ELSEVIER

Journal of Organometallic Chemistry 643–644 (2002) 285–291

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Coordinated olefins, $H_2C{=}CHR$, and phosphanes, PH_2R: a theoretical study of the R substituent effect

G. Frison *, H. Grützmacher *

Laboratory of Inorganic Chemistry, Department of Chemistry, ETH-Hönggerberg, CH-8093 Zurich, Switzerland

Received 12 July 2001; accepted 20 September 2001

Dedicated to Professor François Mathey on the occasion of his 60th birthday

---

Abstract

Five olefin complexes and five phosphane platinum(0) complexes of the type $[Pt(PH_3)_2L]$ ($L = H_2C{=}CHR$ or PH_2R; R = H, CN, F, OH, NH_2) were investigated by DFT methods using the B3LYP functionals to investigate the effects of the substituent R on the donation and back-donation in the bonding of these ligands. A charge decomposition analysis (CDA) proved to be particularly useful in this respect. Some expected trends are well reproduced, i.e. for olefins, particularly for $H_2C{=}CHCN$, back-donation is important while for phosphanes, particularly for PH_2NH_2, electron donation prevails. The variation of the substituent R has a larger effect in phosphane complexes indicating that the electronic properties of a transition metal complex may be more easily controlled by changing the substituent via a coordinated phosphane than via an olefin. Interestingly, the intrinsic interaction energies ΔE_{int} are larger for olefins than for phosphanes indicating that olefins may be better ligands than the latter under special conditions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bonding concepts; CDA analyses; DFT calculations; Olefin complexes; Phosphane complexes; Platinum

---

1. Introduction

Undoubtedly olefins and phosphanes belong to the most often used ligands in coordination chemistry and the ‘fine tuning’ of the properties of transition metal complexes is achieved by placing different substituents onto these ligands. It was thus interesting to study the electronic effect on the transition metal center evoked by various electron-withdrawing and -donating substituents placed in olefins and phosphanes. As a model system, we choose $[Pt(PH_3)_2L]$ complexes for several reasons. First, these species offer a good compromise between a ‘model system’ and complexes that are relevant in a ‘real’ laboratory environment. Moreover, such trigonal planar platinum(0) complexes play an important role in transition metal catalyzed reactions [1] and hence understanding the substituent effects transmitted by the ligands is especially important. A further reason for choosing these model complexes relies on the fact that the 14-electron fragment $[Pt(PH_3)_2]$ is neither particularly electron-poor nor electron-rich and therefore ideally suited to discuss metal–ligand binding within the classical concept of donation and back-donation developed by Dewar [2] and Chatt and Duncanson [3]. Finally, similar systems were thoroughly investigated computationally (see selected Refs. [4–8]; a more complete listing is given in [8]) facilitating comparisons. As ligands L we choose monosubstituted olefins, $H_2C{=}CHR$, and phosphanes, PH_2R, where R varies from CN and F as electron-withdrawing to OH and NH_2 as electron-donating substituents.

Numerous platinum(0) complexes containing acrylo nitrile, $H_2C{=}CHCN$, as the ligand were described (for a selection of recent examples see Refs. [9–11]). Monofluoro ethylene, $H_2C{=}CHF$, complexes are less common but have been characterized for nickel(0) [12–14] and ruthenium(II) [15]. Recent calculations with $H_2C{=}CHF$ as the ligand have been performed on rhodium(I) complexes [16]. Although substituted enol ethers, $R_2C{=}CR^1{-}OR^2$, and enamines, $R_2C{=}CR^1{-}NR^2_2$, are well-known ligands in transition metal chemistry [17]

---

* Corresponding authors. Tel.: +41-1-632-2855; fax: +41-1-632-1090.

E-mail address: gruetzmacher@inorg.chem.ethz.ch (H. Grützmacher).

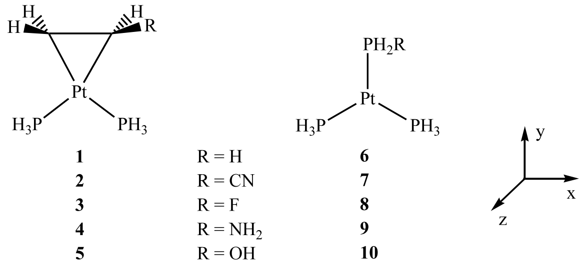
PII: S0022-328X(01)01276-1

their parent molecules, $H_2C{=}CHOH$ and $H_2C{=}CHNH_2$, were studied inadequately in coordination chemistry [18]. Recently, the enamonnium complex $[NiClH(PH_3)_2(H_2C{=}CH{-}NH_3)]^+$ has been theoretically investigated in the context of the hydroammination reaction of olefins [19].

Numerous complexes containing phosphanes of the general formula PR_2X (R = alkyl, aryl; X = F, NR_2, OR) have been described [17]. Remarkably, Mathey et al. could also synthesize the parent molecules PH_2F [20] and PH_2OH [21] stabilized by the $[W(CO)_5]$ fragment. Also, the molecule $PH_2(CN)$ was prepared by a flash-vacuum pyrolysis of a cyano-phosphirane [22] but metal complexes with this molecule have not been described to our knowledge and only a few cyano-phosphane complexes were reported in the literature [23–26].

There is a general agreement on the fact that the metal-to-ligand back-donation, *b*, which has largely π-character, is of more importance for the stability in olefin complexes than in phosphane complexes (see Refs. [4–8] and the literature cited therein). In other words, olefins are considered to be better 'π-acids' as phosphanes, which in turn are better 'σ-bases'. Note, however, that for both type of complexes the σ-type ligand-to-metal donation, *d*, is larger because of the better overlap of the participating orbitals. Only, the stabilizing effect of this donation may be—as any type of ligand-to-metal donation—diminished by repulsive 2-center-4-electron interactions with occupied orbitals of suitable symmetry on the metal center.

It is a priori difficult to estimate the relative importance of ligand substituent effects on these donating, accepting, and repulsive interactions in olefin and phosphane complexes. Therefore, we envisioned a systematic computational study using high-level theoretical methods on the olefin complexes **1**–**5** and phosphane complexes **6**–**10** shown in Scheme 1. Our aim is to analyze the nature of the bonding in these complexes depending on the substituent R and to determine, for which of each of these two-electron donor ligand phosphanes and olefins, the substituent effects are the most pronounced. To this end, we have used the charge decomposition analysis (CDA) procedure, developed by Frenking et al. [27]. This method may be regarded as a 'quantified'-Dewar–Chatt–Duncanson model providing information just about the above-mentioned quantities, i.e. donation, back-donation, and repulsive interactions. This is achieved by inspecting the orbital contributions to the charge distributions in the complex by: (i) the mixing of the filled orbitals of the ligand, L, with the unfilled orbitals at the metal containing fragment, $[ML_n^1]$ (donation, *d*); (ii) the mixing of the unfilled orbitals of L with the filled orbitals at $[ML_n^1]$ (back-donation, *b*); (iii) the mixing of the filled orbitals of L with the filled orbitals at $[ML_n^1]$ (repulsive polarization, *r*); and (iv) the mixing of the unfilled orbitals of L with the unfilled orbitals at $[ML_n^1]$ (residual term, Δ). Although quite recently, the CDA method has already been proven to be a powerful instrument in analyzing the metal–ligand bonding in transition-metal complexes [28].



Scheme 1. Molecules studied in this investigation.

2. Theoretical methods

Full geometry optimizations for systems **1**–**10** were carried out with the use of the B3LYP [29,30] density functional level of theory and with the following basis set. A 6-31G(d) basis set was employed for the first- (H), second- (C, N, O and F), and third-row (P) elements. The Hay and Wadt small-core relativistic effective-core potential with a valence shell of double-ζ quality (441/2111/21) was used on platinum [31]. Sets of five d functions were used in the basis sets throughout these calculations. This corresponds to the standard 'Basis Set II' defined by Frenking and collaborators [32], and the level of theory used in this study will hereafter thus be denoted as B3LYP/II. The optimized structures were characterized by harmonic frequency analysis as minima (all frequencies real). These molecular orbital calculations were performed with the GAUSSIAN 98 programs [33].

CDA [27] was performed using the program CDA 2.1 [34]. The charge distribution in the compounds was calculated with the NBO partitioning scheme [35].

Total energies and complete sets of Cartesian coordinates for the optimized geometries is available from the authors on request.

3. Results and discussion

In Fig. 1 are presented the three-dimensional structures of **1**–**10** obtained from unconstrained geometry optimizations using the B3LYP density functionals. In Tables 1 and 2, key features of the optimized geometries of **1**–**5** and **6**–**10**, respectively, are listed. Experimental geometries of **1**–**10** are not available preventing direct comparison. However, our level of calcu-

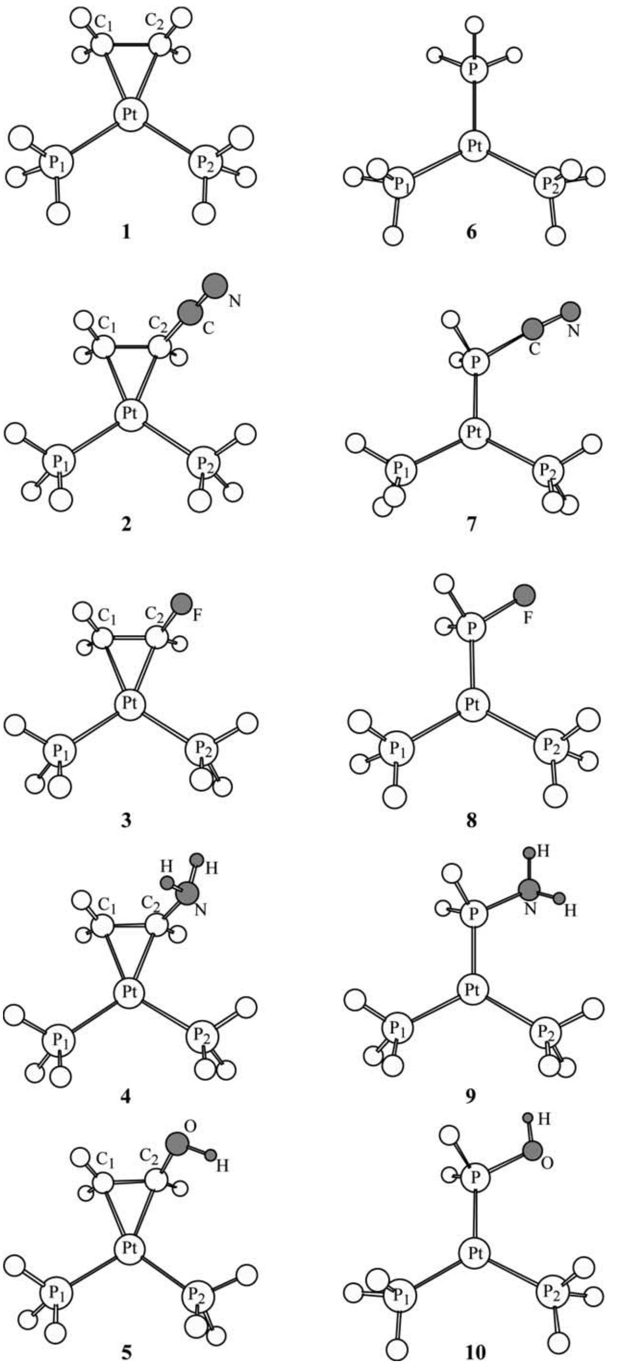


Fig. 1. Three-dimensional optimized structures of **1**–**10** at the B3LYP/II level.

lation is the same as the one utilized previously by Frenking et al. [8] to analyze analogous platinum(0) complexes of strained olefins [Pt(PH_3)$_2$(olefin)] (olefin = C_2H_4 (**11**), C_8H_{10}, C_9H_{12}, $C_{10}H_{14}$, $C_{11}H_{16}$). They have shown that their calculated structures agree reasonably well with the experimental ones, but found that the calculated Pt–C and Pt–P distances are systematically longer (by 0.03–0.05 Å) than the experimental values. The same observation is made here. For instance, in the tris(triphenyl)phosphine complex [Pt(PPh_3)$_3$] [36] the Pt–P bond (2.266 Å) is shorter by 0.04 Å than in the model compound [Pt(PH_3)$_3$] (**6**) (Pt–P: 2.306 Å) despite the fact that the latter is sterically less encumbered. Since this systematic error is very likely to be reproduced in any of the compounds investigated here, we believe that our results still elucidate relative trends in a reliable way.

We begin our discussion with the compounds [Pt(PH_3)$_2$(C_2H_4)] (**1**) and [Pt(PH_3)$_2$(C_2H_3CN)] (**2**). For comparison, we have included the experimental data for [Pt(PPh_3)$_2$(C_2H_4)] (**11**) [37,38] and the symmetrically substituted cyano-olefin complexes {Pt(PPh_3)$_2$[(NC)-HC=CH(CN)]} (**12**) [39] and [Pt(PPh_3)$_2$($C_2(CN)_4$)] (**13**) [40] in Table 1. The calculations predict that **2** has: (i) longer C=C and Pt–P bonds; (ii) shorter Pt–C bonds; (iii) a larger C–Pt–C bond angle; and (iv) a more acute P–Pt–P bond angle than **1**. All these trends due to H by CN substitution agree well with those observed in the experimental geometries of **11**–**13** which gives further confidence to our following discussion based on computational models.

All olefins show an elongation of the C=C bond by about 7% upon complexation to [Pt(PH_3)$_2$] when compared with the free state. For electron-poor olefins H_2C=CH(CN) and H_2C=CHF in **2** and **3**, respectively, this effect is a little larger, for the electron-rich olefins H_2C=CH(NH_2) and H_2C=CH(OH) in **4** and **5** the effect is slightly smaller than for the parent compound H_2C=CH_2. Also, the metal-bonded carbon atoms deviate significantly from planarity in all coordinated olefins as is indicated by $\Theta > 22°$ which measures the angle between the bisector of the H–C_1–H or H–C_2–R bond angles and the C_1–C_2 bond axis (Θ_1 and Θ_2, respectively). Between the structures of the coordinated olefins, only relatively little variation is seen ($22.7° < \Theta < 28.4°$) and these are non-systematic. In Table 1, the atomic charges q according to NBO analysis are included. In all cases the negative charge is accumulated on the olefin and a slightly positive charge resides on the platinum. As expected, this effect is the most pronounced for the cyano-olefin complex **2** ($\Delta q = 0.63e$) while (somewhat unexpected) the degree of charge separation $\Delta q = q(\mathrm{Pt}) - q(\mathrm{H_2CCHR})$ in the other hetero-substituted olefin complexes **3** ($\Delta q = 0.45e$), **4** ($\Delta q = 0.42e$) and **5** ($\Delta q = 0.38e$) differ only marginally from the parent compound **1** ($\Delta q = 0.45e$).

The results for the tris(phosphan)platinum complexes **6**–**10** are listed in Table 2. A notable common feature of the [Pt(PH_3)$_2$(PH_2R)] complexes with $R \neq H$ is that the R substituent lies almost in the plane running through the three phosphorus and the platinum atom (see the small torsion angles P_2–Pt–P–R listed in Table 2). On the other hand, in the parent compound [Pt(PH_3)$_3$] (**6**) no P–H bond is aligned with the central molecular plane. Although we have not investigated this matter systematically, we find that the Pt–P rotation barriers are very low (<3 kJ mol^{-1}). The Pt–P bond lengths towards the substituted phosphane, PH_2R, are shorter in **7**–**10** where $R \neq H$ while the $Pt–PH_3$ bonds—especially those lying to the same side as the P–R bond—are slightly longer than in the parent molecule **6**. In contrast to the olefins, the coordinated phosphanes do not alter their structures significantly

Table 1
Theoretical (**1**–**5** calculated at B3LYP/II) and experimental (**11**–**13**) geometrical parameters (Å and °) and natural charges q

	1	**2**	**3**	**4**	**5**	**11** [a]	**12** [b]	**13** [c]
R	H1	CN	F	NH_2	OH			
Bond lengths								
$C_1=C_2$	1.427	1.445	1.423	1.433	1.420	1.434	1.533	1.494
$\Delta(C_1=C_2)$ [d]	+0.096	+0.106	+0.098	+0.088	+0.094			
Pt–C_1	2.152	2.126	2.143	2.144	2.153	2.112	2.107	2.107
Pt–C_2	2.152	2.149	2.127	2.158	2.171			
Pt–P_1	2.317	2.311	2.343	2.333	2.341	2.268	2.286	2.289
Pt–P_2	2.317	2.335	2.318	2.317	2.307			
C_2–R	1.089	1.438	1.377	1.444	1.397		1.375	1.413
Bond angles								
C_1–Pt–C_2	38.7	39.5	38.9	38.9	38.4	39.7	42.6	41.5
P_1–Pt–P_2	107.3	105.8	106.1	108.0	106.3	111.6	104.4	101.4
Θ_1 [e]	24.1	28.3	26.6	25.4	26.9			
Θ_2 [f]	24.1	24.2	28.1	22.7	28.4			
Natural charges								
$q(H_2CCHR)$	−0.34	−0.47	−0.35	−0.32	−0.29			
q(Pt)	+0.11	+0.16	+0.10	+0.10	+0.09			

[a] From Refs [37,38]; average of X-ray structure values.

[b] From Ref. [39]; average of X-ray structure values.

[c] From Ref. [40]; average of X-ray structure values.

[d] Difference of CC bond length between complexes and the free optimized olefins. A positive value indicates an elongation due to the complexation.

[e] Pyramidalization angle at C_1.

[f] Pyramidalization angle at C_2.

Table 2
Theoretical geometrical parameters (Å and deg) and natural charges q for compounds **6**–**10** calculated at B3LYP/II

	6	**7**	**8**	**9**	**10**
R	H	CN	F	NH_2	OH
Bond lengths					
Pt–P	2.306	2.277	2.245	2.285	2.260
Pt–P_1	2.306	2.305	2.309	2.311	2.305
Pt–P_2	2.306	2.324	2.338	2.313	2.328
P–R	1.419/1.422	1.811	1.632	1.724	1.672
Δ(P–R) [a]	−0.005/−0.002	+0.015	+0.007	−0.003	+0.002
Bond and dihedral angles					
P_1–Pt–P_2	120.0°	120.0	114.9	116.2	116.8
P_2–Pt–P–R	−89.3/28.9	4.7	0.0	8.7	0.9
ΣP [b]	286.3	287.1	292.0	299.5	298.2
Δ(ΣP) [c]	+6.3	+1.9	+2.8	+4.1	+3.0
Natural charges					
$q(PH_2R)$	+0.04	−0.03	+0.02	+0.06	+0.03
q(Pt)	−0.13	−0.12	−0.14	−0.14	−0.13

[a] Difference of P–R bond length between complexes and the free optimized phosphanes. A positive value indicates an elongation due to the complexation.

[b] Sum of the H–P–H and H–P–R bond angles around the phosphorus atoms.

[c] Difference of ΣP between complexes and the free optimized phosphanes. A positive value indicates a decrease of the pyramidality (increase of ΣP).

Table 3
CDA [a] and bonding energies (kcal mol^{-1}) calculated at B3LYP/II

Molecule	R	*d*	*b*	*d*/*b*	*R*	*Δ*	D_e [b]	ΔE_{int} [c]
1	H	0.51	0.38	1.33	−0.43	−0.01	15.4	56.9
2	CN	0.47	0.42	1.13	−0.45	−0.01	17.6	62.8
3	F	0.51	0.40	1.27	−0.44	−0.02	11.9	58.9
4	NH_2	0.51	0.38	1.35	−0.46	−0.02	6.6	54.7
5	OH	0.50	0.37	1.37	−0.43	−0.02	9.9	53.9
6	H	0.38	0.23	1.67	−0.52	0.02	9.7	28.3
7	CN	0.35	0.29	1.20	−0.53	0.02	11.4	30.1
8	F	0.46	0.34	1.35	−0.36	−0.04	19.6	44.3
9	NH_2	0.49	0.27	1.78	−0.44	0.01	14.2	35.8
10	OH	0.47	0.30	1.53	−0.45	0.00	16.3	38.7

[a] Donation *d*, back-donation *b*, repulsive part *r*, and residual term *Δ*.

[b] Dissociation energy of the Pt–P or Pt–CC bond (kcal mol^{-1}).

[c] Interaction energy between the two fragments ($Pt(PH_3)_2$ and olefins or phosphanes) in the geometry that they have in the complex (kcal mol^{-1}).

upon binding to the platinum(0) center, i.e. neither the P–R bond lengths nor the sum of the bond angles, ΣP, change much when compared with the free phosphanes. Significant effects are seen only for the P–CN bond of the cyano-phosphane which becomes 0.015 Å longer and for ΣP of PH_3 which widens by +6.3° on complexation. This finding agrees with experimental observation for aryl/alkyl phosphane complexes [41].

The NBO group charges at the PH_2R phosphane vary between $+0.06e$ for PH_2NH_2 and $-0.03e$ for PH_2CN in accord with the expectation that the first behaves as an electron donating and the second as an electron attracting phosphane. In all complexes, the platinum centre bears a small negative charge, which reveals that the net effect of all three phosphanes in the coordination sphere is to augment the charge density at the metal.

The results of the charge decomposition analyses are compiled in Table 3. In all cases the residual term, *Δ*, is quite small (<0.04) which is a necessary requirement to allow the description of the structures of **1**–**10** as donor–acceptor-complexes [27] and to interpret the bonding in terms of the Dewar–Chatt–Duncanson (DCD) model.

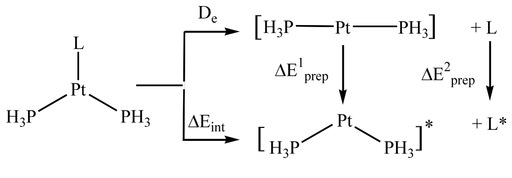
We discuss the olefin complexes **1**–**5** first. As Frenking et al. [8] pointed out, there are four molecular orbitals in the complex, which contribute almost to the same extent to the olefin–Pt donation. The three, which are high in energy, contain the bonding C–C π-orbital of the olefin and the one which is very low in energy contains a significant contribution from the C–C σ-bonding orbital [42]. All four donate dominantly into the $d_{x^2-y^2}$ and d_{z^2} orbital of the platinum center. This feature does not change significantly on the introduction of the substituents R into the olefin, i.e. there are always mostly four molecular orbitals participating in the donation. In the parent complex **1**, there is one molecular orbital, the HOMO-1, which is predominantly involved in back-bonding and contains a large contribution from the C–C anti-bonding π*-orbital of the olefin. This finding is in accord with expectations due to the DCD model. In the complexes **2**–**5** containing the substituted olefins, mainly two molecular orbitals, the HOMO and the HOMO-1, are involved in the back-donation because any of the chosen substituents R interacts via a lone pair (i.e. F, OH, NH_2) or multiple π-bond system (CN) with the coordinated C=C unit in a bonding or anti-bonding way. This leads to the somewhat paradox situation that the HOMO in the substituted olefin complexes is involved in donation and back-donation to almost the same extent. The data in Table 3 show, that as a net effect neither the donation *d* nor the back-donation *b* differs largely dependent on the nature of the substituent R. Nonetheless, the expected trends become clearly visible in the *d*/*b* ratios and acrylo nitrile is the strongest acceptor ($d/b = 1.13$) while the enol is the strongest donor olefin ($d/b = 1.37$).

We now turn our attention to the phosphane complexes **6**–**10**. Again there are a number of molecular orbitals involved in donation (three in **6** and **9**, and four in **7**, **8**, and **10** when only contributions $d > 0.05$ are considered), and back-donation (two in **6**, **7**, and **9**, and three in **8** and **10** with $b > 0.05$). We have not explored the compositions of the molecular orbitals in detail. (One of the advantages of the CDA analysis relies actually in the fact that the delocalized nature of molecular orbitals is kept while it still can be interpreted using classical terms from a localized bonding picture.) Interestingly, based on the *d* values all phosphanes are weaker donors than their olefinic counterparts while the repulsive part *r* is significantly higher for **6**, **7**, and **10**. Only the PH_2F complex **8** shows a lower *r* value than its $H_2C{=}CHF$ counterpart. However all phosphanes are also weaker acceptors and the *d*/*b* ratios in their complexes are larger than those of the corresponding olefin complexes.

In contrast to the latter, some expected trends become more clearly visible within the series of the phosphane complexes. Introduction of a π-donating substituent on the phosphorus centre raises the *d* value in the order $NH_2 > OH > F$ with respect to the parent molecule **6**. This is in accord with the recent calculations by Frenking et al. which showed donation in $[Fe(CO)_4PF_3]$ [$d_{eq} = 0.56$; $d_{ax} = 0.58$] to be higher than *d* in $[Fe(CO)_4PH_3]$ [$d_{eq} = 0.40$; $d_{ax} = 0.43$] [43]. Only the cyano-phosphane in **7** is a weaker donor than PH_3 in **6**.

All heterosubstituted phosphanes PH_2R are better acceptors than PH_3. The molecular orbital which contributes the most to *b* contains a contribution from the σ*-orbital of the P–R bond. Remember that this bond lies in the central molecular plane hence placing the σ* orbital in a perfect position to interact with the occupied d_{xy} orbital on the platinum center. This type of interaction has been also discussed in the context of negative hyper-conjugation [41]. Fluorine is the most electronegative substituent and the corresponding P–F σ*-orbital is the lowest in energy. Consequently, PH_2F shows the largest *b* value for back-donation. However, back-donation is efficiently counterbalanced by its donating ability and the *d*/*b* ratio is larger than for the cyano-phosphane, which is the strongest electron-withdrawing phosphane ($d/b = 1.205$). On the other hand, PH_2NH_2 in **9** is the strongest electron-donating phosphane of all ligands ($d/b = 1.785$) considered in this study.

We plan to investigate the binding in the complexes discussed above in more detail using an energy decompostion scheme (ETS) as was introduced by Ziegler and Rauk [4,44,45]. However, a brief discussion of the binding energies between the organometallic fragment, $[Pt(PH_3)_2]$, and the ligand L will be given here. As is illustrated in Scheme 2, the interaction was evaluated by calculating the adiabatic dissociation energy, D_e, and the interaction energy, ΔE_{int}, which are both listed in Table 3. The energy D_e is required to dissociate the complex $[Pt(PH_3)_2L]$ into the fragments $[Pt(PH_3)_2]$ and L, both in their ground state structures, i.e. $[Pt(PH_3)_2]$ being linear and L showing the structure of the uncomplexed ligand.



Scheme 2. Illustration of the adiabatic dissociation energy, D_e, and the interaction energy, ΔE_{int}. The asterisk indicates the structures of the fragments $[Pt(PH_3)_2]$ and L in the complex $[Pt(PH_3)_2L]$.

The energy ΔE_{int} measures the intrinsic binding between the fragment $[Pt(PH_3)_2]^*$ and L*, both having the same structural parameters as in the complex $[Pt(PH_3)_2L]$. The dissociation energy D_e is lower than ΔE_{int} by the sum of the energies ΔE^1_{prep} and ΔE^2_{prep} which have to be spend to prepare both fragments, $[[Pt(PH_3)_2]$ and L, sterically and electronically for bond formation, i.e. $D_e = \Delta E_{int} - (\Delta E^1_{prep} + \Delta E^2_{prep})$. For the phosphane complexes **6**–**10**, D_e and ΔE_{int} parallel each other, i.e. the fluoro phosphane complex **8** shows the largest and the phosphane complex **6** the smallest D_e and ΔE_{int} values, i.e. all phosphanes, PH_2R are better ligands than the parent phosphane, PH_3. For the olefin complexes **1**–**5** the ordering of D_e and ΔE_{int} is different, however, cyano-ethylene is clearly the strongest bound olefin while the electron-rich olefins in **4** and **5** are significantly weaker bonded than ethylene in the parent complex **1**. Note that the averaged dissociation energies, D^{av}_e, are as expected lower for the olefin complexes ($D^{av}_e = 12.3$ kcal mol^{-1}) than for the phosphane complexes ($D^{av}_e = 14.2$ kcal mol^{-1}), however, the difference is very small and all values lie within the same range. On the contrary, ΔE_{int} is significantly *larger* by about 20 kcal mol^{-1} in the olefin complexes than in the phosphane complexes. Since the distortion of the linear to the bent $[Pt(PH_3)_2]$ fragment [Δ(P–Pt) ~ 0.07 Å, Δ(P–Pt–P) ~ 74° for L = olefin; Δ(P–Pt) ~ 0.06 Å, Δ(P–Pt–P) ~ 62° for L = phosphane) is of the same order of magnitude for all complexes **1**–**10**, the difference between D_e and ΔE_{int} is mainly caused by the distortion of the ligand from L to L* upon complexation. This means that in particular the preparation energy, ΔE^2_{prep}, paid in order to bind an olefin turns this one into a relatively weakly bonded ligand. Although any reasoning about this must await a more detailed ETS analysis, it is plausible to assume that especially the elongation of the strong C=C double bond is responsible for this effect.

4. Conclusions

The bonding in even simple model complexes is already quite complicated and the ligand substituent effects on donation, *d*, and back-donation, *b*, are not easily foreseen and expressed in structural data in a straightforward manner. Here charge decomposition analyses are a useful instrument and may be helpful for the fine-tuning of the properties of transition metal complexes in order to adapt them better for their purpose. Some expectations are confirmed by the CDA, i.e. $H_2C{=}CHCN$ is the strongest electron accepting ligand and PH_2NH_2 is the strongest electron donating ligand. Other results are less obvious and in this respect, the most important result of this study is the observation that substituent effects in coordinated phosphanes are significantly larger than in the corresponding olefins (expressed by the difference of d/b values for **6**–**10**, $\Delta d/b = 0.58$; for **1**–**5**, $\Delta d/b = 0.24$). The binding energies of the various ligands L were estimated in a preliminary form by calculating the adiabatic dissociation energies, D_e, and the intrinsic interaction energies ΔE_{int} which do not include the energies, ΔE_{prep}, necessary to prepare the organometallic fragment $[Pt(PH_3)_2]$ and the ligand L for bond formation. Interestingly and counter intuitive, ΔE_{int} is much larger in olefin complexes than in phosphane complexes. This indicates that olefins, which possess a ground state structure being already close to their structure in the complexed form, shall be excellent ligands. This seems to be the case for complexes of strained olefins where the C=C bond is incorporated in a nonplanar environment within a polycyclic cage [8]. Further theoretical and experimental work in order to gain a more detailed insight into these phenomena is under way.

Acknowledgements

The ETH Zürich and the Swiss National Science Foundation supported this work. We are indebted to the Swiss Center for Scientific Computing (CSCS) and the Competence Centre for Computational Chemistry (C4) of the ETH Zürich for providing computer time.

References

[1] W.A.H. Cornils (Ed.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1 and 2, Wiley–VCH, Weinheim, 1996.
[2] M.J.S. Dewar, Bull. Soc. Chim. Fr. 18 (1951) C71.
[3] J. Chatt, L.A. Duncanson, J. Chem. Soc. (1953) 2939.
[4] T. Ziegler, A. Rauk, Inorg. Chem. 24 (1979) 1558.
[5] K. Morokuma, W.T. Borden, J. Am. Chem. Soc. 113 (1991) 1912.
[6] C. Bo, M. Costas, J.M. Poblet, J. Phys. Chem. 99 (1995) 5914.
[7] G. Frenking, U. Pidun, J. Chem. Soc. Dalton Trans. (1997) 1653.
[8] J. Udin, S. Dapprich, G. Frenking, B.F. Yates, Organometallics 18 (1999) 458.
[9] R.L. Cowan, W.C. Trogler, J. Am. Chem. Soc. 111 (1989) 4750.
[10] Y. Xie, B.R. James, J. Organomet. Chem. 417 (1991) 277.
[11] M.J. Baker, K.N. Harrison, A.G. Orpen, P.G. Pringle, G. Shaw, J. Chem. Soc. Dalton Trans. (1992) 2607.
[12] C.A. Tolman, J. Am. Chem. Soc. 96 (1974) 2780.
[13] J. Ashley-Smith, M. Green, F.G.A. Stone, J. Chem. Soc. A (1969) 3019.
[14] A.D. Berry, Organometallics 2 (1983) 895.
[15] D. Huang, J.C. Bollinger, W.E. Streib, K. Folting, V. Young Jr., O. Eisenstein, K.G. Caulton, Organometallics 19 (2000) 2281.
[16] M. Bühl, M. Håkansson, A.H. Mahmoudkhani, L. Öhrström, Organometallics 19 (2000) 5589.
[17] G. Wilkinson, F.G.A. Stone, E.W. Abel, Comprehensive Organometallic Chemistry II, vol. 12, Pergamon Press, Oxford, 1995.
[18] E.J. Crawford, T.W. Bodnar, A.R. Cutler, J. Am. Chem. Soc. 108 (1986) 6202.
[19] H.M. Senn, P.E. Bloechl, A. Togni, J. Am. Chem. Soc. 122 (2000) 4098.
[20] F. Mercier, F. Mathey, J. Chem. Soc. Chem. Commun. (1984) 782.
[21] F. Mercier, F. Mathey, C. Afiongakpan, J.F. Nixon, J. Organomet. Chem. 348 (1988) 361.
[22] S. Haber, P. Le Floch, F. Mathey, J. Chem. Soc. Chem. Commun. (1992) 1799.
[23] $\{Ni(CO)_2[P(CN)_2(NMe_2)]\}$ and $\{Ni(CO)_2[P(CN)(NMe_2)_2]\}$: H. Nöth, H.J. Vetter, Chem. Ber. 96 (1963) 1479.
[24] $\{Mo(CO)_5[P(CN)Ph_2]\}$ and $\{Mo(CO)_4[P(CN)Ph_2]_2\}$: A. Varshney, G.M. Gray, Inorg. Chim. Acta 248 (1988) 215.
[25] Cyano phosphole and cyano phosphirene as ligands in $[W(CO)_5]$ complexes: S. Holand, F. Mathey, Organometallics 7 (1988) 1796.
[26] $\{Cr_2(CO)_8[P(CN)(CF_3)_2]_2\}$ (Cr = Cr): J.F. Nixon, J.R. Swain, J. Organomet. Chem. 21 (1970) P13.
[27] S. Dapprich, G. Frenking, J. Phys. Chem. 99 (1995) 9352.
[28] G. Frenking, N. Fröhlich, Chem. Rev. 100 (2000) 717.
[29] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[30] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[31] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299.
[32] G. Frenking, I. Antes, M. Böhme, S. Dapprich, A.W. Ehlers, V. Jonas, A. Neuhaus, M. Otto, R. Stegmann, A. Veldkamp, S.F. Vyboishchikov, in: K.B. Lipkowitz, D.B. Boyd (Eds.), Reviews in Computational Chemistry, vol. 8, VCH, New York, 1996, pp. 63–144.
[33] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98, Revision A.9, Gaussian, Inc., Pittsburgh, PA, 1998.
[34] S. Dapprich, G. Frenking, CDA 2.1, Marburg, 1994.
[35] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.
[36] P.A. Chaloner, P.B. Hitchcock, G.T.L. Broadwood-Strong, Acta. Crystallogr. C 45 (1989) 1309.
[37] P.-T. Cheng, C.D. Cook, S.C. Nyburg, K.Y. Wan, Inorg. Chem. 10 (1971) 2210.
[38] P.-T. Cheng, S.C. Nyburg, Can. J. Chem. 50 (1972) 912.
[39] C. Panattoni, R. Graziani, G. Bandoli, D.A. Clemente, U. Belluco, J. Chem. Soc. B (1970) 371.
[40] G. Bombieri, E. Forsellini, C. Panattoni, R. Graziani, G. Bandoli, J. Chem. Soc. A (1970) 1313.
[41] B.J. Dunne, R.B. Morris, A.G. Orpen, J Chem. Soc. Dalton Trans. (1991) 653.
[42] The donation from the C–C σ-bond of the olefins $H_2C{=}CHR$ decreases with increasing electronegativity of the substituent from 0.092 (R = H in **1**) to 0.064 (R = NH_2 in **4**) to 0.060 (R = OH in **5**) to 0.057 (R = CN in **2**) to 0.052 (R = F in **3**).
[43] Y. Chen, M. Hartmann, G. Frenking, Z. Anorg. Allg. Chem. 627 (2001) 985.
[44] T. Ziegler, A. Rauk, Theor. Chim. Acta 46 (1977) 1.
[45] T. Ziegler, A. Rauk, Inorg. Chem. 18 (1979) 1755.