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# Bite-angle bending as a key for understanding group-10 metal reactivity of $d^{10}$ -[M(NHC)<sub>2</sub>] complexes with sterically modest NHC ligands†‡

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Synthesis, characterization and investigations on the reactivity of the novel metal basic, yet isolable 14 VE NHC-complexes [M<sup>0</sup>(iPr<sub>2</sub>Im)<sub>2</sub>] (M = Pd **3**, Pt **4**; iPr<sub>2</sub>Im = 1,3-di-isopropyl-imidazolin-2-ylidene; VE = valence electron; NHC = N-heterocyclic carbene) is reported and compared to the chemistry of the corresponding nickel complex. Quantum chemical analyses reveal that differences in the reactivity of group 10 NHC complexes are caused by differences in the rigidity and thus activation strain associated with bending the corresponding  $d^{10}$ -[M(NHC)<sub>2</sub>] fragments during reaction. These results should have implications for the understanding of the fundamental steps in catalytic cycles, in which such complex fragments are employed.

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## Introduction

Transition metal-mediated activation and functionalization of element–element bonds is a vital area of homogeneous catalysis research. For low-valent, electron-rich transition metal complexes, bond activation is by and large achieved by either  $\sigma$ -bond metathesis or oxidative addition to a metal center, and especially complexes of  $d^8$  transition metals play a crucial role in this chemistry aiming at catalysis.<sup>1,2</sup> In the last two decades, N-heterocyclic carbenes (NHCs) have emerged as one of the most important classes of spectator ligands in organometallic chemistry.<sup>3</sup> Due to their better  $\sigma$ -donor capabilities compared to tertiary phosphines, the employment of NHCs in transition metal complexes can create more electron-rich metal centers. Complexes stabilized with NHCs are expected to exceed the activity of related phosphine compounds for many applications, and NHC complexes of noble metals have already large impact in the field of catalysis.<sup>3</sup> The isolation of unsaturated, metal basic complexes, such as 14 VE (valence electron) species  $d^{10}$ -[ML<sub>2</sub>] or synthons thereof, is highly desirable for investigations

concerning the reactivity of NHC complexes and of elementary steps in catalytic cycles as well as for their use in catalysis.

Over the last years we have explored the manifold chemistry of the {Ni(iPr<sub>2</sub>Im)<sub>2</sub>} complex fragment (iPr<sub>2</sub>Im = 1,3-di-isopropyl-imidazolin-2-ylidene), as provided by dinuclear [Ni<sub>2</sub>(iPr<sub>2</sub>Im)<sub>4</sub>(COD)] (COD = 1,5-cyclooctadiene) or mononuclear [Ni(iPr<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)] (see Scheme 1), in stoichiometric and catalytic reactions.<sup>4</sup> In course of these studies we became more and more interested in synthesizing precursors for [M<sup>0</sup>(iPr<sub>2</sub>Im)<sub>2</sub>] (M = Pd, Pt; see Scheme 1), either complexes [M<sup>0</sup>(iPr<sub>2</sub>Im)<sub>2</sub>] themselves or suitable synthons of them. For M = Ni, a two coordinate complex [M(NHC)<sub>2</sub>] of iPr<sub>2</sub>Im is currently unknown.<sup>5</sup> Investigations on isolated palladium(0) and especially on platinum(0) complexes bearing two NHC ligands are scarce and mainly involve NHCs with sterically demanding nitrogen substituents.<sup>6,7</sup> For palladium, two major pathways for the synthesis of complexes [M(NHC)<sub>2</sub>] have been established: (i) ligand substitution at [Pd(P(*o*Tol)<sub>3</sub>)<sub>2</sub>] (*o*Tol = 2-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>) developed by Herrmann *et al.*<sup>6a</sup> and (ii) ligand substitution at dimeric [(Pd( $\eta^3$ -C<sub>4</sub>H<sub>7</sub>)Cl)<sub>2</sub>] in the presence of sodium dimethylmalonate, developed by Caddick and Cloke *et al.*<sup>6b</sup> The latter

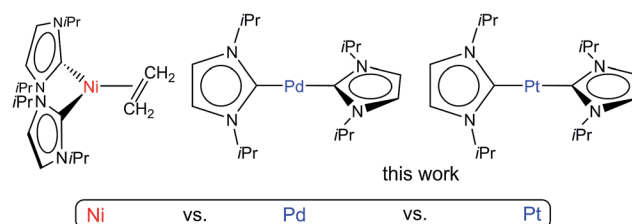
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‡ Dedicated to Prof. Dr. Reinhold Tacke on the occasion of his 65th birthday.



Scheme 1 {M(iPr<sub>2</sub>Im)<sub>2</sub>}-precursors: [Ni(iPr<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)] **A**, [Pd(iPr<sub>2</sub>Im)<sub>2</sub>] and [Pt(iPr<sub>2</sub>Im)<sub>2</sub>].



procedure does not require the unappealing synthesis of the  $[\text{Pd}(\text{P}\{\text{oTol}\}_3)_2]$  precursor,<sup>8</sup> but the stoichiometry has to be controlled carefully due to equilibration in solution, since NHC dissociation from palladium seems to be more facile than generally envisioned.<sup>6c</sup> However, using these methods, complexes such as  $[\text{Pd}(\text{Dipp}_2\text{Im})_2]$  (Dipp = 2,6-diisopropylphenyl),  $[\text{Pd}(\text{Mes}_2\text{Im})_2]$  (Mes = 2,4,6-trimethylphenyl),  $[\text{Pd}(t\text{Bu}_2\text{Im})_2]$ ,  $[\text{Pd}(\text{Ad}_2\text{Im})_2]$  (Ad = adamantyl) and of other NHCs with sterically demanding substituents at nitrogen have been prepared.<sup>6</sup> Furthermore, synthesis of  $[\text{Pd}(\text{Me}_2\text{Im})_2]$  via potassium reduction of  $[\text{Pd}(\text{Me}_2\text{Im})_2\text{Cl}_2]$  and the characterization of this complex including X-ray analysis has been described lately.<sup>6f</sup> In course of these studies, it turned out that complexes of the type  $[\text{Pd}(\text{NHC})_2]$  are extremely air sensitive and form isolable peroxy or peroxocarbonate complexes. Isolation of  $[\text{Pd}(\text{iPr}_2\text{Im})_2]$  has been claimed twice in the literature,<sup>6a,j</sup> but the NMR data provided are in neither case in accordance with a  $D_{2d}$  or  $D_{2h}$  type structure of this complex.

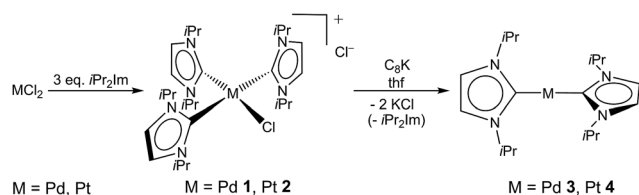
The chemistry of isolated complexes  $[\text{Pt}(\text{NHC})_2]$  is virtually unexplored.<sup>7</sup> Arduengo *et al.*<sup>7a</sup> and Nolan *et al.*<sup>7c</sup> described the synthesis of  $[\text{Pt}(\text{Mes}_2\text{Im})_2]$  and  $[\text{Pt}(\text{Dipp}_2\text{Im})_2]$  starting from the NHC and  $[\text{Pt}(\text{COD})_2]$  or  $[\text{Pt}(\text{COD})(\text{Me})_2]$ , respectively. Intra-molecular C–H activation of the ligand was observed for  $[\text{Pt}(\text{Mes}_2\text{Im})_2]$  in the latter case.<sup>7c</sup> This procedure seems to be further limited since the use of  $t\text{Bu}_2\text{Im}$  leads to formation of  $[\text{Pt}(t\text{Bu}_2\text{Im})(t\text{Bu}_2\text{Im})'(\text{H})(\text{Me})_2]$  (l' denotes coordination at the backbone as an "abnormal" NHC). Additionally, Braunschweig *et al.* reported the synthesis of  $[\text{Pt}(\text{SIMes})_2]$  (SIMes = bis(mesityl)imidazolidin-2-ylidene) via ligand exchange at  $[\text{Pt}(\text{PCy}_3)_2]$ , whereas the same reaction with  $t\text{Bu}_2\text{Im}$  led to mixed substituted  $[\text{Pt}(t\text{Bu}_2\text{Im})(\text{PCy}_3)_2]$ .<sup>7d</sup>

Herein, we report the synthesis, spectroscopic and chemical characterization, and quantum chemical analysis of the complexes  $[\text{Pd}(\text{iPr}_2\text{Im})_2]$  (3) and  $[\text{Pt}(\text{iPr}_2\text{Im})_2]$  (4).

## Results and discussion

### Synthesis and characterization of $[\text{M}^0(\text{iPr}_2\text{Im})_2]$ (M = Pd, Pt)

All attempts to isolate the complexes  $[\text{M}^0(\text{iPr}_2\text{Im})_2]$  (M = Pd, Pt) bearing NHC ligands with modest steric demand by the methods introduced above failed in our hands. However, we have found that complexes  $[\text{M}(\text{iPr}_2\text{Im})_3\text{Cl}]^+\text{Cl}^-$  (M = Pd 1, Pt 2; see Scheme 2) are suitable precursors for the synthesis of 3 and 4. Complexes 1 and 2 have been prepared by the reaction of the metal halides  $\text{MCl}_2$  and three equivalents (or an excess) of the NHC (see Scheme 2).<sup>9</sup> The use of  $\text{K}_2[\text{PtCl}_4]$  instead of  $\text{PtCl}_2$  as platinum source also leads selectively to  $[\text{Pt}(\text{iPr}_2\text{Im})_3\text{Cl}]^+\text{Cl}^-$  (2).



Scheme 2 Synthesis of  $[\text{M}(\text{iPr}_2\text{Im})_3\text{Cl}]^+\text{Cl}^-$  (M = Pd 1, Pt 2) and  $[\text{M}(\text{iPr}_2\text{Im})_2]$  (M = Pd 3, Pt 4).

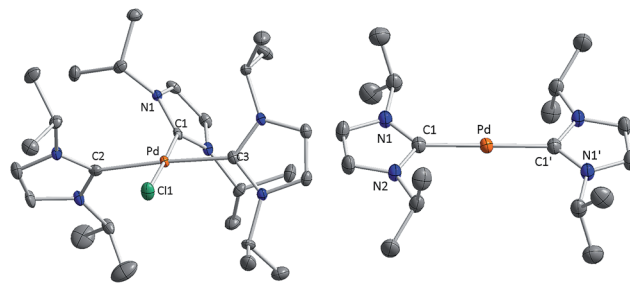


Fig. 1 X-ray crystal structure of the cation of  $[\text{Pd}(\text{iPr}_2\text{Im})_3\text{Cl}]^+\text{Cl}^-$  (1; left) and of  $[\text{Pd}(\text{iPr}_2\text{Im})_2]$  (3; right) in the solid state (ellipsoids set at 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg.) for  $[\text{Pd}(\text{iPr}_2\text{Im})_3\text{Cl}]^+$ : Pd–Cl1 2.3553(9), Pd–C1 2.0181(34), Pd–C2 2.0590(35), Pd–C3 2.0474(30); Cl1–Pd–C1 178.169(95), C2–Pd–C3 175.967(140). Selected bond lengths (Å) for 1: Pd–C1 2.0231 (18).

In some instances the formation of the imidazolium salt  $\text{iPr}_2\text{Im} \cdot \text{HCl}$  as a side product was detected for this reaction. The imidazolium salt and complexes 1 and 2, respectively, are difficult to separate, since these compounds reveal similar solubility in common organic solvents. The NMR spectra of 1 and 2 are those typically observed for a T-shaped alignment of three  $\text{iPr}_2\text{Im}$  ligands and a X-ray analysis of 1 confirms the square planar structure with a T-shaped, propeller-like alignment of the three NHCs ligands of the 16 VE cation (see Fig. 1).

The reduction of 1 and 2 with potassium graphite leads in good yields to the two-coordinated complexes  $[\text{Pd}(\text{iPr}_2\text{Im})_2]$  (3) and  $[\text{Pt}(\text{iPr}_2\text{Im})_2]$  (4) (see Scheme 2), which were isolated as orange (3) or yellow (4) solids. The release of one equivalent  $\text{iPr}_2\text{Im}$  as well as the presence of minor amounts of  $\text{iPr}_2\text{Im} \cdot \text{HCl}$  does not affect the reaction, since 3 and 4 do not react with additional  $\text{iPr}_2\text{Im}$  to afford  $[\text{M}(\text{iPr}_2\text{Im})_3]$ . For nickel, we have shown earlier that threefold coordination is feasible, as exemplified by the synthesis of  $[\text{Ni}(\text{Me}_2\text{Im})_3]$  from the reaction of  $[\text{Ni}(\text{COD})_2]$ ,<sup>4c</sup> and we have also proof for the existence of  $[\text{Ni}(\text{iPr}_2\text{Im})_3]$ . For both, 3 and 4, the analytical data are in agreement with a coordination of the metal with two NHC ligands as proposed in Scheme 2. The  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra reveal one set of signals for the ligands of each complex comprising a doublet for the isopropyl methyl protons (3: 1.34 ppm, 4: 1.33 ppm), a septet for the isopropyl methine protons (3: 6.03 ppm, 4: 6.26 ppm), and a singlet for the olefinic protons of the backbone (3: 6.46 ppm, 4: 6.40 ppm) in the  $^1\text{H}$  NMR spectrum. The  $^{195}\text{Pt}$  NMR spectrum of 4 shows a resonance at  $\delta = -5943$  ppm, which is close to  $^{195}\text{Pt}$  NMR shifts reported for other  $[\text{PtL}_2]$  complexes ( $[\text{Pt}(\text{PCy}_3)_2]$ :  $-6501$  ppm,  $[\text{Pt}(\text{SIMes})(\text{PCy}_3)]$ :  $-6151$  ppm,  $[\text{Pt}(t\text{Bu}_2\text{Im})(\text{PCy}_3)]$ :  $-6156$  ppm,  $[\text{Pt}(\text{SIMes})_2]$ :  $-5462$  ppm vs.  $[\text{Pt}(\text{PPh}_3)_3]$ :  $-4583$  ppm).<sup>7a,d,10</sup>

Single crystals of  $[\text{Pd}(\text{iPr}_2\text{Im})_2]$  (3) suitable for X-ray diffraction have been obtained via slow diffusion of the solvent from a saturated solution of 3 in diethyl ether. The compound crystallizes in the space group  $P2_1/c$  with the palladium atom located on a crystallographically imposed inversion center.

Both imidazole rings of 3 are coplanar arranged, which leads to a  $D_{2h}$  symmetric compound with Pd–C bond lengths of 2.0231(18) Å (Fig. 1). However, for steric reasons, a  $D_{2d}$



symmetric structure with staggered NHC ligands should be expected. A search on all currently known X-ray crystal structures of  $d^{10}$ -[M(NHC)<sub>2</sub>] complexes reveal that the dihedral angles between the NHC nitrogen and NHC carbene carbon atoms increases for bulky substituents.<sup>5a,6,7,11</sup> Calculations on [M(H<sub>2</sub>Im)<sub>2</sub>] presented earlier<sup>12</sup> predict a D<sub>2d</sub> type structure also for sterically less demanding NHCs. However, calculations on [M(iPr<sub>2</sub>Im)<sub>2</sub>] (M = Ni, Pd, Pt) performed at BP86/def2-TZVPP level (see ESI†) reveal a shallow potential for the rotation of the NHC ligands and differences in energy between a D<sub>2d</sub> and D<sub>2h</sub> type structure below 5 kJ mol<sup>-1</sup> in favor of a staggered alignment. Thus, we attribute the reason for experimentally observed D<sub>2h</sub> type symmetry of **3** to packing forces.

### Reactivity of [Pt(iPr<sub>2</sub>Im)<sub>2</sub>] (**4**)

We reported earlier stable NHC nickel  $\eta^2$ -olefin,  $\eta^2$ -alkyne, and  $\eta^2$ -ketone complexes [Ni(iPr<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -C<sub>2</sub>R<sub>4</sub>)], [Ni(iPr<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -C<sub>2</sub>R<sub>2</sub>)], and [Ni(iPr<sub>2</sub>Im)( $\eta^2$ -CO{-O=CR<sup>1</sup>R<sup>2</sup>})].<sup>4</sup> Due to the fact that complexes **3** and **4** did not react with additional NHC in solution, we became interested to investigate reactions of these two-coordinated complexes with  $\pi$ -acceptor ligands such as olefins, alkynes and ketones. In stark contrast to [Ni(iPr<sub>2</sub>Im)<sub>2</sub>], its Pd congener **3** merely shows weak interactions with ethylene giving [Pd(iPr<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)] (**5**), which is very unstable even under an atmosphere of the olefin (see ESI†). However, if a solution of [Pt(iPr<sub>2</sub>Im)<sub>2</sub>] (**4**) is pressurized with 3 bars ethylene, [Pt(iPr<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)] (**6**) is formed in quantitative yield and remains stable under an ethylene atmosphere (Scheme 3). This compound reveals one set of resonances for the NHC ligand (in C<sub>6</sub>D<sub>6</sub> at 1.04, 5.48, 6.47 ppm), substantially shifted from the signals of **4** (1.33, 6.26, 6.40 ppm; see Fig. 2). More significantly, resonances of the  $\eta^2$ -coordinated ethylene ligand were detected at 1.99 ppm with a <sup>195</sup>Pt-coupling constant <sup>2</sup>J<sub>PtH</sub> of 54.7 Hz in the <sup>1</sup>H NMR spectrum and at 13.3 ppm (<sup>1</sup>J<sub>PtC</sub> = 253.8 Hz) in the <sup>13</sup>C NMR spectrum of **6**. If the ethylene pressure is reduced, complex **4** reforms in quantitative yield. This cycle can be

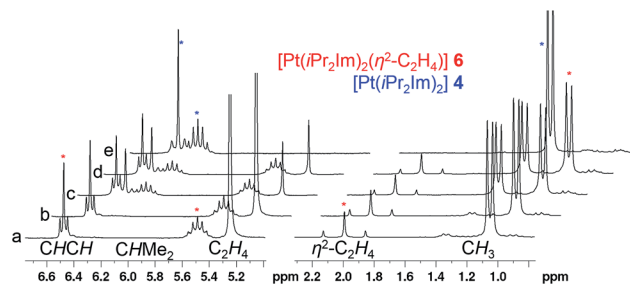


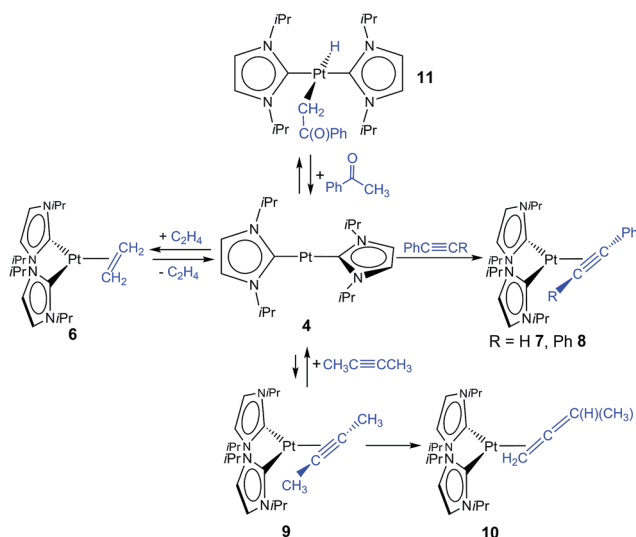
Fig. 2 <sup>1</sup>H NMR of [Pt(iPr<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -C<sub>2</sub>H<sub>4</sub>)] **6** in C<sub>6</sub>D<sub>6</sub>: (a) sample of [Pt(iPr<sub>2</sub>Im)<sub>2</sub>] **4** after pressurizing with ethylene to give **6**, (b) same sample after 14 d (revealing the stability of the complex in solution), (c) same sample after replacing the ethylene atmosphere with argon (revealing that **4** was formed from **6** after ethylene has been partially removed), (d) same sample after 5 h at room temperature; (e) sample after removal of all volatile material and addition of fresh C<sub>6</sub>D<sub>6</sub> (= complex **4**).

repeated for several times without any loss of complex **4**. To our surprise, no reaction has been observed between **4** and more electron rich alkenes such as 1,5-cyclooctadiene or cyclooctene.

Accordingly, we were interested in the reactivity of complex **4** with respect to different alkynes such as phenyl and diphenyl acetylene, and 2-butyne (see Scheme 3). For nickel, we reported earlier the formation of stable nickel alkyne complexes [Ni(iPr<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -RC≡CR')].<sup>4a,c</sup> The reaction of phenyl acetylene and diphenyl acetylene with **4** afforded the alkyne complexes [Pt(iPr<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -HC≡CPh)] (**7**) and [Pt(iPr<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -PhC≡CPh)] (**8**) as the main products.

If 2-butyne is used for the reaction with **4**, quantitative conversion cannot be observed (Scheme 3). For the reaction of **4** and 2-butyne in an equimolar stoichiometry an equilibrium was reached that contains approximately 33% of the reaction product [Pt(iPr<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -MeC≡CMe)] (**9**) and 66% of the starting material [Pt(iPr<sub>2</sub>Im)<sub>2</sub>] (**4**). After prolonged standing in solution the isomerization of the 2-butyne ligand to an 1,2-butadiene (allene) ligand in the coordination sphere of platinum can be observed. Complex [Pt(iPr<sub>2</sub>Im)<sub>2</sub>( $\eta^2$ -H<sub>2</sub>C=C=C(H)Me)] (**10**) has been identified in solution in a mixture containing **4**, **9**, and **10** using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The resonances of the allene ligand for complex **10** were detected at 2.06 ppm (CH<sub>2</sub>), 6.02 ppm (CH) and 2.57 ppm (CH<sub>3</sub>) in the proton NMR spectrum with <sup>195</sup>Pt coupling to the CH<sub>2</sub> (<sup>2</sup>J<sub>PtH</sub> = 54.2 Hz) and CH (<sup>3</sup>J<sub>PtH</sub> = 47.0 Hz) signals, which is in agreement with an 1,2-coordination of the allene ligand as proposed in Scheme 3. The assignment of the resonances was confirmed by a <sup>1</sup>H-<sup>1</sup>H COSY experiment (see ESI†). The allene carbon atoms attached to platinum reveal resonances at -4.3 ppm and 158.4 ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. Complex **10** represents to our knowledge one of the few examples of an allene complex formed from the isomerization of an alkyne ligand in the coordination sphere of platinum.<sup>13</sup>

The reaction of **4** with acetophenone leads to an equilibrium between **4** and the  $\alpha$ -C-H bond activation product *trans*-[Pt(iPr<sub>2</sub>Im)<sub>2</sub>(H)(-CH<sub>2</sub>-C(O)Ph)] (**11**) (Scheme 3). Other likely reaction products such as a  $\eta^2$ -ketone complex or a complex resulting from *ortho*-metallation of the phenyl ring of the



Scheme 3 Reactions of [Pt(iPr<sub>2</sub>Im)<sub>2</sub>] (**4**) with  $\pi$ -acceptor ligands.



ketone have not been observed. The formation of **11** is quantitative if an excess of acetophenone is used at elevated temperatures (80 °C). The hydride ligand of **11** gives rise to a resonance at  $-10.11$  ppm ( $^1J_{\text{PtH}} = 1133.3$  Hz) and the metal bound methylene unit to a resonance at 3.22 ppm ( $^2J_{\text{PtH}} = 70.6$  Hz) in the proton NMR spectrum. Notably, benzene solutions of compound **11** are not stable and slowly decompose to starting material. We have demonstrated earlier that  $[\text{Ni}_2(\text{iPr}_2\text{Im})_4(\text{COD})]$  reacts with ketones to give stable and thermally robust nickel ketone complexes  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-}\{\text{O}=\text{C}\text{R}^1\text{R}^2\})]$  (see Fig. 3). DFT calculations (BP86/def2-TZVPP) on the relative stabilities of complexes  $[\text{M}(\text{iPr}_2\text{Im})_2(\eta^2\text{-}\{\text{O}=\text{C}\text{PhMe}\})]$  and *trans*- $[\text{M}(\text{iPr}_2\text{Im})_2(\text{H})(-\text{CH}_2\text{-C}(\text{O})\text{Ph})]$  for nickel and platinum (see Fig. 3 and ESI†) reveal a significant stabilization ( $-41.7$  kJ mol $^{-1}$ ) of the platinum complex **11** with respect to an  $\eta^2$ -ketone complex. A platinum  $\eta^2$ -ketone complex would be unstable with respect to cleavage into **4** and acetophenone, according to these calculations. For nickel, the DFT calculations reveal the opposite trend, *i.e.* the  $\eta^2$ -ketone complex is the global minimum, stabilized by  $-57.1$  kJ mol $^{-1}$  with respect to  $[\text{Ni}(\text{iPr}_2\text{Im})_2]$  and acetophenone and  $-60.9$  kJ mol $^{-1}$  with respect to  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\text{H})(-\text{CH}_2\text{-C}(\text{O})\text{Ph})]$  (see Fig. 3).

Catalytic C–H bond activation reactions at positions  $\alpha$  to the carbonyl group are currently of interest because they provide atom economic entries into the  $\alpha$ -functionalization of organic carbonyl compounds.<sup>14</sup> Compound **11** represents to our knowledge the first well characterized example of an  $\alpha$ -CH bond activation product of a ketone at platinum (0) to give the corresponding hydrido  $\alpha$ -keto-alkyl complex.<sup>15,16</sup> Further investigations on the reactivity of **11** are underway.

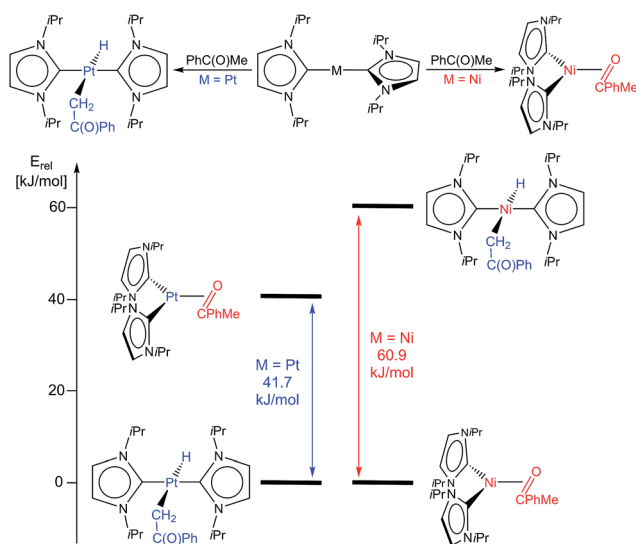


Fig. 3 Top: contrary reactivity of  $[\text{Ni}(\text{iPr}_2\text{Im})_2]$  (as provided by  $[\text{Ni}_2(\text{iPr}_2\text{Im})_4(\text{COD})]$  and  $[\text{Pt}(\text{iPr}_2\text{Im})_2]$  towards acetophenone: Formation of the  $\eta^2$ -ketone complexes  $[\text{Ni}(\text{iPr}_2\text{Im})_2(\eta^2\text{-}\{\text{O}=\text{C}\text{PhMe}\})]$  for nickel and the  $\alpha$ -C–H bond activation product *trans*- $[\text{Pt}(\text{iPr}_2\text{Im})_2(\text{H})(-\text{CH}_2\text{-C}(\text{O})\text{Ph})]$  (**11**) for platinum. Bottom: results of DFT calculations (BP86/def2-TZVPP; see ESI†) on the relative stabilities of the  $\alpha$ -C–H bond activation products *trans*- $[\text{M}(\text{iPr}_2\text{Im})_2(\text{H})(-\text{CH}_2\text{-C}(\text{O})\text{Ph})]$  and  $\eta^2$ -ketone complexes  $[\text{M}(\text{iPr}_2\text{Im})_2(\eta^2\text{-}\{\text{O}=\text{C}\text{PhR}^2\})]$  for  $\text{M} = \text{Pt}$  (left side) and  $\text{M} = \text{Ni}$  (right side).

## Calculations on model systems

In order to understand the reasons for these differences in nickel, palladium and platinum chemistry, we have performed calculations on model systems  $[\text{M}(\text{H}_2\text{Im})_2(\eta^2\text{-C}_2\text{H}_4)]$  using the ADF program at the ZORA-BLYP/TZ2P level.<sup>17</sup> The calculated bond energies for the ethylene ligand dissociation in complexes  $[\text{M}(\text{H}_2\text{Im})_2(\eta^2\text{-C}_2\text{H}_4)]$  into  $[\text{M}(\text{H}_2\text{Im})_2]$  and ethylene clearly reveal the trend observed experimentally, *i.e.* that ethylene binds significantly more strongly to the nickel than to the palladium and platinum complexes:  $-104.2$  kJ mol $^{-1}$  (Ni),  $-25.0$  kJ mol $^{-1}$  (Pd) and  $-20.5$  kJ mol $^{-1}$  (Pt; see Table 1, Fig. 4 and ESI†).

We have analyzed the metal–ethylene bonding in  $[\text{M}(\text{H}_2\text{Im})_2(\eta^2\text{-C}_2\text{H}_4)]$  complexes using the activation strain model and ADF's energy decomposition analysis (EDA).<sup>17b,c</sup> Thus, the bond energy  $\Delta E$  is decomposed into the strain energy  $\Delta E_{\text{strain}}$  associated with the deformation of the fragments  $[\text{M}(\text{H}_2\text{Im})_2]$  and  $\text{C}_2\text{H}_4$  during the bond formation reaction plus the mutual interaction  $\Delta E_{\text{int}}$  between the deformed fragments. The latter is further decomposed into classical electrostatic attraction  $\Delta V_{\text{elstat}}$ , steric (Pauli) repulsion  $\Delta E_{\text{Pauli}}$ , and bonding orbital interactions  $\Delta E_{\text{oi}}$ .<sup>17b</sup> The results are given in Table 1. Note that the orbital interaction  $\Delta E_{\text{oi}}$  is least stabilizing for the 4d metal palladium:  $-415.1$  kJ mol $^{-1}$  (Ni);  $-334.5$  kJ mol $^{-1}$  (Pd);  $-523.4$  kJ mol $^{-1}$  (Pt).<sup>18</sup> Our analyses show that, in line with the work of Dewar, Chatt and Duncanson,<sup>19</sup> the bonding can be described as ligand to metal  $\sigma$ -donation and a  $\pi$ -back donation from the metal to the unoccupied  $\pi^*$ -orbital of ethylene. In agreement with studies presented earlier,<sup>20,21</sup> the orbital interaction of  $\pi$ -symmetry has for each metal a larger impact compared to the orbital interaction of  $\sigma$ -symmetry and increases for  $[\text{M}(\text{H}_2\text{Im})_2(\eta^2\text{-C}_2\text{H}_4)]$  from Pd ( $-249.6$  kJ mol $^{-1}$ ,

Table 1 Energy decomposition analysis [kJ mol $^{-1}$ ] of the metal–ethylene bond in  $[\text{M}(\text{H}_2\text{Im})_2(\eta^2\text{-C}_2\text{H}_4)]$  complexes<sup>a</sup>

M	$\Delta V_{\text{elstat}}$	$\Delta E_{\text{Pauli}}$	$\Delta E_{\text{steric}}$	$\Delta E_{\text{oi}}$	$\Delta E_{\text{int}}$	$\Delta E_{\text{strain}}$	$\Delta E$
Ni	-543.5	+741.8	+198.4	-417.1	-245.0	+140.8	-104.2
Pd	-521.3	+695.7	+174.4	-334.5	-184.2	+159.2	-25.0
Pt	-773.2	+1038.2	+265.0	-523.4	-284.1	+263.6	-20.5

<sup>a</sup> Computed at ZORA-BLYP/TZ2P; for full data, see Table S1;  $\Delta E = \Delta E_{\text{strain}} + \Delta E_{\text{int}}$ ;  $\Delta E_{\text{int}} = \Delta V_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{oi}} + \Delta E_{\text{disp}}$  (see text and ref. 17).

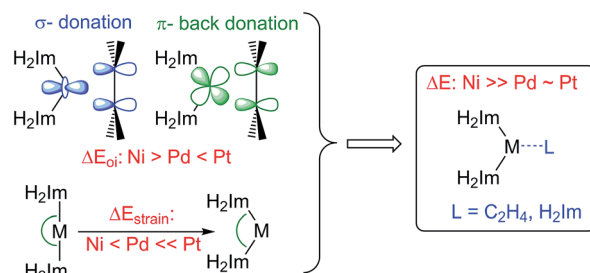


Fig. 4 Analysis of metal–ethylene bonding in  $[\text{M}(\text{H}_2\text{Im})_2(\eta^2\text{-C}_2\text{H}_4)]$  complexes using the activation strain model and ADF's energy decomposition analysis (EDA) (see text).



75% of  $\Delta E_{\text{oi}}$ ) to Ni ( $-317.4 \text{ kJ mol}^{-1}$ , 76%) to Pt ( $-369.0 \text{ kJ mol}^{-1}$ , 71%). The interaction energy  $\Delta E_{\text{int}}$  follows this trend in  $\Delta E_{\text{oi}}$ :  $-245.0 \text{ kJ mol}^{-1}$  (Ni);  $-184.2 \text{ kJ mol}^{-1}$  (Pd);  $-284.1 \text{ kJ mol}^{-1}$  (Pt).

We find that the overall bond energies  $\Delta E$  is significantly weakened for palladium ( $-25.0 \text{ kJ mol}^{-1}$ ) and platinum ( $-20.5 \text{ kJ mol}^{-1}$ ) compared to nickel ( $-104.2 \text{ kJ mol}^{-1}$ ). The main reason lies in an increase in strain energy  $\Delta E_{\text{strain}}$  going from Ni to Pd and especially Pt. This strain  $\Delta E_{\text{strain}}$  appears to stem mainly from the bending of the  $[\text{M}(\text{H}_2\text{Im})_2]$  fragment from its preferred linear geometry towards smaller L–M–L bite angles. While the deformation energies of the ethylene ligand (for Pd:  $+42.2$ ; Ni:  $+48.6$  and Pt:  $+74.3 \text{ kJ mol}^{-1}$ ) depend on the strength of  $\pi$ -back donation, the origin of the deformation energies for the  $[\text{M}(\text{H}_2\text{Im})_2]$  fragment are more subtle and increase from Ni ( $+92.2 \text{ kJ mol}^{-1}$ ) to Pd ( $+117.0 \text{ kJ mol}^{-1}$ ) to Pt ( $+189.3 \text{ kJ mol}^{-1}$ ). Bending of linear  $[\text{M}(\text{H}_2\text{Im})_2]$  is costly in energy, and it has to be emphasized that this energy loss upon bending is by and large an electronic effect. In addition to steric factors, it has been shown earlier that fourteen-electron dicoordinate group-10 metal complexes  $\text{d}^{10}\text{-}[\text{ML}_2]$  adopt linear geometries mainly due to a significant destabilization of one of the occupied, in the linear case nonbonding d orbitals ( $\text{d}_{xz}$ ; for a schematic Walsh diagram see ESI†).<sup>22</sup> An alternative but, ultimately equivalent way of understanding the resistance of  $\text{d}^{10}\text{-}[\text{ML}_2]$  complexes to L–M–L bending is that such bending destabilizes the interaction  $\Delta E_{\text{int}}$  between ML and L through increasing Pauli repulsion between the ligands' lone-pair orbital lobes and a destabilization of the ML  $\text{d}_{z^2}$  hybrid orbital.<sup>22e</sup> For the good  $\sigma$ -donating NHC ligands, the  $\text{d}^{10}\text{-}[\text{ML}_2]$  bending strain is relatively high in the case of the noble metals Pd and Pt and – in combination with the weak orbital interaction  $\Delta E_{\text{oi}}$  term for Pd – is mainly responsible for the weak metal olefin bond. Note that NHC-coordinated palladium and platinum olefin complexes are known to be stable if one utilizes chelating bidentate NHC ligands, for which the linearization of the  $[\text{M}(\text{NHC})_2]$  moiety is not possible.<sup>23</sup> The importance of  $[\text{M}(\text{NHC})_2]$ -bending to this chemistry can also be illustrated with the aid of an analysis on the stability of the model complexes  $[\text{M}(\text{H}_2\text{Im})_3]$  with respect to a cleavage into  $[\text{M}(\text{H}_2\text{Im})_2]$  and  $\text{H}_2\text{Im}$  (Table 2). The deformation energies of the  $\text{H}_2\text{Im}$  ligand are small and lie between 1 and 3  $\text{kJ mol}^{-1}$  (for Pd:  $+1.0$ ; Pt:  $+1.9$  and Ni:  $+2.8 \text{ kJ mol}^{-1}$ ), while the strain energies  $\Delta E_{\text{strain}}$  for the  $[\text{M}(\text{H}_2\text{Im})_2]$  fragments are much higher and increase substantially going from Ni ( $+70.7 \text{ kJ mol}^{-1}$ ) to Pd ( $+90.5 \text{ kJ mol}^{-1}$ ) to Pt ( $+130.4 \text{ kJ mol}^{-1}$ ). Thus, the energy gain  $\Delta E_{\text{int}}$  obtained from the interaction of  $[\text{M}(\text{H}_2\text{Im})_2]$

with  $\text{H}_2\text{Im}$  is almost used up for palladium and platinum due to the L–M–L bending strain of  $[\text{M}(\text{H}_2\text{Im})_2]$ . As a result, we calculate a significant overall binding energy for Ni ( $-107.9 \text{ kJ mol}^{-1}$ ) and a much more reduced binding energy for the metals with larger radii Pd ( $-25.6$ ) and Pt ( $-26.5 \text{ kJ mol}^{-1}$ ).

Our DFT calculations show the same trend in bond energy  $\Delta E$  for the full complexes  $[\text{M}(\text{iPr}_2\text{Im})_2(\text{L})]$  as discussed above for the truncated models  $[\text{M}(\text{H}_2\text{Im})_2(\text{L})]$  (see ESI†). In agreement with the experiment, these calculations reveal that addition of another  $\text{iPr}_2\text{Im}$  ligand to  $[\text{M}(\text{iPr}_2\text{Im})_2]$  should be repulsive for palladium ( $+4.4 \text{ kJ mol}^{-1}$ ) and platinum ( $+13.1 \text{ kJ mol}^{-1}$ ). In addition, we calculated even smaller BDEs for 2-butyne complexes  $[\text{M}(\text{iPr}_2\text{Im})_2(\eta^2\text{-C}_2\text{Me}_2)]$  than for the ethylene complexes  $[\text{M}(\text{iPr}_2\text{Im})_2(\eta^2\text{-C}_2\text{H}_4)]$  of palladium and platinum.

## Conclusions

We have reported the synthesis, characterization and first investigations concerning the reactivity of the novel complexes  $[\text{M}^0(\text{iPr}_2\text{Im})_2]$  ( $\text{M} = \text{Pd}$  **3**,  $\text{Pt}$  **4**), stabilized with an NHC ligand of low steric demand. These complexes represent rare examples of metal basic, yet isolable 14 VE complexes of the type  $\text{d}^{10}\text{-}[\text{ML}_2]$ . Complexes **3** and **4** do not react with additional NHC and the reaction with selected  $\pi$ -acidic ligands leads in some cases, if at all, to  $\pi$ -complexes, which are much less stable compared to the corresponding nickel complexes. The reactions presented here are illustrative examples of the differences one can observe by changing the central atom in a complex going from a 3d metal to a 4d or 5d metal atom within the same ligand framework and clearly show that L–M–L bending strain of  $\text{d}^{10}\text{-}[\text{ML}_2]$  is a key to understand group 10 metal reactivity. This is a new appearance of the concept of bite-angle flexibility that was recently introduced in the context of metal-mediated C–H bond activation.<sup>22f</sup>

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M	$\Delta E_{\text{steric}}$	$\Delta E_{\text{oi}}$	$\Delta E_{\text{int}}$	$\Delta E_{\text{strain}}$	$\Delta E$
Ni	+123.4	–278.5	–181.3	+73.4	–107.9
Pd	+132.4	–224.7	–117.1	+91.5	–25.6
Pt	+225.8	–357.3	–158.8	+132.3	–26.5

<sup>a</sup> Computed at ZORA-BLYP/TZ2P; for full data, see Table S2;  $\Delta E = \Delta E_{\text{strain}} + \Delta E_{\text{int}}$ ;  $\Delta E_{\text{int}} = \Delta V_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{oi}} + \Delta E_{\text{disp}}$  (see text and ref. 17).



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