hand, a metal-containing fragment of low electrophilicity exhibits strong σ-acceptor and weak π-back-donor capacity, both factors favoring the in-plane orientation. However, it should be stressed that the balance between the electrophilic character of the metal-containing fragment and the nucleophilic character of the unsaturated hydrocarbon ligand in the *cis*-[PtH$_2$(CO)(η^2-ene)] complexes renders both orientations of the C═C double bond competitive, and therefore it is a dilemma that leads to the coexistence of both conformers in equilibrium in solutions.

The most characteristic structural differences between the *cis*-[PtH$_2$(CO)(η^2-ene∥)] (in-plane orientation) and *cis*-[PtH$_2$(CO)(η^2-ene⊥)] (upright orientation) could be summarized as follows:

In the upright orientation the η^2-ene coordination is symmetric, forming a platinacyclopropene ring that corresponds to

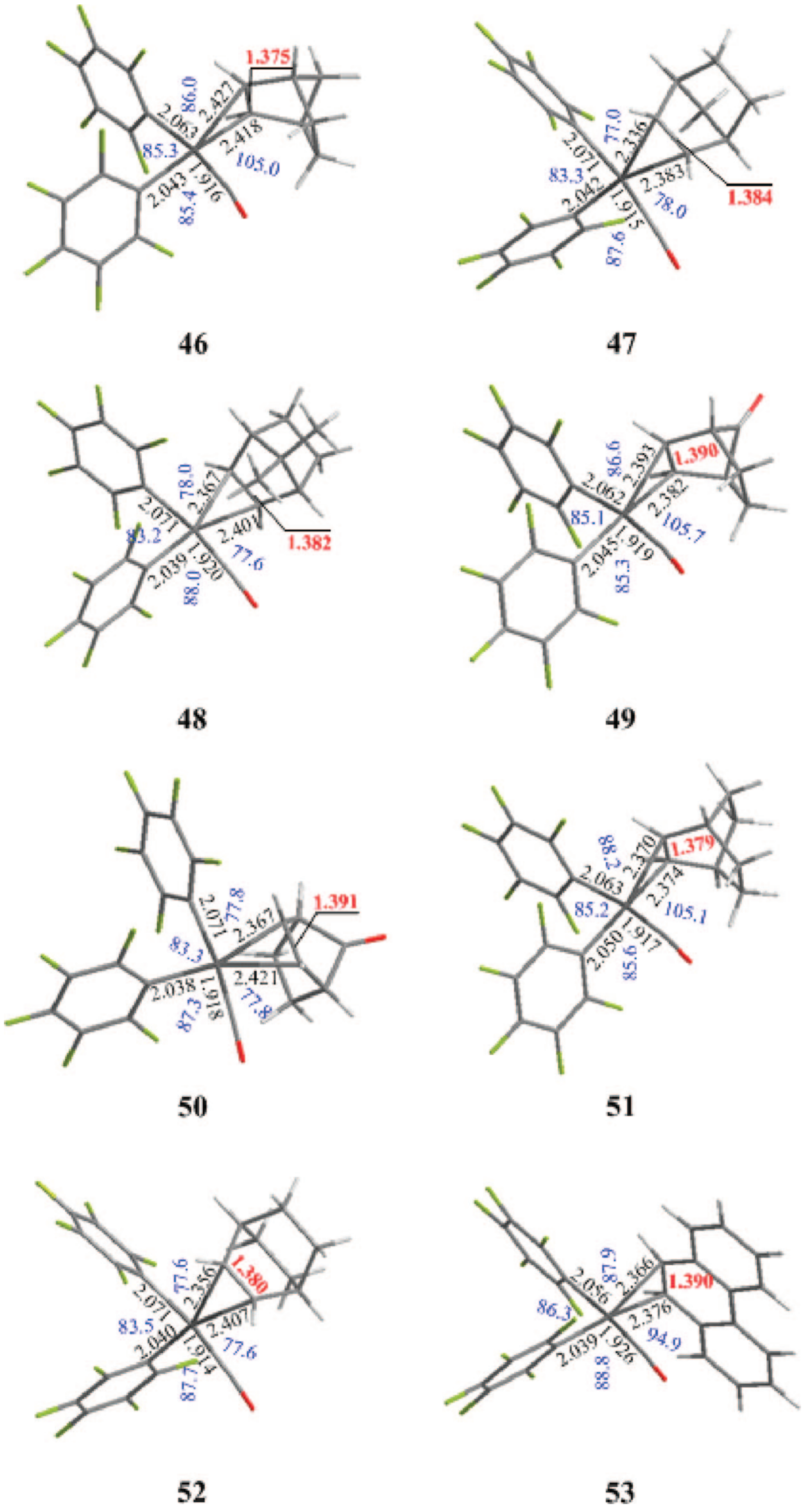


Figure 4. Equilibrium geometries (bond lengths in Å, angles in deg) of the *cis*-[Pt(C_6F_5)$_2$(CO)(η^2-ene)] complexes computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) level of theory.

a perfect isosceles triangle. In contrast, in the in-plane coordination the two Pt−C bonds are not equivalent, their bond lengths differing by 0.029−0.061 Å. It is interesting to notice that the Pt−C bond that is vicinal to the Pt−CO bond is longer than the Pt−C bond vicinal to the Pt−H bond. A remarkable bending back of both the *cis*-H and the CO ligands away from the coordinated C═C double bond is also observed. The bending back of the CO ligand is higher than that of the *cis*-H ligand, and it is more pronounced in the in-plane than in the upright conformation of the double bond. Both the Pt−C bond elongation and the bending back of the CO ligand result from steric repulsive interactions between the π-MOs of the coordinated C═C double bond and the relatively high-lying occupied fragment orbitals (OFOs) of the metal-containing fragment comprised mainly of π-MO localized on the CO ligand. Finally, the elongation of the coordinated C═C double bond is higher in the in-plane than in the upright conformation. Thus, in the in-plane conformation the C═C double bond is elongated by 0.051 to 0.081 Å, while in the upright conformation the elongation amounts to 0.029 to 0.071 Å. Noteworthy is the

Table 4. Selected Electronic Parameters of the *cis*-[Pt(C_6F_5)$_2$(CO)(η^2-ene)] Complexes Computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) Level

Complex	E_{rel}[a]	E_{int}[b]	q_{Pt}	q_{olefin}	P_π	ΔP_π	P_{π^*}	ΔP_{π^*}	$\Delta E(2)$[c]
cis-[Pt(C_6F_5)$_2$(CO) (η^2-Ethene⊥)], **36**	0.0	**-37.16**	0.51	0.12	1.710	**0.290**	0.163	**0.163**	31.05
cis-[Pt(C_6F_5)$_2$(CO) (η^2-Ethene‖)], **37**	3.4	**-35.98**	0.48	0.10	1.726	**0.274**	0.172	**0.172**	24.66
cis-[Pt(C_6F_5)$_2$(CO)(η^2-perfluoroethene⊥)], **38**	0.0	**-44.60**	0.52	0.07	1.671	**0.325**	0.455	**0.180**	61.71
cis-[Pt(C_6F_5)$_2$(CO)(η^2-(*Z*)-but-2-ene⊥*syn*)], **39**	0.0	**-39.16**	0.55	0.14	1.701	**0.264**	0.199	**0.136**	26.18
cis-[Pt(C_6F_5)$_2$(CO)(η^2-(*Z*)-but-2-ene⊥*anti*)], **40**	3.4	**-37.23**	0.49	0.16	1.709	**0.256**	0.184	**0.121**	20.66
cis-[Pt((C_6F_5)$_2$(CO)(η^2-cyclopropene⊥)], **41**	0.0	**-33.53**	0.55	0.11	1.709	**0.224**	0.157	**0.121**	26.37
cis-[Pt((C_6F_5)$_2$(CO)(η^2-(*Z*)-5-methylenecyclohept-1-ene⊥)], **42**	0.0	**-39.58**	0.55	0.14	1.704	**0.261**	0.194	**0.143**	27.32
cis-[Pt((C_6F_5)$_2$(CO)(η^2-(*Z*)-5-methylenecyclohept-1-ene‖)], **43**	3.6	**-36.28**	0.52	0.12	1.727	**0.238**	0.183	**0.132**	19.19
cis-[Pt(C_6F_5)$_2$(CO)(η^2-bicyclo[2.1.0]pent-2-ene)⊥], **44**	0.0	**-44.32**	0.57	0.11	1.678	**0.281**	0.247	**0.193**	33.61
cis-[Pt(C_6F_5)$_2$(CO)(η^2-bicyclo[2.1.0]pent-2-ene‖)], **45**	4.6	**-41.67**	0.47	0.11	1.679	**0.280**	0.247	**0.193**	27.90
cis-[Pt(C_6F_5)$_2$(CO)(η^2-norbornene⊥)], **46**	9.7	**-32.68**	0.52	0.16	1.749	**0.209**	0.143	**0.085**	15.06
cis-[Pt(C_6F_5)$_2$(CO)(η^2-norbornene‖)], **47**	0.0	**-39.79**	0.50	0.13	1.697	**0.261**	0.218	**0.160**	22.56
cis-[Pt(C_6F_5)$_2$(CO)(η^2-7,7-dimethyl-norbornene‖)], **48**	0.0	**-36.33**	0.53	0.12	1.714	**0.242**	0.218	**0.157**	20.38
cis-[Pt(C_6F_5)$_2$(CO)(η^2-1-carbonyl-norbornene⊥)], **49**	1.7	**-31.26**	0.54	0.13	1.724	**0.207**	0.219	**0.135**	19.28
cis-[Pt(C_6F_5)$_2$(CO)(η^2-1-carbonyl-norbornene‖)], **50**	0.0	**-33.41**	0.45	0.12	1.702	**0.229**	0.244	**0.160**	18.93
cis-[Pt(C_6F_5)$_2$(CO)(η^2-bicyclo[2.2.2]oct-2-ene⊥)], **51**	1.9	**-37.15**	0.54	0.15	1.720	**0.239**	0.185	**0.125**	14.84
cis-[Pt(C_6F_5)$_2$(CO)(η^2-bicyclo[2.2.2]oct-2-ene‖)], **52**	0.0	**-38.57**	0.50	0.13	1.707	**0.252**	0.207	**0.147**	19.98
cis-[Pt(C_6F_5)$_2$(CO)(η^2-Phenanthrene⊥)], **53**	0.0	**-32.36**	0.50	0.13	1.664	**0.134**	0.306	**0.108**	16.64

[a] Relative electronic energy (in kcal/mol). [b] Interaction energy (in kcal/mol) between the *cis*-[Pt(C_6F_5)$_2$(CO)] and olefin fragments. [c] Second-order stabilization energy for the [*n*(Pt)→π^*(C=C)] donor−acceptor interaction.

Table 5. Selected Electronic Parameters of a Few *cis*-[PtX_2(CO)] Elecrophiles Computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) Level

cis-[PtX_2(CO)] electrophile	ε_{HOMO} (eV)	ε_{LUMO} (eV)	μ (eV)	η (eV)	**ω (eV)**	Q_{Pt}
cis-[Pt{CH(CH_3)$_3$}$_2$(CO)]	-4.697	-1.851	-3.274	2.846	**1.883**	0.35
cis-[Pt(CH_3)$_2$(CO)]	-7.422	-3.163	-5.293	4.259	**3.289**	0.36
cis-[Pt(C_6H_5)$_2$(CO)]	-7.022	-3.269	-5.146	3.753	**3.528**	0.37
cis-[Pt(CF_3)$_2$(CO)]	-8.361	-4.061	-6.211	4.300	**4.486**	0.28
cis-[Pt(CN)$_2$(CO)]	-9.571	-5.596	-7.584	3.975	**7.235**	0.48
cis-[PtF_2(CO)]	-9.283	-5.670	-7.477	3.613	**7.737**	0.90
cis-[PtBr_2(CO)]	-8.051	-5.266	-6.659	2.785	**7.961**	0.50
cis-[Pt(N_3)$_2$(CO)]	-7.875	-5.321	-6.598	2.554	**8.523**	0.64

higher elongation of the C=C double bond in the perfluoroethene complexes, found to be 0.081 and 0.071 Å in the in-plane and the upright conformation, respectively.

Let us now go deeper into the electronic structure and bonding properties of the *cis*-[PtH_2(CO)(L)] (L = unsaturated hydrocarbon ligand) complexes to understand the orientation mode of the coordinated C=C double bond to the Pt(II) metal center. The major bonding interactions follow the DCD bond model involving σ-donation from the π-MO of the coordinated alkene ligand to the lowest unoccupied fragment orbital (LUFO) of the metal-containing fragment and π-back-donation from the highest occupied fragment orbitals (OFOs) of the metal-containing fragment to the π^*-MO of the alkene ligand. The estimated interaction energies between the metal-containing and the unsaturated hydrocarbon fragments (Table 2) for the *cis*-[PtH_2(CO)(η^2-ene‖)] and *cis*-[PtH_2(CO)(η^2-ene⊥)] complexes range from −37.40 to −50.11 kcal/mol and −25.97 to −41.82 kcal/mol, respectively. It is interesting to notice that the unsaturated hydrocarbon ligands (except perfluoroethene) acquire a total positive natural atomic charge around 0.01−0.08 |e| in the upright orientation and negative natural atomic charge around −0.01 to −0.13 |e| in the in-plane orientation. In the perfluoroethene complex the coordinated perfluoroethene ligand acquires a negative natural atomic charge of −0.03 |e| in the upright orientation, as well. Obviously in the in-plane orientation π-back-donation exceeds σ-donation, while the opposite is true in the upright orientation. Moreover, the platinum(II) metal center acquires a positive natural atomic charge around 0.17 to 0.23 |e|, which is higher in the *cis*-[PtH_2(CO)(η^2-ene⊥)] than the *cis*-[PtH_2(CO)(η^2-ene‖)] complexes.

The degree of σ-donation and π-back-donation in the *cis*-[PtH_2(CO)(η^2-ene)] complexes can be separately evaluated by the electron populations P_π and P_{π^*} of the involved natural bond orbitals (NBOs) localized on the coordinated C=C double bond.[35] It can be seen that both the σ-donation and π-back-donation are stronger in the in-plane than in the upright orientations (compare the variation of the population of the π natural bond orbital (P_π, *e*) with respect to free olefin, ΔP_π, and the variation of the population of the π^* natural bond orbital (P_{π^*}, *e*) with respect to free olefin (ΔP_{π^*} values given in Table 2). The estimated ΔP_π values range from 0.183 to 0.275 *e* in the in-plane and from 0.082 to 0.264 *e* in the upright orientation. The higher values (0.275 and 0.264 *e*) are characteristic of the perfluoroethene ligand followed by those of the ethene and bicyclo[2.1.0]pent-2-ene ligands. On the other hand, the estimated ΔP_{π^*} values are found in the range 0.200−0.320 *e* and 0.106−0.193 *e* in the in-plane and upright orientation, respectively. The stronger π-back-donation occurs in the in-plane orientation of the cyclopropene ligand and the lower one in the upright orientation of the phenanthrene ligand. The higher π-back-donation in the in-plane than in the upright orientation of the unsaturated hydrocarbon ligands is also reflected in the higher stabilization energy $\Delta E(2)$ for the *n*(Pt)→π^*(C=C) interaction resulting from second-order perturbation theory given by[36]

$$\Delta E(2) = n_i F_{ij}/(\varepsilon_i - \varepsilon_j) \qquad (2)$$

This equation evaluates the magnitude of the donor−acceptor interaction in terms of the spatial overlap of the NBO, using the off-diagonal Fock (Kohn−Sham) matrix elements F_{ij} and the difference in energy between the NBOs, $\varepsilon_i - \varepsilon_j$, weighted

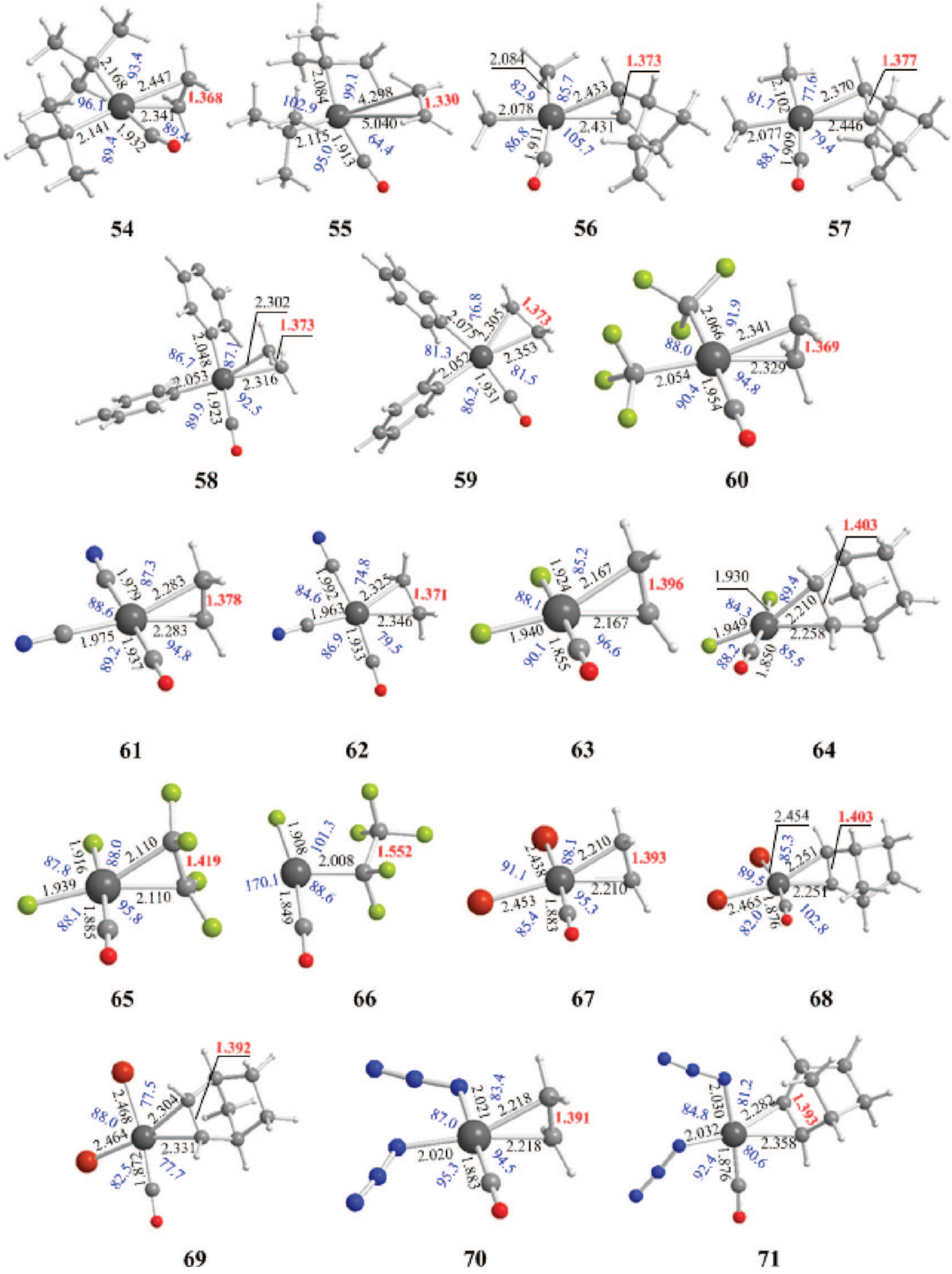


Figure 5. Equilibrium geometries (bond lengths in Å, angles in deg) of the *cis*-[PtX$_2$(CO)(η^2-ene)] complexes computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) (E = nonmetal element) level of theory.

by the occupancy of the donor NBO, n_i. Representative 3D isosurface plots of the $n(\mathrm{Pt})\rightarrow\pi^*(\mathrm{C{=}C})$ hyperconjugative interactions in both the upright and in-plane orientations of the coordinated C=C double bond are given in Scheme 1. Analogous are the 3D isosurface plots of the $n(\mathrm{Pt})\rightarrow\pi^*(\mathrm{C{=}C})$ hyperconjugative interactions in all PtX$_2$(CO)(η^2-ene) complexes studied herein.

Electronic Properties and Conformational Preferences of the *cis*-[PtCl$_2$(CO)(η^2-ene)] Complexes. To assess the effect of the electrophilic character of the metal-containing fragment on the conformational preference of the unsaturated hydrocarbon ligands, we calculated next the geometric and electronic structures of the *cis*-[PtCl$_2$(CO)(η^2-ene)] complexes formed upon coordination of the unsaturated hydrocarbon ligands, with the *cis*-[PtCl$_2$(CO)] fragment exhibiting the higher electophilicity (ω = 9.18 eV). We calculated the possible equilibrium geometries of the *cis*-[PtCl$_2$(CO)(η^2-ene)] complexes at the B3P86/SDD(Pt)∪6-31G-

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Table 6. Selected Electronic Parameters of Some *cis*-[PtX$_2$(CO)(η^2-ene)] Complexes Computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) Level

Complex	E_{rel}[a]	E_{int}[b]	q_{Pt}	q_{olefin}	P_π	ΔP_π	$P_{\pi*}$	$\Delta P_{\pi*}$	$\Delta E(2)$[c]
cis-[Pt{CH(CH$_3$)$_3$}$_2$(CO)(η^2-Ethene$\perp$)], **54**	1.5	**-16.80**	0.50	0.05	1.785	**0.215**	0.161	**0.161**	18.49
cis-[Pt{CH(CH$_3$)$_3$}$_2$(CO)(η^2-Ethene$\parallel$)], **55**	0.0	**-0.53**	0.37	0.00	1.996	**0.004**	0.001	**0.001**	0.06
cis-[Pt(CH$_3$)$_2$(CO)(η^2-norbornene$\perp$)], **56**	0.0	**-23.70**	0.47	0.08	1.788	**0.170**	0.161	**0.103**	17.68
cis-[PtCH$_3$)$_2$(CO)(η^2-norbornene$\parallel$)], **57**	0.2	**-26.53**	0.43	0.06	1.762	**0.196**	0.202	**0.144**	19.67
cis-[Pt(C$_6$H$_5$)$_2$(CO) (η^2-Ethene$\perp$)], **58**	0.0	**-28.33**	0.49	0.07	1.749	**0.251**	0.177	**0.177**	31.04
cis-[Pt(C$_6$H$_5$)$_2$(CO)(η^2-Ethene$\parallel$)], **59**	2.4	**-28.55**	0.44	0.04	1.758	**0.242**	0.194	**0.194**	26.45
cis-[Pt(CF$_3$)$_2$(CO)(η^2-ethene$\perp$)], **60**	0.0	**-33.60**	0.36	0.11	1.748	**0.252**	0.131	**0.131**	25.91
cis-[Pt(CN)$_2$(CO)(η^2-ethene$\perp$)], **61**	0.0	**-45.22**	0.49	0.15	1.685	**0.315**	0.160	**0.160**	29.30
cis-[Pt(CN)$_2$(CO)(η^2-ethene$\parallel$)], **62**	4.5	**-41.51**	0.45	0.14	1.712	**0.288**	0.146	**0.146**	21.23
cis-[PtF$_2$(CO)(η^2-ethene$\perp$)], **63**	0.0	**-62.45**	0.88	0.10	-	-	-	-	-
cis-[PtF$_2$(CO)(η^2-norbornene$\perp$)], **64**	0.0	**-64.50**	0.87	0.12	-	-	-	-	-
cis-[PtF$_2$(CO)(η^2-perfluoroethene$\perp$)], **65**	0.0	**-70.53**	0.52	-0.04	-	-	-	-	-
cis-[PtF$_2$(CO)(η^2-perfluoroethyl)], **66**	32.8	**-261.19**	0.84	0.07	-	-	-	-	-
cis-[PtBr$_2$(CO)(η^2-ethene$\perp$)], **67**	0.0	**-48.27**	0.49	0.12	1.610	**0.390**	0.243	**0.243**	40.18
cis-[PtBr$_2$(CO)(η^2-norbornene$\perp$)], **68**	0.0	**-52.10**	0.50	0.17	-	-	-	-	-
cis-[PtBr$_2$(CO)(η^2-norbornene$\parallel$)], **69**	4.0	**-45.79**	0.44	0.17	1.620	**0.338**	0.245	**0.187**	23.54
cis-[Pt(N$_3$)$_2$(CO)(η^2-ethene$\perp$)], **70**	0.0	**-46.37**	0.70	0.11	1.618	**0.382**	0.250	**0.250**	38.72
cis-[Pt(N$_3$)$_2$(CO)(η^2-norbornene//)], **71**	0.0	**-43.73**	0.69	0.16	1.634	**0.324**	0.257	**0.199**	25.50

[a] Relative electronic energy (in kcal/mol). [b] Interaction energy (in kcal/mol) between the *cis*-[PtX$_2$(CO)] electrophile and the unsaturated hydrocarbon ligands. [c] Second-order stabilization energy for the [n(Pt)→π*(C=C)] donor−acceptor interactions.

(d,p)(E) level of theory starting from geometries involving either in-plane or upright η^2-coordination of the C=C double bond. The equilibrium geometries of the *cis*-[PtCl$_2$(CO)(η^2-ene)] complexes along with selected structural parameters computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) level of theory are shown in Figure 2. Selected electronic parameters of the *cis*-[PtCl$_2$(CO)(η^2-ene)] complexes are compiled in Table 3.

In contrast to the *cis*-[PtH$_2$(CO)(η^2-ene)] complexes, where both orientations of the unsaturated hydrocarbon correspond to local minima on the PES, in the *cis*-[PtCl$_2$(CO)(η^2-ene)] complexes only one of the orientations could be located as a minimum in the PES, that of the upright orientation of the C=C double bond independently of the starting geometry, except for the complexes of the perfluoroethene, norbornene, 7,7-dimethylnorbornene, and bicyclo[2.2.2]oct-2-ene ligands. For the latter complexes both orientations correspond to minima in the PES, with the upright orientation at 1.0 and 3.8 kcal/mol higher energy than the in-plane orientation. Noteworthy is the in-plane orientation of perfluoroethene, where the *cis*-chloride ligand has migrated to a carbon atom of the coordinated perfluoroethene, thus forming a chlorotetrafluoroethyl ligand, CF$_2$ClCF$_2$−, coordinated to the platinum(II) metal center. The C−C bond length in the coordinated CF$_2$ClCF$_2$− ligand corresponds to a single C−C bond (1.553 Å). In complex **30** the coordinated 7,7-dimethylnorbornene ligand does not adopt the perfect upright orientation but is tilted about the Pt−olefin rotational axis (the tortional Cl−Pt−C−C angle is −49.9°), while the two Pt−C bond lengths differ significantly, by 0.214 Å.

One of the most characteristic structural features of the *cis*-[PtCl$_2$(CO)(η^2-ene)] complexes is (i) the elongation of the coordinated C=C double bond by 0.048−0.097 Å. The higher elongation occurs in the perfluoroethene complex **21** and the lower one in the phenanthrene, **35**, 7,7-dimethylnorbornene, **31**, and norbornene, **29**, complexes, while in complex **22** the large elongation of 0.229 Å is indicative of the transformation of the coordinated perfluoroethene to a coordinated CF$_2$ClCF$_2$− ligand. Another characteristic feature is (ii) the slippage of the *cis*-PtCl$_2$(CO) fragment along the axis of the coordinated C=C double bond, resulting in the nonequivalence of the Pt−C bond lengths in norbornene, **29**, 7,7-dimethylnorbornene, **30**, **31**, and bicyclo[2.2.2]oct-2-ene, **34**, complexes adopting the in-plane orientation of the C=C double bond; the Pt−C bond, which is vicinal to the Pt−CO bond is longer than the Pt−C bond vicinal to the Pt−Cl bond by 0.038, 0.214, 0.099, and 0.057 Å, respectively. Another characteristic feature is (iii) a remarkable bending back of both the *cis*-Cl and CO ligands away from the coordinated C=C double bond. Both the Pt−C bond elongation and the bending back of the *cis*-Cl ligand result from stereoelectronic repulsive interactions between the π-MOs of the coordinated C=C double bond and the relatively high-lying OFOs of the *cis*-PtCl$_2$(CO) fragment (Scheme 2) comprised mainly of nonbonding p$_\pi$-MOs localized on the *cis*-Cl ligand.

The estimated interaction energies of the *cis*-[PtCl$_2$(CO)(η^2-ene)] complexes ranging from −45.99 to −61.13 kcal/mol are higher than the corresponding interaction energies of the *cis*-[PtH$_2$(CO)(η^2-ene)] complexes. This observation is compatible with the stronger *trans* effect of the hydride than the chloride ligand. For complex **22** the interaction energy is much higher (−127.85 kcal/mol), because of the contribution from the strong C−Cl interactions forming the CF$_2$ClCF$_2$− ligand, which is strongly bound to the Pt(II) metal center.

It is interesting to notice that the unsaturated hydrocarbon ligands (except chlorotetrafluoroethyl in **22**) acquire a total positive natural atomic charge ranging from 0.10 to 0.20 |e|. In the chlorotetrafluoroethyl complex **22** the coordinated chlorotetrafluoroethyl ligand acquires a negative natural atomic charge of −0.13 |e|. Moreover, the platinum(II) metal center acquires a positive natural atomic charge of 0.53 to 0.60 |e|.

The degree of σ-donation and π-back-donation in the *cis*-[PtCl$_2$(CO)(η^2-ene)] complexes has been separately evaluated by the electron populations P_π and $P_{\pi*}$ of the involved NBOs localized on the coordinated C=C double bond (Table 3). Surprisingly, in most cases the NBO analysis failed to analyze the respective σ-donation and π-back-donation interactions. However, in the cases where these interactions were analyzed, the estimated ΔP_π and $\Delta P_{\pi*}$ values were found in the range

0.231−0.351 and 0.158−0.211 *e*, respectively. The much stronger σ-acceptor and the weaker π-back-donor capacity of the *cis*-[$PtCl_2(CO)$] fragment compared to those of the *cis*-[$PtH_2(CO)$] one could be due to the higher electrophilicity of the former in conjunction with the stronger *trans* effect of the chloride than the hydride ligand.

These observations clearly illustrate the key role of the σ- and π-back-bonding interactions in determining the conformational preference of the unsaturated hydrocarbon ligands upon coordination with the platinum-containing electrophilic fragments. These interactions can be modulated by the electrophilicity and nucleophilicity of the platinum-containing electrophile and the unsaturated hydrocarbon nucleophiles, respectively. *Thus, it can be concluded that the coordinated unsaturated hydrocarbon ligands exclusively prefer the upright orientation when the σ-type metal−ligand interactions are higher than the π-back-bonding interactions. This could be achieved by coordinating a strong unsaturated hydrocarbon nucleophile to a strong platinum-containing fragment electrophile.*

Electronic Properties and Conformational Preferences of the *cis*-[$Pt(C_6F_5)_2(CO)(\eta^2$-ene)] Complexes. We studied next the unsaturated hydrocarbon complexes of the electrophilic metal-containing fragment *cis*-[$Pt(C_6F_5)_2(CO)$], exhibiting an intermediate electrophilic character (ω = 5.83 eV). We calculated the possible equilibrium geometries of the *cis*-[$Pt(C_6F_5)_2(CO)(\eta^2$-ene)] complexes at the B3P86/SDD(Pt)∪6-31G(d,p)(E) level of theory starting from geometries involving either in-plane or upright η^2-coordination of the C=C double bond. The equilibrium geometries of the *cis*-[$Pt(C_6F_5)_2(CO)(\eta^2$-ene)] complexes along with selected structural parameters computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) level of theory are shown in Figures 3 and 4, while selected electronic parameters have been collected in Table 4.

The behavior of the *cis*-[$Pt(C_6F_5)_2(CO)(\eta^2$-ene)] complexes with respect to the conformational preference of the coordinated unsaturated hydrocarbon is intermediate between those of the *cis*-[$PtH_2(CO)(\eta^2$-ene)] and *cis*-[$PtCl_2(CO)(\eta^2$-ene)] complexes. Thus, the *cis*-[$Pt(C_6F_5)_2(CO)(\eta^2$-ene)] complexes can be classified into two categories.

The first category involves the complexes where only the upright orientation of the unsaturated hydrocarbon corresponds to a minimum in the PES. Here belong the perfluoroethene, **38**, (*Z*)-but-2-ene, **39**, **40**, cyclopropene, **41**, and phenanthrene, **53**, complexes. The second category involves the complexes where both orientations of the coordinated C=C double bond correspond to local minima in the PES. In this category belong the ethene, **36**, **37**, (*Z*)-5-methylenecyclohept-1-ene, **42**, **43**, bicyclo[2.1.0]pent-2-ene, **44**, **45**, norbornene, **46**, **47**, 1-carbonylnorbornene, **49**, **50**, and bicyclo[2.1.2]oct-2-ene, **51**, **52**, complexes. The 7,7-dimethylnorbornene complex, **48**, adopts only the equilibrium geometry with the in-plane orientation of the coordinated C=C double bond. In general, the unsaturated hydrocarbons yielding the first category of complexes have nucleophilicities in the range 0.154−0.250 eV. On the other hand, the unsaturated hydrocarbons yielding the second category of complexes have nucleophilicities in the range 0.133−0.238 eV. *It is evident that the nucleophilicity of the unsaturated hydrocarbon ligands in conjunction with steric effects (due to the more bulky C_6F_5 ligand) plays a key role in modulating the conformational preference upon coordination with a platinum-containing fragment of intermediate electrophilicity.*

The most salient structural features of the *cis*-[$Pt(C_6F_5)_2(CO)(\eta^2$-ene)] complexes are analogous to those of the *cis*-[$PtH_2(CO)(\eta^2$-ene)] and *cis*-[$PtCl_2(CO)(\eta^2$-ene)] complexes. Thus the coordinated C=C double bond is elongated by 0.033−0.075 and 0.040−0.054 Å in the upright and in-plane orientations, respectively. These values being intermediate between those of the *cis*-[$PtH_2(CO)(\eta^2$-ene)] and *cis*-[$PtCl_2(CO)(\eta^2$-ene)] complexes justifies the crucial role of the electrophilicity of the metal-containing fragment in the structural parameters of the complexes. In all *cis*-[$Pt(C_6F_5)_2(CO)(\eta^2$-ene)] complexes the two Pt−C bond distances of the η^2-bonded unsaturated hydrocarbon are not equivalent in both the in-plane and the upright orientation of the C=C double bond. It is important to stress here that, in contrast to the *cis*-[$PtH_2(CO)(\eta^2$-ene)] and *cis*-[$PtCl_2(CO)(\eta^2$-ene)] complexes, where the two Pt−C bond distances are not equivalent only in the in-plane orientation of the C=C double bond, in the *cis*-[$Pt(C_6F_5)_2(CO)(\eta^2$-ene)] complexes the two Pt−C bond distances differ also by 0.008−0.023 Å in the complexes with the upright orientation. This could be due to steric effects of the bulkier C_6F_5 than the hydride and chloride ligands. Certainly, the larger differences amounting to 0.037−0.051 Å are found in the in-plane orientation. Finally, noteworthy is the location of two local minima on the PES of the *cis*-[$PtCl_2(CO)$(*Z*-but-2-ene)] complex corresponding to the *syn*- and *anti*-conformation of the upright coordinated *Z*-but-2-ene with respect to the coordinated carbonyl ligand. The *syn*-conformer is slightly more stable than the *anti*-conformer by about 3.4 kcal/mol.

Perusal of Table 4 illustrates that the estimated interaction energies of the *cis*-[$Pt(C_6F_5)_2(CO)(\eta^2$-ene)] complexes ranging from −31.32 to −44.60 kcal/mol are closer to those of the *cis*-[$PtH_2(CO)(\eta^2$-ene)] complexes (slightly higher), which is compatible with the electrophilicity index of 5.83 eV of the *cis*-[$Pt(C_6F_5)_2(CO)$] fragment as compared to the electrophilicity index of 3.84 and 9.18 eV of the *cis*-[$PtH_2(CO)$] and *cis*-[$PtCl_2(CO)$] fragments, respectively.

In all *cis*-[$Pt(C_6F_5)_2(CO)(\eta^2$-ene)] complexes the coordinated unsaturated hydrocarbon ligands acquire a total positive natural atomic charge ranging from 0.07 to 0.16 |e|. Surprisingly these values are closer to those of the *cis*-[$PtCl_2(CO)(\eta^2$-ene)] than the *cis*-[$PtH_2(CO)(\eta^2$-ene)] complexes. Moreover, the platinum(II) metal center acquires a positive natural atomic charge of 0.48 to 0.57 |e|. These values are also closer to those of the *cis*-[$PtCl_2(CO)(\eta^2$-ene)] than the *cis*-[$PtH_2(CO)(\eta^2$-ene)] complexes. The estimated ΔP_π and $\Delta P_{\pi*}$ values in the *cis*-[$Pt(C_6F_5)_2(CO)(\eta^2$-ene)] complexes are found in the range 0.134−0.325 and 0.108−0.193 *e*, respectively. Finally, the estimated stabilization energies $\Delta E(2)$ for the n(Pt)→π*(C=C) interactions related with the π-back-donation process range from 15.06 to 61.71 kcal/mol. These values compare better with those of the *cis*-[$PtH_2(CO)(\eta^2$-ene||)] than the *cis*-[$PtCl_2(CO)(\eta^2$-ene||)] complexes.

Predicting the Conformational Preference in *cis*-[$PtX_2(CO)(\eta^2$-ene)] Complexes. To test further the predictive power of the electrophilicity index ω of the *cis*-[$PtX_2(CO)$] fragments in conjunction with the nucleophilicity of the unsaturated hydrocarbon ligands on the conformational preference of the coordinated C=C double bond (upright or in-plane), calculations were performed on a series of complexes of selected unsaturated hydrocarbon ligands (ethene, norbornene, or perfluoroethene) with the electrophilic *cis*-[$PtX_2(CO)$] (X = $CH(CH_3)_3$, CH_3, C_6H_5, CF_3, CN, F, Br, and N_3) fragments, which span a wide range of electrophilicity indices, ranging from 1.883 to 8.523 eV (Table 5).

The equilibrium geometries of the *cis*-[$PtX_2(CO)(\eta^2$-ene)] complexes along with selected structural parameters computed at the B3P86/SDD(Pt)∪6-31G(d,p)(E) level of theory are shown in Figure 5, while selected electronic parameters have been collected in Table 6.

The behavior of the *cis*-[$PtX_2(CO)(\eta^2$-ene)] complexes with respect to the conformational preference of the coordinated unsaturated hydrocarbon is effectively determined by the electrophilicity of the *cis*-[$PtX_2(CO)$] electrophile. Thus all *cis*-[$PtX_2(CO)(\eta^2$-ene)] complexes involving weak *cis*-[$PtX_2(CO)$] electrophiles (ω values in the range 1.883 to 4.486 eV) behave exactly like the *cis*-[$PtH_2(CO)$] electrophile ($\omega = 3.84$ eV). On the other hand, all *cis*-[$PtX_2(CO)(\eta^2$-ene)] complexes involving strong *cis*-[$PtX_2(CO)$] electrophiles (ω values in the range 7.235 to 8.523 eV) behave exactly like the *cis*-[$PtCl_2(CO)$] electrophile ($\omega = 9.18$ eV).

The behavior of the *cis*-[$Pt(CN)_2(CO)$] electrophile with an intermediate electrophilicity index of 7.067 eV matches that of the *cis*-[$Pt(C_6F_5)_2(CO)$] electrophile ($\omega = 5.83$ eV).

Noteworthy is the strong steric effect introduced by the bulky ^{t}Bu and Me ligands, which inhibits the in-plane orientation of the unsaturated hydrocarbon ligands. Thus in the in-plane orientation of ethene the ethene molecule is pushed away from the platinum metal center to a distance of about 4.5 Å. In general the estimated interaction energies parallel the electrophilicity of the *cis*-[$PtX_2(CO)$] elecrophiles. It is also important to notice that in the in-plane orientation of perfluoroethene in complex **66** the *cis*-fluoride ligand has migrated to the carbon atom of the coordinated perfluoroethene, thus forming a perfluoroethyl complex. The estimated interaction energy between the perfluoroethyl and the *cis*-[$PtF_2(CO)$] elecrophile was found to be −261.19 kcal/mol. Such migration processes, being crucial steps in the catalytic hydrogenation, hydrosilylation, hydrocyanation, hydroamination, etc., of unsaturated hydrocarbons, occur easily in the in-plane orientation, and therefore platinum complexes that favor the in-plane orientation should be superior catalysts than those favoring the upright orientation.

In all *cis*-[$PtX_2(CO)(\eta^2$-ene)] complexes the coordinated unsaturated hydrocarbon ligands acquire a total positive natural atomic charge ranging from 0.04 to 0.17 $|e|$. Moreover, the platinum(II) metal center acquires a positive natural atomic charge of 0.36 to 0.88 $|e|$. The estimated ΔP_π and ΔP_{π^*} values in the complexes were found in the range 0.170−0.390 and 0.103−0.250 e, respectively. As it would be expected, the higher values of ΔP_π and lower values of ΔP_{π^*} characterize the complexes of the more electrophilic *cis*-[$PtF_2(CO)$] fragment. Finally, the estimated stabilization energies $\Delta E(2)$ for the $n(\mathrm{Pt}) \rightarrow \pi^*(\mathrm{C{=}C})$ were found in the range 17.68 to 40.18 kcal/mol, which is comparable to those found for the *cis*-[$PtX_2(CO)(\eta^2$-ene)] (X = H, Cl, C_6F_5) complexes.

Conclusions

In the present work we have employed an array of NBO and CDA-based analysis tools in conjunction with hybrid density functional calculations at the B3P86/SDD(Pt)∪6-31G(d,p)(E) level to unravel the origin of the in-plane or upright conformational preference of η^2-coordinated C═C double bonds in a series of square-planar d^8 metal complexes formulated as *cis*-[$PtX_2(CO)(L)$] (X = H, Cl, C_6F_5; L = unsaturated hydrocarbon ligand). Specifically, we have considered the nucleophilicity of the unsaturated hydrocarbon ligands with respect to *cis*-[$PtH_2(CO)$], *cis*-[$PtCl_2(CO)$], and *cis*-[$Pt(C_6F_5)_2(CO)$] electrophiles having low ($\omega = 3.84$ eV), intermediate ($\omega = 5.83$ eV), and high ($\omega = 9.18$ eV) electrophilicity.

In general terms, the unsaturated hydrocarbon ligands with the higher π-nucleophilicity index (strong nucleophiles), exhibiting strong σ-donor and weak π-acceptor capacities, slightly prefer the in-plane orientation of the η^2-coordinated C═C double bond upon coordination with the relatively weak *cis*-[$PtX_2(CO)$] electrophiles, while those with the lower π-nucleophilicity index (weak nucleophiles), exhibiting weak σ-donor and strong π-acceptor capacities, slightly prefer the upright orientation. On the other hand, a metal-containing fragment of low electrophilicity exhibits strong σ-acceptor and weak π-back-donor capacity, both factors favoring the in-plane orientation.

In contrast to the complexes of the *cis*-[$PtX_2(CO)$] electrophiles of low electrophilicity, where both orientations of the unsaturated hydrocarbon correspond to local minima on the PES, in the complexes of the *cis*-[$PtX_2(CO)$] electrophiles with high electrophilicity ($\omega > 7.0$ eV) only one of the orientations could be located as a minimum on the PES, that of the upright orientation of the C═C double bond independently of the starting geometry. *It is concluded that the coordinated unsaturated hydrocarbon ligands exclusively prefer the upright orientation when the σ-type metal−ligand interactions are higher than the π-back-bonding interactions. Generally, this could be achieved by coordinating a strong unsaturated hydrocarbon nucleophile to a strong platinum-containing electrophile.*

Finally, the behavior of the unsaturated hydrocarbon complexes of the *cis*-[$PtX_2(CO)$] electrophiles of intermediate electrophilicity (ω values in the range 5.0−7.0 eV) with respect to the conformational preference of the coordinated unsaturated hydrocarbon is intermediate between those of the *cis*-[$PtX_2(CO)$] electrophiles with low and high electrophilicity. *In this case it is evident that the nucleophilicity of the unsaturated hydrocarbon ligands in conjunction with steric effects play a key role in fine-tuning the conformational preference upon coordination with a cis-[$PtX_2(CO)$] electrophile of intermediate electrophilicity.*

Supporting Information Available: Complete ref 19. The Cartesian coordinates and energies of all stationary points are compiled in Table S1. This information is available free of charge via the Internet at http://pubs.acs.org.

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