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NHC Complexes

Bis-NHC Chelate Complexes of Nickel(0) and Platinum(0)**

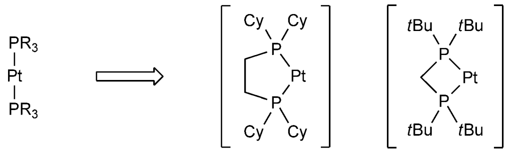
*Matthias Brendel, Carolin Braun, Frank Rominger, and Peter Hofmann**

Dedicated to the MPI für Kohlenforschung on the occasion of its centenary

Abstract: *For a long time d^{10}-ML_2 fragments have been known for their potential to activate unreactive bonds by oxidative addition. In the development of more active species, two approaches have proven successful: the use of strong σ-donating ligands leading to electron-rich metal centers and the employment of chelating ligands resulting in a bent coordination geometry. Combining these two strategies, we synthesized bis-NHC chelate complexes of nickel(0) and platinum(0). Bis(1,5-cyclooctadiene)nickel(0) and -platinum(0) react with bisimidazolium salts, deprotonated in situ at room temperature, to yield tetrahedral or trigonal-planar bis-NHC chelate olefin complexes. The synthesis and characterization of these complexes as well as a first example of C–C bond activation with these systems are reported. Due to the enforced cis arrangement of two NHCs, these compounds should open interesting perspectives for bond-activation chemistry and catalysis.*

Transition-metal-mediated activation and functionalization of C–H, C–C, and strong C–X bonds is a vital area of research in homogeneous catalysis. For low-valent, electron-rich complexes of late transition metals bond activation is mainly achieved by oxidative addition to the metal center.[1] Metal fragments isolobal to singlet methylene exhibit the ideal energetic and geometric characteristics crucial for the design of highly reactive systems.

In the 1970s Stone et al. observed completely different behavior for two nearly identical linear bisphosphine platinum(0) complexes **A** formed from appropriate precursor complexes (Scheme 1).[2] An MO analysis revealed that the frontier orbitals of d^{10}-ML_2 fragments substantially depend in terms of energy and hybridization on the L-M-L angle. In the case of linear complexes like **A**, the different reactivity can hence be explained by the fact that the steric bulk of the phosphines in the fragment limits the accessible degree of deviation from linearity during the oxidative addition step.[3]



A **B** **C**

Scheme 1. Bisphosphine platinum(0) systems active in bond-activation reactions (R = Me, Et; Cy = cyclohexyl).

Complexes with chelating bisphosphine ligands enforcing a bent coordination geometry show enhanced reactivity: The platinum(0) fragment **B** with bis(dicyclohexylphosphino)-ethane as the ligand, formed by reductive elimination of neopentane from the corresponding neopentylhydrido-platinum(II) complex (P-Pt-P angle of 87.2°), activates a large variety of C–H bonds.[4] With an even smaller bite angle of 74.7° the analogous bis(di-*tert*-butylphosphino)-methaneplatinum neopentyl hydride showed very unusual reactivity patterns, presumably via intermediate **C**.[5] In the reaction with tetramethylsilane both C–H and C–Si bonds are activated,[5a] and epoxides undergo unprecedented C–C bond activation forming 3-platinaoxetanes.[5c]

In the last two decades N-heterocyclic carbenes (NHCs) have emerged as one of the most important classes of spectator ligands in organometallic chemistry.[6] Due to their stronger σ-donor character compared to tertiary phosphines, the employment of NHCs can create more electron-rich metal centers. Thus, the activity of d^{10}-ML_2 fragments bearing NHCs is expected to exceed that of related phosphine complexes. NHCs are superior to phosphines in catalytic processes in which bond activation is followed by oxidation as the latter are prone to oxidation.[7]

The investigation of platinum(0) complexes bearing two NHCs is scarce.[8] The only example for bond-activation chemistry was reported by Nolan et al. for $Pt(IMes)_2$ (IMes = 1,3-dimesitylimidazol-2-ylidene), who observed intramolecular C–H activation of the ligand.[8d] Nickel(0) bis-NHC complexes are more established; they were found to be active in stoichiometric bond activations and as catalysts for cross-coupling reactions.[8a,b,9] Comprehensive studies were performed by Radius et al. using $[Ni_2(IiPr)_4(cod)]$ (cod = 1,5-cyclooctadiene; IiPr = 1,3-diisopropylimidazol-2-ylidene) as the precursor for various bond activations.[10]

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[*] M. Brendel, C. Braun, Dr. F. Rominger, Prof. Dr. P. Hofmann
Institute of Organic Chemistry
Ruprecht-Karls-University Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
E-mail: ph@oci.uni-heidelberg.de
Prof. Dr. P. Hofmann
Catalysis Research Laboratory (CaRLa)
Im Neuenheimer Feld 584, 69120 Heidelberg (Germany)

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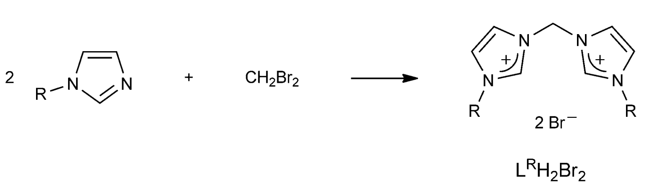
Based on the current state of research with respect to reactive d^{10}-ML_2 systems, it seemed challenging to synthesize compounds by employing chelating bis-NHC ligands that enforce a *cis* configuration at the metal center.[11] Already in the first application of NHC complexes in homogeneous catalysis, bis-NHC chelate complexes of palladium(II) were studied.[12a] Complexes bearing this type of ligand are now established for most late transition metals in all prevalent oxidation states.[12b] Bis-NHC chelate complexes are known for platinum(II) and platinum(IV) and were first studied by Strassner et al.[13] Nickel(II) complexes of these ligands were already investigated by the groups of Herrmann and Green fifteen years ago.[14] However, to the best of our knowledge, compounds of this type are unprecedented for platinum(0) and only three examples have been reported for nickel(0).[15,20]

In our study we employed the aryl-substituted bis-NHC L^{Dipp} (Dipp = 2,6-diisopropylphenyl) and the alkyl-substituted L^{tBu}. The bisimidazolium salts used as precursors are easily accessible by microwave-assisted S_N2 reactions of the corresponding imidazoles with dibromomethane (Scheme 2).



Scheme 2. Microwave-assisted synthesis of bisimidazolium salts used as precursors for the bis-NHC ligands employed in this study. R = Dipp: xylenes, 190°C, 2 h, 79%; R = *t*Bu: THF, 130°C, 5 h, 74%.

As the isolated biscarbenes are very sensitive towards air and not stable at room temperature, we chose to deprotonate the bisimidazolium salts in situ. When lithium hexamethyldisilazide (LiHMDS) serves as a base, lithium adducts are formed. The signals for their carbene carbon atoms in ^{13}C NMR spectra are shifted to higher field by $\Delta\delta = 8.2$ ppm (L^{Dipp}) and 2.8 ppm (L^{tBu}) compared to the free biscarbenes synthesized by deprotonation with KHMDS.

Addition of [Ni(cod)$_2$] to deprotonated $L^{Dipp}H_2Br_2$ in THF at room temperature immediately leads to a deep red solution (Scheme 3, see the Supporting Information (SI)). After removal of the volatiles in vacuo, a mixture of water and toluene is added to the crude product. It is important to add these solvents at the same time, as the product reacts with toluene in the presence of small amounts of remaining base to give a yet unidentified product. Water hydrolyzes the base and secures complete separation of the lithium bromide. The addition of water prior to toluene affects the yield adversely. Separation of the phases and washing of the product with hexane leads to the desired pure complex [L^{Dipp}Ni(η^4-cod)] (**1**) in 50% yield.

The orange compound **1** is extremely oxygen-sensitive in solution and as a solid. In dichloromethane or chloroform the complex is not stable. The ^1H NMR spectrum of **1** shows a singlet for the methylene bridge of the bis-NHC ligand, which means that boat-to-boat inversion of the six-membered nickelacycle occurs rapidly at room temperature. The olefinic protons of the cod ligand give rise to one singlet with an integral of four protons at $\delta = 3.66$ ppm, indicating η^4-coordination. Red single crystals suitable for X-ray diffraction analysis were grown by layering a THF solution of **1** with pentane. The solid-state structure has a distorted tetrahedral geometry with a bite angle of the bis-NHC ligand of 93.8° (Figure 1). This is significantly smaller than that in the Radius system, in which the two mono-NHCs span an angle of 118.1°.[10a]

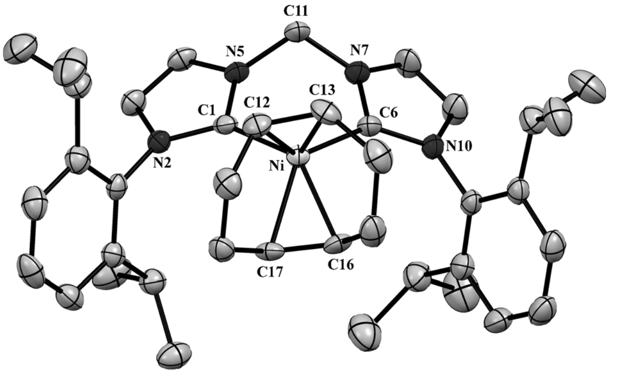
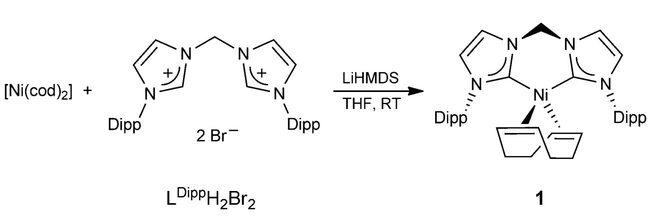
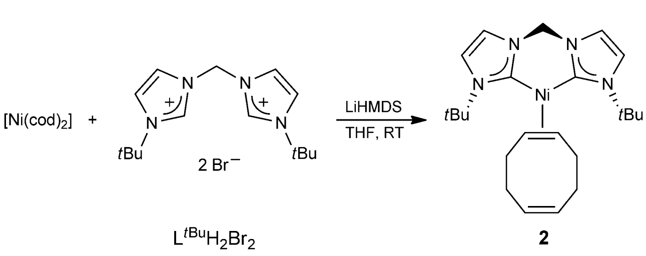


Figure 1. Solid-state structure of **1**.[16a] Ellipsoids at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–C1 1.938(3), Ni–C6 1.953(3), Ni–C12 2.136(3), Ni–C13 2.114(3), Ni–C16 2.065(3), Ni–C17 2.075(3), C12–C13 1.383(5), C16–C17 1.355(5); C1-Ni-C6 93.83(13).

In an analogous manner the alkyl-substituted bisimidazolium salt $L^{tBu}H_2Br_2$ can be used to synthesize the nickel(0) complex **2** (Scheme 4, see SI). The synthesis and purification of **2** are similar to that of **1** but using diethyl ether instead of toluene. Complex **2** is isolated in 34% yield as an orange solid. The ^1H NMR spectrum differs significantly from that of **1**. Because the ligand's methylene bridge shows two doublets, boat-to-boat inversion of the nickelacycle does not occur at



Scheme 3. Synthesis of [L^{Dipp}Ni(η^4-cod)] (**1**).



Scheme 4. Synthesis of [L^{tBu}Ni(η^2-cod)] (**2**).

room temperature due to the steric bulk of the *tert*-butyl groups. Surprisingly, the chemical shifts for the two double bonds of the olefin ligand differ distinctly. One multiplet at $\delta = 2.92$ ppm corresponds to a coordinated double bond. The second signal appears in the range of a noncoordinated olefin at $\delta = 6.08$ ppm. This indicates η^2-coordination, which is unusual for this diene.[17]

When a solution of **2** in hexane was cooled to −30 °C, orange single crystals were obtained. The solid-state structure of **2** confirms the η^2-coordination of cod, which adopts a chair conformation (Figure 2). Several attempts at locating potential energy minima with DFT calculations for a tetrahedral complex with η^4-coordination were unsuccessful and led to η^2-coordination instead. The steric demand of the two bis-NHC ligands differs greatly. The area close to the metal center is far more crowded in the complex bearing L^{tBu} due to the *tert*-butyl group, and the usual chelating coordination of the cod ligand in **2** is impeded. The bite angle of the chelate ligand is 91.0° and therefore smaller than in **1**.

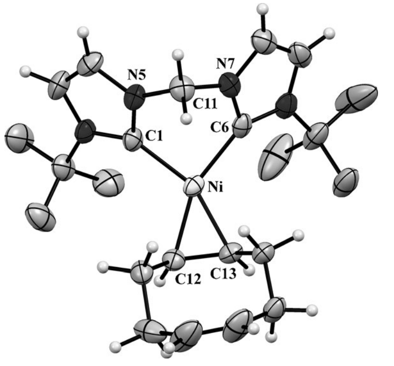
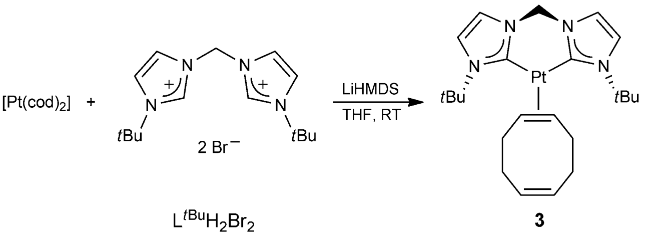


Figure 2. Solid-state structure of **2**.[16b] Ellipsoids at the 50% probability level; hydrogen atoms of the *tert*-butyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni–C1 1.905(3), Ni–C6 1.921(4), Ni–C12 1.951(4), Ni–C13 1.955(3), C12–C13 1.426(5); C1-Ni-C6 91.00(16).

The approach is not limited to nickel compounds. Addition of $[Pt(cod)_2]$ to deprotonated $L^{tBu}H_2Br_2$ leads to the platinum(0) complex **3** (Scheme 5, see SI). In a procedure analogous to that used for the nickel complexes the pale yellow compound is isolated in a yield of 56%. The ^{1}H NMR spectrum is similar to that of **2**. Recognizable by two doublets for the protons of the methylene bridge, boat-to-boat inversion of the platinacycle does not occur at room temperature. The platinum atom couples with one of these protons ($^4J(Pt,H) = 14.6$ Hz), which is identified by NOESY as the one oriented towards the metal center. As in the nickel complex, two multiplets at $\delta = 2.08$ and 5.60 ppm for the olefinic double bonds suggest η^2-coordination of the cod ligand.



Scheme 5. Synthesis of $[L^{tBu}Pt(\eta^2\text{-cod})]$ (**3**).

Slow evaporation of a solution of **3** in diethyl ether solution provided yellow single crystals (Figure 3). The unit cell contains two independent molecules with η^2-coordinated cod in a twist and a chair conformation, respectively. The bite angles of the chelate ligand are 84.6° and 83.7°, just between the bite angles in the bisphosphine systems **B** and **C** described above.

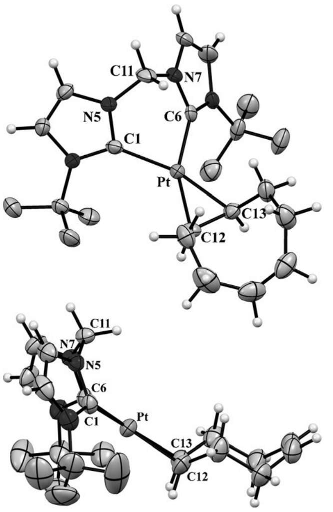
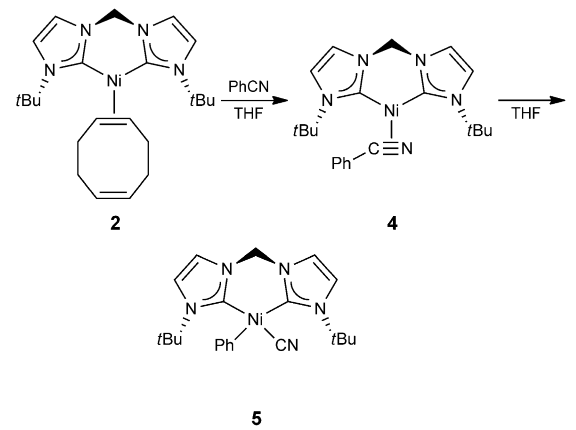


Figure 3. Solid-state structures of **3**.[16c] Ellipsoids at the 50% probability level; hydrogen atoms of the *tert*-butyl groups are omitted for clarity. The unit cell contains two independent molecules with different conformations of the cod ligand. Selected bond lengths [Å] and angles [°]: twist (top): Pt–C1 2.049(6), Pt–C6 2.052(6), Pt–C12 2.077(6), Pt–C13 2.091(6), C12–C13 1.468(8); C1-Pt-C6 84.6(2); chair (bottom): Pt–C1 2.065(7), Pt–C6 2.052(6), Pt–C12 2.072(6), Pt–C13 2.082(7), C12–C13 1.461(11); C1-Pt-C6 83.7(2).

First studies testing the reactivity of these new complexes look promising. The cod ligand is readily replaced by electron-deficient olefins (see SI). To corroborate that the compounds are precursors for reactive 14 valence electron fragments, nickel complex **2** is reacted with benzonitrile (Scheme 6, see SI). The nitrile replaces the weakly coordinated olefin rapidly at room temperature forming the η^2-nitrile complex **4**. The side-on coordination results in a large shift of the singlet for the nitrile carbon atom to lower field in the ^{13}C NMR spectrum compared to the free nitrile ($\delta =$ 173 ppm vs. 119 ppm) and a lower stretching frequency $\nu_{C\equiv N}$ in the IR spectrum ($\tilde{\nu} = 1713$ cm^{-1} vs. 2235 cm^{-1}). At room temperature the substrate is slowly activated via oxidative addition. The resulting nickel(II) complex **5** has a stretching frequency of $\tilde{\nu} = 2101$ cm^{-1} for the cyano ligand. After five hours at 65 °C in [D$_8$]THF the conversion is complete.

Due to the alkyl substitution, complex **2** is more electron-rich than **1** and therefore undergoes C−C activation significantly faster. In contrast to the bis(diisopropylphosphino)ethane nickel(0) fragment with a similar bite angle,[18] the



Scheme 6. C–C bond activation of benzonitrile.

activation is irreversible with the bis-NHC system. When solutions of the intermediate and the product of the C–C activation were slowly cooled from 65 °C to room temperature single crystals formed which confirm the postulated structures (Figure 4). In the context of investigations directed towards acrylate synthesis from ethylene and carbon dioxide performed in our laboratories,[19] the bis-NHC chelate nickel(0) complex **2** is found to be more efficient than bisphosphine ligand systems in the formation of nickelalactones, which is the first step of the catalytic cycle.

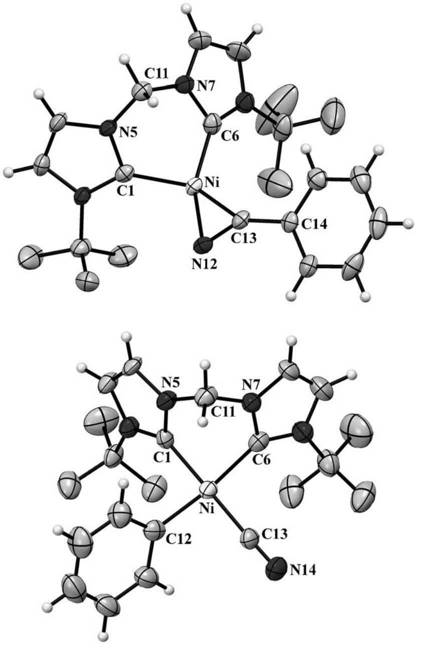


Figure 4. Solid-state structures of **4** and **5** (see SI). Ellipsoids at the 50% probability level; hydrogen atoms of the *tert*-butyl groups and noncoordinated THF molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: **4** (top): Ni–C1 1.932(5), Ni–C6 1.893(5), Ni–N12 1.924(4), Ni–C13 1.841(5), N12–C13 1.234(6); C1-Ni-C6 91.7(2), N12-C13-C14 134.2(5); **5** (bottom): Ni–C1 1.896(6), Ni–C6 1.937(6), Ni–C12 1.931(7), Ni–C13 1.856(7), C13–N14 1.159(8); C1-Ni-C6 86.7(2), C12-Ni-C13 88.2(3).

In summary, we have developed a short and efficient approach to new bis-NHC chelate complexes of nickel(0) and platinum(0). These types of compounds complete the range of accessible complexes in the search for active d^{10}-ML$_2$ systems for stoichiometric bond activations and new homogeneous catalysts for, for example, cross-coupling reactions, hydrocyanation, and selective functionalizations of unreactive molecules.

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[16] Intensity data were collected on a Bruker APEX II diffractometer at 200(2) K, Mo Kα irradiation, $\lambda = 0.71073$ Å, 0.5° ω-scans covered the complete reciprocal space, empirical absorption correction with SADABS,[16d] structures refined against F^2 with a full-matrix least-squares algorithm using SHELXL,[16e] hydrogen atoms were treated using appropriate riding models except noted otherwise. a) CCDC 983372 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, $0.13 \times 0.12 \times 0.12$ mm^3, monoclinic, $P2_1/n$, $a = 14.881(1)$, $b = 15.636(1)$, $c = 16.040(1)$ Å, $\beta = 115.206(2)°$, $V = 3376.8(4)$ Å^3, $Z = 4$, $\rho = 1.250$ g cm^{-3}, $\theta_{\max} = 25.74°$, mean redundancy 5.58, 36656 reflections measured, 6434 unique ($R_{\mathrm{int}} = 0.0609$), $\mu = 0.61$ mm^{-1}, $T_{\min} = 0.85$, $T_{\max} = 0.94$, 421 parameters refined, olefinic hydrogen atoms were refined isotropically, $R1(F) = 0.047$, $wR(F^2) = 0.111$ for observed reflections, residual electron density -0.39 to 0.66 e Å^{-3}; b) CCDC 991443 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, $0.24 \times 0.23 \times 0.17$ mm^3, orthorhombic, $Fdd2$, $a = 53.344(2)$, $b = 11.8460(5)$, $c = 14.7010(6)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 9289.7(7)$ Å^3, $Z = 16$, $\rho = 1.222$ g cm^{-3}, $\theta_{\max} = 26.76°$, mean redundancy 9.06, 23913 reflections measured, 4324 unique ($R_{\mathrm{int}} = 0.0422$), $\mu = 0.85$ mm^{-1}, $T_{\min} = 0.82$, $T_{\max} = 0.89$, 267 parameters refined, olefinic hydrogen atoms H12 and H13 were refined isotropically, $R1(F) = 0.032$, $wR(F^2) = 0.071$ for observed reflections, residual electron density -0.24 to 0.29 e Å^{-3}; c) CCDC 983373 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, $0.14 \times 0.11 \times 0.11$ mm^3, monoclinic, $P2_1/n$, $a = 13.3820(4)$, $b = 18.1117(6)$, $c = 19.4204(7)$ Å, $\beta = 100.7324(9)°$, $V = 4624.6(3)$ Å^3, $Z = 8$, $\rho = 1.619$ g cm^{-3}, $\theta_{\max} = 25.048°$, mean redundancy 3.52, 29254 reflections measured, 8187 unique ($R_{\mathrm{int}} = 0.0355$), $\mu = 6.08$ mm^{-1}, $T_{\min} = 0.54$, $T_{\max} = 0.62$, 517 parameters refined, $R1(F) = 0.034$, $wR(F^2) = 0.079$ for observed reflections, residual electron density -1.33 to 2.75 e Å^{-3}. d) G. M. Sheldrick, Bruker Analytical X-ray-Division, Madison, Wisconsin, **2012**; e) G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112 – 122.

[17] For the only examples of the nickel triad, see a) A. Gunale, H. Pritzkow, W. Siebert, D. Steiner, A. Berndt, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1111 – 1113; *Angew. Chem.* **1995**, *107*, 1194 – 1196; b) M. E. Tauchert, T. R. Kaiser, A. P. V. Göthlich, F. Rominger, D. C. M. Warth, P. Hofmann, *ChemCatChem* **2010**, *2*, 674 – 682.

[18] J. J. Garcia, W. D. Jones, *Organometallics* **2000**, *19*, 5544 – 5545.

[19] M. L. Lejkowski, R. Lindner, T. Kageyama, G. É. Bódizs, P. N. Plessow, I. B. Müller, A. Schäfer, F. Rominger, P. Hofmann, C. Futter, S. A. Schunk, M. Limbach, *Chem. Eur. J.* **2012**, *18*, 14017 – 14025.

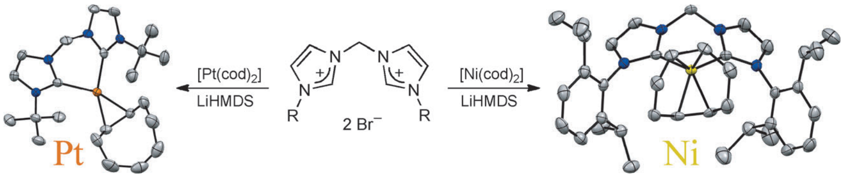
[20] Note added in proof: For the first fully characterized bis-NHC nickel(0) chelate complex, see N. D. Harrold, G. L. Hillhouse, *Chem. Sci.* **2013**, *4*, 4011 – 4015.

Communications

NHC Complexes

M. Brendel, C. Braun, F. Rominger,
P. Hofmann* ________ ▮▮▮▮–▮▮▮▮

Bis-NHC Chelate Complexes of Nickel(0) and Platinum(0)



Adjusting the bite: d^{10}-ML$_2$ fragments are well known to activate unreactive bonds by oxidative addition. Starting from lithium carbene adducts formed in situ, nickel and platinum olefin complexes of such fragments bearing chelating bis-NHCs were synthesized. Combining these strong electron donors with the bent coordination geometry enforced by chelation opens interesting perspectives for bond-activation chemistry and catalysis.