

Direct Access to Parent Amido Complexes of Rhodium and Iridium through N–H Activation of Ammonia**

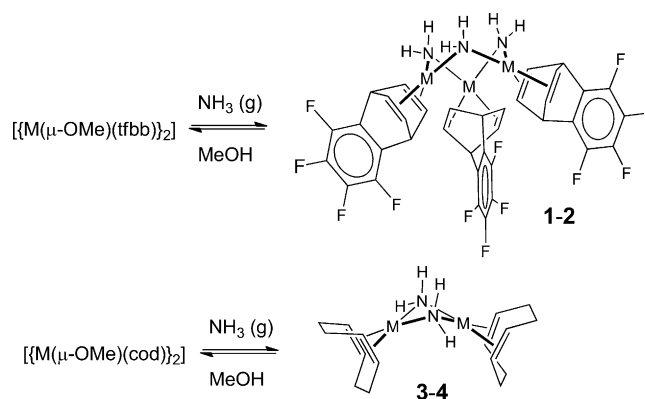
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Ammonia is a low-cost and potentially valuable building block for almost every nitrogen-containing compound required by industry. There is an obvious interest in utilizing this chemical as feedstock in catalytic organic transformations to produce higher-value products, an issue that has begun to be explored with some degree of success.^[1] However, most of late transition metal catalyzed reactions do not occur with ammonia. Several factors have been invoked to explain this lack of reactivity:^[2] 1) The high strength of the N–H bond of ammonia (107 kcal mol^{−1}) makes its activation very difficult to achieve by metal centers; 2) the catalyst often deactivates through the formation of stable Werner ammine (M←NH₃) adducts; and 3) the low acidity of ammonia prevents its participation in proton exchange reactions that could lead to N–H activation.

In order to achieve a metal-mediated functionalization of ammonia, an imperative requisite should be the formation of M–NH₂ bonds directly from ammonia (i.e. rather than leading to stable M←NH₃ adducts).^[3] So far, only few early examples involving interaction of NH₃ with iridium complexes followed an oxidative addition profile.^[4] This concept was elegantly illustrated by Hartwig et al., who reported on the formal oxidative addition of ammonia to an electron-rich Ir^I pincer system, leading to the first structurally characterized terminal amido hydrido Ir^{III} complex.^[5] In spite of the efficacy of this N–H activation, uptake and homolytic breakage of ammonia by late transition metal complexes still remains a difficult goal.^[6] We assumed that a good approach to induce

the formation of M–NH₂ bonds, circumventing the formation of Werner adducts, should rely on an appropriate design of organometallic precursors. Herein we report on a synthetic protocol that uses gaseous ammonia as “NH₂” source to generate stable novel parent bridging and terminal amido Rh^I and Ir^I complexes under very mild conditions.

We chose as metallic precursors dinuclear complexes bearing alkoxo-bridging ligands, well suited to induce N–H activation.^[7] In this way, treatment of the methoxo-bridged compounds $[M(\mu\text{-OMe})(\text{tfbb})_2]$ (M = Rh, Ir; tfbb = tetrafluorobenzobarrelene) with gaseous ammonia in diethyl ether at atmospheric pressure rapidly afforded the parent amido-bridged trinuclear complexes $[M(\mu_2\text{-NH}_2)(\text{tfbb})_3]$ (M = Rh (**1**), Ir (**2**)) which were isolated in good yields. On the other hand, reactions of the cod complexes $[M(\mu\text{-OMe})(\text{cod})_2]$ (cod = 1,5-cyclooctadiene) with gaseous ammonia yielded dinuclear amido-bridged complexes $[M(\mu\text{-NH}_2)(\text{cod})_2]$ (M = Rh (**3**), Ir (**4**)) in excellent yields (Scheme 1). All the



Scheme 1. Synthesis of parent amido-bridged complexes $[M(\mu\text{-NH}_2)(\text{tfbb})_3]$ (**1**, **2**) and $[M(\mu\text{-NH}_2)(\text{cod})_2]$ (**3**, **4**) (M = Rh, Ir).

reactions leading to complexes **1–4** were found to be reversible. For example, monitoring by NMR spectroscopy the reaction of **3** with MeOH in a 1:1 ratio in [D₆]benzene showed upon 10 min, when the equilibrium was considered to be reached, the presence of unchanged **3**, the original methoxo-bridged complex $[Rh(\mu\text{-OMe})(\text{cod})_2]$ and the mixed amido-alkoxo species $[Rh(\text{cod})_2(\mu\text{-OMe})(\mu\text{-NH}_2)]$ in a 0.4:0.3:1 ratio along with released ammonia (see Supporting Information). Excess of substrates (i.e. NH₃ or MeOH) are required to drive the reactions to completion either way, as observed experimentally.

Complexes **1–4** have been fully characterized by elemental analysis, spectrometric techniques, and multinuclear NMR

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(^1H , $^{13}\text{C}\{^1\text{H}\}$, and bidimensional g-HMQC ^1H - ^{15}N) data. Additionally, an X-ray structural analysis has been carried out for complexes **1**, **2**, and **3** (Figures 1 and 2).^[8] The most striking structural feature of these complexes relies on the

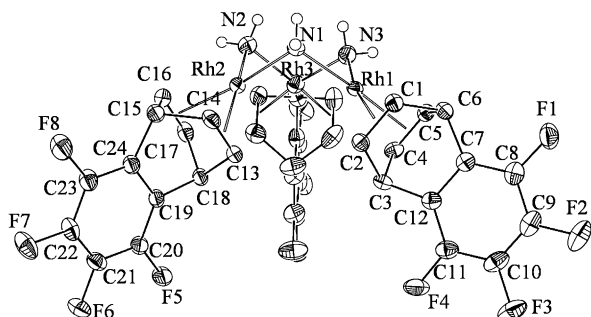


Figure 1. Molecular diagram of complex **1**. Selected bond lengths [Å] and angles [°]: Rh1–N1 2.058(2), Rh1–N3 2.075(3), Rh2–N1 2.089(2), Rh2–N2 2.066(3), Rh3–N2 2.084(3), Rh3–N3 2.068(3), mean Rh–Ct 2.001(3); N1–Rh1–N3 86.9(1), N1–Rh2–N2 88.1(1), N2–Rh3–N3 88.4(1)°. Ct represents the midpoints of the olefinic bonds.

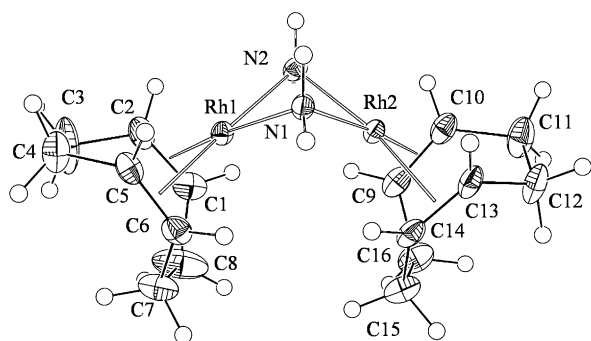


Figure 2. ORTEP diagram of complex **3**. Selected bonds lengths [Å] and angles [°] (only data for one independent molecule is given here): Rh1–N1 2.092(2), Rh1–N2 2.078(3), Rh2–N1 2.088(2), Rh2–N2 2.064(2), mean Rh–Ct 2.003(5); N1–Rh1–N2 76.64(9), N1–Rh2–N2 76.95(10). Ct represents the midpoints of olefinic bonds.

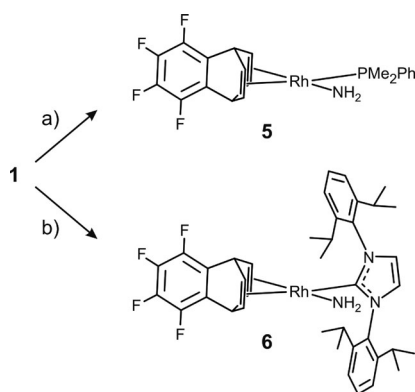
different nuclearity of the tfbb compounds **1** and **2** in comparison to the cod complex **3**, apparently only induced by the nature of the diolefin. Complexes **1** and **2** are trinuclear and isostructural, and exhibit three square-planar metal centers bridged by three μ_2 -NH₂ groups, forming a Rh₃N₃ six-membered metallacycle with a cone disposition.^[9] Inter-metallic distances fall in the range 3.2043(3)–3.3981(2) Å (**1**) and 3.2135(4)–3.4222(4) Å (**2**), all of them excluding clear metal–metal interactions.

On the contrary, complex **3** is dinuclear, and crystallizes with two crystallographically independent but chemically identical molecules in the unit cell. The rhodium atoms lie on slightly distorted square-planar geometries and are held together by two amido bridging groups; the whole structure is folded around the N–N vector with dihedral angles of 68.36(6)° and 58.45(7)° between the two metal coordination planes of each molecule. The intermetallic separations (2.7785(3) and 2.8603(3) Å) are much shorter than those observed in the tfbb analogs.

Calculations at the DFT level have been carried for amido di- and trinuclear complexes of Rh and Ir bearing tfbb and cod as ancillary ligands. The obtained gas-phase optimized geometries of structures **1**–**4** are in good agreement with X-ray values. Stationary points on the potential energy surfaces have been found for the experimentally unobserved trinuclear complexes of Rh and Ir bearing the cod ligand. These structures show a distortion from the C_{3v} symmetry due to short hydrogen–hydrogen contacts (1.966 Å) between neighboring cod units, pointing out a destabilization of trinuclear cod complexes due to steric repulsion. In contrast, such steric hindrance is reduced for trinuclear tfbb complexes due to the smaller size of the ligand (See Supporting Information).

Complexes **1**–**4** showed a temperature-dependent behavior in solution. At room temperature, both the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** and **2** showed two signals for the tfbb ligands (CH and =CH, respectively), indicating an averaged D_{3h} symmetry, and a resonance due to the NH₂ moiety at 0.35 (**1**) and 2.67 ppm (**2**) (^{15}N NMR: 5.5 ppm (**1**); –1.73 ppm (**2**)). Cooling the solutions of **1** and **2** led to the freezing of the fluxional motions, and single species with C_{3v} symmetry were observed, according with the solid-state structure found for both complexes. For instance, at –50 °C the ^1H NMR spectrum of **1** showed the CH and =CH protons as sets of two resonances, while the amido protons were observed as two resonances at 0.23 and 0.44 ppm. This dynamic behavior responds to a fast exchange between the two possible conformers (cone and partial cone), which show approximately C_{3v} and C_2 symmetries, respectively. Line-shape NMR variable-temperature analysis allowed an estimation of the activation energy for the envelope flipping motions, which were 42.1 and 52.3 kJ mol^{–1} for complexes **1** and **2**, respectively. These results are supported by gas-phase calculations (see Supporting Information). Partial cone structures of **1** and **2** have been found, being 17.1 and 20.0 kJ mol^{–1} less stable than the respective cone conformer. Transition structures have been found for the fluxional motion, yielding activation energies of 40.4 and 44.9 kJ mol^{–1} for **1** and **2**, respectively, in good agreement with experimental values. On the other hand, the pattern of the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of both cod complexes **3** and **4** at room temperature were similar to each other, indicating a dynamic motion which could not be frozen at –90 °C in [D₈]toluene. The D_{2h} symmetry detected, in contrast to the expected C_{2v} symmetry observed in the solid state, responded to a four-membered “MNMN” metallacycle inversion,^[10] which is fast on the NMR time scale therefore producing averaged NMR signals that reflected a planar conformation.

Access to terminal parent amido complexes of Rh^I was straightforward by splitting the amido bridges of complex **1** with donor ligands, like dimethylphenylphosphane and the N-heterocyclic carbene 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr). Treatment of **1** with PMe₂Ph in a 1:3 molar ratio gave [Rh(tfbb)(NH₂)(PMe₂Ph)] (**5**) in 61 % yield. In a similar way, addition of IPr to **1** in a 3:1 molar ratio led to the formation of mononuclear complex [Rh(tfbb)(IPr)(NH₂)] (**6**) in 44 % yield (Scheme 2). Complexes **5** and **6** featured an unprecedented Rh^I–NH₂ moiety, which was confirmed by ^{15}N - ^1H HMQC spectroscopy ($\delta(^1\text{H})$ = –0.54 (**5**), 1.23 ppm



Scheme 2. Synthesis of complexes **5** and **6**. a) 3 equiv PMe_2Ph , toluene, -15°C ; b) 3 equiv IPr , toluene, RT.

(**6**); $\delta(^{15}\text{N}) = -11.8$ (**5**), 67.6 ppm (**6**)). The diolefins appeared as a set of three resonances in their ^1H NMR spectra, which indicated the presence of a mirror plane, while the $\text{tfbb}:\text{NH}_2:\text{L}$ ($\text{L} = \text{PMe}_2\text{Ph}$, IPr) ratio was 1:1:1 in both cases. In **6**, the presence of a sole septuplet for the $i\text{Pr}$ protons is explained taking into account the added effects of a rotational process that exchanges unsymmetrical isopropyl groups, and the mirror plane that bisects the imidazol ring of IPr and contains the Rh , N , and the C -carbenic atoms.^[11]

In general, access to parent amido low-valent late transition metal complexes is rather limited, perhaps due to the absence of aromatic substituents at nitrogen, which adds stabilization to the system by electronic delocalization.^[12] There are synthetic routes towards these compounds mainly based on salt metathesis reactions,^[13–15] however they need strong bases and do not use ammonia directly for their formation. Only few examples of these elusive species have been recently reported to be prepared from ammonia without change of the redox state of the metals; they are based on deprotonative N-H cleavage by a μ_3 -oxo triruthenium cluster^[16] and by a diaryl Fe complex.^[17] Furthermore, it has been shown how ammonia is activated by bifunctional iridium^[18] or ruthenium^[19] complexes through metal–ligand cooperation. The reactions described herein proceed as well through an N-H heterolytic cleavage of ammonia, assisted intramolecularly by a methoxo basic ligand attached to the metal. Once the amido complexes are formed, no exchange with ND_3 was observed. Under mild conditions, no reaction of the terminal amido Rh complexes with olefins was detected. However, with terminal acetylenes, clear evidence of alkynyl complexes along with polymer formation was observed. We anticipate that diolefin amido rhodium complexes described herein catalyze very efficiently the homogeneous polymerization of phenylacetylene, being the trinuclear tfbb complex **1** much more active than the dinuclear cod complex **2**.

In conclusion, we have developed a method that allows the high-yield access to Rh^{I} and Ir^{I} parent amido complexes directly from gaseous ammonia, creating a unique platform where to explore the reactivity and catalytic performance of these rare and relevant species.^[20] Two important points should be underlined about the synthetic strategy we enlighten here: 1) it provides a direct entry into previously

unknown Rh-NH_2 complexes, and 2) this protocol is not limited to a specific system, but on the contrary, it may be extended to other metals bearing alkoxo bridging ligands. Finally, we believe that the ability to generate M-NH_2 complexes directly from ammonia follows the right direction towards the discovering of new catalytic processes involving the functionalization of ammonia, a highly desirable and valuable target that we are currently exploring.

Experimental Section

1: Gaseous ammonia was bubbled through a yellow suspension of $[\text{Rh}(\mu\text{-OMe})(\text{tfbb})_2]$ (0.25 g, 0.35 mmol) in diethyl ether (20 mL) at -15°C , giving rise to the crystallization of an orange microcrystalline solid within 5 min. The bubbling of ammonia was continued for 30 min and the solid was collected by filtration via cannula, washed with hexanes and then vacuum-dried (0.21 g, 88%). ^1H NMR (300 MHz, $[\text{D}_6]\text{benzene}$, 25°C , TMS): $\delta = 5.41$ (m, 6H; CH), 2.83 (m, 12H; $=\text{CH}$) (tfbb), 0.35 ppm (br s, 6H; NH_2); ^1H NMR (300 MHz, CD_2Cl_2 , -50°C , TMS): $\delta = 5.89$ (m, 3H), 5.35 (m, 3H) (CH), 3.38 (m, 6H), 3.20 (m, 6H) ($=\text{CH}$) (tfbb), 0.44 (br s, 3H), 0.23 ppm (br s, 3H) (NH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, $[\text{D}_6]\text{benzene}$, 25°C , TMS): $\delta = 139.2$ (dm, $^1J(\text{C},\text{F}) = 248$ Hz), 138.2 (dm, $^1J(\text{C},\text{F}) = 255$ Hz) (CF), 127.8 (m, C_q), 52.3 (d, $^1J(\text{C},\text{Rh}) = 10$ Hz; $=\text{CH}$), 40.2 ppm (d, $^3J(\text{C},\text{Rh}) = 4$ Hz; CH) (tfbb); $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, $[\text{D}_6]\text{benzene}$): $\delta = -147.9$ (d, $^3J(\text{F},\text{F}) = 25$ Hz), -160.5 ppm (d, $^3J(\text{F},\text{F}) = 25$ Hz); $^{15}\text{N-H}$ HMQC (40 MHz, $[\text{D}_6]\text{benzene}$, 25°C , NH_3): $\delta = 5.5$ (br s; NH_2); MS ($\mu\text{-TOF}^+$): m/z 369.9 [$M^+/3 + \text{Na} + \text{H}$]; elemental analysis calcd (%) for $\text{C}_{36}\text{H}_{24}\text{F}_{12}\text{N}_3\text{Rh}_3$: C 41.77, H 2.34, F 22.02, N 4.06; found: C 41.65, H 2.23, F 21.95, N 4.01.

5: To a solution of **1** (0.12 g, 0.12 mmol) in toluene (4 mL) kept at -15°C , pure dimethylphenylphosphane (0.05 g, 52 μL , 0.36 mmol) was added slowly via syringe. The resulting orange solution was stirred for 15 min and then the volume was evaporated to dryness by reduced pressure. The resulting orange solid was washed with hexanes, filtered via cannula and dried under vacuum (0.11 g, 61%). ^1H NMR (400 MHz, $[\text{D}_8]\text{toluene}$, 25°C , TMS): $\delta = 8.00$ (m, 2H; H_o Ph), 7.10 (m, 3H; $\text{H}_m + \text{H}_p$ Ph) (PMe_2Ph), 5.49 (s, 2H; CH), 3.12 (m, 4H; $=\text{CH}$) (tfbb), 1.12 (m, 6H; Me), -0.54 ppm (br s, 2H; NH_2); ^1H NMR (400 MHz, $[\text{D}_8]\text{toluene}$, 25°C , TMS): $\delta = 8.05$ (m, 2H; H_o Ph), 7.14 (m, 3H; $\text{H}_m + \text{H}_p$ Ph) (PMe_2Ph), 5.57 (s, 2H; CH), 3.18 (m, 2H; $=\text{CH}$), 3.02 (m, 2H; $=\text{CH}$) (tfbb), 1.21 (m, 6H; Me), -0.36 ppm (br s, 2H; NH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, $[\text{D}_6]\text{benzene}$, 25°C): $\delta = -13.6$ ppm (d, $^1J(\text{P},\text{Rh}) = 170$ Hz); $^{13}\text{C}\{^1\text{H}\}$ -APT NMR plus HSQC (100.6 MHz, $[\text{D}_8]\text{toluene}$, -20°C , TMS): $\delta = 142.1$ (dd, $^1J(\text{C},\text{P}) = 18$ Hz, $^2J(\text{C},\text{Rh}) = 17$ Hz; C_{ipso} Ph), 139.9 (dm, $^1J(\text{C},\text{F}) = 242$ Hz), 138.2 (dm, $^1J(\text{C},\text{F}) = 269$ Hz) (CF tfbb), 131.63 (dd, $^2J(\text{C},\text{P}) = 6$ Hz, $^3J(\text{C},\text{Rh}) = 6$ Hz; C_o), 128.7 (s, C_p), 127.6 (d, $^3J(\text{C},\text{P}) = 4$ Hz; C_m) (Ph), 48.5 (d, $^1J(\text{C},\text{Rh}) = 10$ Hz; $=\text{CH}$), 40.3 ppm (d, $^2J(\text{C},\text{Rh}) = 3$ Hz; CH) (tfbb); $^{19}\text{F}\{^1\text{H}\}$ NMR (282 MHz, $[\text{D}_6]\text{benzene}$): $\delta = -144.4$ (d, $^3J(\text{F},\text{F}) = 23$ Hz), -157.1 ppm (d, $^3J(\text{F},\text{F}) = 25$ Hz); $^{15}\text{N-H}$ HMQC (40 MHz, $[\text{D}_6]\text{benzene}$, 25°C , NH_3): $\delta = -11.8$ ppm; MS ($\mu\text{-TOF}^+$): m/z 467.0 [$M^+ - \text{NH}_2$]; elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{19}\text{F}_4\text{NPRh}$: C 49.71, H 3.96, N 2.90; found: C 49.68, H 3.89, N 2.81.

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- [8] Data for **1**: $C_{36}H_{24}F_{12}N_3Rh_3 \cdot C_6H_{14}$, $M = 1121.48$, space group $P2_1/n$, $a = 13.5763(8)$, $b = 13.3187(8)$, $c = 21.4824(13)$ Å; $\beta = 99.062(2)^\circ$; $V = 3835.9(4)$ Å³; $Z = 4$; $R_1 = 0.0344$, 9620 reflections, $I > 2\sigma(I)$; $wR(F^2) = 0.0880$, GoF = 1.033 (10940 unique). Data for **2**: $C_{36}H_{24}F_{12}N_3Ir_3 \cdot C_6H_{14}$, $M = 1389.42$, space group $P2_1/n$, $a = 13.5872(6)$, $b = 13.3741(6)$, $c = 21.3459(10)$ Å; $\beta = 98.951(1)^\circ$; $V = 3831.7(3)$ Å³; $Z = 4$; $R_1 = 0.0262$, 8669 reflections, $I > 2\sigma(I)$; $wR(F^2) = 0.0680$, GoF = 1.019 (9967 unique). Data for **3**: $C_{16}H_{28}N_2Rh_2$, $M = 454.22$, space group $P1$, $a = 6.9014(4)$, $b = 11.6776(7)$, $c = 21.2575(13)$ Å; $\alpha = 104.3290(10)$, $\beta = 98.7070(10)$; $\gamma = 90.4370(10)^\circ$, $V = 1638.9(2)$ Å³; $Z = 4$; $R_1 = 0.0208$, 7277 reflections, $I > 2\sigma(I)$; $wR(F^2) = 0.0706$, GoF = 1.002 (8225 unique). CCDC 831649 (**1**), 831650 (**2**), and 831651 (**3**) 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.
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