Terminal Imido Rhodium Complexes^[**]

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Dedicated to Prof. Pablo Espinet on occasion of his 65 birthday

Abstract: Compounds of the late transition metals with multiple $M=X$ bonds ($X = CR_2, NR, O$) represent a synthetic challenge, partly overcome by preparative chemists, but with noticeable lacks in the second and third rows. For example, there are no isolated examples of terminal imido rhodium complexes known to date. Here, we showcase the isolation, characterization, and some preliminary reactivity studies of the first rhodium complexes $[Rh(PhBP_3)(NR)]$ ($PhBP_3 = PhB(CH_2PPh_2)_3$) with a multiple and terminal $Rh=N$ bond. These imidos result from reactions of organic azides with the corresponding rhodium(I) complex having a labile ligand, and display a pseudo-tetrahedral core geometry with an almost linear $Rh-N-C$ arrangement ($177.5(2)^\circ$) and a short $Rh-N$ bond ($1.780(2) \text{ \AA}$). We also show that the $Rh=N$ bond undergoes protonation at nitrogen or addition of H_2 , as well as can engage in nitrene group transfer and cycloaddition reactions.

Complexes with a terminal imido functionality bound to a single late transition metal center (Groups 8-11) are or have been proposed as intermediates in novel C-H bond functionalization reactions such as amination and aziridination through the use of N-atom transfer protocols,^[1] and yet the isolated of such compounds still remain relatively uncommon.^[2] The lack of characterization of such active intermediates that can mediate catalytic C-N bond formation is rather unfortunate, and claims for a fundamental understanding of metal-imido or metal-nitrene species are warranted. Unfortunately, the preparation of such interesting species can be difficult, especially when such system can participate in reactions such as H-atom transfer reactions involving aliphatic C-H bonds.^[3]

The high $p\pi$ electron loading of the imido group renders multiple bond character and strong $M=N$ bonds possible for metals with low d^n electron counts, i.e., for early transition metals and high oxidation states, but destabilizes the interaction with late transition metals in tetragonal structures with filled $d\pi$ orbitals.^[4] This typically makes their isolation difficult. However, the use of low-coordinate architectures that possess empty $d\pi$ metal orbitals has enabled various groups to uncover the synthesis and reactions of a number of terminal imido complexes of cobalt^[5] and nickel^{[1e],[6]} with geometries ranging from pseudo-tetrahedral, trigonal-planar and even linear structures, and with d^6 to d^8 configurations. Specifically, when moving to the heavier congeners of group 9,

Bergman's Ir imido complexes with the general formula $Cp^*Ir\equiv NR$ ($R = \text{aryl, alkyl, silyl}$)^[7] still stand as the sole structurally characterized compound with a terminal imido ligand. Surprisingly, rhodium,^[8] the link between Co and Ir, has yet to show tendency to stabilize a terminal imido ligand.

Indirect evidence for the existence of a transient imido complex $[(C_5Me_5)RhNR]$ ($R = 2,6\text{-}i\text{-Pr}_2C_6H_3$) was obtained from the isolation of the tetrazene $[(C_5Me_5)Rh(mesN_4R)]$ as a result of the condensation of the species generated in situ with $mesN_3$.^[9] Unfortunately, the related dinuclear complex $\{[(C_5Me_5)Rh(\mu\text{-}NTs)]_2\}$ yields also the same type of product.^[10] Other examples of rhodium imidos were reported by McGlinchey and Stone, but such species have been ill-characterized.^[11] As a result, just two families of d^8 -rhodium imido complexes are known, namely, the dinuclear dppm-bridged amido/imido tautomers,^[12] and polynuclear complexes based on triply bridging " $\mu_3\text{-NC}_6\text{H}_4\text{Me}$ " imido ligands.^[13] More recently, a related Rh(II) complex with a single imido group bridging the metal-metal bond has been reported.^[14]

Our initial attempts to isolate imido compounds from reactions of Rh(III) complexes via deprotonation of coordinated amines, as reported by Danopoulos and Wilkinson,^[9] were unsuccessful. We then hypothesized whether a low-coordinate precursor was required to generate imido species with a multiple $N=Rh$ bond through oxidation. For this reason, we focused our attention on the *fac*- $Rh[PhBP_3]$ fragment, as highlighted by Peters with iron and cobalt ($PhBP_3 = PhB(CH_2PPh_2)_3$).^[4a] Herein we report the successful synthesis and full characterization of the first rhodium complexes bearing a terminal imido ligand and also report some exploratory reactions involving the $Rh=N$ multiple bond.

We chose a relatively bulky adamantyl azide as a nitrene source by reaction with the complex $[Rh(PhBP_3)(C_2H_4)(NCMe)]$ (**1**).^[15] Upon addition and warming of the solution in toluene a slow change of color from yellow to brown was observed, which yielded the imido complex $[Rh(PhBP_3)(NAd)]$ (**2**) as amber-like crystals after subsequent workup. No intermediates were observed when the reaction was monitored by NMR spectroscopy (1H , ^{31}P ; C_6D_6). Aromatic azides react also with **1** in toluene to yield purple solutions of the corresponding imido complexes $[Rh(PhBP_3)(NR)]$ ($R = 2,6\text{-}i\text{-Pr}_2C_6H_3$ (**3**), C_6F_5 (**4**)). Complex **3** was isolated as a purple microcrystalline solid, while **4** was characterized in situ.

For complex **2**, we were fortunate to obtain reliable X-ray diffraction data of a single crystal,^[16] and the structure revealed a rhodium atom confined in an almost perfect tetrahedral with overall C_{3v} symmetry due to its bonding to three equivalent phosphorus atoms of the tripodal $PhBP_3$. The fourth site is represented by the imido ligand, having a $Rh-N_{\text{imido}}$ bond distance ($1.780(2) \text{ \AA}$) that is short by about $0.3 \text{ \AA}$ when compared to similar species having bridging amido or imido ligands,^{[10],[13],[17]} but similar to that observed for $[IrCp^*NR]$.^[7] The short distance together with an almost linear $Rh-N_{\text{imido}}-C_{\text{Ad}}$ angle ($177.5(2)^\circ$) are indicative of such ligand having multiple $Rh-N$ bond character. Although the adamantyl group was found to be disordered in two positions and these were modelled, for the purpose of clarity we display only one as shown in Figure 1.

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Figure 1. Left: structure (ORTEP at 50% level) of complex [Rh(PhBP₃)NAd] (**2**) (only the C^{ipso} atoms of the phenyl groups from PPh₂ are shown for clarity) (left). Selected bond distances (Å) angles (°): Rh–P1, 2.2629(7); Rh–P2, 2.2839(7); Rh–P3, 2.2591(7); Rh–N, 1.780(2); N–C46, 1.431(3); P1–Rh–N, 127.83(8); P2–Rh–N, 127.51(7); P3–Rh–N, 126.39(8); axis(B,Rh)–N, 179.59(9). Rh–N–C46, 177.5(2). Right: Space filling representation of complex **2**.

Repetitive attempts to grow up single crystals of complexes **3** or **4** gave systematically very small and geminated microcrystals, preventing crystallographic structure determination. Nonetheless, complexes **2-4** display a characteristic doublet ($J_{P,Rh} \approx 110$ Hz) in the $^{31}P\{^1H\}$ NMR spectra distinctive of species of high symmetry, as shown by the structure of **2**. All of them possess identical connectivity, which is clearly detected by the couplings of the phosphorus nuclei with carbon, proton, or fluorine nuclei of the groups R bonded to the imido nitrogen. Moreover, their hydrodynamic radii (r_H), evaluated by DOSY experiments, exhibit similar values (6.84, 6.69, and 6.36 Å, for **2**, **3**, and **4**, respectively), which evidences that they are mononuclear in solution and exclude plausible monomer/dimer equilibria. Furthermore, these radii are close to the averaged molecular ones calculated by DFT methods (7.07 and 6.74 Å, for **2a** and **4a**, respectively).

Complexes **2-4** are thermally stable, but highly sensitive to moisture, being **2** the least sensitive. Their solutions in C₆D₆ are immediately hydrolyzed by traces of water giving the free amine and uncharacterized beige solids insoluble in common organic solvents. Hence, the imido nitrogen is a Brønsted base that abstracts protons from water. In this sense, complex **2** reacts cleanly with protic acids such as HBF₄·Et₂O (2 molar-equiv) in acetonitrile to give the amine H₂NAd and [Rh(PhBP₃)(NCMe)₃](BF₄)₂.^[15] No other compounds except the starting complex were observed in this reaction when using a 1:1 molar ratio.

To gain insight into the electronic structure of complexes **2-4** and the characteristics of the Rh–N bond, DFT calculations [b3lyp, LanL2Tz(f)/6-311G(d)/6-31G(d,p)] were carried out on complexes [Rh(PhBP₃)(NR)] (R = Ad (**2a**), C₆F₅ (**4a**)) and on a model compound of **3** (**3a**), in which the ^{*i*}Pr substituents on the imido aryl were replaced by hydrogen. The results of the calculation for **2a** give geometrical parameters that are in good agreement with the experimentally determined structure of **2** (Figure S4 and Table S1). For the aryl imido complexes **3a** and **4a**, the symmetry of the calculated structure is lowered away from C₃ by distortion of the metal coordination sphere. An off-axis distortion in which the Rh–N vector is bent away from the B–C vector gives rise to a core slightly distorted towards a trigonal pyramid. In addition, the Rh–N–C angles (166.73 °, 170.68 °, respectively) are more bent than for the alkylimido **2**, which is typical for arylimido complexes.^[4b,18] The ground-state frontier MOs diagram for **2a** is shown in Figure 2. The LUMO and LUMO+1 correspond to two antibonding combinations of the metal-based orbitals 2e_a and 2e_s (of parentage d_{xz} and d_{yz}) with the p_x and p_y orbitals of the imido nitrogen. The respective bonding combinations, HOMO-39 and HOMO-40, are found lower

in energy, so that they correspond to two Rh–N π -bonds. The σ -component mainly arises from the overlap between the filled d_{z²} orbital (1a₁) with a filled sp orbital of the nitrogen, as observed in HOMO-2 and HOMO-63. Under this perspective, the Rh–N bond would lack the σ -component, hence more in accord with a double bond. Nonetheless, the topology of the d_{z²}-based MOs clearly suggests a further mixing with the empty low-lying 2a₁ orbital of the [Rh(PhBP₃)]²⁺ fragment (see inset in Figure 2). This symmetry-allowed mixing stabilizes the dz² orbital, mitigating the destabilizing effect of populating the Rh–N σ^* interaction. Moreover, the measured metrical parameters imply that the Rh–N bond should actually be considered close to a triple bond according to the bond distance computed for a Rh–N triple bond, 1.80 Å, using the method put forth by Pauling.^[19] On the whole, the bonding in this imido complex seems to be similar to that of pseudo-tetrahedral cobalt(III) imido complexes with tripodal ligands.^{[4b],[5a-f]}

Figure 2. Frontier MOs energy level diagram for complex **2a** showing relevant MOs involved in the multiple Rh=N bond. The blue inset shows the frontier MOs for the fragment [Rh(PhBP₃)]²⁺, while the red inset display those of the NAd fragment involved in the Rh=N bond.

Similar computed MO diagrams result for complexes **3a** and **4a**, but the relevant MOs are not degenerate and the HOMO–LUMO gap (3.00 eV for **3a** and **4a**) is smaller than for **2a**. In addition, although the natural charge of the Rh atom from a NBO analysis of **2a-4a** is quite similar (≈ 0.120), this is highly negative and noticeably larger for the nitrogen atom in **4a** (−0.7711) than in **3a** (−0.7018) and **2a** (−0.6983), which is indicative of a more polar Rh=N bond in **4a**. Both data are consistent with the experimental grade of reactivity of complexes: **4a** > **3a** > **2a** (vide infra).

We explored the reactivity of these imidos. Accordingly, group transfer of the imido functionality in **2** occurred in the presence of excess CO to form [Rh(PhBP₃)(CO)₂]^[20] and the isocyanate AdNCO in 16 hours (Scheme 1). A similar, but much faster reaction occurs when treating complex **3** with CO, which was completed in a matter of minutes to produce the same rhodium carbonyl complex and the isocyanate, 2,6-^{*i*}Pr₂C₆H₃NCO. Both isocyanates were characterized by their characteristic $\nu(\text{NCO})$ IR band between 2300 and 2250 cm^{−1} and ¹H NMR spectra. Related imide carbonylations are known for several late transition metal imides.^{[7],[21]}

Scheme 1. Synthesis and reactions of complexes 2-4.

In more unique reactions, exposure of a C₆D₆ solution of **2** or **4** to 5 atm of H₂ at 23 °C resulted in hydrogenation of the Rh=NR linkage to yield the dihydride rhodium complexes [Rh(PhBP₃)(H)₂(H₂NAd)] (**5**) and [Rh(PhBP₃)(H)₂(NCMe)],^[15] respectively, which were characterized by NMR spectroscopic methods. The reaction is very slow for **2** at room temperature taking five days to reach completion, while for **4** the hydrogenation is complete in 30 min. No diamagnetic intermediates were observed on monitoring the reactions by ¹H and ³¹P NMR spectroscopy. Since the metal is electrophilic, as shown by the previous reaction and the Rh positive charge while the nitrogen supports a negative charge, most probably hydrogen adds to the multiple Rh=N bond in a heterolytic way to produce an unobserved pentacoordinated amido-hydride complex of formula [Rh(PhBP₃)(H)(NHR)], which adds a second molecule of dihydrogen to render the amine-dihydride complexes. Since no intermediates are observed, we propose the first step to be slow en route to the final product. While the amine AdNH₂ remains coordinated in **5**, free amine C₆F₅NH₂ was found at the end of the reaction of **4**, as the result of the displacement by acetonitrile present in the reaction medium.

Complex **2** is sluggishly reactive and does not further transform with the azides N₃Ad, and N₃C₆F₅. However complex **4** is so reactive that it reacts immediately with N₃C₆F₅ to give the tetrazaene complex [Rh(PhBP₃){N₄(C₆F₅)₂}] (**6**). The synthesis of tetrazaene complexes from organic azides and low-valent metal precursors is well-precedented,^[22] although examples of rhodium tetrazaene complexes are quite scarce. In the solid state structure of complex **6**, the C₆F₅ groups are placed at the 1,4-positions of the tetrazaene, which is consistent with a dipolar 1,3-cycloaddition of the azide to the Rh=N bond (Scheme 1). Thus, the mechanism follows that proposed in the synthesis of tetrazenes from organic azides and isolated or transient metal-imido intermediates.^[22] Also in the structure of **6** (Figure 3) the rhodium atom displays a distorted trigonal bipyramidal environment, as a result of being gripped by the tripodal PhBP₃ and chelating N₄(C₆F₅)₂ ligands. The three Rh–P bond distances were found to be different, with the P-atom at the apical position (P3) being the longest. Both Rh–N bond distances are in the range of typical single Rh–N bonds with the equatorial one (Rh–N1) being the shortest. Within the tetrazaene ligand, the central N2–N3 bond distance is close to that of a double N=N bond while N1–N2 and N3–N4 bond distances are smaller than those of single N–N bonds. These short distances and the strictly planar ‘RhN₄’ metallacycle (maximum deviation for the plane 0.012 Å) indicate a delocalization in the ring. Accordingly, a major contribution to the electronic structure of **6** arises from the canonic form [Rh^{III}{(C₆F₅)₂N₄}²⁻] with a dianionic tetrazenide ligand, but the metal environment geometry and the N–N bond distances stand for a non-negligible representation of the tetrazadiene-Rh(I) form.

Figure 3. Structure (ORTEP at 50% level) of complex [Rh(PhBP₃){N₄(C₆F₅)₂}] (**6**) (only the C^{ipso} atoms of the phenyl groups from PPh₂ are shown for clarity). Selected bond distances (Å) and angles (°): Rh–P1, 2.3168(8); Rh–P2, 2.2926(9); Rh–P3, 2.4081(9); Rh–N1, 2.008(3); Rh–N4, 2.053(3); N1–N2, 1.397(4), N2–N3, 1.259(4); N3–N4, 1.371(4); P3–Rh–N4, 166.41(8); P1–Rh–N1, 149.76(8); P2–Rh–N1, 123.34(8); P1–Rh–P2, 86.83(3); N1–Rh–N4, 74.0(1); Rh–N1–N2, 118.0(2); N1–N2–N3, 114.3(3); N2–N3–N4, 116.4(3); N3–N4–Rh, 116.3(2).

The difference in reactivity of the aryl (**3**, **4**) versus the alkyl (**2**) imido complexes is not only determined by the electronic structure of these complexes but also by their kinetics. The Rh–N bond is protected in same way by the steric encumbrance provided by the phenyl groups of the tripod ligand, which encircle it with the planes almost aligned in the direction of the bond (see Figure 2 right). Presumably, the bent arrangement of the imido ligand in **3** and **4** and the reduced bulkiness of the aryl versus adamantyl groups permit the access to a wider array of substrates at the rhodium–imido bond.

Moreover, the bulkiness of the PhBP₃ ligand along with that of the adamantly group on the nitrogen avoid the formation of a dimer of the type [{Rh(PhBP₃)(μ-NR)}₂]. Further, even for the smaller C₆F₅ group, DFT calculations show the dimer to be very congested in the region between the rhodium atoms and 17.9 kcal mol⁻¹ higher in enthalpy than the monomer (see Supporting Information), which also corroborates these rhodium-imido complexes are mononuclear.

In summary, the first rhodium complexes containing terminal alkyl and aryl imido ligands have been prepared and characterized. These compounds are thermally stable and diamagnetic and the solid-state structure for an alkyl-imido derivative displays a linear Rh–N–C linkage with a short Rh–N distance whereby the metal ion is confined in a pseudo-tetrahedral environment.^[23] These characteristics are a consequence of a special and multiple Rh=N bond consisting primarily in two Rh–N π-bonds. Our findings fill a gap in the chemistry of Group 9 metals. Preliminary studies indicate that rhodium imides are somewhat ambiphilic and can therefore undergo protonation at nitrogen as well as hydrogenation at the Rh=N bond. These systems also engage in nitrene group transfer, and cycloaddition reactions, although their reactivity is strongly modulated by the organic group bound to nitrogen.

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Multiple Bonds

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Terminal Imido Rhodium Complexes: A Missing Link

A missing link: Terminal imido rhodium complexes with a multiple $\text{Rh}=\text{N}$ bond have been prepared, providing thus a type of compound that has remained elusive to synthesis. The finding fills a gap in the chemistry of Group 9 metals. Preliminary studies indicate rhodium imides are somewhat ambiphilic and can therefore undergo protonation at nitrogen as well as hydrogenation at the $\text{Rh}=\text{N}$ bond. These systems also engage in nitrene group transfer and cycloaddition reactions.