Journal of Organometallic Chemistry 755 (2014) 93–100

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Comparison of coordination mode of some biphosphine ligands in cyclometalated organoplatinum(II) complexes

Ahmad R. Esmaeilbeig*, Mohsen Golbon Haghighi, Sahebeh Nikahd, Sara Hashemi, Mohammad Mosarezaee, Mehdi Rashidi, S. Masoud Nabavizadeh*

Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71467-13565, Iran

ARTICLE INFO

Article history:
Received 11 November 2013
Received in revised form
7 January 2014
Accepted 10 January 2014

Keywords:
Organoplatinum
Phosphine ligands
DFT calculations

ABSTRACT

The reaction of the cyclometalated complexes [PtR(CN)(SMe_2)], **1**, in which R is Me or 4-MeC_6H_4, and CN is either ppy (deprotonated 2-phenylpyridine) or bhq (deprotonated benzo-h-quinoline), with 1,2-bis[bis(pentafluorophenyl)phosphino]ethane (dfppe), were studied. When 0.5 equiv of dfppe was added, the binuclear cyclometalated Pt(II) complexes [$Pt_2R_2(CN)_2$(μ-dfppe)], **2i**–**l**, were formed, which are the first examples of diplatinum complexes with bridging dfppe ligands. When the ligand dfppe was reacted with complex **1** in the ratio of 1:1, only in the case of R = Me and CN = ppy, the complex [Pt(Me)(κ^1-ppy)(κ^2-dfppe)], **4d**, was obtained, in which the ppy ligand is monodentate and dfppe is chelating, and in other cases the dimers **2j**–**l** were formed. The results were compared, using density functional theory (DFT), with other diphosphine ligands, 1,1-bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe) to clarify the electronic and steric effects of diphosphine ligands on their coordination mode ability.

1. Introduction

2-Phenypyridine or benzo[h]quinoline (abbreviated as HCN) and biphosphines (PP) are two of the most common and important classes of ligands employed in organometallic chemistry. The coupling of these two ligand types is of current interest, since the resulting hybrid CN–PP ligands are expected to affect complex properties. The cyclometalated platinum(II) complexes containing deprotonated 2-phenylpyridine (ppy) or benzo[h]quinoline (bhq) have already been reported as interesting complexes [1–11].

In this paper we report the effect of the presence of electron-withdrawing substituents near the phosphorus atoms of the PP ligand on its coordination mode when it is reacted with cycloplatinated(II) complexes [PtR(CN)(SMe_2)], in which R = Me or 4-MeC_6H_4 and CN = ppy or bhq. To this purpose, an electron-poor diphosphine formally derived from substitution of phenyl hydrogens of dppe (1,2-bis(diphenylphosphino)ethane) with electronegative fluorine atoms (i. e. 1,2-bis[bis(pentafluorophenyl) phosphino]ethane = dfppe) is employed. The majority of the reported transition metal complexes with dfppe are mononuclear complexes bearing a single or two chelating dfppe ligand and dimeric complexes with bridging dfppe [12–17]. However, to the best of our knowledge, diplatinum complexes containing bridging dfppe are not known. We have recently reported some mono- and binuclear platinum(II) complexes, in each of which biphosphine ligands such as 1,1-bis(diphenylphosphino)methane (dppm), dppe and 1,1′-bis(diphenylphosphino)ferrocene (dppf) act as monodentate, chelating or bridging ligands [1,18–20].

2. Experimental section

The ^{1}H NMR spectra were recorded by using a Bruker Avance DPX 250 or DRX 500 spectrometer with TMS as reference. The ^{31}P NMR spectra were recorded using a Bruker Avance DRX 500 spectrometer with 85% H_3PO_4 as reference. The microanalyses were performed using a Thermofinigan Flash EA–1112 CHNO rapid elemental analyzer. The complexes [PtR(CN)(SMe_2)], R = Me or 4-MeC_6H_4 and CN = deprotonated 2-phenylpyridine (ppy) or deprotonated benzo[h]quinoline (bhq) were made by the known methods [18]. 1,2-Bis[bis(pentafluorophenyl)phosphino]ethane (dfppe) and dppm were purchased from commercial sources.

2.1. [Pt(Me)(κ^2-ppy)(κ^1-dppm)], **3a**

To a solution of [Pt(Me)(ppy)(SMe_2)], **1a**, (43 mg, 0.1 mmol) in acetone (20 mL) was added dppm (40 mg, 0.1 mmol). The mixture

* Corresponding authors. Tel.: +98 711 613 7110; fax: +98 711 646 0788.
E-mail addresses: esmaeilbeig@chem.susc.ac.ir (A.R. Esmaeilbeig), nabavi@chem.susc.ac.ir, nabavizadeh@yahoo.com (S.M. Nabavizadeh).

0022-328X/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2014.01.008

was stirred at room temperature for 1 h. After removal of the solvent by evaporation, a residue was obtained which was washed several times with hexane and dried under vacuum. It was isolated as a yellow powder. Yield 60%; mp = 115 °C (decomp). Anal. Calcd. for $C_{37}H_{33}NP_2Pt$: C, 59.4; H, 4.4; N, 1.9; Found: C, 59.6; H, 4.3; N, 2.1. Selected NMR in $CDCl_3$: $\delta(^1H)$ = 0.86 [d, 3H, $^3J_{PH}$ = 8 Hz, $^2J_{PtH}$ = 83 Hz, MePt], 3.37 [d, 2H, $^2J_{PH}$ = 8 Hz, $^3J_{PtH}$ = 19 Hz, CH_2P_2]; 6.52 [ddd, 1H, $^3J^{56}_{HH}$ = 6 Hz, $^3J^{54}_{HH}$ = 7 Hz, $^4J^{53}_{HH}$ = 1 Hz, H^5]; $\delta(^{31}P)$ = 19.9 [d, $^2J_{PP}$ = 72 Hz, $^1J_{PtP}$ = 2082 Hz, 1 P], δ = −25.2 [d, $^2J_{PP}$ = 72 Hz, $^3J_{PtP}$ = 64 Hz, 1 P].

2.2. [Pt(Me)(κ¹-ppy)(κ²-dfppe)], **4d**

Dfppe (76 mg, 0.1 mmol) was added to a solution of [Pt(Me)(ppy)(SMe_2)], **1a**, (43 mg, 0.1 mmol) in acetone (20 mL). The mixture was stirred at room temperature for 20 h. After removal of the solvent by evaporation, a residue was obtained which was further purified by washing with cold ether. The product, as a white solid, was dried under vacuum. Yield 65%, mp = 240 °C (decomp). Anal. Calcd. for $C_{38}H_{15}F_{20}NP_2Pt$: C, 40.7; H, 1.4; N, 1.3; Found: C, 41.0; H, 1.7; N, 1.4. Selected NMR in $CDCl_3$: δ(1H) = 0.78 [br. s, 3H, $^2J_{PtH}$ = 76 Hz, MePt]; 2.70 [br, 4H, CH2P]; 6.75–8.75 [aromatic hydrogens]; $\delta(^{31}P)$ = 9.9 [br. s, $^1J_{PtP}$ = 1693 Hz, P trans to ppy]; 16.7 [br. s, $^1J_{PtP}$ = 1615 Hz, P trans to Me].

2.3. [$Pt_2(Me)_2(ppy)_2$(μ-dfppe)], **2i**

Dfppe (38 mg, 0.05 mmol) was added to a solution of [Pt(Me)(ppy)(SMe_2)], **1a**, (43 mg, 0.1 mmol) in acetone (20 mL). The mixture was stirred at room temperature for 20 h. After removal of the solvent by evaporation, a residue was obtained which was washed with cold ether to give the product as a white solid. Yield 76%, mp = 177 °C (decomp). Anal. Calcd. for $C_{50}H_{26}F_{20}N_2P_2Pt_2$: C, 40.4; H, 1.8; N, 1.9; Found: C, 40.7; H, 1.7; N, 1.7. Selected NMR in $CDCl_3$: $\delta(^1H)$ = 0.47 [d, $^3J_{PH}$ = 10 Hz, $^2J_{PtH}$ = 80 Hz, 6H, MePt]; 3.39 [br. s, 4H, CH_2P]; 6.39–8.20 [aromatic hydrogens]; $\delta(^{31}P)$ = 9.0 [s, $^3J_{PP}$ = 69 Hz, $^1J_{PtP}$ = 1898 Hz, PtP].

The following complexes were made similarly by using the appropriate starting complexes **1** and dfppe:

2.4. [$Pt_2(Me)_2(bhq)_2$(μ-dfppe)], **2j**

Yield 80%, mp = 179 °C (decomp). Anal. Calcd. for $C_{54}H_{26}F_{20}N_2P_2Pt_2$: C, 42.3; H, 1.7; N, 1.8; Found: C, 42.7; H, 1.6; N, 2.1. Selected NMR in $CDCl_3$: $\delta(^1H)$ = 0.46 [d, $^3J_{PH}$ = 10 Hz, $^2J_{PtH}$ = 82 Hz, 6H, MePt]; 3.74 [br. s, 4H, CH_2P]; 8.02 [br. d, $^3J^{56}_{HH}$ = 5 Hz, 2H, H^6 of bhq]; $\delta(^{31}P)$ = 10.6 [s, $^3J_{PP}$ = 74 Hz, $^1J_{PtP}$ = 2037 Hz, PtP].

2.5. [$Pt_2(4\text{-}MeC_6H_4)_2(ppy)_2$(μ-dfppe)], **2k**

Yield 70%, mp = 250 °C (decomp). Anal. Calcd. for $C_{62}H_{34}F_{20}N_2P_2Pt_2$: C, 45.4; H, 2.1; N, 1.7; Found: C, 45.9; H, 2.5; N, 1.7. Selected NMR in $CDCl_3$: $\delta(^1H)$ = 2.10 [s, 6H, MeC]; 3.33 [br. s, 4H, CH_2P]; 6.53 [d, $^3J^{m}_{HHo}$ = 7 Hz, 4H, H^m]; 6.90 [d, $^3J^{m}_{HHo}$ = 7 Hz, $^3J_{PtH}$ = 56 Hz, 4H, Ho]; 8.07 [br. d, $^3J^{56}_{HH}$ = 5 Hz, 2H, H^6 of ppy]; $\delta(^{31}P)$ = 9.4 [br. s, $^1J_{PtP}$ = 1774 Hz, PtP].

2.6. [$Pt_2(4\text{-}MeC_6H_4)_2(bhq)_2$(μ-dfppe)], **2l**

Yield 75%, mp = 240 °C (decomp). Anal. Calcd. for $C_{66}H_{34}F_{20}N_2P_2Pt_2$: C, 47.0; H, 2.0; N, 1.7; Found: C, 47.5; H, 2.0; N, 1.7. Selected NMR in $CDCl_3$: $\delta(^1H)$ = 2.1 [s, 6H, MeC]; 3.75 [br. s, 4H, CH_2P]; 6.54 [d, $^3J^{m}_{HHo}$ = 7 Hz, 4H, H^m]; 6.98 [d, $^3J^{m}_{HHo}$ = 7 Hz, $^3J_{PtH}$ = 57 Hz, 4H, Ho]; 8.27 [br. d, $^3J^{56}_{HH}$ = 5 Hz, 2H, H^6 of bhq]; $\delta(^{31}P)$ = 9 [s, $^3J_{PP}$ = 75 Hz, $^1J_{PtP}$ = 2045 Hz, PtP].

3. Computational details

Density functional calculations were performed with the program suite Gaussian03 [21] using the B3LYP level of theory [22–24]. The LANL2DZ basis set [25–28] was chosen to describe Pt. The 6-31G(d) basis set was used for other atoms. The solvent effects were calculated by the CPCM model in acetone. The geometries of complexes were fully optimized by employing the density functional theory without imposing any symmetry constraints. To evaluate and ensure the optimized structures of the molecules, frequency calculations were carried out using analytical second derivatives. In all cases only real frequencies were obtained for the optimized structures.

4. Results

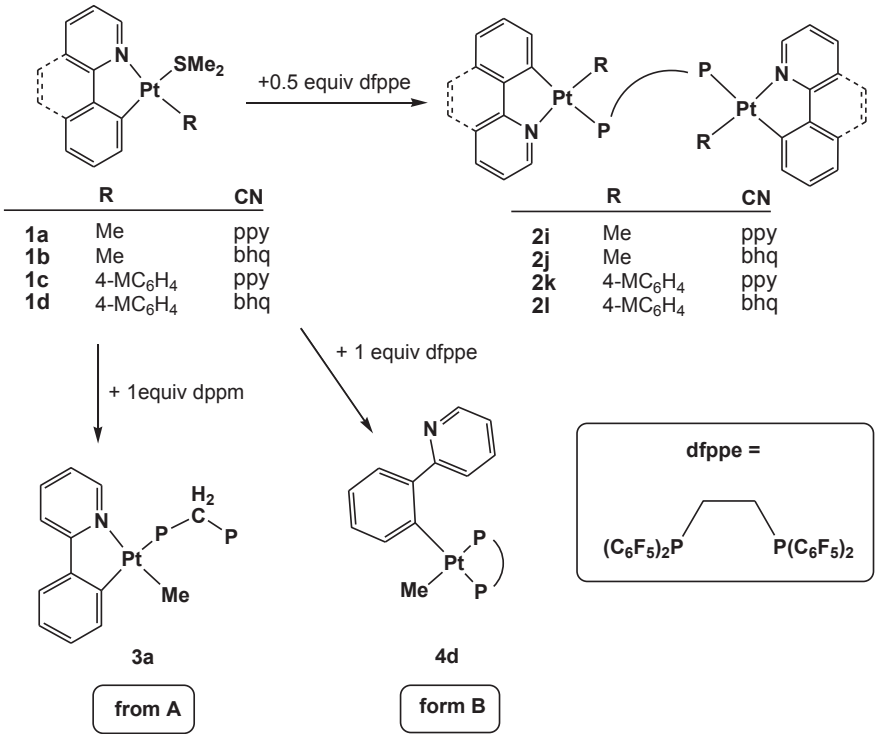
4.1. Synthesis and characterization of new complexes

We have recently reported some mono- and binuclear platinum(II) complexes, containing biphosphine ligands such as dppm, dppe and dppf. In these complexes diphosphine ligands act as monodentate, chelating or bridging ligands [1,18–20] (see Scheme 1S in Supporting Information for summery of these reactions). The reactions studied in the present work are summarized in Scheme 1.

The starting complexes [PtR(CN)(SMe_2)], **1**, in which R = Me or 4-MeC_6H_4 and CN = ppy or bhq, were prepared as reported previously [18,20]. As is depicted in Scheme 1 and Scheme 1S, the reaction of a solution of the dimethylsulfide complexes **1** with 0.5 equiv of PP ligands (PP is dppm, dppe or dfppe), followed by replacement of the labile ligand SMe_2 with the P ligating atoms of PP, at room temperature afforded the bridging PP complexes [$Pt_2R_2(CN)_2$(μ-PP)], **2**, in good yields. The complexes **2a**–**h** (see Scheme 1S) containing bridging dppm and dppe were also prepared as described previously [18,20,29]. In the present work, the analogous complexes [$Pt_2R_2(CN)_2$(μ-dfppe)], **2i**–**l**, were synthesized and characterized by ^1H and ^{31}P NMR spectroscopy (see Supporting Information for the detailed discussion about the spectroscopic data for complex **2j**). The ^{31}P NMR data of [$Pt_2R_2(CN)_2$(μ-dfppe)]dimers, **2i**–**l**, along with those known for [$Pt_2R_2(CN)_2$(μ-dppe)], **2e**–**h**, are reported in Table 1S (Supporting Information). As can be seen, there is a steady increase in the values of the Pt–P coupling constants, which shifts, for example, from 1898 Hz for **2i** to 2085 Hz for **2e**. This behavior can be associated with the increasing electron-withdrawing character of the dfppe ligand.

The monomeric complexes [Pt(4-MeC_6H_4)(CN)(κ¹-dppm)], CN = ppy, **3b**, or bhq, **3c**, were also prepared as described previously [20]. The analogous complex [PtMe(ppy)(κ¹-dppm)], **3a**, was synthesized by the reaction of [PtMe(ppy)(SMe_2)], **1a**, with dppm in a 1:1 ratio according to Scheme 1. The free phosphorus atom of the dppm ligand in complex **3a** did not displace the nitrogen-donor from metal to give complex [PtMe(κ¹-C-ppy)(κ²-dppm)], analogous to complex **4d** (see Scheme 1). The structure of complex **3a** was readily deduced from its ^1H and ^{31}P NMR spectra (see Supporting Information for the detailed discussion about the spectroscopic data for complex **3a**).

The complexes [PtR(κ¹-CN)(κ²-dppe)], (**4a**, R = Me, CN = ppy; **4b**, R = 4-MeC_6H_4, CN = ppy; **4c**, R = 4-MeC_6H_4, CN = bhq), have been made by the reaction of [Pt(R)(CN)(SMe_2)], **1**, with dppe in a 1:1 ratio (Scheme 1S) [18]. Surprisingly, in the related reactions of complexes **1** with dfppe, in the 1:1 ratio, diplatinum complexes **2j**–**l** and 0.5 equiv of unreacted dfppe were obtained (see Fig. 1S-b), except in the case of complex **1a** which only complex [Pt(Me)(κ¹-ppy)(κ²-dfppe)], **4d**, with chelating biphosphine was formed (see Fig. 1S-c). The latter was isolated as a stable yellow solid which was



Scheme 1.

characterized by its ^{1}H and ^{31}P NMR spectra (see Supporting Information for spectroscopic data).

4.2. DFT – computed geometries for the dimers **2i–j**

The structures of new diplatinum complexes containing dfppe as bridging ligand, **2i–j**, were further investigated by density functional theory and are shown in Fig. 1; the selected bond lengths and bond angles are listed in Table 1. The geometries are best described as distorted square-planar and the bond angles around the Pt center range from 79° to 101.5°. The chelating CN bite angles, i.e. (CN)C-Pt-N(CN), amount to 79.0°–79.5°, which are significantly smaller than 90°, implying that the chelate is probably under strain. The complexes have the dihedral angle PCCP = 162°–165°.

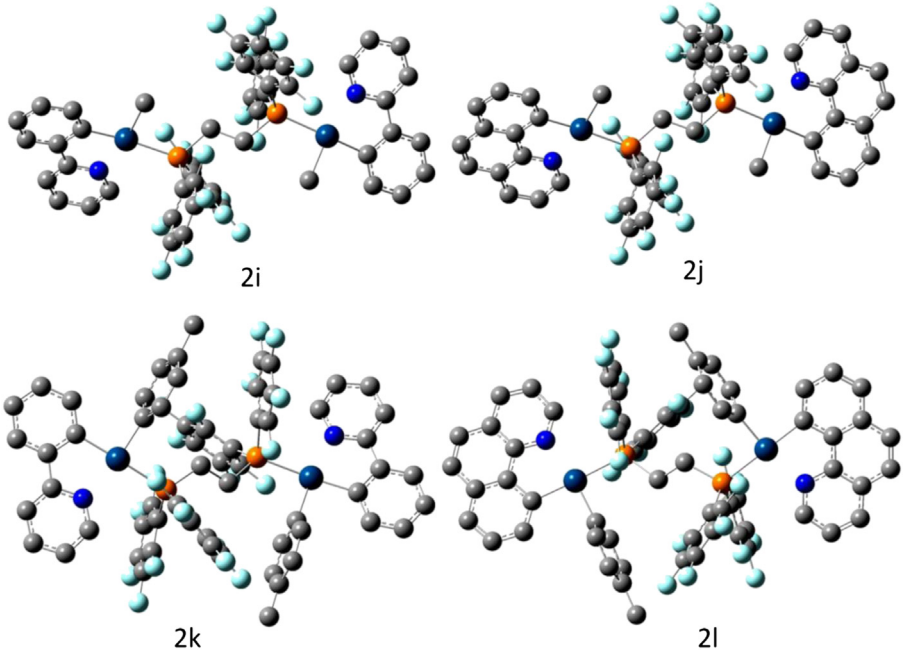


Fig. 1. The DFT-optimized structures of dimers **2**. The H atoms are omitted for more clarity.

Table 1
The selected DFT-optimized bond lengths (Å) and angles (°) for the dimers **2**.

Complex	Bond distance				Angle			
	Pt–C (R)	Pt–C (CN)	Pt–N (CN)	Pt–P	(R) C–Pt–C (CN)	(CN) C–Pt–N (CN)	(CN) N–Pt–P	P–Pt–C (R)
$[Pt_2Me_2(ppy)_2(\mu\text{-dfppe})]$, **2i**	2.075	2.039	2.213	2.392	91.7	79.0	101.5	88.2
$[Pt_2Me_2(bhq)_2(\mu\text{-dfppe})]$, **2j**	2.074	2.045	2.226	2.388	91.6	79.5	100.7	89.0
$[Pt_2(4\text{-}MeC_6H_4)_2(ppy)_2(\mu\text{-dfppe})]$, **2k**	2.032	2.040	2.205	2.419	91.8	79.0	100.0	89.5
$[Pt_2(4\text{-}MeC_6H_4)_2(bhq)_2(\mu\text{-dfppe})]$, **2l**	2.030	2.044	2.225	2.412	91.0	79.5	99.8	90.1

5. Discussion

We were interested in assembling the cyclometalated complexes to form more complex structures for potential applications in molecular materials. In this regard, the reaction of the complexes **1** with general formula $[PtR(CN)(SMe_2)]$ (see Scheme 1 and Scheme 1S; R = Me or 4-MeC_6H_4; CN = ppy or bhq) with dppm, dppe or dfppe ligands in 1:0.5 M ratio gave the symmetrical bridged diplatinum complexes **2**. When the ratio of 1:1 was used, the short bite angle diphosphine ligand, dppm, does not displace the pyridine donor and forms only a monodentate dppm complex, **A**. The chelate ring in complex **1** can be opened by reaction with a chelating diphosphine, dppe, to give the monodentate 2-pyridilphenyl platinum complex **B**. As shown in Scheme 1, complex **A** has a free phosphine donor while **B** has a free pyridyl group. Surprisingly, when the ligand dfppe was reacted with complex **1** in the ratio of 1:1, the complex **B** was only obtained when R = Me and CN = ppy, and in other cases the dimers **2** were formed (see Scheme 1S). It seems that there is a competition between chelation by the diphosphine ligand and by the CN-donor ligand. We have performed a series of calculations in order to investigate the relative stabilities of the isomers **A** and **B** as a function of R (=Me or Ph), CN (=ppy or bhq) and PP (=dppm, dppe or dfppe) ligands. Here, we have used the naming form **A** (general formula $[PtR(\kappa^2\text{-CN})(\kappa^1\text{-PP})]$), and **B** (general formula $[PtR(\kappa^1\text{-CN})(\kappa^2\text{-PP})]$) for monodentate and chelating PP, respectively, for ease of discussion (see Scheme 1).

The lowest energy structures of the complexes $[PtR(\kappa^2\text{-CN})(\kappa^1\text{-PP})]$ (isomer **A**) and $[PtR(\kappa^1\text{-CN})(\kappa^2\text{-PP})]$ (isomer **B**), as calculated by DFT calculations, are shown in Figs. 2–4 and their selected bond lengths and angles are reported in Table 2S (see Supporting Information).

5.1. Effect of R ligand

Energy differences between forms **A** and **B** (or $\Delta E = E_A - E_B$) of the complexes [PtMe(CN)(PP)] are lower than the ΔE of [PtPh(CN)(PP)] in acetone as solvent. As an example, ΔE for complex [PtMe(ppy)(dppe)] is −2.8 kJ mol^{-1}, while this value for complex including Ph group, [PtPh(ppy)(dppe)], is equal to −19.8 kJ mol^{-1}. The lowest energy optimized structures of these complexes are shown in Fig. 2. More negative value of ΔE obtained for Ph shows that the electron-withdrawing ability of the Ph ligand and more importantly its steric hindrance favor more isomer **A** over isomer **B**.

5.2. Effect of CN ligand

The CN ligands presented in this study are deprotonated 2-phenylpyridine (ppy) or deprotonated benzo[h]quinoline (bhq) and as is clear from their structures, they are flexible and rigid ligands, respectively. Considering the energy differences between forms **A** and **B** (ΔE), the complexes [PtR(bhq)(PP)] have more negative ΔE values compare to those for [PtR(ppy)(PP)]. For example ΔE values for complexes [PtMe(bhq)(dppe)] and [PtMe(ppy)(dppe)] are −14.8 and −2.8 kJ mol^{-1}, respectively. The lowest energy structures of the complexes [PtMe(bhq)(dppe)] and [PtMe(ppy)(dppe)], (for both isomers **A** and **B**) as calculated by DFT calculations, are shown in Fig. 3. More negative calculated values for ΔE in the case of CN = bhq predicts a greater preference for the κ^2-*C*-isomer (form **A**) for the bhq compared to the ppy complex. So the chelate Pt(bhq) is expected to be relatively favored compared to the chelate Pt(ppy) ring, based on the fact that bhq is more rigid than ppy. The calculated results are in agreement with experimental finding [18]. Attempts to prepare the complex $[PtMe(\kappa^1\text{-bhq})(dppe)]$, were unsuccessful indicating that the rigid ligand bhq is less favored than the more flexible ppy when bound in the κ^1 form.

5.3. Effect of PP ligand

The DFT-calculated structures of isomers **A** and **B** for the complexes [PtMe(ppy)(dppm)] and [PtMe(ppy)(dfppe)] are shown in Fig. 4. The energy differences between isomers **A** and **B** (or ΔE) when PP = dppm is more negative than that when PP = dfppe or dppe. For example, the ΔE values for complexes [PtMe(py)(dppm)] and [PtMe(ppy)(dfppe)] are −33.9 and −9.9 kJ mol^{-1}, respectively. It means that the isomer **A** is the favored isomer in the case of dppm while the formation of isomer **B** is likely when PP is

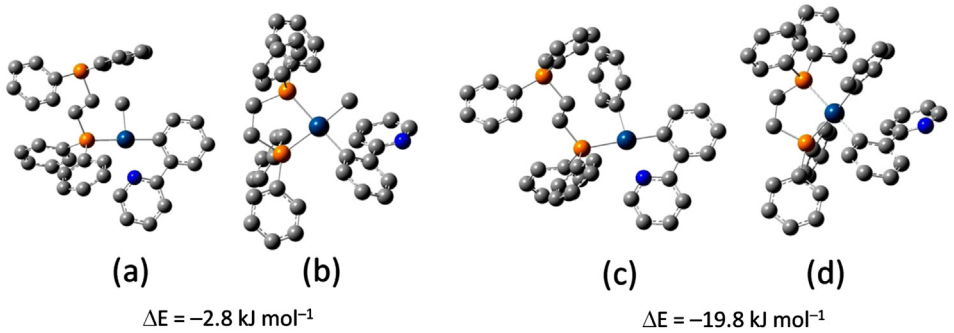


Fig. 2. DFT-calculated structures of (a) $[PtMe(\kappa^2\text{-ppy})(\kappa^1\text{-dppe})]$ (isomer **A**), (b) $[PtMe(\kappa^1\text{-ppy})(\kappa^2\text{-dppe})]$ (isomer **B**), (c) $[PtPh(\kappa^2\text{-ppy})(\kappa^1\text{-dppe})]$ (isomer **A**), (d) $[PtPh(\kappa^1\text{-ppy})(\kappa^2\text{-dppe})]$ (isomer **B**).

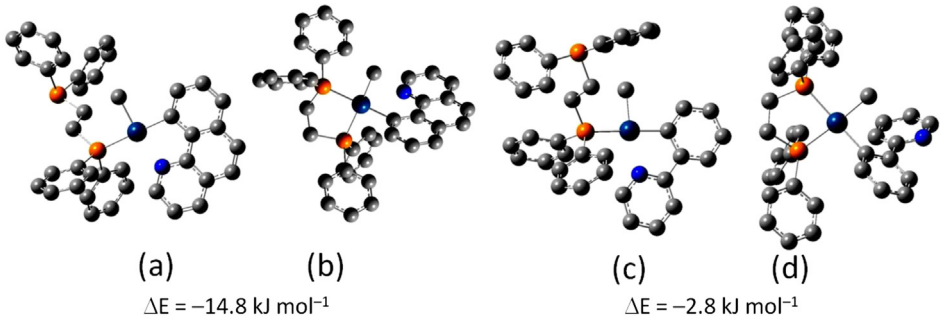


Fig. 3. DFT-calculated structures of (a) [PtMe(κ^2-bhq)(κ^1-dppe)] (isomer **A**), (b) [PtMe(κ^1-bhq)(κ^2-dppe)] (isomer **B**), (c) [PtMe(κ^2-ppy)(κ^1-dppe)] (isomer **A**), (d) [PtMe(κ^1-ppy)(κ^2-dppe)] (isomer **B**).

dfppe. This is in agreement with experimental findings. For the complexes studied in the present work, there is a dependence on the ligand PP = dppm, dppe, or dfppe. Only with dppm is the isomer **A** favored, while both dppe and dfppe favor isomer **B**. It is well known that the four-membered Pt(dppm) chelate ring is strained whereas the five-membered Pt(dfppe) chelate ring is not [30,31], and so this can rationalize the observation of isomer **A** when PP = dppm and isomer **B** when PP = dfppe or dppe.

In general, the isomeric form **B** of dfppe ligand can only be formed when R = Me and CN = ppy, by the reaction of [Pt(Me)(ppy)(SMe_2)] with dfppe in a 1:1 ratio. When R is Ph or CN is bhq, the dfppe acts as bridging ligand and a dimer is formed, while in the same condition with similar starting complexes **1**, dppe forms monomeric complexes **B**. It seems that when R = Ph, coordination around the dfppe chelating **B** is more sterically hindered than that of Me, probably responsible for the formation of **A**. This complex is also unstable and can react with more platinum complex precursor (having labile SMe_2 ligand) to give the unusual diphosphine bridged binuclear complexes, even when PP = dfppe. In the case of CN = bhq, the rigidity of this ligand compared to ppy and also lower Lewis basicity of dfppe compared to dppe (due to the presence of electron-withdrawing fluoroaryl ligands) makes the formation of isomer **B** difficult, responsible for the formation of dimer for the case in which PP = dfppe.

5.4. DFT investigation of product formation

In order to gain further insight into the dimer formation, DFT calculations were carried out for the complexes and intermediates, using parameters for the solvent acetone and a mechanism described in Scheme 2 is suggested to occur during the reaction progress. The complex **1a** contains a labile SMe_2 ligand and two Pt–C bonds. The SMe_2 dissociation step is facilitated by the strong *trans* influence of the metalated C atom of ppy, which weakens the Pt–SMe_2 bond. In the first step the PP (=dppm or dfppe) ligand displaces the labile ligand SMe_2 to give the intermediate complex [PtMe(ppy)(PP-κ^1P)], **A**, in which PP-κ^1P is monodentate PP ligand and 0.5 equiv of the starting complex **1a** is remained unreacted. The energy barriers for this step are 25.9 and 80.7 kJ mol^{-1} for dppm and dfppe, respectively (see Fig. 5). These values are in agreement with experimental findings showing the formation of dangling dppm is easier than dfppe complexes. The complex **A** forms an equilibrium with the chelating PP isomer complex [PtMe(PP)(ppy-κ^1C)], **B**, in which ppy-κ^1C is the deprotonated ppy ligand that is C-ligated with the dangling N atom. The intermediates **B** are higher in energy than isomers **A** (33.9 and 10.0 kJ mol^{-1} for dppm and dfppe, respectively), so the equilibrium shifts to isomers **A**. In the second step, the complex **A** is reacted with remaining second half of the starting complex **1a** to produce the final diplatinum complex [$Pt_2Me_2(ppy)_2$(μ-PP)], **2a** or **2j**.

5.5. Frontier molecular orbitals

Qualitative representations of the highest occupied and lowest unoccupied molecular orbitals in the newly synthesized cycloplatinated complexes **3a**, **4d** and **2i** are presented in Fig. 6. The energies of the relevant frontier orbitals of complexes **2i**–**2l** are also shown in Table 2. The HOMO–LUMO gap of **3a** is equal to 4.069 eV. The highest occupied MO of **3a** is mainly Pt d_z^2 orbital with small contribution of the p_π orbitals of the ppy ligand. The LUMO is predominately localized on the ppy orbitals. The value of the energy separations between the HOMO and LUMO of **4d** and **2i** are

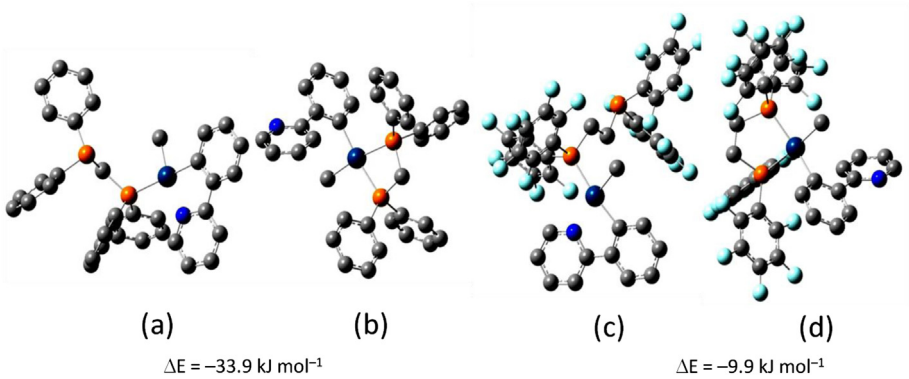
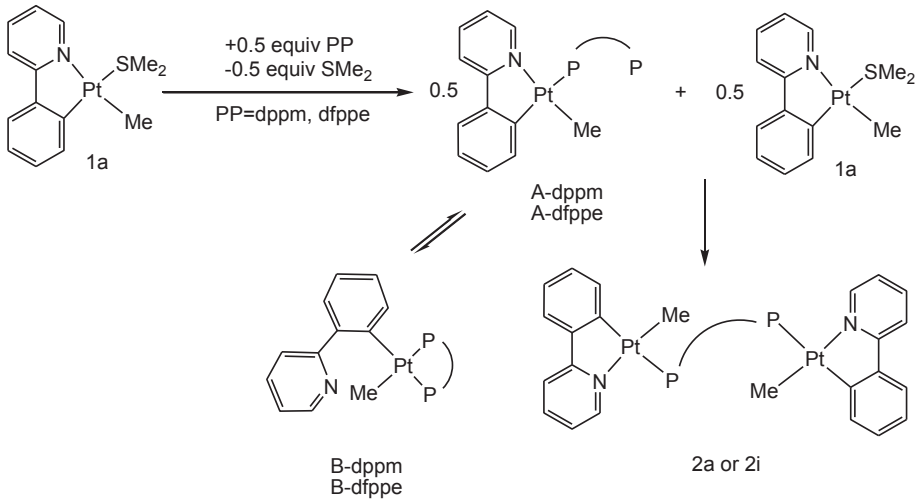


Fig. 4. DFT-calculated structures of (a) [PtMe(κ^2-ppy)(κ^1-dppm)] (isomer **A**), (b) [PtMe(κ^1-ppy)(κ^2-dppm)] (isomer **B**), (c) [PtMe(κ^2-ppy)(κ^1-dfppe)] (isomer **A**), (d) [PtMe(κ^1-ppy)(κ^2-dfppe)] (isomer **B**).



Scheme 2. Suggested mechanism for formation of diplatinum(II) complexes.

smaller than that of **3a** and equal to 3.813 and 3.830 eV, respectively. The highest occupied molecular orbital of **4d** is essentially the d_z^2 orbital of Pt atom with small contribution of ppy ligand and the LUMO of this complex is manly localized on dfppe ligand. The HOMO and LUMO of complex **2i** can also be ascribed as combination of Pt d_z^2 + ppy and dfppe ligand, respectively.

Table 3 shows the atomic charges of the platinum center for the complexes shown in Fig. 5, obtained from the natural bond orbital (NBO) analysis [32]. The calculated charge on the Pt atom of **A**-dppm and **A**-dfppe complexes are less positive than that for complex **1a**, which is the result of charge transfer from platinum to P atom in forming complexes **A**-dppm and **A**-dfppe (Table 3). As is clear from Table 3, the positive charge on the platinum atom in the complex **A**-dfppe (0.113) is higher than that on the platinum atom in the complex **A**-dppm (0.096). This higher positive charge on the platinum atom in the complex **A**-dfppe, which means lower electron density at the platinum center, is due to the presence of electron-withdrawing fluoroaryl ligands.

Also, the Pt charge in isomers **B** (i.e. **B**-dppm and **B**-dfppe) is negative in comparison with the positive charge on Pt atom of isomers **A** (i.e. **A**-dppm and **A**-dfppe), which is probably the result of the coordination of the more electronegative nitrogen atom of CN ligands to Pt center of isomers **A**.

6. Conclusion

We have now extended the cyclometalated platinum(II) complexes containing deprotonated 2-phenylpyridine or benzo[h] quinoline to synthesis unknown examples of square planar platinum(II) complexes containing bridging dfppe ligands as illustrated by the structures of complexes **2i**–**l** (Scheme 1, Fig. 1). These

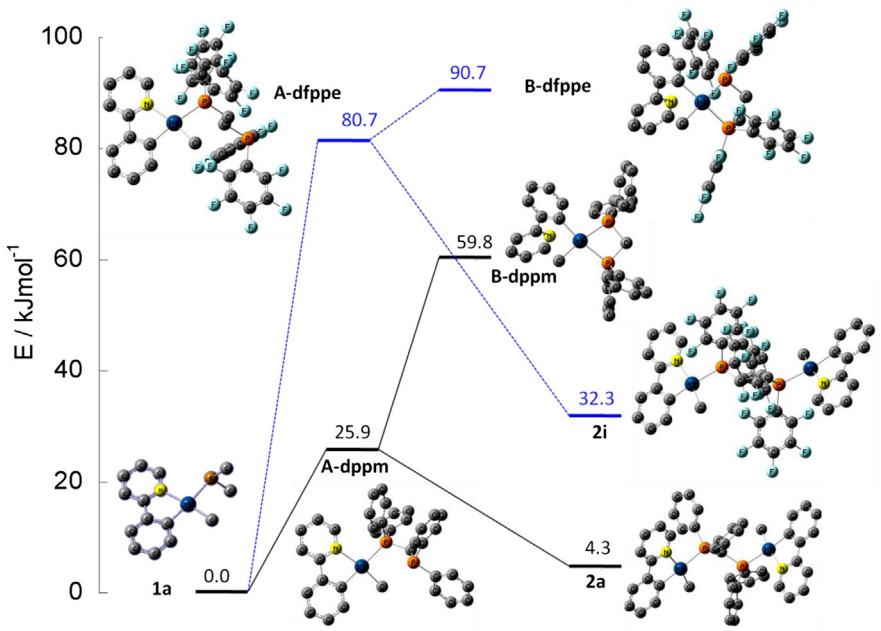


Fig. 5. Calculated structures and energies (kJ mol^{-1}) of intermediates and compounds in the reaction of **1a** with dppm or dfppe in acetone solution. Energies are with respect to **1a** and free molecules of SMe_2 and PP are included in the related compounds.

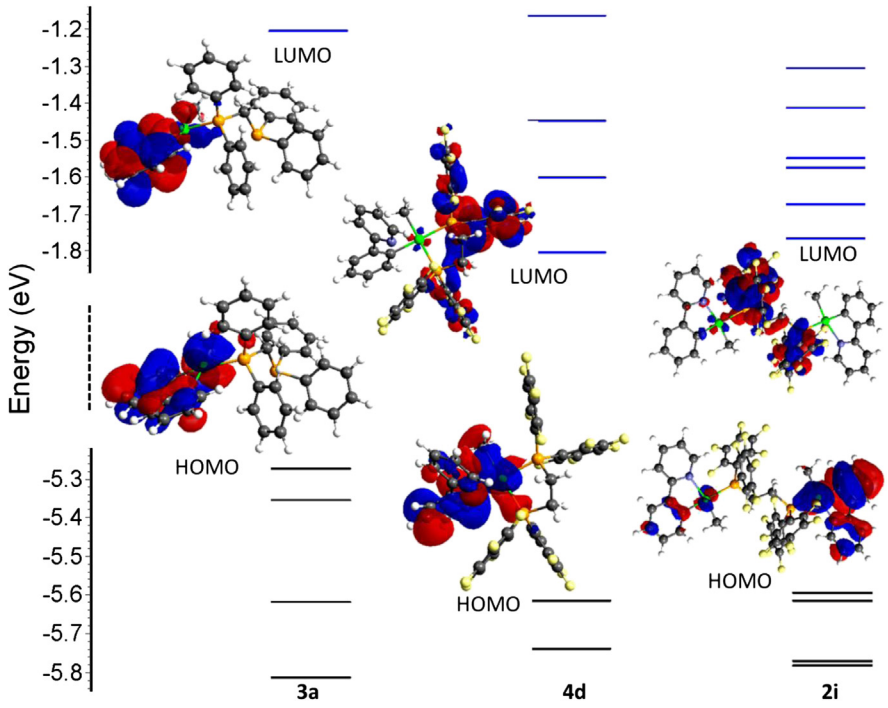


Fig. 6. Qualitative frontier molecular orbitals for complexes **3a**, **4d** and **2i**.

Table 2
Energies (eV) of the relevant frontier orbitals of selected complexes.

	Orbital	*E* (eV)
3a	HOMO	−5.276
	LUMO	−1.207
4d	HOMO	−5.617
	LUMO	−1.804
2i	HOMO	−5.597
	LUMO	−1.767

dimeric complexes are synthesized according to Scheme 1 in a 1:0.5 M ratio of Pt precursor and dfppe ligand.

In the synthesis of monomeric complexes, there are two potentially bidentate ligands (i.e. CN and PP) and one of them must be monodentate because the platinum(II) center prefers square-planar stereochemistry. There is a fine balance such that the complexes with PP = dppe and dfppe prefer the isomeric form **B** (with chelating PP and CN as C-ligated with the dangling N atom) whereas the complexes with PP = dppm prefer the form **A** (in which CN acts as chelating ligand and dppm is monodentate). In particular, in the case of dfppe, the reaction of complexes **1** in molar ratio of 1:1 gave either **B** (only when R = Me and CN = ppy) or dimer **2** (with 0.5 equiv of the unreacted dfppe). The reported dimeric species containing dfppe as bridging ligand are the first examples of platinum(II) complexes (Scheme 1) because the tendency for chelation of dfppe is strong in square planar platinum complexes and the formation of complexes with bridging dfppe is unusual.

Table 3
NPA charges on Pt atoms of the complexes presented in Fig. 5.

1a	A-dppm	A-dfppe	B-dppm	B-dfppe	**2a**	**2i**
0.156	0.096	0.113	−0.113	−0.095	0.122	0.088

Acknowledgments

The support of the Shiraz University Research Councils is acknowledged. We are grateful to Dr. F. Niroomand Hosseini for valuable assistance and many good suggestions.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.01.008.

References

[1] S.M. Nabavizadeh, H. Amini, H.R. Shahsavari, M. Namdar, M. Rashidi, R. Kia, B. Hemmateenejad, M. Nekoeinia, A. Ariafard, F.N. Hosseini, Organometallics 30 (2011) 1466–1477.
[2] M. Ghedini, T. Pugliese, M. La Deda, N. Godbert, I. Aiello, M. Amati, S. Belviso, F. Lelj, G. Accorsi, F. Barigelletti, Dalton Trans. (2008) 4303–4318.
[3] N. Ghavale, A. Wadawale, S. Dey, V.K. Jain, J. Organomet. Chem. 695 (2010) 1237–1245.
[4] S.K. Yen, D.J. Young, H.V. Huynh, L.L. Koh, T.S.A. Hor, Chem. Commun. (2009) 6831–6833.
[5] C. Anderson, M. Crespo, J. Morris, J.M. Tanski, J. Organomet. Chem. 691 (2006) 5635–5641.
[6] A. Chakraborty, J.C. Deaton, A. Haefele, F.N. Castellano, Organometallics 32 (2013) 3819–3829.
[7] C.-J. Lin, Y.-H. Liu, S.-M. Peng, J.-S. Yang, J. Phys. Chem. B 116 (2012) 8222–8232.
[8] A. Santoro, A.C. Whitwood, J.G. Williams, V.N. Kozhevnikov, D.W. Bruce, Chem. Mater. 21 (2009) 3871–3882.
[9] H.-Y. Hsieh, C.-H. Lin, G.-M. Tu, Y. Chi, G.-H. Lee, Inorg. Chim. Acta 362 (2009) 4734–4739.
[10] A. Bossi, A.F. Rausch, M.J. Leitl, R. Czerwieniec, M.T. Whited, P.I. Djurovich, H. Yersin, M.E. Thompson, Inorg. Chem. 52 (2013) 12403–12415.
[11] J.R. Berenguer, E. Lalinde, M.T. Moreno, S. Sánchez, J. Torroba, Inorg. Chem. 51 (2012) 11665–11679.
[12] M.F. Ernst, D.M. Roddick, Inorg. Chem. 28 (1989) 1624–1627.
[13] E.L. Diz, A. Neels, H. Stoeckli-Evans, G. Süss-Fink, Polyhedron 20 (2001) 2771–2780.
[14] R.H. Heyn, C.H. Görbitz, Organometallics 21 (2002) 2781–2784.
[15] G. Suardi, B.P. Cleary, S.B. Duckett, C. Sleigh, M. Rau, E.W. Reed, J.A.B. Lohman, R. Eisenberg, J. Am. Chem. Soc. 119 (1997) 7716–7725.

[16] C. Crotti, E. Farnetti, T. Celestino, M. Stener, S. Fontana, Organometallics 23 (2004) 5219–5225.
[17] T. Korenaga, K. Abe, A. Ko, R. Maenishi, T. Sakai, Organometallics 29 (2010) 4025–4035.
[18] M.G. Haghighi, M. Rashidi, S.M. Nabavizadeh, S. Jamali, R.J. Puddephatt, Dalton Trans. 39 (2010) 11396–11402.
[19] S.M. Nabavizadeh, M.D. Aseman, B. Ghaffari, M. Rashidi, F.N. Hosseini, G. Azimi, J. Organomet. Chem. 715 (2012) 73–81.
[20] S.M. Nabavizadeh, M.G. Haghighi, A.R. Esmaeilbeig, F. Raoof, Z. Mandegani, S. Jamali, M. Rashidi, R.J. Puddephatt, Organometallics 29 (2010) 4893–4899.
[21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A.S. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN 03, Revision B03, Gaussian, Inc, Pittsburgh PA, 2003.
[22] A.D. Becke, J. Chem. Phys. 98 (1993) 5648–5652.
[23] B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chem. Phys. Lett. 157 (1989) 200–206.
[24] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785–788.
[25] W.R. Wadt, P.J. Hay, J. Chem. Phys. 82 (1985) 284–298.
[26] R.L. Cook, J.G. Morse, Inorg. Chem. 21 (1982) 4103–4105.
[27] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270–283.
[28] L.E. Roy, P.J. Hay, R.L. Martin, J. Chem. Theory Comput. 4 (2008) 1029–1031.
[29] S. Jamali, R. Czerwieniec, R. Kia, Z. Jamshidi, M. Zabele, Dalton Trans. 40 (2011) 9123–9130.
[30] R. Puddephatt, Chem. Soc. Rev. 12 (1983) 99–127.
[31] B. Chaudret, B. Delavaux, R. Poilblanc, Coord. Chem. Rev. 86 (1988) 191–243.
[32] E. Glendening, A. Reed, J. Carpenter, F. Weinhold, NBO Version 3.1, Gaussian, Inc., Wallingford, CT, 2004 included in Gaussian 03.