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Amido/Imido Complexes

The Dehydrogenation of Alcohols through a Concerted Bimetallic Mechanism Involving an Amido-Bridged Diiridium Complex**

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The catalytic functionalization of ammonia into higher-value nitrogen-containing products is currently a hot topic.[1] However, the productive participation of ammonia as a substrate in homogeneous catalysis is normally hampered by the intrinsically high strength of the N–H bond, which is very difficult for metal centers to activate.[2] Therefore, it is convenient to find alternative ways to achieve the formation of [M–NH_2] species directly from ammonia as a step towards accomplishing its subsequent functionalization.[3] Since the oxidative addition of ammonia to a single iridium center was unambiguously demonstrated by Hartwig et al.,[4] further research has led to the recognition that NH_3 is able to participate in metal-mediated N–H bond cleavage processes that may ultimately lead to the formation of parent amido and imido late-transition-metal species.[5]

Sound advances in this field have been recently reported, in which the clever design of metallic precursors often dictates the success of these strategies. In this way, efficient synthetic pathways towards these compounds that involve both homolytic[6] and heterolytic[7,8] activation of ammonia have been disclosed, and researchers are beginning to unfold the chemistry around otherwise unusual late M–NH_2 complexes. Within this context, it is even more intriguing and challenging to achieve multiple metal-mediated ammonia activation, which could lead to the formation of rare late-transition-metal imido complexes. Such species are valuable intermediates in useful catalytic transformations, such as nitrogen transfer reactions,[9] and indeed very important in the context of dinitrogen fixation and reduction.[10]

However, the scarceness of methods to generate M–NH_2 complexes (preferably from ammonia) has prevented exploration of the reactivity and catalytic performance of low-valent late-transition-metal parent amido complexes. It is interesting to mention in this context the key role of amido intermediates in Noyori type catalytic reactions.[11] Herein, we report on the alcohol-induced transformation of a dinuclear amido-bridged iridium complex into higher nuclearity Ir_3 and Ir_4 imido clusters, the formation of which is a direct consequence of alcohol dehydrogenation.

We recently reported on the heterolytic activation of ammonia mediated by the methoxo-bridged compound [{Ir(cod)(μ-OMe)}$_2$] (cod = 1,5-cyclooctadiene) to afford the amido dinuclear complex [{Ir(cod)(μ-NH_2)}$_2$] (**1**).[8] During our ongoing research on metal-mediated ammonia activation, we found that bubbling gaseous NH_3 into a solution of [{Ir(cod)(μ-OMe)}$_2$] in THF and then allowing it to stand under a layer of hexanes for several days resulted in the expected complex **1** in high yield. However, the product was mixed with a crop of red crystals, which were identified by X-ray analysis as [Ir_4(cod)$_4$(μ_4-η^2-$HNCH_2NH$)(μ_4-NH)] (**2**), and variable amounts of orange crystals, which were characterized as [Ir_3(cod)$_3$(μ_3-NH)$_2$(μ_2-H)] (**3**).

Complexes **2** and **3** were characterized in the solid state by elemental analysis and X-ray diffraction techniques.[12] Whereas **2** was found to be rather insoluble, **3** was further characterized by spectrometric techniques and multinuclear NMR spectroscopy. Complex **2** is a novel tetrairidium cluster (Figure 1), in which the Ir_4 framework exhibits a saddle rectangular geometry, with metals that alternate an equal distance above and below (0.065(2) Å) the mean plane defined by the four iridium atoms. The tetrametallic rectangle is face-capped with a nonsymmetrical parent imido ligand that coordinates in a μ_4-fashion, in which the N1 atom is clearly closer to the Ir2 and Ir4 vertices (see the values for Ir–N1 distances in Figure 1). QTAIM analysis of the solid-state model indicates slightly different electron densities at the four N1–Ir bond critical points (range 0.0705–0.1078 a.u.), and also shows small negative values of the Laplacian, which suggests a covalent character for all N1–Ir bonds (see the Supporting Information). The opposite face is supported by an unexpected, newly formed μ_4-$HNCH_2NH$ bis-amido ligand, which coordinates to the four metals by bridging two iridium centers with each nitrogen atom, with Ir–N distances of 2.063–2.094(4) Å. Short metal–metal bond lengths are observed between the iridium centers bridged by nitrogen atoms of the μ_4-$HNCH_2NH$ amido fragment (Ir1–Ir2: 2.7544(3) and Ir3–Ir4: 2.7009(3) Å), while longer intermetallic separations are found in the other two edges of the metal rectangle (Ir1–Ir4: 2.9151(3) and Ir2–Ir3: 2.9537(3) Å). The plane formed by the imido and the methylenediamido fragments displays a dihe-

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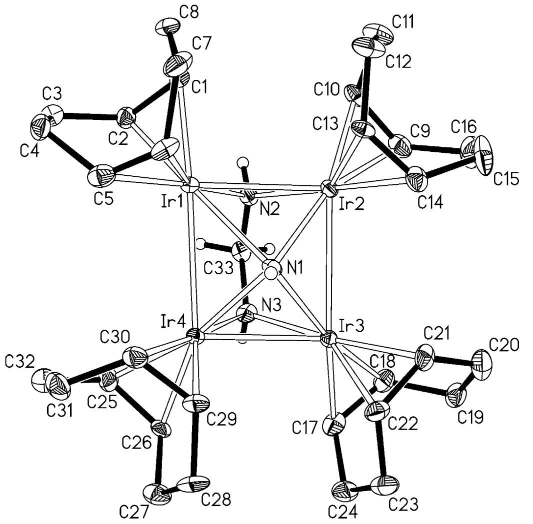


Figure 1. Crystal structure of complex **2**. Selected bond lengths [Å] and angles [°]: Ir1–N1 2.317(4), Ir1–N2 2.063(4), Ir2–N1 2.117(4), Ir2–N2 2.094(4), Ir3–N1 2.221(4), Ir3–N3 2.082(5), Ir4–N1 2.105(4), Ir4–N3 2.091(4), mean Ir–Ct 2.007(16), N2–C33 1.458(7), N3–C33 1.453(7); N1-Ir1-N2 76.85(16), N1-Ir2-N2 80.81(17), N1-Ir3-N3 77.78(17), N1-Ir4-N3 80.22(17), Ir1-N2-Ir2 82.98(16), Ir3-N3-Ir4 80.66(16). Ellipsoids set at 50% probability. Only hydrogen atoms for the bridging ligands have been shown. Ct = the midpoints of the olefinic bonds.

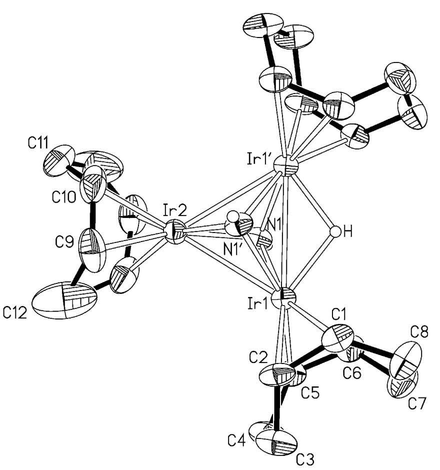


Figure 2. Crystal structure of complex **3**. Selected bond lengths [Å] and angles [°]: Ir1–N1 2.018(3), Ir1–N1′ 2.030(3), Ir2–N1 2.019(4), mean Ir–Ct 2.002(14), Ir1–Ir2 2.7758(2), Ir1–Ir1′ 2.8572(3), Ir1–H 1.788(19); Ir1′-Ir1-Ir2 59.025(4), Ir1-Ir2-Ir1′ 61.950(8), N1-Ir1-N1′ 73.58(16), N1-Ir2-N1′ 73.79(19), Ir1-N1-Ir2 86.90(13), Ir1-N1-Ir1′ 89.90(13). Ellipsoids set at 50% probability. Atoms marked with (′) are related to the corresponding unmarked atoms through a twofold axis. Ct = the midpoints of the olefinic bonds.

dral angle of 88.9(5)° with the tetrametallic plane. However, the four diolefins from the cyclooctadiene ligands do not coordinate perpendicular to the Ir_4 plane, but rather are slightly twisted towards the less sterically demanding imido ligand, avoiding any potential intermolecular interaction with this polar group. To the best of our knowledge, this is the first example of a low-valent late-transition-metal mixed parent imido/amido complex.

Complex **3** possesses an isosceles-triangular Ir_3 core (Figure 2), doubly capped by two μ_3-NH imido ligands, which form a trigonal bipyramid comprised of the three metal atoms in the equatorial plane and the N atoms of the two imido fragments in the apical positions, at a distance of 1.212(3) Å from the trimetallic plane. The whole molecule exhibits a crystallographic twofold axis of symmetry with only half the molecule as an independent part. A short metal–metal distance of 2.7758(2) Å is observed between Ir1 and Ir2, whereas the equivalent iridium atoms (Ir1 and Ir1′) are separated by 2.8572(3) Å; both distances are within the appropriate range for metal–metal bonds. In fact, electron counting for **3** gives the expected 48 e^- for a metallic triangle. The hydride ligand, clearly observed in the NMR measurements (see below), was included in the model as a bridging hydride, based on electrostatic potential calculations, and is also situated on the twofold axis, connecting the two crystallographically related Ir atoms.

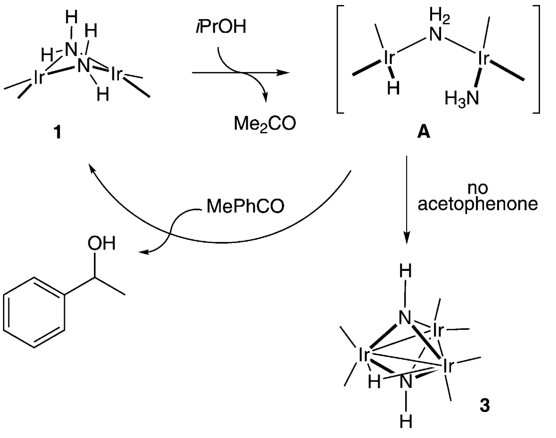
The ^1H, $^{13}C\{^1H\}$-APT, and HSQC NMR spectra of **3** in $[D_8]$toluene were consistent with a C_{2v} symmetry at all temperatures. Accordingly, both the olefinic protons and carbon atoms were observed as a set of three signals, whereas the imido ligands were located at low field as a broad singlet, and the bridging hydride was seen at $\delta = -20.27$ ppm. The signal from the imido ligands and that of the bridging hydride occurred in a 2:1 ratio.Selective NOE experiments confirmed the hydride to be bridging the two equivalent Ir1 and Ir1′ metals. The equivalent imido nitrogen atoms were detected at $\delta = 160.4$ ppm by ^1H-^{15}N HMQC spectroscopy, which is a far low-field shift compared with the bridging amido ligands.[8]

It seems reasonable that the methanol released in the reaction of the methoxo iridium complex with gaseous NH_3 should be the origin of the CH_2 fragment of the methylenediamido ligand present in cluster **2**. To check this possibility, we monitored the reaction of amido complex **1** with methanol at room temperature in $[D_8]$toluene by NMR spectroscopy. After six days, we observed the presence of unreacted **1**, the formation of the mixed-bridging complex $[Ir_2(cod)_2(\mu\text{-}OMe)(\mu\text{-}NH_2)]$, and cluster **3** in a 1:0.5:0.2 ratio. Further heating at 65 °C gave a mixture of **1**/**3** in a 0.2:1 ratio, along with an insoluble red solid that analysis showed to be cluster **2**. These observations suggested that the released methanol could be slowly dehydrogenated by **1** affording formaldehyde,[13] which ultimately would be responsible for the transformation of **1** into cluster **2**.[14] To test this statement, we carried out the reaction of amido complex **1** with formaldehyde. Treatment of **1** with paraformaldehyde in THF for six days reproducibly produced red crystals of complex **2**, $[Ir_4(cod)_4(\mu_4\text{-}\eta^2\text{-}HNCH_2NH)(\mu_4\text{-}NH)]$, in 38% yield.[15]

Further information about this process of alcohol dehydrogenation was obtained by following the reaction of **1** with the model isopropyl alcohol in $[D_8]$toluene at 65 °C by NMR spectroscopy. We observed the gradual production of acetone along with clean and quantitative formation of **3** within 16 h; interestingly, no other iridium species could be detected under these conditions. On the other hand, the partial incorporation of deuterium at the imido and hydride positions in **3** was detected by ^2H spectroscopy during deuterium labeling experiments carried out with **1** and $(CD_3)_2CDOD$ at

70 °C. As expected, complex **1** is a catalyst precursor for the transfer hydrogenation of acetophenone from *i*PrOH to afford 1-phenylethanol (see the Supporting Information).

The experimental observations can be tentatively explained by considering the formation of an unusual diiridium hydrido intermediate species **A**, as a consequence of a hydrogen transfer process (Scheme 1). The composition and dinuclear nature of this species are supported by theoretical calculations (see below). This reactive Ir^I species **A** seems to be responsible for the observed catalytic hydrogen transfer reactions from isopropyl alcohol to acetophenone to yield 1-phenylethanol; however, in the absence of acetophenone, or when its concentration has substantially decreased, dehydrogenation of *i*PrOH by **1** yields the stable cluster **3**, as confirmed by ^{1}H NMR spectroscopy, an observation that allowed us to prepare cluster **3** in excellent yield.



Scheme 1. Catalytic cycle proposed for the transfer hydrogenation of acetophenone with *i*PrOH and **1**, including the formation of **3** in the absence of acetophenone.

The catalytic dehydrogenation of methanol or isopropyl alcohol to respectively yield formaldehyde or acetone is a favorable process, as was shown by Noyori in a theoretical study on amido/amine ruthenium complexes,[16] in which the operative pathway implies a cyclic six-membered transition state. However, in our specific case a similar pathway is not favorable.[17] Theoretical calculations at the M06 level have been carried out to substantiate the catalytic cycle proposed in Scheme 1. The ring structure of the amido complex **1** can be opened by the decoordination of one Ir–NH_2 dative bond to yield **1′**, a process with an activation energy of 24.0 kcal mol^{-1}. Structure **1′** possesses an $-NH_2$ unit bearing a lone pair, and the Ir–Ir distance is shortened from 2.898 Å (1) to 2.731 Å (**1′**) (Figure 3 a).

The concerted dehydrogenation of isopropanol by **1′** takes place through an eight-membered-ring pericyclic mechanism (Figure 3 b). First, a hydrogen bond is formed between the nitrogen lone pair of **1′** and *i*PrOH, which leads to the transition structure **TS2**, with an activation energy of 13.5 kcal mol^{-1}. Similar to the metal-ligand bifunctional mechanism proposed by Noyori, [16] both hydrogen atoms are transferred simultaneously to the Ir and NH_2 ligand.

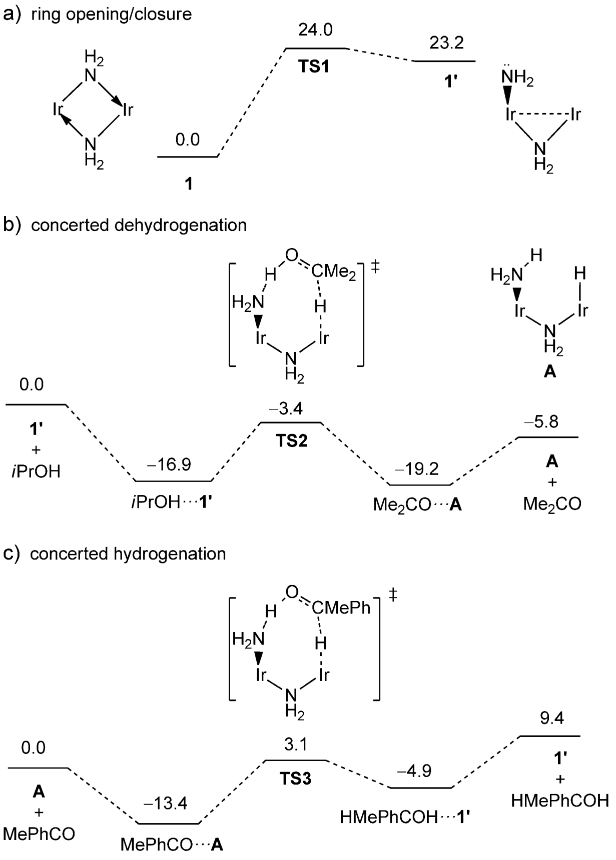


Figure 3. Computed DFT potential-energy profile for the catalytic hydrogen transfer from *i*PrOH to acetophenone. Energies given in kcal mol^{-1} relative to **1** (a), **1′**+*i*PrOH (b), and **A**+MePhCO (c).

However, owing to the starting bimetallic ring structure and the steric hindrance enforced by the cyclooctadiene ligands, cooperative participation of the NH_2-Ir-NH_2-Ir moiety is required. Amine hydrido diiridium intermediate **A** is formed and, in presence of acetophenone, the hydrogen atoms are transferred from **A** through transition structure **TS3**, with an activation energy of 16.5 kcal mol^{-1}, to close the catalytic cycle (Figure 3 c).

Although the multiple activation of ammonia by early-transition-metal precursors in high oxidation states to yield imido complexes is well documented,[18] there is only one report involving a double activation of ammonia mediated by polyhydrido and μ_3-oxo triruthenium clusters, which activate ammonia to form μ_3-NH imido linkages.[19] In this context, the transformation of a methoxo diiridium compound to imido clusters **2** and **3** upon interaction with ammonia can be viewed as a formal multiple activation of ammonia. The mere existence of parent imido complexes of late transition metals (Co triad and after) in low oxidation states is extremely rare, a situation explained in terms of $d\pi/p\pi$ repulsions between the metal and the nucleophilic nitrogen centers.[20] Most of these species are based on N-aryl/tosyl-substituted derivatives, the enhanced electron-withdrawing properties of which help to stabilize them by forming strong M–N bonds.[21] Consequently, there are few examples of parent imido late-transition-metal complexes from Group 9 characterized to date,[22,7a] and none of them prepared directly from ammonia.

In summary, the work presented herein not only emphasizes the importance of late-transition-metal amido (M$-$NH$_2$) bonds in the context of the dehydrogenation of alcohols and amido/imido cluster formation, but also reveals an unprecedented bimetallic mechanism that allows a concerted net hydrogen transfer through a proposed eight-membered dimetallacycle.

Experimental Section

Synthesis of **2**: Solid paraformaldehyde (16 mg, 15 μL, 0.55 mmol, 1.08 g L^{-3}) was added by syringe to a solution of **1** (0.14 g, 0.22 mmol) in deoxygenated THF (10 mL), and then stirred for 6 days. At this point, a red solid (**2**) was separated by filtration through a cannula, washed with hexanes, and dried under vacuum (53 mg, 38 %). IR (solid): $\tilde{\nu} = 3232$, 3170 cm^{-1}; elemental analysis calcd (%) for C$_{33}$H$_{53}$Ir$_4$N$_3$: C 31.44, H 4.24, N 3.33; found: C 31.23, H 4.23, N 3.21.

Synthesis of **3**: **1** (0.15 g, 0.24 mmol), toluene (20 mL) and isopropyl alcohol (4.8 mmol, 0.4 mL) were placed in a Schlenk tube modified with a Dean Stark apparatus, which was half-filled with toluene topped with a condenser. The mixture was stirred at 65 °C for 16 h. The volatiles were then removed under vacuum to afford an orange solid that was washed with diethyl ether (2 × 10 mL) and then dried under vacuum (0.13 g, 85 %). ^{1}H NMR (300 MHz, [D$_8$]toluene, 0 °C, TMS): $\delta = 8.76$ (br s, 2 H; NH), 3.93 (m, 4 H), 3.87 (m, 4 H), 3.63 (m, 4 H) (=CH, cod), 2.56 (m, 8 H), 2.41 (m, 16 H) (CH$_2$ cod); -20.27 ppm (s, 1 H; Ir$-$H); ^{13}C{^{1}H} NMR+HSQC (100 MHz, [D$_8$]toluene, 0 °C, TMS): $\delta = 65.1$, 58.0, 57.3 (all s; = CH), 34.5, 33.8, 33.7 ppm (all s, CH$_2$) (cod); ^{15}N-^{1}H HMQC (40 MHz, [D$_8$]toluene, 0 °C, NH$_3$): $\delta = 160.4$ ppm (br s; NH); MS (μ-TOF$^+$): m/z 931.2 (M^+-3H); IR (solid): $\tilde{\nu} = 3312$ (NH$_2$), 2150 cm^{-1} (Ir$-$H); elemental analysis calcd (%) for C$_{24}$H$_{39}$Ir$_3$N$_2$: C 30.92, H 4.22, N 3.01; found: C 30.81, H 4.18, N 2.98.

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[12] Crystal data for **2**: C$_{33}$H$_{53}$Ir$_4$N$_3$, $M = 1260.58$, yellow irregular prism, $0.08 \times 0.07 \times 0.04$ mm^3, triclinic, P-1, $a = 11.4462(6)$, $b = 12.0256(6)$, $c = 12.9238(7)$ Å; $\alpha = 70.2100(10)$, $\beta = 86.2030$ (10), $\gamma = 66.8810(10)$°; $V = 1534.86(14)$ Å^3; $Z = 2$; $\mu = 17.314$ mm^{-1}, min. and max. transmission factors 0.636 and 0.746; $2\theta_{\max} = 57.30$°; 18918 reflections collected, 7212 unique [$R_{\text{int}} = 0.0238$]; number of data/restraints/parameters: 7212/1/379; final $Gof = 1.040$; $R_1 = 0.0241$ [6174 reflections, $I > 2\sigma(I)$]; $wR(F^2) = 0.0541$ for all data. Crystal data for **3**: C$_{24}$H$_{39}$Ir$_3$N$_2$, $M = 932.17$, red prism, $0.213 \times 0.135 \times 0.130$ mm^3, monoclinic, $C2/c$, $a = 16.6274(7)$, $b = 10.9487(4)$, $c = 13.4154(5)$ Å; $\beta = 99.0310$ (10)°; $V = 2411.98(16)$ Å^3; $Z = 4$; $\mu = 16.524$ mm^{-1}, min. and max. transmission factors 0.085 and 0.188; $2\theta_{\max} = 61.04$°; 13862 reflections collected, 34545 unique [$R_{\text{int}} = 0.0276$]; number of data/restraints/parameters: 34545/3/153; final $Gof = 1.098$; $R_1 = 0.0226$ [3271 reflections, $I > 2\sigma(I)$]; $wR(F^2) = 0.0566$ for all data. CCDC 872933 (**2**) and 872934 (**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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