Metal—ligand bond dissociation energies in the Ni, Pd, and Pt complexes with N-heterocyclic carbenes: effect of the oxidation state of the metal (0, +2)

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A DFT study was carried out of how the nature of metal, the oxidation state of the metal (0 and +2), as well as the structures of N-heterocyclic carbene (NHC) and other ligands influence the heterolytic dissociation energies of the metal—ligand bond in the complexes M-NHC (M = Ni, Pd, Pt). It was shown that a change in the oxidation state of the metal can be followed by a considerable change in the M—NHC bond dissociation energy (up to nearly 21 kcal mol^{-1}), which is also strongly influenced by the ligand in the *trans*-position to NHC.

Key words: N-heterocyclic carbenes, coordination compounds, nickel, palladium, platinum, bond dissociation energies, catalysis.

Nickel, palladium, and platinum complexes with N-heterocyclic carbenes (NHC) are widely used as homogeneous catalysts.[1—6] They are also intensively studied as luminescent materials[7—9] and cancer drugs.[10—12] Wide use of metal complexes with NHC (M-NHC) is underlain by higher stability of such systems compared to other types of homogeneous catalysts since the M—NHC bond is very strong.[1,2,13] However, M-NHC complexes can decompose in solutions due to dissociation of the M—NHC bond, which often occurs in rather mild conditions.[14—20] Dissociation of the metal—ligand bond is of great importance for catalysis and other practical applications because it usually causes deactivation of catalysts[6,21—23] or changes in the nature of active centers and in the mechanism of catalysis.[24—27] Contrary to this, elimination of auxiliary ligands is often necessary to activate the catalyst, M-NHC.[16]

Thus, the catalytic properties of complexes M-NHC depend strongly on their ability to break down with heterolytic dissociation of the metal—ligand bond. Therefore, the heterolytic bond dissociation energy (BDE),[28] which can be calculated by quantum chemistry methods, is often used to predict the catalytic properties of complexes.[29—31] To date, both experimental and theoretical BDE values have been determined for various complexes M-NHC.[32—40] For instance, the influence of (i) the structure of the NHC ligand on the M—NHC bond dissociation energies ($BDE_{M—NHC}$) in complexes with Ni[32,34,37] and Pd[36,37,39,40] and (ii) halide ligands on the BDE in complexes Pd^{II}-NHC[39] were studied. Steric factors, especially, bulky substituents at nitrogen atoms of the NHC ligands affect strongly the $BDE_{M—NHC}$ values.[29,30] However, it should be noted that the oxidation state of the metal usually changes in the course of catalysis and these changes can influence the stability of the metal—ligand bonds. For instance, the catalytic cycles of the cross-coupling, hydrogenation, and CH-activation reactions very often involve interconversions of the intermediates M^0-NHC and M^{II}-NHC.[1—4] Therefore, prediction of catalytic activity and stability of complexes requires taking account of the mutual influence of the oxidation state of the metal and the nature of the NHC ligand and other ligands on the BDE values. It is commonly accepted that reduction of the complexes $M^{II}L$ (L is ligand) to M^0L considerably reduces their thermodynamic stability.[41] However, it was shown that $BDE_{Ni—NHC}$ in the Ni^0-NHC complexes can be higher than in the Ni^{II}-NHC complexes with the same NHC ligands.[35] Note that systematic studies of the effect of the oxidation state of the metal on the metal—ligand BDE have not been reported as yet.

In this work we used the density functional quantum chemical calculations to study the joint effect of the oxidation state of the metal (0 and +2) and the nature of the NHC ligand and other ligands on the metal—ligand BDE in the Ni, Pd, and Pt complexes belonging to the abundant structure types $(NHC)M^0L$ and $(NHC)M^{II}(X)_2L$, where NHC = 1,3-dimethylimidazol-2-ylidene, 1,3-dimethylbenzimidazol-2-ylidene, 1,4-dimethyl-1,2,4-triazol-5-ylidene; X = Cl^-, Br^-, I^-; L = Py, NHC, I^-.

Calculation Methods

Calculations were carried out within the framework of the density functional theory (DFT) using the Gaussian-09 program.[42] To choose the optimum computational method, the most often used DFT methods including PBE1PBE, B3LYP,

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B3LYP-D3, M06, M06-2X, M06-L, wB97XD, B3PW91, M11, M11-L, and MN12-L were tested. The best agreement between the calculated values of the geometric parameters of complexes $(IMe)_2Pd^0$ and $(IMe)_2PdI_2$ and those determined from X-ray diffraction (XRD) experiments (Table 1, Fig. 1)**[43,44]** was used as the criterion of choice. The 6-311++G(2d,2p) basis set**[45—47]** was used for the C, H, N, O, Cl, and Br atoms and the LanL2DZ basis set**[48,49]** was used for the I and Pd atoms. The PBE1PBE-

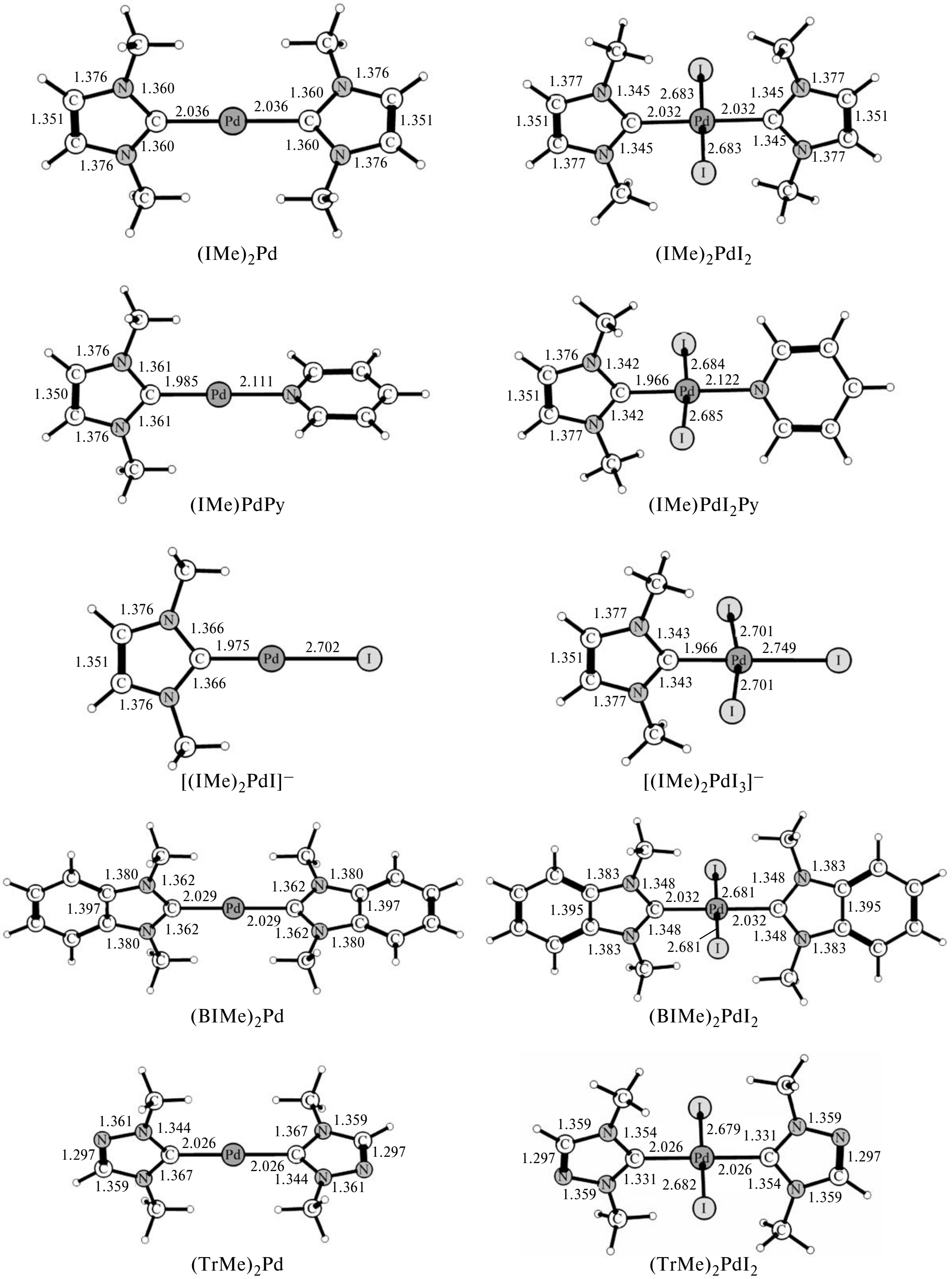


Fig. 1. Molecular structures of complexes Pd^0-NHC (on the left) and Pd^{II}-NHC (on the right) and selected bond lengths (d/Å) obtained from PBE1PBE//6-311++G(2d,2p)&LANL2dZ ($CHCl_3$, IEFPCM) calculations.

Table 1. Bond lengths (*d*) in complexes $(IMe)_2Pd^0$ and $(IMe)_2PdI_2$ determined by XRD[43,44] and obtained from DFT quantum chemical calculations

Связь	*d*/Å		
	XRD	DFT	
		PBE1PBE	B3LYP
	Complex $(IMe)_2Pd^0$		
Pd—C	2.006	2.036	2.059
$N—C_{carbene}$	1.360	1.360	1.366
N—CH	1.376	1.376	1.384
HC—CH	1.346	1.351	1.352
$N—CH_3$	1.454	1.445	1.455
	Complex $(IMe)_2PdI_2$		
Pd—C	2.033	2.032	2.058
Pd—I	2.608	2.683	2.735
$N—C_{carbene}$	1.342	1.345	1.352
N—CH	1.392	1.377	1.384
HC—CH	1.345	1.351	1.352
$N—CH_3$	1.463	1.447	1.458

optimized geometric parameters of the complexes appeared to be the closest to the experimental values (Table 1). For the sake of comparison, Table 1 also lists the geometric parameters calculated by the B3LYP method which provides poorer agreement between the results of calculations and experimental data. Therefore, further calculations were carried out using the PBE1PBE method[50,51] and the 6-311++G(2d,2p) basis set for the C, H, N, O, Cl, and Br atoms and the LanL2DZ basis set for the I, Pd, Pt, and Ni atoms. The character of the stationary points located on the potential energy surface was confirmed by calculating thermal vibration frequencies. The solvent effect was included in the IEF-PCM approximation using $CHCl_3$ as solvent.[52—55]

The character of electronic interactions between atoms was assessed by the NBO method.[56,57] The degree of involvement of the electron density of the ligand in the formation of a metal—ligand σ-bond was determined by calculating the NPA charge transfer (Δq) from the corresponding ligand atom participating in the bond formation to the metal atom[39] using the natural population analysis (NPA). The metal—ligand π-backbonding energy, E_{BB}, was evaluated using NBO analysis of second-order perturbations as the stabilization energy of the interaction between the Lewis type occupied donor d-orbital (i) of the metal and the vacant acceptor π*-orbital (j) of the ligand (L or NHC):[38,39,56]

$$E_{BB} = q_i F_{i,j}^2/(\varepsilon_j - \varepsilon_i),$$

where q_i is the population of the donor orbital, ε_i and ε_j are the diagonal matrix elements (orbital energies), and $F_{i,j}$ is the off-diagonal NBO Fock matrix element.

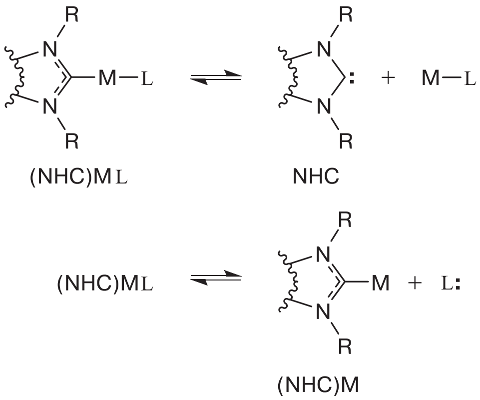
Results and Discussion

Figures 1 and 2 present the optimized molecular structures of the model complexes Pd-NHC used to evaluate the effect of the oxidation state of the metal on the metal—ligand BDE. The model complexes Ni-NHC and Pt-NHC are structurally similar to the complexes Pd-NHC shown in Fig. 1.

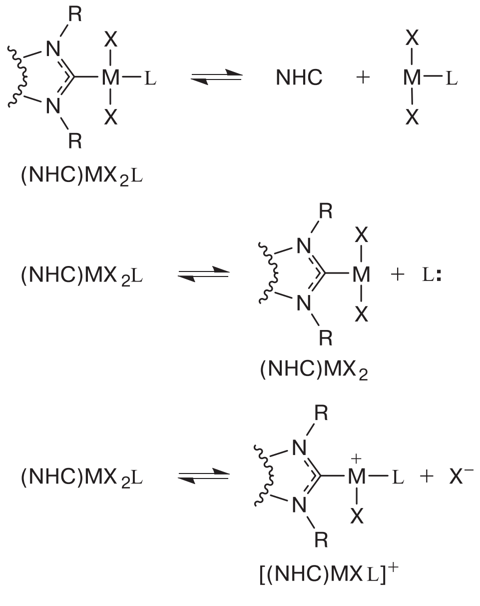
Complexes (NHC)ML containing no chelating ligands have a linear geometry;[43,58—62] however, complexes of the general formula $(NHC)M(X)_2L$ can exist as *cis*- and *trans*-isomers.[63]. Isomers of the complexes $(NHC)M(X)_2L$ with *trans*-arrangement of the ligands NHC and L are thermodynamically more stable in chloroform and other solvents of low polarity.[64] In this work, all calculations were carried out for the *trans*-isomers of the complexes $(NHC)M(X)_2L$ since they better resemble the linear geometry of the complexes (NHC)ML. The influence of steric factors was minimized by considering the NHC ligands with *N*-methyl substituents.

The metal—ligand bond dissociation processes and the resulting fragments whose energies were used in the BDE calculations are shown in Schemes 1 and 2.

Scheme 1



Scheme 2



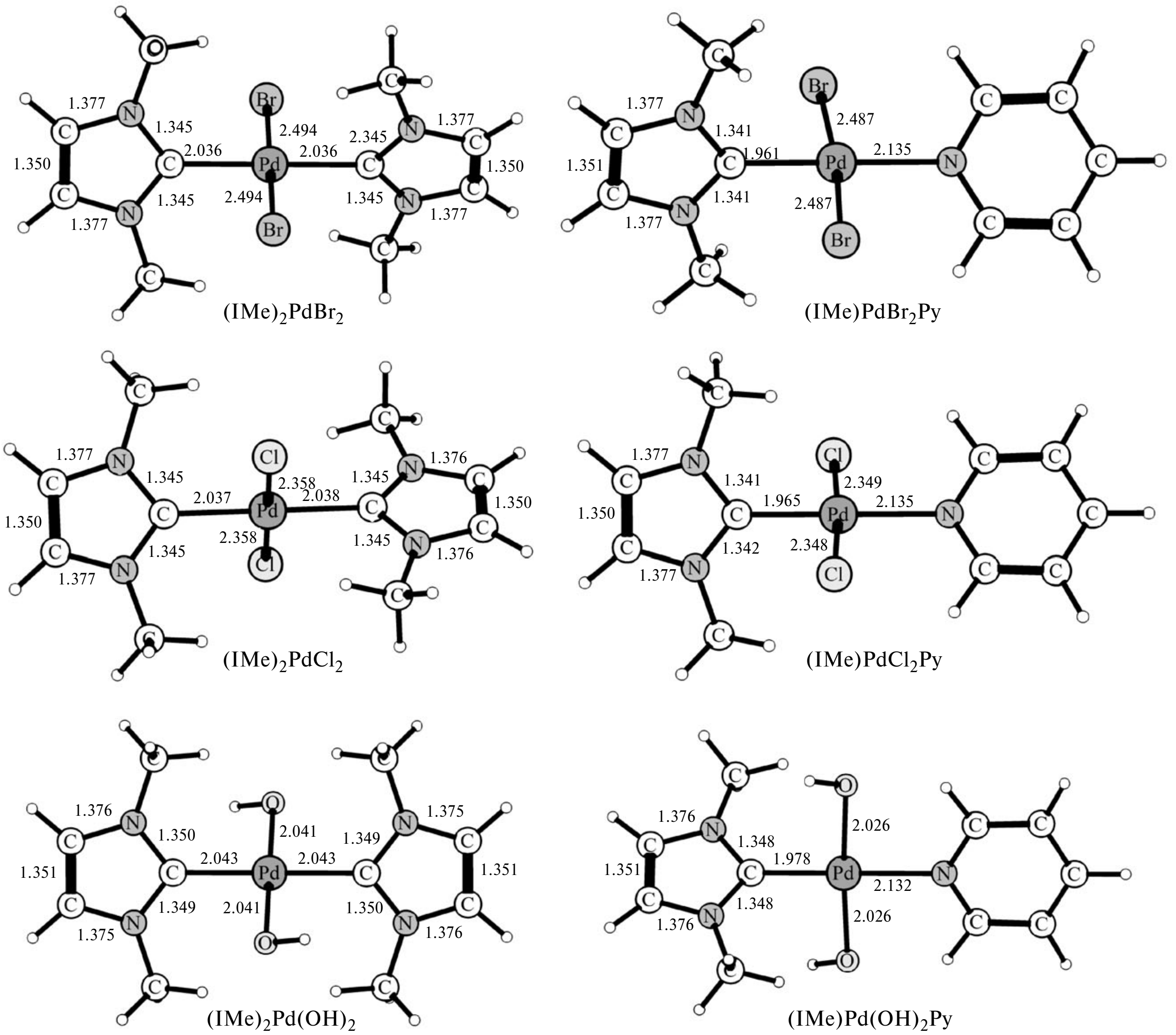

$(IMe)_2PdBr_2$ $(IMe)PdBr_2Py$
$(IMe)_2PdCl_2$ $(IMe)PdCl_2Py$
$(IMe)_2Pd(OH)_2$ $(IMe)Pd(OH)_2Py$

Fig. 2. Molecular structures of complexes Pd^{II}-NHC and selected bond lengths (*d*/Å) obtained from PBE1PBE//6-311++G(2d,2p)&LANL2dZ ($CHCl_3$, IEFPCM) calculations.

The BDE_{M-NHC} values for the complexes M^0-NHC and M^{II}-NHC were calculated using the equations

$$BDE_{M-NHC} = (E_{NHC} + E_{ML}) - E_{(NHC)ML}, \quad (1)$$

$$BDE_{M-NHC} = (E_{NHC} + E_{MX_2L}) - E_{(NHC)MX_2L}. \quad (2)$$

By analogy, the BDE_{M-L} values were calculated using the equations

$$BDE_{M-L} = (E_{(NHC)M} + E_L) - E_{(NHC)ML}, \quad (3)$$

$$BDE_{M-L} = (E_{(NHC)MX_2} + E_L) - E_{(NHC)MX_2L}, \quad (4)$$

and the BDE_{M-X} values were obtained from the equation

$$BDE_{M-X} = (E_{[(NHC)MXL]^+} + E_{X^-}) - E_{(NHC)MX_2L}. \quad (5)$$

In Eqs (1)—(5), $E_{(NHC)ML}$ and $E_{(NHC)MX_2L}$ are the total energies of the complexes; E_{NHC}, E_{ML}, E_{MX_2L}, E_L, $E_{(NHC)MX_2}$, $E_{[(NHC)MXL]^+}$, and E_{X^-} are the total energies of the fragments formed as a result of heterolytic dissociation of the corresponding bond in the complex.

Table 2 presents the calculated metal—ligand bond dissociation energies in the M^0-NHC and M^{II}-NHC complexes. The BDE_{Ni-NHC}, BDE_{Pd-NHC}, and BDE_{Pt-NHC} values (see Table 2) agree with the published data obtained from DFT calculations of complexes bearing small substituents at nitrogen atoms of the NHC ligands.[29,34,37—40] From the data of Table 2 it follows that the M—NHC bond dissociation energy can be strongly influenced by not only the nature of the metal and other ligands, but also the oxidation state of the metal.

Table 2. Dissociation energies of M—NHC ($\mathrm{BDE_{M-NHC}}$), M—L ($\mathrm{BDE_{M-L}}$) and M—X bonds ($\mathrm{BDE_{M-X}}$) in complexes $\mathrm{M^0}$-NHC and $\mathrm{M^{II}}$-NHC obtained from PBE1PBE//6-311++G(2d,2p)&LANL2dZ ($\mathrm{CHCl_3}$, IEFPCM) calculations (in kcal $\mathrm{mol^{-1}}$)

Complex $\mathrm{M^0}$-NHC	$\mathrm{BDE_{M-NHC}}$	$\mathrm{BDE_{M-L}}$ (L)	Complex $\mathrm{M^{II}}$-NHC	$\mathrm{BDE_{M-NHC}}$	$\mathrm{BDE_{M-L}}$ (L)	$\mathrm{BDE_{M-X}}$
		M = Ni			M = Ni	
$\mathrm{(IMe)_2Ni}$	49.6	49.6 (IMe)	$\mathrm{(IMe)_2NiI_2}$	50.5	50.5 (IMe)	49.4 ($\mathrm{I^-}$)
(IMe)NiPy	55.8	33.8 (Py)	$\mathrm{(IMe)NiI_2Py}$	64.7	29.6 (Py)	49.7 ($\mathrm{I^-}$)
$\mathrm{[(IMe)NiI]^-}$	63.3	22.6 ($\mathrm{I^-}$)	$\mathrm{[(IMe)NiI_3]^-}$	57.1	21.6 ($\mathrm{I^-}$)	29.5 ($\mathrm{I^-}$)
$\mathrm{(BIMe)_2Ni}$	50.8	50.8 (BIMe)	$\mathrm{(BIMe)_2NiI_2}$	50.1	50.1 (BIMe)	52.1 ($\mathrm{I^-}$)
$\mathrm{(TrMe)_2Ni}$	49.7	49.7 (TrMe)	$\mathrm{(TrMe)_2NiI_2}$	49.8	49.8 (TrMe)	54.7 ($\mathrm{I^-}$)
		M = Pd			M = Pd	
$\mathrm{(IMe)_2Pd}$	43.6	43.6 (IMe)	$\mathrm{(IMe)_2PdI_2}$	50.8	50.8 (IMe)	50.7 ($\mathrm{I^-}$)
	—	—	$\mathrm{(IMe)_2PdBr_2}$	48.5	48.5 (IMe)	48.8 ($\mathrm{Br^-}$)
	—	—	$\mathrm{(IMe)_2PdCl_2}$	48.0	48.0 (IMe)	50.8 ($\mathrm{Cl^-}$)
	—	—	$\mathrm{(IMe)_2Pd(OH)_2}$	44.6	44.6 (IMe)	69.0 ($\mathrm{OH^-}$)
(IMe)PdPy	51.9	23.0 (Py)	$\mathrm{(IMe)PdI_2Py}$	72.5	25.3 (Py)	51.3 ($\mathrm{I^-}$)
	—	—	$\mathrm{(IMe)PdBr_2Py}$	70.9	24.6 (Py)	50.4 ($\mathrm{Br^-}$)
	—	—	$\mathrm{(IMe)PdCl_2Py}$	68.9	25.2 (Py)	52.8 ($\mathrm{Cl^-}$)
	—	—	$\mathrm{(IMe)Pd(OH)_2Py}$	61.2	25.3 (Py)	72.8 ($\mathrm{OH^-}$)
$\mathrm{[(IMe)PdI]^-}$	49.6	20.6 ($\mathrm{I^-}$)	$\mathrm{[(IMe)PdI_3]^-}$	60.2	21.3 ($\mathrm{I^-}$)	31.9 ($\mathrm{I^-}$)
$\mathrm{(BIMe)_2Pd}$	44.1	44.1 (BIMe)	$\mathrm{(BIMe)_2PdI_2}$	50.1	50.1 (BIMe)	52.3 ($\mathrm{I^-}$)
$\mathrm{(TrMe)_2Pd}$	43.2	43.2 (TrMe)	$\mathrm{(TrMe)_2PdI_2}$	50.0	50.0 (TrMe)	55.3 ($\mathrm{I^-}$)
		M = Pt			M = Pt	
$\mathrm{(IMe)_2Pt}$	59.4	59.4 (IMe)	$\mathrm{(IMe)_2PtI_2}$	60.0	60.0 (IMe)	54.8 ($\mathrm{I^-}$)
(IMe)PtPy	76.8	31.5 (Py)	$\mathrm{(IMe)PtI_2Py}$	83.8	30.2 (Py)	55.5 ($\mathrm{I^-}$)
$\mathrm{[(IMe)PtI]^-}$	79.8	23.2 ($\mathrm{I^-}$)	$\mathrm{[(IMe)PtI_3]^-}$	75.8	22.0 (I)	35.2 ($\mathrm{I^-}$)
$\mathrm{(BIMe)_2Pt}$	60.0	60.0 (BIMe)	$\mathrm{(BIMe)_2PtI_2}$	59.8	59.8 (BIMe)	57.2 ($\mathrm{I^-}$)
$\mathrm{(TrMe)_2Pt}$	59.1	59.1 (TrMe)	$\mathrm{(TrMe)_2PtI_2}$	59.6	49.8 (TrMe)	59.7 ($\mathrm{I^-}$)

The $\mathrm{BDE_{M-NHC}}$ values increase in the order Pd < Ni < < Pt for the structurally similar complexes $\mathrm{M^0}$-NHC and in the order Ni ⩽ Pd < Pt for the complexes $\mathrm{M^{II}}$-NHC. The effect of the oxidation state of the metal in the structurally similar complexes $\mathrm{M^0}$-NHC and $\mathrm{M^{II}}$-NHC on the $\mathrm{BDE_{M-NHC}}$ values is ambiguous and depends on both the metal M and the ligands L and X (see Table 2). The $\mathrm{BDE_{Pd-NHC}}$ in complexes $\mathrm{Pd^{II}}$-NHC is 1.0—20.6 kcal $\mathrm{mol^{-1}}$ higher than in the complexes $\mathrm{Pd^0}$-NHC with the same ligands L. The complexes $\mathrm{Pd^{II}}$-NHC are characterized by much higher NPA charge transfer from the carbon atom of the NHC ligand to the metal atom (Table 3) and, correspondingly, by the stronger Pd—NHC σ-bond, whereas the energy of π-backbonding from Pd to NHC changes insignificantly. In the bis-NHC complexes of Ni and Pt, the oxidation state of the metal has little effect on $\mathrm{BDE_{M-NHC}}$, which is nearly 50 kcal $\mathrm{mol^{-1}}$ for the former and about 60 kcal $\mathrm{mol^{-1}}$ for the latter. Probably, in these types of complexes weakening of the σ-bond characterized by nearly twofold decrease in Δq (NHC→M) on going from $\mathrm{M^{II}}$ to $\mathrm{M^0}$ (in absolute value) is compensated by an increase in the π-backbonding energy E_{BB} (Table 3). For the complexes with L = Py an increase in the oxidation state of the metal is followed by an increase in $\mathrm{BDE_{M-NHC}}$ by 8.9 kcal $\mathrm{mol^{-1}}$ for Ni-NHC and by 7 kcal $\mathrm{mol^{-1}}$ for Pt-NHC. The opposite effect was obtained for the complexes with L = $\mathrm{I^-}$, *viz*., $\mathrm{BDE_{Ni-NHC}}$ for $\mathrm{(IMe)NiI^-}$ is 6.2 kcal $\mathrm{mol^{-1}}$ higher than for $\mathrm{(IMe)NiI_3^-}$, while $\mathrm{BDE_{Pt-NHC}}$ for the complex with $\mathrm{Pt^0}$ is 4 kcal $\mathrm{mol^{-1}}$ higher than for the complex with $\mathrm{Pt^{II}}$ (see Table 2). A possible explanation is that the change in the oxidation state of the metal influences the σ- and π-backbonding energies in different manner depending on the ligand L (see below).

From the results obtained it follows that the stability of the catalytic complexes Pd-NHC can be significantly reduced in the reactions whose catalytic cycle involves reduction of palladium to $\mathrm{Pd^0}$, whereas the nickel and platinum complexes are less sensitive to changes in the oxidation state of the metal.

Noteworthy is that the nature of the heterocycle in the NHC ligand has little effect on $\mathrm{BDE_{M-NHC}}$ (see Table 2). However, the influence of the ligand L in *trans*-position relative to the other ligand, NHC, on $\mathrm{BDE_{M-NHC}}$ is significant. Calculations of the complexes with the imidazole NHC ligands gave the lowest $\mathrm{BDE_{M-NHC}}$ for the molecules with L = IMe while the highest ones were obtained for the anionic complexes (L = $\mathrm{I^-}$) or for the complexes with pyridine ligands (L = Py). Probably, a strong effect of different ligands L in the electrically neutral complexes on $\mathrm{BDE_{Pd-NHC}}$ can be explained by the *trans*-effect with a large contribution from the σ-donor

Table 3. NPA charge transfer values (Δq) and the π-backbonding energies (E_{BB}/kcal mol^{-1}) obtained from PBE1PBE//6-311++G(2d,2p)&LANL2dZ (CHCl$_3$, IEFPCM) calculations

Complex M^0-NHC	Δq		E_{BB} (M→NHC)	Complex M^{II}-NHC	Δq		E_{BB} (M→NHC)
	NHC→M	L→M^0			NHC→M	L→M^{II}	
		M = Ni				M = Ni	
$(IMe)_2Ni$	−0.117	−0.117	16.1	$(IMe)_2NiI_2$	−0.258	−0.258	5.8
(IMe)NiPy	−0.122	+0.018	2.1	$(IMe)NiI_2Py$	−0.292	−0.018	2.0
$[(IMe)NiI]^-$	−0.127	−0.364	39.1	$[(IMe)NiI_3]^-$	−0.301	−0.516	7.4
$(BIMe)_2Ni$	−0.092	−0.092	11.3	$(BIMe)_2NiI_2$	−0.255	−0.255	1.9
$(TrMe)_2Ni$	−0.091	−0.091	11.9	$(TrMe)_2NiI_2$	−0.238	−0.238	6.2
		M = Pd				M = Pd	
$(IMe)_2Pd$	−0.151	−0.151	12.0	$(IMe)_2PdI_2$	−0.285	−0.285	8.6
—	—	—	—	$(IMe)_2PdBr_2$	−0.286	−0.286	7.5
—	—	—	—	$(IMe)_2PdCl_2$	−0.283	−0.283	6.8
—	—	—	—	$(IMe)_2Pd(OH)_2$	−0.247	−0.247	8.9
(IMe)PdPy	−0.164	+0.008	3.8	$(IMe)PdI_2Py$	−0.348	−0.010	3.3
—	—	—	—	$(IMe)PdBr_2Py$	−0.359	−0.007	3.2
—	—	—	—	$(IMe)PdCl_2Py$	−0.358	−0.008	3.1
—	—	—	—	$(IMe)Pd(OH)_2Py$	−0.276	−0.008	11.3
$[(IMe)PdI]^-$	−0.160	−0.328	24.0	$[(IMe)PdI_3]^-$	−0.354	−0.505	11.9
$(BIMe)_2Pd$	−0.136	−0.136	9.1	$(BIMe)_2PdI_2$	−0.281	−0.281	2.9
$(TrMe)_2Pd$	−0.130	−0.130	9.1	$(TrMe)_2PdI_2$	−0.265	−0.265	8.9
		M = Pt				M = Pt	
$(IMe)_2Pt$	−0.160	−0.160	18.4	$(IMe)_2PtI_2$	−0.256	−0.256	13.4
(IMe)PtPy	−0.198	+0.010	6.0	$(IMe)PtI_2Py$	−0.308	−0.017	3.7
$[(IMe)PtI]^-$	−0.195	−0.408	39.4	$[(IMe)PtI_3]^-$	−0.322	−0.541	18.4
$(BIMe)_2Pt$	−0.143	−0.143	14.7	$(BIMe)_2PtI_2$	−0.252	−0.252	4.3
$(TrMe)_2Pt$	−0.139	−0.139	14.5	$(TrMe)_2PtI_2$	−0.240	−0.240	14.2

ability of the ligand L. A comparison of the calculated ligand—metal charge transfer values (Δq) in the complexes with L = NHC and L = Py shows (see Table 3) that such ligands L, as NHC, are strong σ-donors ($\Delta q = -0.117$ for the complex $(IMe)_2Ni$) and exhibit a pronounced *trans*-effect, thus facilitating the dissociation of the *trans*-NHC ligand. Pyridine is a weak σ-donor ($\Delta q = +0.018$ in the complex (IMe)NiPy) which exhibits a weak *trans*-effect and influences the M—NHC bond to a much lesser extent. High BDE_{M-NHC} obtained for the anionic complexes (L = I^-) seem to be due to a considerable enhancement of π-backbonding from M to NHC, which strengthens the M—NHC bond in spite of increased σ-donor effect of the ligand L (see Table 3). For instance, E_{BB} (Ni→NHC) in complex $[(IMe)NiI]^-$ is 39.1 kcal mol^{-1}, being much higher than the π-backbonding energy in the electrically neutral complexes Ni^0-NHC (2.1—16.1 kcal mol^{-1}) (see Table 3).

We also considered the effect of *cis*-ligands X on BDE_{M-NHC} taking complexes Pd^{II}-NHC with various halide ions and OH^- as the ligands X and NHC or Py as the ligand L (see Figs 1 and 2, Table 2). Both types of complexes (L = NHC, Py) demonstrate a same-type effect of the ligands X on BDE_{Pd-NHC}, *viz.*, the Pd—NHC bond dissociation energy decreases in the order $I^- > Br^- > Cl^- > OH^-$ while the bond in question expectably elongates from 1.966 to 1.978 Å for L = Py and from 2.032 to 2.043 Å for L = IMe (see Figs 1 and 2). In the halide complexes, changes in BDE_{Pd-NHC} are relatively small (to 3.6 kcal mol^{-1}), being much more pronounced for the hydroxyl complexes. For instance, BDE_{Pd-NHC} in the complex $(IMe)Pd(OH)_2Py$ is 11.3 kcal mol^{-1} lower than in the complex $(IMe)PdI_2Py$ (see Table 2). A considerable decrease in BDE_{Pd-NHC} on going from the halide to hydroxyl complexes is accompanied by a large decrease in charge transfer Δq (NHC→Pd) (see Table 3).

A comparison of other metal—ligand BDE values bonds shows that spontaneous elimination is most likely expected for the iodide anion *trans*-arranged relative to NHC in the anionic complexes and for Py, namely, BDE_{M-I} is about 21—23 kcal mol^{-1} and BDE_{M-Py} is in the range of 23—34 kcal mol^{-1} (see Table 2). These ligands should eliminate most easily from the Pd complexes, especially Pd^0-NHC (see Table 2). The ease of Py dissociation to a great extent underlies the application of the $(NHC)MX_2Py$ complexes in catalysis.[2—4] The dissociation energies of the *cis*-ligands X in the complexes M^{II}-NHC are rather high and for, *e.g.*, I^- vary in the range of nearly 30—60 kcal mol^{-1}. The fact that the BDE_{Pd-I} values are somewhat overestimated compared to the BDE_{Pd-Br} and

$\mathrm{BDE_{Pd-Cl}}$ ones is probably due to the use of the other basis set (LanL2DZ) for the iodine atoms.

By and large, bis-NHC complexes $(\mathrm{NHC})_2\mathrm{MX}_2$ are the least prone to elimination of the ligands X and L. Probably, this often hampers activation of these complexes and provides an explanation for the reduced catalytic activity in many reactions compared to the mono-NHC complexes.[1—4]

An analysis of the calculated geometric parameters of the molecules shows that the metal—ligand bond lengths (Table 4) by and large correlate with the calculated BDE (see Table 2). Considering the $\mathrm{Pd^{II}}$-NHC complexes with the iodide ligands X, the strongest Pd—NHC bond is also the shortest one (complex $(\mathrm{IMe})\mathrm{PdI_2Py}$, $\mathrm{BDE_{Pd-NHC}} = 72.5$ kcal mol^{-1}, $d_{\mathrm{Pd-NHC}} = 1.966$ Å), while the weakest Pd—NHC bond is also the longest one (complex $(\mathrm{IMe})_2\mathrm{PdI}_2$, $\mathrm{BDE_{Pd-NHC}} = 50.8$ kcal mol^{-1}, $d_{\mathrm{Pd-NHC}} = 2.032$ Å). However, the change in the M—NHC bond length is not always proportional to the change in $\mathrm{BDE_{M-NHC}}$. For instance, the Pd—NHC bond in complex $[(\mathrm{IMe})\mathrm{PdI}]^-$ is shorter than in (IMe)PdPy (1.975 *vs.* 1.985 Å, respectively), whereas the former complex is characterized by somewhat lower $\mathrm{BDE_{Pd-NHC}}$ than the latter (49.6 *vs.* 51.9 kcal mol^{-1}, respectively). It should be noted that the M—NHC bonds in all anionic complexes $[(\mathrm{IMe})\mathrm{MI}]^-$ and $[(\mathrm{IMe})\mathrm{PdI_3}]^-$ are much shorter than in the electrically neutral complexes, which can be explained by an increase in the contribution of π-backbonding from M to NHC (see Table 3). The correlation between the BDE values and the Pd—NHC bond lengths in the complexes $(\mathrm{IMe})\mathrm{PdX_2Py}$ is also violated. For instance, one has $\mathrm{BDE_{Pd-NHC}} = 72.5$ kcal mol^{-1} for $(\mathrm{IMe})\mathrm{PdI_2Py}$ and 68.9 kcal mol^{-1} for $(\mathrm{IMe})\mathrm{PdCl_2Py}$, whereas the Pd—NHC bond in the iodide complex is slightly longer (1.966 Å) than in the chloride one (1.965 Å). The M—L and M—X bond lengths also correlate with the bond dissociation energies and are close to the values determined by XRD in the structurally similar complexes Ni-NHC,[65—69] Pd-NHC,[24,43,44,70—72] and Pt-NHC.[25,58,73—76] Other geometric parameters of the molecules agree with the XRD data.

Summing up, the M—NHC bond dissociation energies can be strongly influenced by the oxidation state of the metal M and by the nature of the ligand L in *trans*-position relative to the NHC ligand. Complexes Pd-NHC are the most sensitive to the changes in the oxidation state of the metal, *viz.*, reduction of $\mathrm{Pd^{II}}$ to $\mathrm{Pd^0}$ can be accompanied by a large decrease in $\mathrm{BDE_{Pd-NHC}}$ (to nearly 21 kcal mol^{-1}), which should be taken into account in the design of catalytic processes. For all types of complexes, an increase in the σ-donor ability of the ligands L and X leads to a decrease in $\mathrm{BDE_{M-NHC}}$. Bis-NHC complexes $(\mathrm{NHC})_2\mathrm{MX}_2$

Table 4. Metal—ligand bond lengths (*d*/Å) in complexes $\mathrm{M^0}$-NHC and $\mathrm{M^{II}}$-NHC obtained from PBE1PBE//6-311++G(2d,2p)&LANL2dZ ($\mathrm{CHCl_3}$, IEFPCM) calculations

Complex $\mathrm{M^0}$-NHC	$d_{\mathrm{M-NHC}}$	$d_{\mathrm{M-L}}$ (L)	Complex $\mathrm{M^{II}}$-NHC	$d_{\mathrm{M-NHC}}$	$d_{\mathrm{M-L}}$ (L)	$d_{\mathrm{M-X}}$
	M = Ni				M = Ni	
$(\mathrm{IMe})_2\mathrm{Ni}$	1.865	1.865 (IMe)	$(\mathrm{IMe})_2\mathrm{NiI_2}$	1.909	1.909 (IMe)	2.571, 2.571 ($\mathrm{I^-}$)
(IMe)NiPy	1.839	1.867 (Py)	$(\mathrm{IMe})\mathrm{NiI_2Py}$	1.870	1.951 (Py)	2.574, 2.576 ($\mathrm{I^-}$)
$[(\mathrm{IMe})\mathrm{NiI}]^-$	1.791	2.524 ($\mathrm{I^-}$)	$[(\mathrm{IMe})\mathrm{NiI_3}]^-$	1.866	2.619 (I)	2.602, 2.608 ($\mathrm{I^-}$)
$(\mathrm{BIMe})_2\mathrm{Ni}$	1.858	1.858 (BIMe)	$(\mathrm{BIMe})_2\mathrm{NiI_2}$	1.907	1.907 (BIMe)	2.563, 2.563 ($\mathrm{I^-}$)
$(\mathrm{TrMe})_2\mathrm{Ni}$	1.857	1.857 (TrMe)	$(\mathrm{TrMe})_2\mathrm{NiI_2}$	1.902	1.902 (TrMe)	2.561, 2.565 ($\mathrm{I^-}$)
	M = Pd				M = Pd	
$(\mathrm{IMe})_2\mathrm{Pd}$	2.036	2.036 (IMe)	$(\mathrm{IMe})_2\mathrm{PdI_2}$	2.032	2.032 (IMe)	2.683, 2.683 ($\mathrm{I^-}$)
	—	—	$(\mathrm{IMe})_2\mathrm{PdBr_2}$	2.036	2.036 (IMe)	2.494, 2.494 ($\mathrm{Br^-}$)
	—	—	$(\mathrm{IMe})_2\mathrm{PdCl_2}$	2.037	2.038 (IMe)	2.358, 2.358 ($\mathrm{Cl^-}$)
	—	—	$(\mathrm{IMe})_2\mathrm{Pd(OH)_2}$	2.043	2.043 (IMe)	2.041, 2.041 ($\mathrm{OH^-}$)
(IMe)PdPy	1.985	2.111 (Py)	$(\mathrm{IMe})\mathrm{PdI_2Py}$	1.966	2.122 (Py)	2.684, 2.685 ($\mathrm{I^-}$)
	—	—	$(\mathrm{IMe})\mathrm{PdBr_2Py}$	1.961	2.135	2.487, 2.487 ($\mathrm{Br^-}$)
	—	—	$(\mathrm{IMe})\mathrm{PdCl_2Py}$	1.965	2.135 (Py)	2.348, 2.349 ($\mathrm{Cl^-}$)
	—	—	$(\mathrm{IMe})\mathrm{Pd(OH)_2Py}$	1.978	2.132 (Py)	2.026 ($\mathrm{OH^-}$)
$[(\mathrm{IMe})\mathrm{PdI}]^-$	1.975	2.702 ($\mathrm{I^-}$)	$[(\mathrm{IMe})\mathrm{PdI_3}]^-$	1.966	2.749 ($\mathrm{I^-}$)	2.701, 2.701 ($\mathrm{I^-}$)
$(\mathrm{BIMe})_2\mathrm{Pd}$	2.029	2.029 (BIMe)	$(\mathrm{BIMe})_2\mathrm{PdI_2}$	2.032	2.032 (BIMe)	2.681, 2.681 ($\mathrm{I^-}$)
$(\mathrm{TrMe})_2\mathrm{Pd}$	2.026	2.026 (TrMe)	$(\mathrm{TrMe})_2\mathrm{PdI_2}$	2.026	2.026 (TrMe)	2.678, 2.682 ($\mathrm{I^-}$)
	M = Pt				M = Pt	
$(\mathrm{IMe})_2\mathrm{Pt}$	2.001	2.001 (IMe)	$(\mathrm{IMe})_2\mathrm{PtI_2}$	2.027	2.027 (IMe)	2.690, 2.690 ($\mathrm{I^-}$)
(IMe)PtPy	1.943	2.063 (Py)	$(\mathrm{IMe})\mathrm{PtI_2Py}$	1.967	2.107 (Py)	2.689, 2.689 ($\mathrm{I^-}$)
$[(\mathrm{IMe})\mathrm{PtI}]^-$	1.917	2.699 ($\mathrm{I^-}$)	$[(\mathrm{IMe})\mathrm{PtI_3}]^-$	1.956	2.768 (I)	2.699, 2.700 ($\mathrm{I^-}$)
$(\mathrm{BIMe})_2\mathrm{Pt}$	1.994	1.994 (BIMe)	$(\mathrm{BIMe})_2\mathrm{PtI_2}$	2.025	2.025 (BIMe)	2.691, 2.691 ($\mathrm{I^-}$)
$(\mathrm{TrMe})_2\mathrm{Pt}$	1.992	1.992 (TrMe)	$(\mathrm{TrMe})_2\mathrm{PtI_2}$	2.020	2.020 (TrMe)	2.689, 2.693 ($\mathrm{I^-}$)

are characterized by rather high $\mathrm{BDE_{M-NHC}}$ and $\mathrm{BDE_{M-X}}$, which can make their activation in catalytic systems difficult. Complexes $(\mathrm{NHC})\mathrm{MX_2Py}$ as well as anionic complexes $[(\mathrm{NHC})\mathrm{MX_3}]^-$ have strong M—NHC bonds, but can readily lose the ligand Py or halide anion in *trans*-position relative to the NHC ligand; this should facilitate the formation of activated forms of M-NHC in the course of catalysis. The calculated BDE values are in good agreement with experimental data and can be used to predict the activity and stability of the catalytic systems M-NHC.

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