EurJIC
European Journal of Inorganic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

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To be cited as: Eur. J. Inorg. Chem. 10.1002/ejic.201600925

Link to VoR: http://dx.doi.org/10.1002/ejic.201600925

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C–N Bond Coupling Reactions of Ammonia with Acetone Promoted by Iridium and Rhodium Complexes: Experimental and DFT Studies

M. Pilar Betoré,[a] Pilar García-Orduña,[a] Fernando J. Lahoz,[a] Miguel A. Casado,*[a] Víctor Polo,*[b] Luis A. Oro[a,c]

Abstract: Treatment of acetone solutions of the known chlorido-bridged complexes [{M(μ-Cl)(cod)}$_2$] (M = Ir, Rh; cod = 1,5-cyclooctadiene) under an ammonia atmosphere afforded the cationic complexes [M(cod)(κ*N*,κ*N*-NH$_2$–C(CH$_3$)$_2$–CH$_2$–C(CH$_3$)=NH)]Cl (M = Ir (**3**), Rh (**4**)). The molecular structures of **3** and **4** showed the formation of six-membered metallacycles due to the presence of a 4-imino-2-methylpentan-2-amino κ*N*,κ*N*-chelated ligand. Alternatively, the cations [M(cod)(NCCH$_3$)$_2$]BF$_4$ (M = Ir, Rh) reacted with gaseous ammonia at atmospheric pressure affording bis ammine complexes [M(cod)(NH$_3$)$_2$]BF$_4$ (M = Ir (**5**), Rh (**6**)), which were found to react with acetone forming cations [M(cod)(κ*N*,κ*N*-NH$_2$–C(CH$_3$)$_2$–CH$_2$–C(CH$_3$)=NH)]BF$_4$ (M = Ir (**7**), Rh (**8**)). DFT studies reveal that the transformation of **6** → **8** is mediated by NH$_3$ molecules acting as an external base. The reaction is triggered by deprotonation of an ammonia ligand forming a metal-amido intermediate which further transforms to an acetimino ligand *via* aldol condensation. The terminal methyl group of one acetimino ligand is deprotonated by NH$_3$ yielding an enamine ligand which can react with the imine ligand *via* concerted nucleophilic addition affording the metallacycle which is stabilized by protonation.

Introduction

The catalytic functionalization of ammonia promoted by late transition metal-based complexes is a topic of interest.[1] The main barrier to overcome such target is concerned with the high strength of the N–H bond of ammonia, which makes very difficult for the metals to fulfil its activation. Additionally, the high tendency of late transition metal complexes to bind ammonia forming stable Werner-like adducts often precludes the N–H activation of ammonia. However, the clever design of some ligand architectures has led to a rational N–H activation of ammonia, a required process to achieve its further functionalization. In this context Hartwig *et al*. reported in 2005 the oxidative addition of the N–H bond of ammonia to an iridium(I) complex stabilized by a pincer ligand with an alkyl-based, electron donating skeleton, forming a monomeric hydrido amido iridium(III) complex,[2] an approach further illustrated by a carbosilane pincer ligand in combination with iridium.[3] More recently the construction of non-innocent, polyfunctional ligands has allowed the heterolytic N–H activation of ammonia through metal-ligand cooperation.[4] It should be mentioned, however, that early metal-based complexes are much more active in the N–H activation of ammonia, which usually involves the formation or participation of parent amido and imido species.[5]

In this line, our ongoing research on N–H activation of ammonia mediated by iridium and rhodium complexes has made clear that the design of the organometallic precursors has a high impact in the ammonia activation processes. In this way we have shown that methoxo-bridged complexes of Ir^{I} and Rh^{I} leads to a facile heterolytic N–H scission of ammonia, yielding parent amido-bridged complexes,[6] a body of work that allowed us studying the unconventional reactivity of parent amido complexes of iridium and rhodium.[7] Furthermore, the choice of cationic complexes of the type [Ir(cod)(P–P)]$^+$ (P–P = bis(diphenylphosphane)ethane, bis(diphenylphosphane)propane, bis(diphenylphosphane)butane; cod = 1,5-cyclooctadiene) afforded the products of a formal oxidative addition of ammonia to iridium [{Ir(μ-NH$_2$)H(P–P)(NH$_3$)}$_2$]$^{+2}$.[8] One of the most pursued targets relies on C–N bond formation directly with ammonia,[9] a phenomenon often hampered by the intrinsic nature of the substrate. However, remarkable advances have been made in this context, where well designed late metal-based catalysts have been optimized to allow the catalytic C–N coupling between ammonia and a number of functionalized compounds such as alcohols,[10] alkynes,[11] ketones, amines[12] and allylic substrates[13] affording new *N*-containing functionalized compounds directly from ammonia.

In this contribution we found out that the known chlorido-bridged complexes [{M(μ-Cl)(cod)}$_2$] (M = Ir, Rh) react with gaseous ammonia in acetone affording "M(cod)" cations with a κ*N*,κ*N*-chelated 4-imino-2-methylpentan-2-amino molecule. In order to

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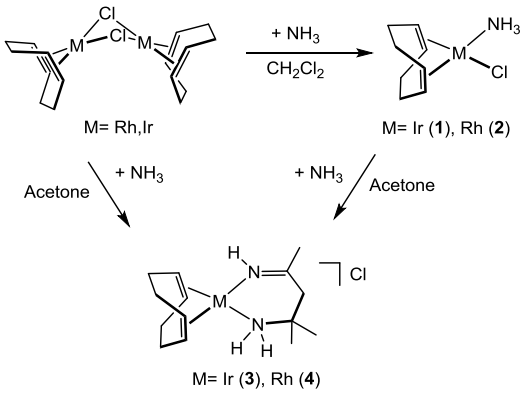
Supporting information for this article is given via a link at the end of the document. CCDC-1495850-1495852 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

gain more insights into the formation of C–N and C–C bonds mediated by transition metal complexes, a detailed mechanistic study combining experimental and computational methodologies has been conducted in this piece of work. Based on the experimental observations, a plausible reaction mechanism has been proposed at the DFT level, revealing the existence of unstable but accessible reaction intermediates, the role of the metallic centre or the ammonia N–H cleavage and C–N and C–C bond formations.

Results and Discussion

Exposure of dichloromethane solutions of the known chlorido-bridged complexes [{M(μ-Cl)(cod)}$_2$] (M = Ir, Rh; cod = 1,5-cyclooctadiene) to gaseous ammonia (2 bar) afforded mononuclear ammine complexes [MCl(cod)(NH$_3$)] (M = Ir (**1**), Rh[14] (**2**)) in good yields. Complexes **1** and **2** were sparingly soluble in organic solvents, a situation that did not allow their full characterization in solution. However the ^{1}H NMR spectra of **1**-**2** in CD_3CN showed a similar pattern, where the =CH protons of the diene were observed as broad signals at 3.74 ppm (**1**) and at 4.08 ppm (**2**), which indicates that fluxional processes are operating in solution at room temperature, if one takes into account that the complexes have a C_s symmetry (Scheme 1). Furthermore, the ammonia ligands gave rise sharp resonances in **1** and as a broad resonance in **2** (δ(^{1}H): 2.13 (**1**), 1.67 (**2**) ppm) in their respective ^{1}H NMR spectra. Additionally, mass spectrometry and microanalytical data of complexes **1** and **2** were consistent with the proposed formulation (See Experimental Section). In this line, the IR spectra of **1**-**2** showed strong absorptions around 3200 cm^{-1}, which confirmed the presence of an ammonia ligand in the complexes.[15] When attempting to obtain single crystals of **1** and **2** for a X-ray diffraction study, we found out that both complexes reacted with acetone affording new species further characterized as the mononuclear cationic complexes [M(cod)(κ*N*,κ*N*-NH$_2$–C(CH$_3$)$_2$–CH$_2$–C(CH$_3$)=NH)]Cl albeit in low yields (M = Ir (**3**, 35%); Rh (**4**, 40%)). The yields of the aforementioned reactions were substantially increased by reactions of complexes **1** and **2** with gaseous ammonia in acetone (M = Ir (**3**, 60%); Rh (**4**, 89%)) respectively, or alternatively by stirring acetone solutions of the chlorido-bridged complexes [{M(μ-Cl)(cod)}$_2$] (M = Ir, Rh) under an ammonia atmosphere (See the Experimental Section). It should be noted that ammonia and acetone are found to react by themselves affording acetimine, an unstable compound that after short periods of storage gives acetonine (2,2,4,4,6-pentamethyl-2,3,4,5-tetrahydropyrimidine).[16] While good quality single crystals of complex **3** were grown from a saturated solution in deuterated acetonitrile, single crystals of complex **4** were obtained from a saturated solution of the complex in acetone. The molecular structures of complexes **3** and **4** are shown in Figures 1 and 2, respectively, while relevant bond distances and angles are collected in Table 1.



Scheme 1. Synthesis of complexes **1**-**4**.

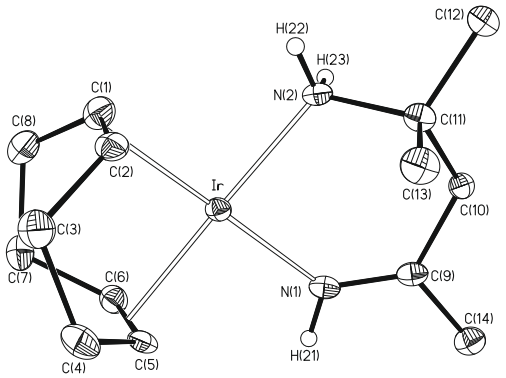


Figure 1. Molecular structure of complex **3**. The chloride anion has been omitted for clarity.

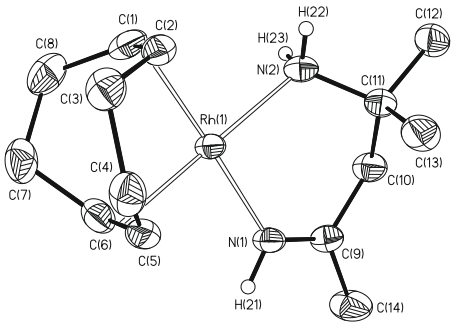


Figure 2. Molecular structure of complex **4**. The chloride anion has been omitted for clarity.

Table 1. Main distances (Å) and angles (°) of complexes **3** and **4**. (M = Ir, Rh).

	3	**4**	**4**
M–N1	2.055(3)	2.059(2)	2.062(2)
M–N2	2.111(3)	2.106(2)	2.109(2)
M–Ct1	2.007(4)	2.018(3)	2.022(3)
M–Ct2	2.001(3)	2.017(3)	2.022(3)

N1–C9	1.287(4)	1.271(4)	1.281(3)
N2–C11	1.495(4)	1.478(3)	1.489(3)
N1-M-N2	87.58(11)	89.86(9)	86.94(10)
N1-M-Ct1	178.17(12)	176.51(12)	178.82(11)
N1-M-Ct2	178.17(12)	91.32(12)	92.14(12)
N2-M-Ct1	93.06(12)	91.10(11)	93.23(11)
N2-M-Ct2	93.06(12)	176.60(12)	178.84(11)
Ct1-M-Ct2	87.86(14)	87.91(13)	87.71(13)

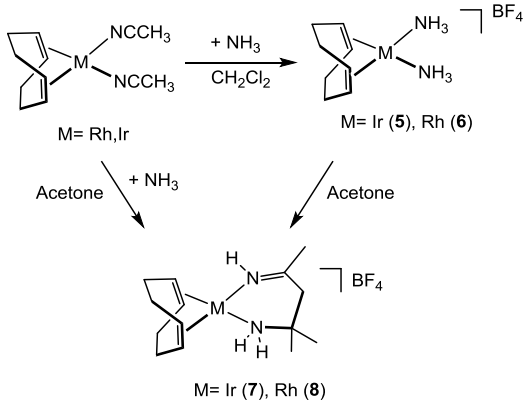
Ct(1) and Ct(2) represent the midpoints of the olefinic C(1)=C(2), and C(5)=C(6) bonds in both compexes, respectively.

Both mononuclear molecular structures share some common features although they differ in the crystal packing, as asymmetric unit of complex **4** contains two crystallographically independent but chemically equivalent molecules. Mean difference between both molecules of complex **4** concerns the metallacycle conformation (see below). The metal coordination sphere of **3** and **4** complexes exhibits a hardly distorted square planar geometry defined by the coordination of the cod ligand in its usual η^4-*C*=*C* mode and a 4-imino-2-methylpentan-2-amino newly formed molecule κ*N*,κ*N*-coordinated to the metal atom. The resultant six-membered M–N(1)–C(9)–C(10)–C(11)–N(2) (M = Ir, Rh) metallacycles adopt half chair conformations with similar deviations from the planarity (**3**: Q = 0.5445(2) Å, φ = 94.1(4)°, θ = 136.2(3)°, $^6H_5$ conformation; **4**: Q = 0.539(3) Å, φ = 59.7(3)°, θ = 123.2(3)°, $^6H_1$ conformation and Q = 0.539(3) Å, φ = –79.7(4)°, θ = 44.0(3)°, $^5H_6$ conformation)[17] Bond lenghts and angles describing the six-membered metallacycles are comparable to those observed in (κ*N*,κ*N*-NH_2–$C(CH_3)_2$–CH_2–$C(CH_3)$=NH) fragment in reported complexes containing ruthenium(II),[18] cobalt(III),[19] copper(II),[20,21] palladium(II),[22] nickel,[23] platinum(II),[24] rhodium(III)[25] and iridium(III).[26] The M–N(amino) bond lengths (M–N(2): 2.111(3) Å (**3**); 2.106(2) and 2.109(2) Å (**4**)) are slightly longer than those corresponding to the M–N(imino) (M–N(1) (2.055(3) Å (**3**); 2.059(2) and 2.062(2) Å(**4**)), a situation explained in terms of the hybridization of the nitrogen atoms. Hydrogen atoms of amino and imino groups are involved in N–H···Cl interactions with the chloride anion, stabilizing the solid state structure (see Supporting Information).

Cationic complexes **3** and **4** were found to be soluble in methanol and sparingly soluble in acetonitrile, which allowed us their characterization in solution. The ^{1}H NMR spectra of **3** and **4** in CD_3OD showed the =CH protons of the cod as sets of two broad signals around 4 ppm, a situation that fits with the C_s symmetry observed in the solid state for both cationic complexes. Moreover, the nitrogen-containing ligand was observed as sets of three sharp singlets for the methyl and the methylene fragments, although the amino and imino protons were not observed most probably as a consequence of proton exchange with the deuterated solvent. However when performing the ^{1}H NMR spectra of **3** and **4** in CD_3CN, the =NH fragments were observed at low field (δ 9.31 ppm (**3**); 8.65 ppm (**4**)) while the protons from the $–NH_2$ moiety were observed as sharp signals (δ 3.68 ppm (**3**), 2.03 ppm (**4**)). Additionally, mass spectrometry and microanalytical data of species **3** and **4** were consistent with the above proposed formulation (See Experimental Section); in this line, the IR spectra of the solids showed strong absorptions around 3000 cm^{-1}, which indicated the presence of nitrogen ligands in the complexes, and around 1600 cm^{-1} which indicated de presence of the C=N double bonds.

The low solubility of complexes **3**-**4** precluded a deep characterization in solution, which led us to prepare the analogous cationic complexes with a bulkier anion. In order to achieve this, we started from the known cationic solvate complexes $[M(cod)(NCCH_3)_2]BF_4$ (M = Ir, Rh) which were in turn prepared from the chlorido-bridged complexes $[\{M(\mu\text{-}Cl)(cod)\}_2]$ (M = Ir, Rh) and $AgBF_4$ in acetonitrile as microcrystalline yellow solids in excellent yields. Exposure of dichloromethane solutions of the cationic complexes $[M(cod)(NCCH_3)_2]BF_4$ (M = Ir, Rh) to gaseous ammonia (2 bar) rapidly afforded bright yellow solids in moderate yields which were further characterized as the mononuclear bis ammine complexes $[M(cod)(NH_3)_2]BF_4$ (M = Ir (**5**, 64%), Rh (**6**, 60%); Scheme 2). The ^{1}H NMR spectra of **5** and **6** in CD_3CN showed the resonances for the chemically equivalent =CH protons of cod as broad resonances centred at 3.75 ppm (**5**) and 4.02 ppm (**6**), while the ammonia ligands were observed as a broad resonances in both cases (δ 3.10 ppm (**5**); 1.92 ppm (**6**)). The $^{13}C\{^1H\}$-APT NMR spectra of **5** and **6** showed only two resonances for the carbon atoms of the cod ligands by virtue of the C_{2h} symmetry of the complexes; in this way, the =CH carbon atoms were observed as a singlet (δ 65.1 ppm) for **5** and a doublet (δ 81.3 ppm, $^1J_{Rh-C}$ = 13 Hz) for **6**. We were able to observe the ammonia ligand in the ^1H-^{15}N HMBC NMR spectrum of complex **6** ($\delta(^{15}N)$ 133.6 ppm), a value far more positive than those found in some ammine iridium(III) complexes.[8] Additionally, mass spectrometry and microanalytical data of species **5** and **6** were consistent with the above proposed formulation (See Experimental Section).

The treatment of cations **5** and **6** with acetone afforded bright yellow solids in good yields characterized as the cations $[M(cod)(\kappa N,\kappa N\text{-}NH_2\text{–}C(CH_3)_2\text{–}CH_2\text{–}C(CH_3)\text{=}NH)]BF_4$ (M = Ir (**7**), Rh (**8**)). It was experimentally verified that the yields were almost identical by stirring acetone solutions of the $[M(cod)(NCCH_3)_2]BF_4$ (M = Ir, Rh) under an ammonia atmosphere (Scheme 2).



Scheme 2. Synthesis of complexes **5**-**8**.

Complexes **7-8** were found to be quite soluble in several organic solvents, which allowed their full spectroscopic characterization in solution (See Experimental Section). The ^{1}H NMR spectra of **7** and **8** in CD_3CN showed a similar pattern that resembled those shown by chloride species **3** and **4**, respectively; the =NH protons were observed at 9.72 ppm and 8.86 ppm for **7** and **8**, respectively, while the NH_2 protons were located at 3.79 ppm (**7**) and 2.99 ppm (**8**) as broad signals. Additionally, we located the nitrogen signals of the κ*N*,κ*N*-chelated ligand by ^{1}H-^{15}N HMBC NMR spectroscopy, where the =NH fragment was observed at very low field (δ(^{15}N) 217.8 ppm (**7**), 224.7 ppm (**8**)) while the amine nitrogen atom from the –NH_2 moiety were observed at 31.0 ppm (**7**) and 29.8 ppm (**8**). While the carbon and proton resonances of the 4-imino-2-methylpentan-2-amino newly formed molecule were perfectly observed in the ^{1}H and the ^{13}C{^{1}H}-APT NMR spectra, respectively, the shape and number of the =CH resonances of the cod ligands indicated that at room temperature both complexes **7** and **8** are undergoing some fluxional processes in solution (See the Experimental Section). As a matter of fact, the =CH resonances were observed as broad resonances at 4.04 ppm (**7**) and 4.07 ppm (**8**), a situation that reflects a C_{2h} symmetry, instead of the expected C_s symmetry. While the pattern of the ^{1}H NMR spectrum of rhodium complex **8** in CD_3CN was not significantly altered from 25 °C to –80 °C, the iridium cation **7** did change the ^{1}H NMR pattern at low temperatures. In this way, at –80 °C the =CH protons of the cod were observed as two well-separated signals at 3.86 and 3.73 ppm, reflecting at this temperature the real C_s symmetry in solution. This situation was further confirmed by the resolution of the molecular structure of isostructural complex **8** on a single crystal by X-ray methods (See the Supporting Information). The freezing of the fluxional processes associated with iridium complex **7** at low temperatures allowed us calculating the thermodynamic parameters involved with the dynamic process. Rate constants were estimated from NMR line-shape analysis, ranging from 0.1 s^{-1} (193 K) to 400 s^{-1} (293 K). The enthalpy ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) were found to be 8.6 ± 0.1 kcal mol^{-1} and −16.5 ± 0.7 cal mol^{-1} K^{-1} (Eyring analysis, see the Supporting Information). Finally, the MALDI-TOF spectra of **7** and **8** showed peaks at *m/z*: 415.1729 and 325.1143, respectively, values whose isotopic distribution matched perfectly that expected for the respective [M(cod)(κ*N*,κ*N*-NH_2–$C(CH_3)_2$–CH_2–$C(CH_3)$=NH)]$^{+}$ (M = Ir, Rh).

DFT Mechanistic Study

In order to ascertain the role of the metal in the formation of the 4-imino-2-methylpentan-2-amino compound described herein, we carried out DFT studies by using theoretical methods. The reaction pathway for the formation of the rhodium complex **8** from **6** has been studied using computational methods at the DFT level (B3LYP-D3(PCM)/def2-SVP) in order to unveil the reaction mechanism at the molecular level. As ammonia molecules present in solution may act as an external base assisting the deprotonation of the organometallic cationic bis(ammine) complex [Rh(cod)$(NH_3)_2$]$^{+}$ (**8**), two additional ammonia molecules interacting *via* hydrogen bonds have been including in the calculations allowing the presence of NH_4^{+}-charged intermediates; the counterion has been omitted in the calculations. The number of hydrogen bond interactions formed by NH_3 or H_2O molecules has been considered carefully in order to obtain a balanced description of all structures calculated along the reaction pathway. The complete reaction from **6** to **8** involves the following steps: i) reaction of the two coordinated ammonia molecules with external acetone to form two acetimino ligands *via* aldol condensation; ii) an imine-enamine tautomerization process of one of the ligands, and iii) an intramolecular C–C bond coupling process yielding the metallacycle **8**. The energetic profile calculated at the DFT level for the first ammonia-imine transformation *via* aldol condensation with acetone is shown in Figure 3, indicating explicitly the hydrogen atoms taking part in hydrogen bonding interactions and proton transfer processes.

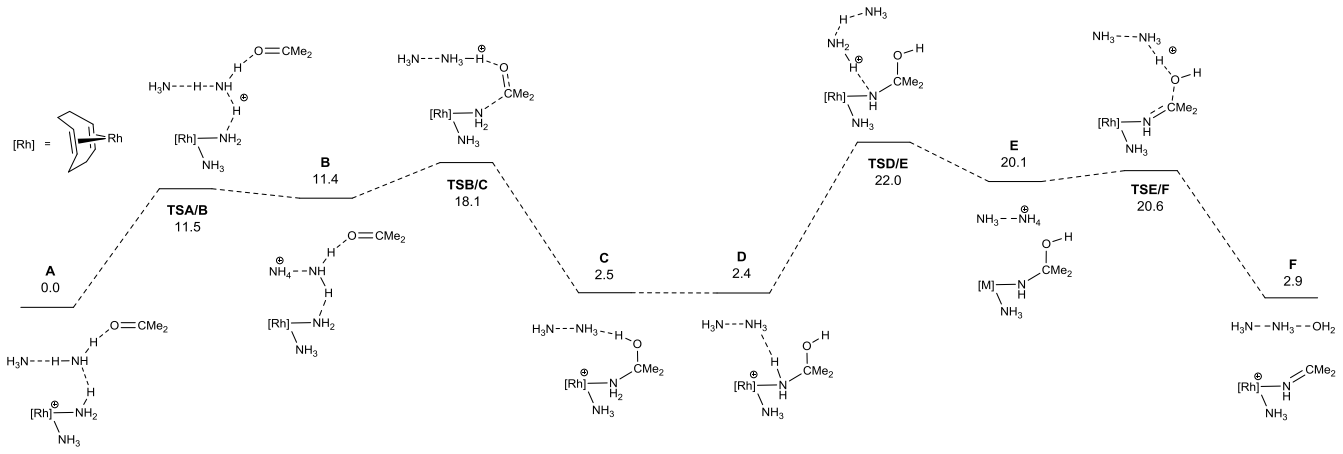
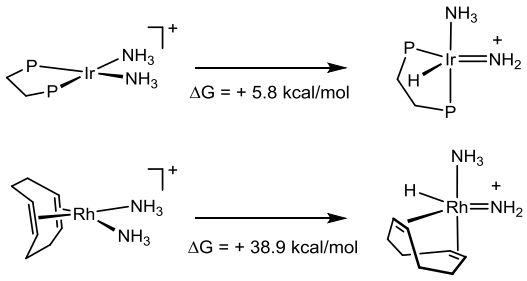


Figure 3. Gibbs energy reaction profile (in kcal/mol and relative to **A**) calculated for the ammonia to imine transformation assisted by two NH_3 molecules. Key hydrogen bonding interactions are shown.

The reaction starts by the deprotonation of an ammonia molecule coordinated to the metal by external ammonia molecules via **TSA/B** with an energetic barrier of 11.5 kcal/mol. This process has been previously proposed by some of us in a recent work[8] for a similar iridium complex bearing bis(phosphane) auxiliary ligands instead of cod. In both cases a metal–amido intermediate is formed which is very reactive. It was reported for the $[Ir(dppe)(NH_3)_2]^+$ complex (dppe = bis(diphenylphosphane)ethane) the oxidative addition of the N–H bond to the metal yielding a hydrido intermediate with an increment in energy of 5.8 kcal/mol. For the $[Rh(cod)(NH_3)_2]^+$ analogous species studied in this work, such hydrido intermediate is extremely unstable, rising the energy up to 38.9 kcal/mol (see Scheme 3). Alternatively, the metal amido intermediate **B** may undergo a nucleophilic attack to the C(sp^2) carbon of one solvent acetone molecule while the proton is transferred from the NH_4^+ group to the oxygen atom of acetone. This process is characterized by **TSB/C** structure presenting an energetic barrier of 18.1 kcal/mol and it is a very early and flat transition structure as pointed out by the C–N interatomic distance of 2.76 Å and the very low imaginary frequency of 44.1i cm^{-1}. A metallic complex bearing a hemiaminal ligand **C** is reached. This intermediate can evolve towards the mono-acetimino product **F** plus water in a stepwise manner by a second deprotonation from the nitrogen atom coordinated to the metal of the hemiaminal ligand. This process is obtained via **TSD/E** showing a relative energy of 22.0 kcal/mol and forming again a NH_4^+ intermediate **E**. A molecule of water is released by the concomitant proton transfer from the NH_4^+ to the oxygen and the heterolytic C–O bond dissociation while the lone pair at the nitrogen forms the N=C double bond as it is shown in **TSE/F**. Although the obtained acetimino intermediate **F** is slightly endergonic, the formed water molecule should be further stabilized by hydrogen bond formation with solvent acetone molecules which are not considered in the PCM solvent model.



Scheme 3. Relative Gibbs energies for the oxidative addition of N–H bond to the metals for "Ir(dppe)" and "Rh(cod)" bis(ammine) cations, respectively.

The second part of the reaction, which goes from the acetimino intermediate **F** to the bis(acetimino) complex **G**, is essentially the same as the transformation of **A** to **F** shown in Figure 3, and involves the reaction of the ammonia molecule coordinated to the metal with an acetone molecule to form the acetimino ligand. The corresponding energetic profile for structures **A'** to **F'** has been calculated yielding very similar results to those reported above (see the Supporting Information for details). The final part of the transformation of **6** to **8** involves the formation of the C–C bond in an organometallic complex bearing two acetimino ligands. A mechanistic proposal has been reported by Vicente *et. al*[24] for a "Rh(η^3-Cp*)Cl" organometallic fragment consisting of an imine-enamine tautomerization of one of the ligands, which is followed by a C–C coupling process that gives the imino-imido intermediate, while the proton migration to the imido nitrogen concludes the transformation. In the aforementioned work, no external base was available to facilitate the proton transfer and the ligands of the metal play a key role.

The energetic profile for the formation of the metallacycle from the bis(acetimino) complex **G** is shown in Figure 4. Hence, intermediate **G** may become deprotonated on one methyl fragment by external NH_3 molecules *via* **TSG/H** transition structure, leading to the enamine neutral intermediate **H**. Instead of protonation of the negatively charged imido nitrogen, an electronic rearrangement involving the two double bonds and the lone pair of nitrogen may occur, yielding the new C–C bond *via* **TSH/I** transition structure as it is shown in Figure 5. Although the bond/lone pair reorganizations at **TSH/I** are concerted, the metal does not participate in the electronic reorganization and therefore it cannot be classified as a pericyclic rearrangement. The energetic barrier for this process is 23.9 kcal/mol and leads to the metallacyclic intermediate **I**. The final product can be obtained by protonation of the negatively charged imido nitrogen through a low energy **TSI/J** transition structure and yielding a very exergonic product **G** (-19.4 kcal/mol) and making the reaction irreversible.

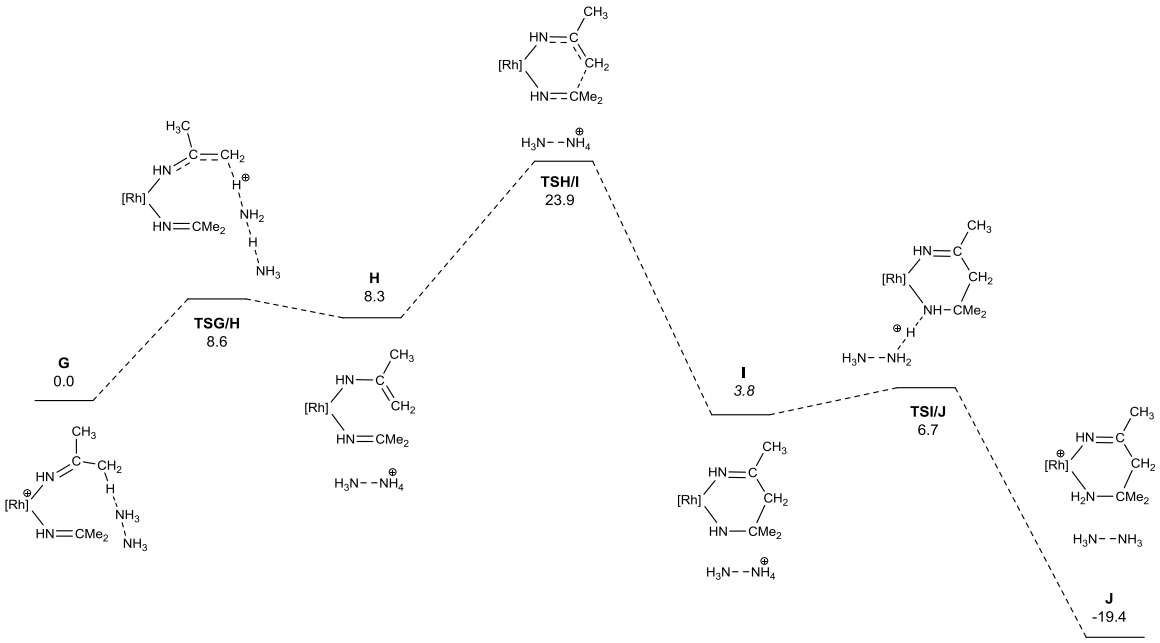


Figure 4. Gibbs energy reaction profile (in kcal/mol and relative to **A**), calculated for the nucleophilic addition of enamine to imine to yield the metallacycle assisted by two NH_3 molecules.

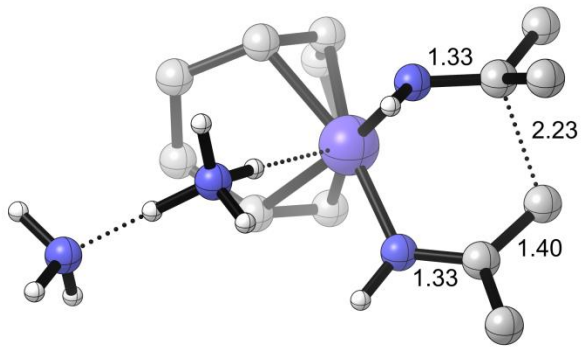


Figure 5. Geometrical representation of the DFT optimized structure **TSH/I**, selected key distances in Å. Hydrogen atoms bonded to carbon atoms are omitted for clarity.

Conclusions

In this contribution we have shown that 1,5-cyclooctadiene complexes of iridium(I) and rhodium(I) act as templates for the C–N and C–C bond formation between ammonia and acetone, leading eventually to the formation of a 4-imino-2-methylpentan-2-amino molecule, which becomes κ*N*,κ*N*-coordinated to the metals forming six-membered metallacycles. The mechanism operative in the M(d^8)-mediated (M = Ir, Rh) C–N and C–C bond formation has been studied in detail by theoretical methods. The mechanistic steps are deprotonation by the external base, nucleophilic addition of the carbonyl group of acetone and water removal by protonation of the –OH group and formation of the imine. Enamine is obtained by deprotonation of the acetimine by NH_3 molecules and the metallacycle is formed by the nucleophilic addition of the enamine to the imine. The role of the metal is limited to promote the deprotonation of the ammonia ligand yielding metal-amido intermediates accessible at the experimental working conditions which can afford the aldol condensation with acetone.

Experimental Section

All manipulations were performed under a dry argon atmosphere using Schlenk-tube techniques. Solvents were obtained from a Solvent Purification System (Innovative Technologies) or were dried by standard procedures and distilled under argon prior to use. Gaseous NH_3 was commercially obtained and used without further purification. Complexes [{M(μ-Cl)(cod)}$_2$] (M = Rh,[27] Ir),[28] and [M(cod)(NCCH$_3$)$_2$]BF$_4$ (M = Rh,[29] Ir),[30] were prepared as previously described in the literature. Deuterated solvents CD_3CN, CD_3OD and $(CD_3)_2CO$ were dried using activated molecular sieves. Carbon, hydrogen and nitrogen analyses were performed with a Perkin-Elmer 2400 Series II CHNS/O microanalyzer. IR spectra of solid samples were recorded with a Perkin-Elmer 100 FT-IR spectrometer (4000−400 cm^{-1}) equipped with attenuated total reflectance. ^{1}H, ^{13}C{^{1}H} and ^{1}H-^{15}N hmbc NMR spectra were recorded on Bruker Avance 300 (300.1276 and 75.4792 MHz) and Bruker Avance 400 (400.1625 and 100.6127 MHz) spectrometers. NMR chemical shifts are reported in ppm relative to tetramethylsilane and are referenced to partially deuterated solvent resonances. Coupling constants (*J*) are given in hertz. Spectral assignments were achieved by combination of ^{1}H-^{1}H cosy, ^{1}H-^{1}H noesy, ^{13}C apt, and ^{1}H-^{13}C hsqc experiments. MALDI-TOF mass spectra were obtained on a Bruker MICROFLEX spectrometer using 1,8-dihydroxy-9,10-dihydroanthracen-9-one (dithranol), as matrix.[31]

Synthesis of [IrCl(cod)(NH$_3$)] (1). An orange solution of [{Ir(μ-Cl)(cod)}$_2$] (0.10 g, 0.15 mmol) in CH_2Cl_2 (6 mL) was stirred under an ammonia atmosphere (2 bar) at room temperature. After an hour a yellow microcrystalline solid precipitated out the solution; this was collected by filtration with a cannula and the resulting yellow solid was washed with hexanes and then vacuum-dried. Yield: 0.07 g (66%). ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ 3.74 (br, 4H, =CH cod), 2.15 (m, 4H, CH_2 cod), 2.13 (s, 3H, NH_3), 1.46 (m, 4H, CH_2 cod). IR (solid, cm^{-1}): υ(N–H), 3186 (s), 3251 (s), 3283 (s). MS (MALDI-TOF$^+$): *m/z* 334.0777 [M$^+$ + O − Cl]. Anal. Calcd for $C_8H_{15}ClIrN$: C, 27.23; H, 4.28; N, 3.97. Found: C, 27.07; H, 4.12; N, 4.31.

Synthesis of [RhCl(cod)(NH$_3$)] (2). An orange solution of complex [{Rh(μ-Cl)(cod)}$_2$] (0.100 g, 0.20 mmol) in CH_2Cl_2 (6 mL) was stirred under an ammonia atmosphere (2 bar) at room temperature. After an hour a yellow microcrystalline solid precipitated out the solution; this was collected by filtration with a cannula and the resulting yellow solid was washed with hexanes and then vacuum-dried. Yield: 0.09 g (82%). ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ 4.08 (br, 4H, =CH cod), 2.37 (m, 4H), 1.77 (m, 4H) (CH_2 cod), 1.67 (br, 3H, NH_3). IR (solid, cm^{-1}): υ(N–H), 3148 (s), 3213 (s), 3311 (s). Mass MS (MALDI-TOF$^+$): *m/z* 252.024 [M$^+$ + Na + H − Cl]. Anal. Calcd for $C_8H_{15}ClNRh$: C, 36.46; H, 5.74; N, 5.31. Found: C, 36.34; H, 5.54; N, 5.06.

Synthesis of [Ir(cod)(κ*N*,κ*N*-NH$_2$–C(CH$_3$)$_2$–CH$_2$–C(CH$_3$)=NH)]Cl (3). An orange suspension of [{Ir(μ-Cl)(cod)}$_2$] (0.100 g, 0.15 mmol) in acetone (6 mL) was stirred under gaseous ammonia (2 bar) at room temperature, forming upon 16 hours an orange suspension. The solid was isolated by filtration with a cannula and the resulting orange powder was washed with diethyl ether and then vacuum-dried. Yield: 0.08 g (60%). Orange single crystals were grown from a saturated solution of **3** in CD_3CN standing at room temperature. ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ 9.31 (br, 1H, =NH), 3.87 (br, 2H, NH_2), 3.68 (br, 4H, =CH cod), 2.63 (s, 2H, CH_2), 2.10 (m, 4H, CH_2 cod), 2.09 (s, 3H, CH_3), 1.52 (m, 4H, CH_2 cod), 1.32 (s, 6H, CH_3). ^{1}H NMR (300 MHz, CD_3OD, 25 °C): δ 3.86 (br, 2H), 3.76 (br, 2H) (=CH cod), 2.63 (s, 2H, CH_2), 2.27 (s, 3H, CH_3), 2.23 (m, 4H), 1.73 (m, 4H) (CH_2 cod), 1.32 (s, 6H, CH_3). IR (solid, cm^{-1}): υ(N–H), 3031 (s), 3090 (s), 3142 (s); υ(C=N), 1642 (s). MS (MALDI-TOF$^+$): *m/z* 417.1849 (100%, M$^+$). Anal. Calcd for $C_{14}H_{26}ClIrN_2$: C, 37.36; H, 5.82; N, 6.23. Found: C, 36.92; H, 5.71; N, 6.45.

Synthesis of [Rh(cod)(κ*N*,κ*N*-NH$_2$–C(CH$_3$)$_2$–CH$_2$–C(CH$_3$)=NH)]Cl (4). An orange-yellow suspension of [{Rh(μ-Cl)(cod)}$_2$] (0.100 g, 0.20 mmol) in acetone (6 mL) was stirred under an ammonia atmosphere (2 bar) at room temperature, forming upon 16 hours a yellow suspension. This was isolated by filtration with a cannula and the resulting yellow powder was washed with diethyl ether and then vacuum-dried. Yellow single crystals were grown from a saturated solution of **4** in $(CD_3)_2CO$ standing at room temperature. Yield: 0.13 g (89%). ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ 8.65 (br, 1H, =NH), 4.05 (br, 4H, =CH cod), 2.48 (s, 2H, CH_2), 2.38 (m, 4H, CH_2 cod), 2.03 (br, 2H, NH_2), 1.78 (m, 4H, CH_2 cod). ^{1}H NMR (300 MHz, CD_3OD, 25 °C): δ 4.06 (br, 2H), 4.02 (br, 2H) (=CH cod), 2.51 (s, 2H, CH_2), 2.35 (m, 4H, CH_2 cod), 2.09 (s, 3H, CH_3), 1.90 (m, 4H, CH_2 cod), 1.26 (s, 6H, CH_3). IR (solid, cm^{-1}): υ(N–H), 3039 (s), 3099 (s), 3126 (s); υ(C=N), 1650 (s). Mass Calcd for $RhC_{14}H_{26}N_2$: 325.1146; MS (MALDI-TOF$^+$): *m/z* 325.1147 (100%, M$^+$). Anal. Calcd for $C_{14}H_{26}ClN_2Rh$: C, 46.61; H, 7.27; N, 7.77. Found: C, 46.25; H, 6.99; N, 7.52.

Synthesis of [Ir(cod)(NH$_3$)$_2$]BF$_4$ (5). A yellow solution of complex [Ir(cod)(NCCH$_3$)$_2$]BF$_4$ (0.04 g, 0.09 mmol) in CH_2Cl_2 (6 mL) was stirred under ammonia (2 bar) at room temperature, forming a yellow suspension instantaneously. The solid was collected by filtration with a cannula, washed with diethyl ether and dried under vacuum. Yield: 0.02 g (64%). ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ 3.75 (br, 4H, =CH cod), 3.10 (s, 6H, NH_3), 2.16 (m, 4H), 1.57 (m, 4H) (CH_2 cod). ^{13}C{^{1}H}-APT NMR (75 MHz, CD_3CN, 25 °C): δ 65.1 (s, =CH cod), 31.9 (s, CH_2 cod). IR (solid, cm^{-1}): υ(N–H), 3340 (s), 3275 (s), 3204 (s). MS (MALDI-TOF$^+$): *m/z* 334.0777 [M$^+$ − NH_3 + O]. Anal. Calcd for $C_8H_{18}BF_4N_2Ir$: C, 22.81; H, 4.31; N, 6.65. Found: C, 21.31; H, 4.39; N, 6.38.

Synthesis of [Rh(cod)(NH$_3$)$_2$]BF$_4$ (6). A yellow solution of complex [Rh(cod)(NCCH$_3$)$_2$]BF$_4$ (0.04 g, 0.12 mmol) in CH_2Cl_2 (6 mL) was stirred under ammonia (2 bar) at room temperature, forming rapidly a yellow suspension. The solid was collected by filtration with a cannula, washed with diethyl ether and then dried under vacuum. Yield: 0.02 g (60%). ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ 4.02 (br, 4H, =CH cod), 2.37(m, 4H, CH_2 cod), 1.92 (s, 6H, NH_3), 1.83 (m, 4H, CH_2 cod). ^{13}C{^{1}H}-APT NMR (75 MHz, CD_3CN, 25 °C): δ 81.3 (d, $^1J_{Rh-C}$ = 13 Hz, =CH cod), 31.3 (s, CH_2 cod). ^{1}H-^{15}N HMBC (41 MHz, CD_2Cl_2, 25 °C): δ 133.6 (NH_3). IR (solid, cm^{-1}): υ(N–H), 3360 (s), 3292 (s), 3205 (s). MS (MALDI-TOF$^+$): *m/z* 252.0243 [M$^+$ − 2NH_3 + CH_3CN]. Anal. Calcd for $C_8H_{18}BF_4N_2Rh$: C, 28.95; H, 5.47; N, 8.44. Found: C, 29.01; H, 5.46; N, 7.88.

Synthesis of [Ir(cod)(κ*N*,κ*N*-NH$_2$–C(CH$_3$)$_2$–CH$_2$–C(CH$_3$)=NH)]BF$_4$ (7). An orange solution of [Ir(cod)(NCCH$_3$)$_2$]BF$_4$ (0.100 g, 0.21 mmol) in acetone (6 mL) was stirred under gaseous ammonia (2 bar) at room temperature, forming upon 16 hours a yellow solution. This was concentrated and the addition of diethyl ether induced the precipitation of

a yellow solid. This was isolated by filtration with a cannula, washed with diethyl ether and then dried under vacuum. Yield: 0.05 g (49%). ^{1}H NMR (300 MHz, CD_3CN, 25 ^{o}C): δ 9.72 (br, 1H, =NH), 4.04 (br, 4H, =CH cod), 3.79 (br, 2H, NH_2), 2.59 (s, 2H, CH_2), 2.22 (m, 4H, CH_2 cod), 2.17 (s, 3H, CH_3), 1.70 (m, 4H, CH_2 cod), 1.30 (s, 6H, CH_3). ^{1}H NMR (400 MHz, CD_3CN, –80 ^{o}C): δ 10.72 (br, 1H, =NH), 4.32 (br, 2H, NH_2), 3.86 (br, 2H), 3.73 (br, 2H) (=CH cod), 2.78 (s, 2H, CH_2), 2.33 (s, 3H, CH_3), 2.10 (m, 4H), 1.59 (m, 4H) (CH_2 cod), 1.33 (s, 6H, CH_3). ^{13}C{^{1}H}-APT NMR (75 MHz, CD_3CN, 25 ^{o}C): δ 188.0 (s, C=NH), 67.2 (s, =CH cod), 51.4 (s, C–NH_2), 48.6 (s, CH_2), 31.9 (s, CH_2 cod), 29.9 (s, CH_3), 28.6 (s, CH_3). ^{1}H-^{15}N HMBC (41 MHz, $(CD_3)_2CO$, –80 ^{o}C): δ 217.8 (NH), 31.0 (NH_2). IR (solid, cm^{-1}): υ(N–H), 3239 (s), 3283 (s); υ(C=N), 1643 (s). MS (MALDI-TOF$^+$): *m/z* 415.1729 (100%, M$^+$). Anal. Calcd for $C_{14}H_{26}BF_4IrN_2$ + 1/2 CH_3CN: C, 34.52; H, 5.31; N, 6.71. Found: C, 34.33; H, 5.07; N, 6.20.

Synthesis of [Rh(cod)(κ*N*,κ*N*-NH_2–$C(CH_3)_2$–CH_2–$C(CH_3)$=NH)]BF_4 (8). A yellow solution of [Rh(CH_3CN)$_2$(cod)]BF_4 (0.100 g, 0.27 mmol) in acetone (6 mL) was stirred under ammonia (2 bar) at room temperature, forming upon 16 hours a yellow solution. This was concentrated and the addition of diethyl ether induced the precipitation of a yellow solid. This was isolated by filtration with a cannula, washed with diethyl ether and then dried under vacuum. Yellow single crystals of this complex were grown by slow diffusion of diethyl ether into a saturated solution of 8 in CD_3CN standing at 3 ^{o}C. Yield: 0.096 g (86%). ^{1}H NMR (300 MHz, CD_3CN, 25 ^{o}C): δ 8.86 (br, 1H, =NH), 4.07 (br, 4H, =CH cod), 2.99 (br, 2H, NH_2), 2.51 (s, 2H, CH_2), 2.37 (m, 4H, CH_2 cod), 2.12 (s, 3H, CH_3), 1.91 (m, 4H, CH_2 cod), 1.29 (s, 6H, CH_3). ^{13}C{^{1}H}-APT NMR (75 MHz, CD_3CN, 25 ^{o}C): δ 186.0 (s, C=NH), 82.6 (s, =CH cod), 50.7 (s, C–NH_2), 48.5 (s, CH_2), 31.2 (s, CH_2 cod), 29.7 (s, CH_3), 29.2 (s, CH_3). ^{1}H-^{15}N HMBC (41 MHz, $(CD_3)_2CO$, –10 ^{o}C): δ 224.7 (NH), 29.8 (NH_2). IR (solid, cm^{-1}): υ(N–H), 3254 (s), 3272 (s), 3303 (s); υ(C=N), 1649 (s). MS (MALDI-TOF$^+$): *m/z* 325.1143 (100%, M$^+$). Anal. Calcd for $C_{14}H_{26}BF_4N_2Rh$: C, 40.81; H, 6.36; N, 6.80. Found: C, 40.69; H, 5.75; N, 6.74.

Determination of Rotational Barrier. Full line-shape analysis of the dynamic ^{1}H NMR spectra of complex **7** was carried out using the programgNMR (Cherwell Scientific Publishing Limited). Activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained by a linear least-squares fit of the Eyring plot. Errors were computed by published methods.[32]

Computational Details

All DFT theoretical calculations have been carried out using the Gaussian program package.[33] The B3LYP method[34] has been employed including the D3 dispersion correction scheme developed by Grimme for both energies and gradient calculations and the "ultrafine" grid.[35] The def2-SVP basis set[36] has been selected for all atoms and the PCM method[37] was chosen to simulate solvent effects (acetone, ε = 20.493), both have been used for geometry optimizations and calculation of Gibbs energy corrections at 298 K and 1 atm. The nature of the stationary points has been check by analytical frequency analysis and transition states were characterized by a single imaginary frequency corresponding to the expected motion of the atoms. Some dihedral angles for the NH_3 external molecules were frozen in some transition states regarding protonation/deprotonation of amido/imine ligands in order to remove spurious imaginary frequencies. Reaction paths were calculated for very flat transition structures connecting the corresponding intermediates. Molecular structures were represented using CYLView software.[38]

Crystal Structure Determination of Complexes 3, 4 and 8. Single crystal X-ray diffraction data were collected with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 100(2) K (complexes **3** and **8**) and 150(2) K (complex **4**) using narrow ω rotations (0.3°) on a Bruker APEX DUO four-circles diffractometer. Intensities were integrated and corrected for absorption effects with SAINT+[39] and SADABS[40] programs, integrated in APEX2 package. The structures were solved by direct methods with SHELXS-2013[41] and refined by full-matrix least-squares refinement in F^2 with SHELXL-2014.[42] Hydrogen atoms of NH and NH_2 and cod groups have been observed in Fourier difference maps and freely refined.

Crystal data for **3**. $C_{14}H_{26}IrN_2{\cdot}Cl{\cdot}C_2D_3N$; *M* = 494.09; orange prism, 0.111 x 0.155 x 0.170 mm^3; monoclinic $P2_1/n$; *a* = 9.1364(4), *b* = 9.6833(4), *c* = 20.3104(9) Å; β = 95.7250(10)°; *V* = 1787.91(13) Å^3; *Z* = 4; ρ_{calc} = 1.836 g cm^{-3}; μ = 7.615 cm^{-1}; min. and max. transmission factors 0.2582 and 0.4588; $2\theta_{max}$ = 58.742°; 20825 reflections collected; 4633 unique reflections [R_{int} = 0.0325]; number of data/restraints/parameters: 4633/0/271; final *GOF* 1.144; R_1 = 0.0255 [4252 reflections, $I > 2\sigma(I)$], wR_2 = 0.0632 for all data; largest difference peak: 2.050 e Å^{-3}. At the end of the refinement five residual density peaks higher than 1 e Å^{-3} have been found. They are close to the metal atom and have no chemical sense.

Crystal data for **4**. $C_{14}H_{26}N_2Rh{\cdot}Cl$; *M* = 360.73; yellow prism, 0.088 x 0.091 x 0.239 mm^3; triclinic *P-1*; *a* = 9.8324(7), *b* = 13.2393(6), *c* = 13.3917(7) Å; α = 78.0917(7), β = 72.5995(7), γ = 71.0076(7)°; *V* = 1561.40(16) Å^3; *Z* = 4; ρ_{calc} = 1.535 g cm^{-3}; μ = 1.251 cm^{-1}; min. and max. transmission factors 0.7556 and 0.8778; $2\theta_{max}$ = 59.264°; 23564 reflections collected; 7953 unique reflections [R_{int} =0.0347]; number of data/restraints/parameters: 7953/1/387; final *GOF* 1.020; R_1 = 0.0325 [6293 reflections, $I > 2\sigma(I)$], wR_2 = 0.0816 for all data; largest difference peak: 1.126 e Å^{-3}.

Crystal data for **8**. $C_{14}H_{26}N_2Rh{\cdot}BF_4$; *M* = 412.09; yellow prism, 0.100 x 0.131 x 0.180 mm^3; monoclinic $P2_1/n$; *a* = 10.3395(4), *b* = 15.7643(7), *c* = 10.3588(4) Å; β = 96.4420(10) °; *V* = 1677.77(12) Å^3; *Z* = 4; ρ_{calc} = 1.631 g cm^{-3}; μ = 1.054 cm^{-1}; min. and max. transmission factors 0.8305 and 0.8986; $2\theta_{max}$ = 59.108°; 32235 reflections collected; 4490 unique reflections [R_{int} = 0.0276]; number of data/restraints/parameters: 4490/0/230; final *GOF* 1.044; R_1 = 0.0288 [4048 reflections, $I > 2\sigma(I)$], wR_2 = 0.0723 for all data; largest difference peak: 1.370 e Å^{-3}.

Acknowledgements

The authors express their appreciation to the financial support of MINECO/FEDER project CTQ2015-67366-P and Diputación General de Aragón (DGA/FSE, group E07). The support from KFUPM-University of Zaragoza research agreement and the Centre of Research Excellence in Petroleum Refining & Petrochemicals (KFUPM) is gratefully acknowledged. V. P. thankfully acknowledges the resources from the supercomputer

"memento", technical expertise and assistance provided by BIFI-ZCAM (Universidad de Zaragoza).

Keywords: Iridium • Rhodium • Ammonia • C–N Coupling • C–C Coupling

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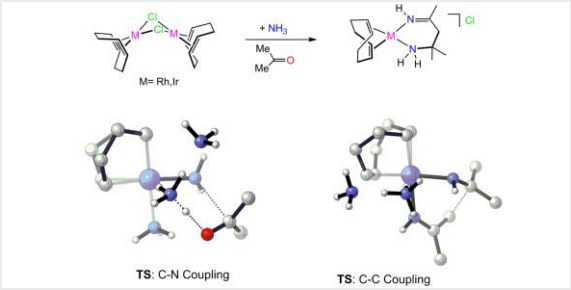

C–N Coupling

M. P. Betoré, P. García-Orduña, F. J. Lahoz, M. A. Casado, V. Polo,* L. A. Oro*

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Title
C–N Bond Coupling Reactions of Ammonia with Acetone Promoted by Iridium and Rhodium Complexes: Experimental and DFT Studies

Rhodium and iridium chlorido complexes react with ammonia in acetone affording new species containing an amino/imino ligand formed by sequential C─N and C─C coupling, as confirmed by DFT methods.