18-Electron Rule

DOI: 10.1002/ange.201105928

Dispersion and Back-Donation Gives Tetracoordinate [Pd(PPh$_3$)$_4$]

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Palladium-catalyzed coupling reactions have received enormous attention in recent years, as illustrated by the Nobel Prize in 2010.[1] Despite this, there are many questions remaining to be answered in the field. One concerns the nature and activation of Pd^0 precatalysts that are frequently employed in couplings. Taking [Pd^0(PPh$_3$)$_4$] as a common example, it is generally agreed that this complex must lose two phosphine ligands to enter catalytic cycles as a [Pd^0(PPh$_3$)$_2$] complex.[2] However, why would the complex do a rare double dissociation from the 18-electron tetrakis complex to reach a doubly unsaturated state? Furthermore, why is the 18-electron complex preferred, when it is well known that Pd^0 has a full shell of d orbitals and only the 5s orbital available for accepting dative bonds?[3] To illuminate some of these issues, we have undertaken a detailed study of the energies and electronic structures of the different [Pd(PPh$_3$)$_n$] complexes.

The 18-electron rule has been an important guideline for studying the coordination chemistry of transition metals. The theory behind it is that each ligand can donate its electron pair(s) to one of nine available valence orbitals (s, p, or d) on the transition metal. However, it is now generally accepted that for most transition metals, the p orbitals are too high in energy to participate in valence bonding, removing a theoretical foundation for the 18-electron rule.[3,4] Inorganic chemists have also long been able to rationalize complex geometries using ligand field theory (LFT) based solely on d orbitals.[5] Using valence bond concepts, Landis and Weinhold have shown that transition metal coordination can be understood in terms of 6 valence orbitals (s and d only) in combination with 3-center-4-electron bonds, so-called ω bonds.[3] The Landis–Weinhold theory can rationalize observed geometries not only of most 18-electron complexes, but also well-known exceptions to the 18-electron rule like the square planar d^8 complexes (e.g., Pd^{II}) and linear d^{10} complexes (e.g., Au^I). However, [Pd^0(PPh$_3$)$_4$] follows the 18-electron rule and apparently violates the Landis–Weinhold theory, which instead predicts the catalytically competent [Pd^0(PPh$_3$)$_2$] as the preferred state, and in fact defines this complex as hypervalent.

In the current study, we will use the labels P$_1$–P$_4$ to designate the number of phosphine ligands bound to Pd^0 (e.g., P$_2$ means [Pd^0(PPh$_3$)$_2$]), with the addition "Cl" showing an anionic complex with a chloride ligand in addition to the phosphines. Our starting point for the current study was a previous investigation at the B3LYP level, where P$_2$ was identified as the preferred state,[6] in violation of crystal data[7] as well as studies of the ligation preference in solution.[8] However, recent improvements allowing inclusion of dispersion interactions into DFT calculations[9,10] have shown that it is now possible to quantify binding energies to transition metals,[11] as well as model processes like the oxidative addition with high accuracy.[12] In here, we have used dispersion-corrected DFT to analyze the energetics as well as the electronic structure of Pd^0 phosphine complexes.

Palladium(0) is known to form 18-electron complexes, which would indicate that the 18-electron rule could be correct. However, 18-electron complexes of Pd^0 appear to form only when one (or more) ligand is a relatively good π acceptor, for example, phosphines or olefins such as dibenzylidene acetone (dba). Low-temperature (−60 °C) NMR experiments by Mann and Musco suggested that P$_4$ (i.e., [Pd(PPh$_3$)$_4$]) dissociates one of the phosphines in solution to form P$_3$.[8] However, in the presence of additional triphenylphosphine they observed two complexes and concluded that P$_4$ and P$_3$ are in equilibrium. Investigations of oxidative addition by Fauvarque et al. suggested that the main species in solution at room temperature is the catalytically incompetent P$_3$ complex, which dissociates one phosphine in an unfavorable equilibrium to form the catalytically active P$_2$ complex.[13]

Our previous results indicated that P$_2$ is the more stable form in solution. However, since the calculations were performed using the B3LYP functional one could expect a poor description of the London dispersion interactions, which could be important for the tri- and tetracoordinated complexes. We therefore decided to employ two methods which account for the dispersion, B3LYP-D[9] and the M06 functional.[10] The geometries were optimized by using B3LYP[14] with the lacvp* basis set,[15] and interestingly we find only slight changes when optimizing with the M06 functional. The results are presented in Table 1 together with the experimental estimates of the relative free energies of the respective complexes.

It is clear from Table 1 that dispersion has a large effect on the ligand dissociation energies. It is also interesting how well the dispersion-corrected free energies correlate with the experimental numbers, regarding the size of the system and the many possible sources of error, including the PBF solvation free energy and the entropic contribution to the free energy where the low frequency modes give the most important contributions. The dispersion correction for the

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201105928.

Table 1: Relative Gibbs free energies in $kJ\,mol^{-1}$.

Reaction	B3LYP	B3LYP[a]	B3LYP-D	M06	Exptl.
P_4 to P_3	−141	−127	14	16 (6)[b]	> 0[c]
P_3 to P_2	−67	−55	40	40 (32)[b]	27[d]
P_2 to P_1	67	62	97	89	–
P_2 to PCl^-	11	−6	42	23	–
PCl^- to P_2Cl^-	58	51	0	4	–

[a] Smaller basis set: LACVP*, Ref. [15]. [b] Numbers in parentheses are BSSE corrected. [c] P_3 can be observed, but excess ligand drives the equilibrium to P_4, Ref. [8]. [d] Estimated from the equilibrium constant reported for the reaction in Ref. [25].

reaction from P_4 to P_3 is $155.5\,kJ\,mol^{-1}$ using Grimme's D addition to B3LYP.[9,16] This large number clearly shows that results using B3LYP are unreliable for association/dissociation of large ligands and that a dispersion correction is essential for this size of system. Formation of P_2 is a facile process, whereas formation of the more active P_1 complex is substantially less favored. Note, however, that the calculated energy difference between P_2 and P_1 is particularly sensitive to solvation. The continuum model[17] employed here may not be sufficient to fully account for the expected solvent coordination to the Pd of P_1.

Looking in more detail at the trends of potential energies in vacuo, we compare the full system with a smaller model ligand, PH_3, where steric interactions are negligible. The results at different levels of theory are shown in Table 2.

Table 2: Potential energies for ligand dissociation, in $kJ\,mol^{-1}$.

Reaction	B3LYP	B3LYP[a]	B3LYP-D	M06
PPh_3				
P_4 to P_3	−47	−33	108	111
P_3 to P_2	12	24	118	118[a]
P_2 to P_1	124	129	159	151
PH_3				
P_4 to P_3	20	18	33	32
P_3 to P_2	36	40	45	46
P_2 to P_1	116	113	121	129

[a] Smaller basis set: LACVP*, Ref. [15].

Interestingly, the best fit to the complete calculations in Table 1 is obtained by using the "traditional" B3LYP functional with a double-ζ valence basis set and the smaller PH_3 ligand, whereas dispersion-corrected functionals for the full system in the absence of Gibbs energy contribution and solvation give severe overbinding. We also see that in the absence of steric crowding, Pd^0 still has a preference for tetrakis coordination, only slightly augmented by dispersion corrections.

Table 3: Analysis of Pd complexes with PPh_3 or PH_3 ligands.

Ligand(s)	Charge[a]	5s Occupancy[b]	4d Occupancy[b]	Pd−P bond [Å]
1 PPh_3	−0.14	0.42	9.72	2.223
2 PPh_3	−0.30	0.64	9.66	2.340
3 PPh_3	−0.02	0.39	9.62	2.394
4 PPh_3	+0.11	0.27	9.61	2.545
1 PH_3	−0.09	0.36	9.73	2.206
2 PH_3	−0.29	0.63	9.66	2.304
3 PH_3	−0.10	0.45	9.64	2.359
4 PH_3	−0.02	0.39	9.61	2.406
2 PH_3[c]	−0.05	0.34	9.70	2.359
3 PH_3[c]	0.00	0.32	9.67	2.406

[a] NPA charge on Pd.[19] [b] Number of electrons in 5s and 4d orbitals, respectively.[20] In all cases, the 5p occupation is ≤ 0.02. [c] Frozen geometry of fragment from the complex with one additional ligand.

Biscoordinated 14-electron palladium complexes, such as P_2, are generally regarded as coordinatively unsaturated, since they have less than 18 valence electrons. However, when analyzing the electron distribution by using NBO,[18] we see only marginal difference in valence orbital utilization for P_1–P_4 (Table 3).[19] A Pd atom has no 5s occupation, 10 electrons in 4d, and a charge of zero. Dative ligands donate into 5s, whereas back-donation occurs from 4d. The total charge is negative on Pd if σ donation dominates over π back-donation. As expected, total back-donation increases (i.e., 4d occupation decreases) with increasing number of ligands. The increase is not additive, in part because the Pd−P distance increases with the number of ligands. Interestingly, the 5s occupation maximizes for P_2, indicating that this complex has the highest covalent character. This is well in line with the Weinhold–Landis theory of ω bonding[3] (i.e., 3c-4e-bonding), where "normal" valence for Pd^0 means one ligand donating into the single unoccupied valence orbital. Complexes like P_2 are formally regarded as hypervalent with one linear ω bond.[3] Partial ds hybridization creates an orbital with two large lobes able to reach far from the Pd nucleus (Figure 1), achieving efficient bonding with two ligands in a linear geometry. In complexes with more than 2 ligands, the linear relationship is lost, and the ligands overlap less efficiently with the unhybridized 5s orbital. In P_4, we can in fact see that back-donation has come to dominate, resulting in an overall electron deficiency on Pd.

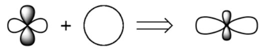

Figure 1. Creation of a linear orbital by ds-hybridization.

By analyzing the smaller model ligand, PH_3, we see that the trends are the same and even the absolute magnitude of populations match fairly well with the full size system. Bond lengths are shorter, and the dative component for the P_3 and P_4 models thus slightly increased, but the back-donation contribution is virtually identical. A dramatic geometry effect can be seen when removing one ligand from the P_3 model without geometry optimization, thus creating a bis-coordinated complex with a P−Pd−P bond angle of 120°. The 5s occupation drops to 0.34, compared to 0.63 for the linear system, clearly showing the strong linear preference of the ω bond. The energy required for the angular distortion is 39 kJ mol^{-1}.

To further investigate the relative contributions of the Pd–ligand interactions, we applied the ALMO-EDA method by Head-Gordon and co-workers[20] to quantify the relative magnitude of forward and backward donation between the defined fragments for the small model system using PH_3 ligands. Figure 2 depicts the interaction energy from the charge transfer from the phosphine(s) to palladium (E_{CT}don), from palladium to the phosphine(s) (E_{CT}back), and the total interaction (E_{CT}tot). The total interaction E_{CT}tot increases for each ligand that binds to palladium as expected since palladium is known to commonly bind four phosphines in solid phase unless the ligands are sterically demanding. Consistently with the NBO-analysis, E_{CT}don increases from mono- to di-coordinate Pd complex, but when the third and fourth phosphines bind the interaction decreases slightly. Thus, the additional association is not due to the electron deficiency on palladium. Instead it results from the strong back-donation. The E_{CT}back term increases significantly for each ligand that binds, and at the tri- and tetracoordinate complexes the interaction due to back-donation exceeds that of ligand-to-metal donation.

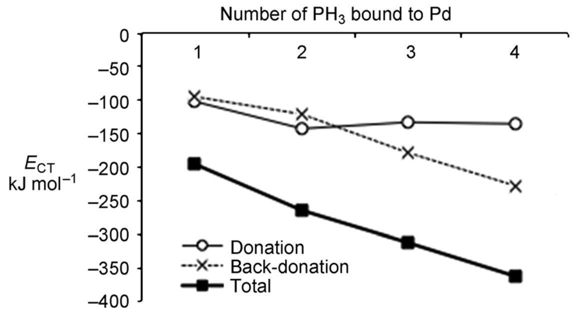

Figure 2. The forward and backward charge transfer terms between palladium and the ligand(s) calculated with ALMO-EDA.

To summarize, formation of tri- and tetracoordinate Pd^0 complexes is driven by metal-to-ligand back-donation. NBO analyses show that the ligand-to-metal donation decreases when the third and fourth ligand coordinates. ALMO-EDA analyses further show that the energy from back-donation dominates over donation when the third and fourth ligand coordinates. These results clearly show that the formation of 18-electron palladium(0) complexes is not due to orbital unsaturation at the metal center but rather to excess of electron density on the metal that can be shared with the ligands. The major role of dispersion is to compensate the too strong steric repulsion seen in DFT. The compliance with the experimentally indicated expectation that Pd^0 easily forms bis-ligated complexes is now substantially improved compared to “traditional” DFT. The inherent cost of forming the mono-ligated complexes that are necessary for some reactions has also been demonstrated.[21] Further, we have shown that dispersion interactions are crucial when describing metal complexes of even medium-sized ligands like PPh_3, but only together with other free energy contributions like solvation and vibrations.[6]

Computational Details

All geometries were optimized at the B3LYP/LACVP* level[14,15] by using Jaguar 7.6.[22] Gibbs free energies were calculated by the following equation $G(\mathrm{kJ\,mol^{-1}}) = E(\mathrm{DFT/basis\ set}) + G_{\mathrm{solv}} + \mathrm{ZPE} + H_{298} + S_{298} + 7.9$ (concentration correction to the free energy of solvation from 1 M(g) → 1 M(aq) to 1 atm(g) → 1 M(aq)). The single-point energy correction is calculated using the M06 with the LACV3P**++ basis set augmented with two f-functions on Pd as suggested by Martin,[23] and by B3LYP with LACV3P**++(2f). Dispersion corrections were calculated using the potential suggested by Grimme.[9] Single-point solvation free energies were calculated at the B3LYP/LACVP* level using the Poisson–Boltzmann solvent model (PBF)[18] implemented in Jaguar 7.6 with standard parameters for tetrahydrofuran, except for the chloride ion were the experimental value of 271 kJ mol^{-1} was used.[24] Thermochemical data were extracted from the normal mode analysis at the B3LYP/LACVP* level, and all geometries were confirmed to have no imaginary vibrational modes. ALMO-EDA calculations were performed using a modified version of Q-Chem 3.1 with the B3LYP functional and the Stuttgart–Bonn pseudopotential and basis set augmented with two f functions on Pd, and the 6-311++G(3df,2pd) on P and H.

Received: August 22, 2011

Keywords: 18-electron rule · density functional theory · dispersion interactions · ligand dissociation · palladium

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