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Multiple Bonds

Terminal Imido Rhodium Complexes**

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Dedicated to Professor Pablo Espinet on the occasion of his 65th birthday

Abstract: *Compounds of the late transition metals with M=X multiple bonds ($X = CR_2$, NR, O) represent a synthetic challenge, partly overcome by preparative chemists, but with noticeable gaps in the second- and third-row elements. For example, there are no isolated examples of terminal imido rhodium complexes known to date. Described herein is 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 imido compounds 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)°] and a short Rh−N bond [1.780(2) Å]. We also show that the Rh=N bond undergoes protonation at the nitrogen atom or addition of H_2, and also engages 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 proceeding through N-atom-transfer protocols,[1] and yet the isolation of such compounds still remain relatively uncommon.[2] The lack of characterization of such active intermediates, which 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 a system can participate in reactions such as H-atom-transfer reactions involving aliphatic C−H bonds.[3]

The high pπ-electron loading of the imido group renders multiple-bond character and strong M=N bonds possible for metals with low d^n electron counts, that is, for early transition metals and high oxidation states, but destabilizes the interaction with late transition metals in tetragonal structures with filled dπ orbitals.[4] This feature typically makes their isolation difficult. However, the use of low-coordinate architectures which possess empty dπ-metal orbitals has enabled various groups to uncover the synthesis and reactions of a number of terminal imido complexes of cobalt[5] and nickel[1c,e,6] having geometries ranging from pseudo-tetrahedral, trigonal-planar, to even linear structures, and with d^6 to d^8 configurations. Specifically, when moving to the heavier congeners of Group 9, the iridium imido complexes reported by Bergman and co-workers, having the general formula [Cp*Ir≡NR] (R = aryl, alkyl, silyl),[7] still stand as the sole structurally characterized compound with a terminal imido ligand. Surprisingly, rhodium,[8] which sits between cobalt and iridium, has yet to show a tendency for stabilizing a terminal imido ligand.

Indirect evidence for the existence of the transient imido complex [(C_5Me_5)RhNR] (R = 2,6-*i*Pr$_2$C$_6$H$_3$) was obtained from the isolation of the tetrazene [(C_5Me_5)Rh(mesN$_4$R)], which resulted from the condensation of the species generated in situ with mesN$_3$.[9] Unfortunately, the related dinuclear complex [{(C_5Me_5)Rh(μ-NTs)}$_2$] also yields the same type of product.[10] Other examples of rhodium imido compounds 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 μ$_3$-NC$_6$H$_4$Me imido ligands.[13] More recently, a related rhodium(II) complex with a single imido group bridging the metal–metal bond was reported.[10c]

Our initial attempts to isolate imido compounds from reactions of rhodium(III) complexes by 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 the imido species with a N=Rh bond through oxidation. For this reason, we focused our attention on the *fac*-Rh[PhBP$_3$] fragment, as highlighted by Saouma and 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 to react with the complex [Rh(PhBP$_3$)(C_2H_4)(NCMe)] (**1**; see Scheme 1).[14] Upon addition and warming of the solution in toluene, a slow change of color from yellow to brown was observed, and the imido complex [Rh(PhBP$_3$)(NAd)] (**2**) was yielded as amberlike crystals after subsequent

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workup. No intermediates were observed when the reaction was monitored by NMR spectroscopy (^{1}H, ^{31}P; C_6D_6). Aromatic azides also react with **1** in toluene to yield purple solutions of the corresponding imido complexes [Rh(PhBP$_3$)(NR)] [R = 2,6-iPr$_2$C$_6$H$_3$ (**3**), C_6F_5 (**4**)]. The complex **3** was isolated as a purple microcrystalline solid, while **4** was characterized in situ.

For **2**, we were fortunate to obtain reliable X-ray diffraction data of a single crystal,[15] and the structure revealed a rhodium atom confined to an almost perfect tetrahedral with an overall C_{3v} symmetry resulting from 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 of 1.780(2) Å, which is shorter by about 0.3 Å when compared to similar species having bridging amido or imido ligands,[10,13,16] 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)°] are indicative of such ligands having a Rh=N multiple bond. Although the adamantyl group was found to be disordered in two positions, for the purpose of clarity we display only one as shown in Figure 1.

Repetitive attempts to grow single crystals of **3** or **4** systematically gave very small and geminated microcrystals, thus preventing crystallographic structure determination. Nonetheless, **2–4** display a doublet ($J_{\text{P,Rh}} \approx 110$ Hz) in the ^{31}P{^{1}H} NMR spectra, which is distinctive of species with high symmetry, as shown by the structure of **2**. All of them possess identical connectivity, which is clearly evident by the couplings of the phosphorus nuclei with carbon, proton, or fluorine nuclei of the groups R bonded to the imido nitrogen atom. 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), thus showing that they are mononuclear in solution and excludes plausible monomer/dimer equilibria. Furthermore, these radii are close to the average molecular ones calculated by DFT methods (7.07 and 6.74 Å, for **2a** and **4a**, respectively).

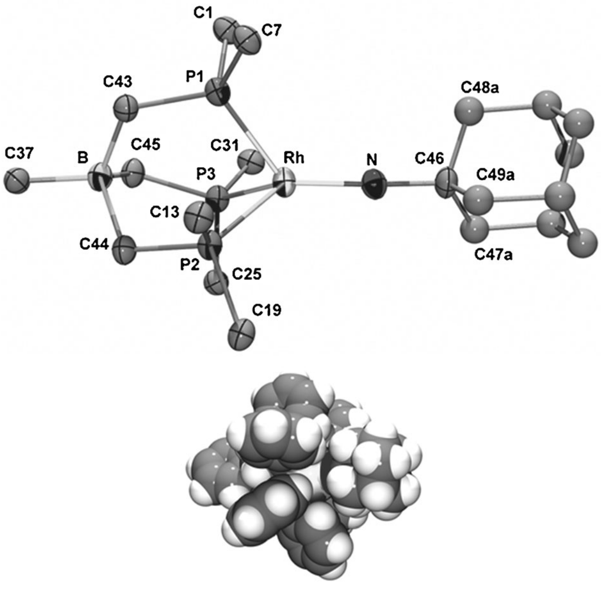

Figure 1. Top: Structure (ORTEP at 50% level) of complex [Rh(PhBP$_3$)NAd] (**2**; only the C^{ipso} atoms of the phenyl groups from PPh$_2$ are shown for clarity). Selected bond distances [Å] angles [°]: Rh–P1 2.2629(7), Rh–P2 2.2839(7), Rh–P3 2.2591(7), Rh–N 1.780(2), N–C46 1.431(3); P1-Rh-N 127.83(8), 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). Bottom: Space-filling representation of **2**.

Complexes **2–4** are thermally stable, but highly sensitive to moisture, with **2** being the least sensitive. Their solutions in C_6D_6 are immediately hydrolyzed by traces of water, thus giving the free amine and uncharacterized beige solids which are insoluble in common organic solvents. Therefore, the imido nitrogen atom is a Brønsted base which abstracts protons from water. In this sense, **2** reacts cleanly with protic acids such as $HBF_4 \cdot Et_2O$ (2 molar equivalents) in acetonitrile to give the amine H$_2$NAd and [Rh(PhBP$_3$)(NCMe)$_3$](BF$_4$)$_2$.[14] 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 structures of **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 the complexes [Rh(PhBP$_3$)(NR)] [R = Ad (**2a**), C$_6$F$_5$(**4a**)] and on a model compound of **3** (**3a**), in which the iPr substituents on the imido aryl were replaced by hydrogen. The results of the calculation for **2a** gave geometrical parameters which are in good agreement with the experimentally determined structure of **2** (see Figure S4 and Table S1 in the Supporting Information). For the aryl imido complexes **3a** and **4a**, the symmetry of the calculated structure moves away from C_3 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 which is slightly distorted towards a trigonal pyramid. In addition, the Rh-N-C angles (166.73° and 170.68°, respectively) are more bent than those for the alkylimido **2**, which is typical for arylimido complexes.[4b,17] The ground-state frontier molecular orbital (MO) 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 atom. The respective bonding combinations, HOMO-39 and HOMO-40, are found to be 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_{z^2} orbital (1a$_1$) with a filled sp orbital of the nitrogen atom, as observed in HOMO-2 and HOMO-63. From this perspective, the Rh–N bond would lack the σ component, and hence be more in accord with a double bond. Nonetheless, the topology of the d_{z^2}–based MOs clearly suggests further mixing with the empty low-lying 2a$_1$ orbital of the [Rh(PhBP$_3$)]$^{2+}$ fragment (see inset in Figure 2). This symmetry-allowed mixing stabilizes the dz^2 orbital, thus 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 to be close to a triple bond according to the bond distance (1.80 Å) computed for a Rh–N triple bond using the method put forth by Pauling.[18] 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]

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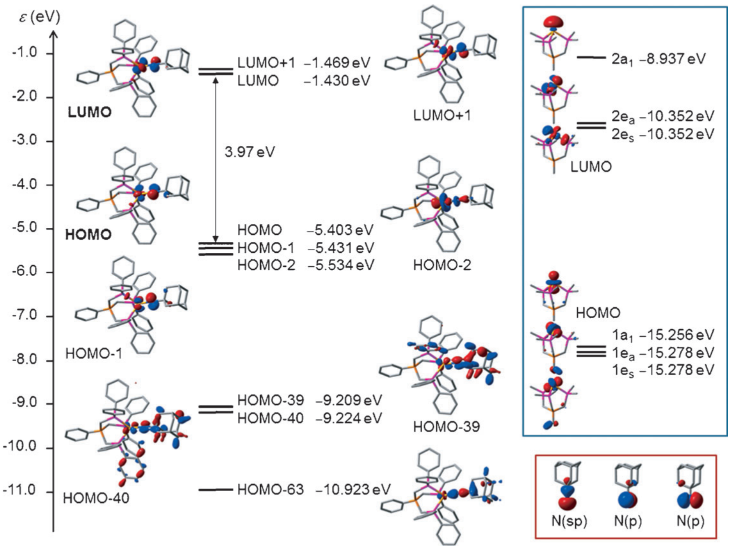
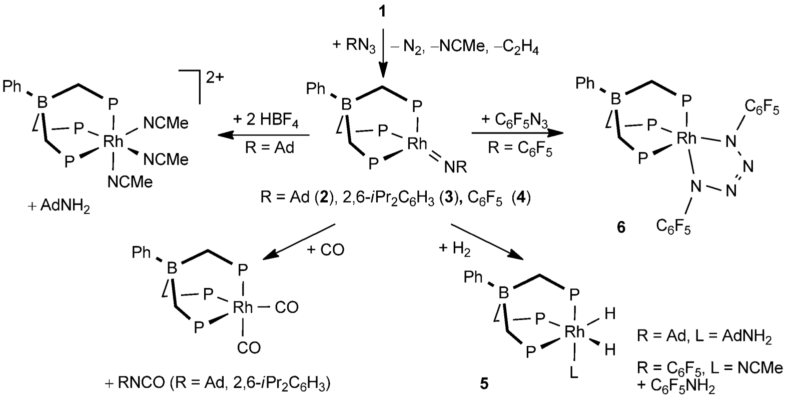


Figure 2. Frontier MO energy level diagram for **2a** showing relevant MOs involved in the Rh=N bond. The inset framed in blue shows the frontier MOs for the fragment $[Rh(PhBP_3)]^{2+}$, while the inset framed in red displays those of the NAd fragment involved in the Rh=N bond.

Similar computed MO diagrams were determined for **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 that for **2a**. In addition, although the natural charge of Rh from an NBO analysis of **2a**–**4a** is quite similar (ca. 0.120), this value is highly negative and noticeably larger for the nitrogen atom in **4a** (−0.7711) than for the one in **3a** (−0.7018) and **2a** (−0.6983), thus indicating a more polar Rh = N bond in **4a**. Both data sets are consistent with the experimental ranking of the reactivity of complexes: **4a** > **3a** > **2a**.



Scheme 1. Synthesis and reactions of complexes **2**–**4**.

We explored the reactivity of these imido compounds. Accordingly, group transfer of the imido functionality in **2** occurred in the presence of excess CO to form $[Rh(PhBP_3)(CO)_2]$[19] and the isocyanate AdNCO in 16 hours (Scheme 1). A similar, but much faster reaction occurs when treating **3** with CO, and was complete in a matter of minutes to produce the same rhodium carbonyl complex and the isocyanate, 2,6-iPr$_2$C$_6$H$_3$NCO. Both isocyanates were characterized by their characteristic ν(NCO) IR band between 2300 and 2250 cm^{-1} and ^{1}H NMR spectra. Related imide carbonylations are known for several late-transition-metal imides.[7,20]

In more unique reactions, exposure of a C_6D_6 solution of **2** and **4** to 5 atm of H_2 at 23 °C resulted in hydrogenation of the Rh = NR linkage to yield the dihydride rhodium complexes $[Rh(PhBP_3)(H)_2(H_2NAd)]$ (**5**) and $[Rh(PhBP_3)(H)_2(NCMe)]$,[14] respectively, which were characterized by NMR spectroscopic methods. The reaction is very slow for **2** at room temperature, thus taking five days to reach completion, while for **4** the hydrogenation is complete in 30 minutes. No diamagnetic intermediates were observed when monitoring the reactions by ^{1}H and ^{31}P NMR spectroscopy. Since the metal is electrophilic, as shown by the previous reaction, and the Rh has positive charge while the nitrogen atom supports a negative charge, it is most likely that hydrogen adds to the Rh=N bond in a heterolytic way to produce an unobserved pentacoordinated amido-hydride complex with the formula $[Rh(PhBP_3)H(NHR)]$, and then adds a second molecule of dihydrogen to generate 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 $AdNH_2$ remains coordinated in **5**, the free amine $C_6F_5NH_2$ was found at the end of the reaction of **4**, as the result of the displacement by acetonitrile which is present in the reaction medium.

Complex **2** is sluggishly reactive and does not further transform with the azides N_3Ad, and $N_3C_6F_5$. However **4** is so reactive that it reacts immediately with $N_3C_6F_5$ to give the tetrazene complex $[Rh(PhBP_3)\{N_4(C_6F_5)_2\}]$ (**6**). The synthesis of tetrazene complexes from organic azides and low-valent metal precursors is well precedented,[21] although examples of rhodium tetrazene complexes are quite scarce. In the solid-state structure of **6**, the C_6F_5 groups are placed at the 1,4-positions of the tetrazene, 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.[21] Also, in the structure of **6** (Figure 3) the rhodium atom displays a distorted trigonal bipyramid environment, as a result of being gripped by the tripodal $PhBP_3$ and chelating $N_4(C_6F_5)_2$ 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 tetrazene 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 RhN_4

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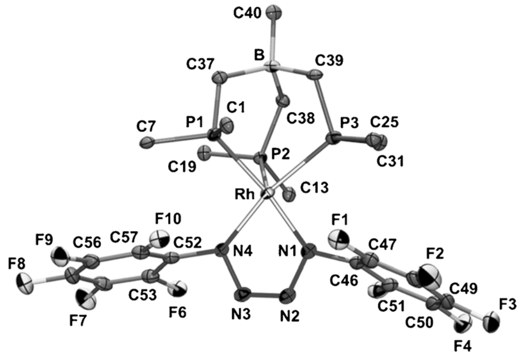

Figure 3. Structure (ORTEP at 50% level) of complex [Rh(PhBP$_3$){N$_4$(C$_6$F$_5$)$_2$}] (**6**; only the C^{ipso} atoms of the phenyl groups from PPh$_2$ are shown for clarity). Selected bond distances [Å] and angles [°]: Rh–P1 2.3168(8), Rh–P2 2.2926(9), Rh–P3 2.4081(9), Rh–N1 2.008(3), Rh–N4 2.053(3), 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).

metallacycle (maximum deviation for the plane 0.012 Å) indicate delocalization in the ring. Accordingly, a major contribution to the electronic structure of **6** arises from the canonic form [Rh^{III}{(C$_6$F$_5$)$_2$N$_4$}$^{2-}$] with a dianionic tetrazenide ligand, but the metal geometry and the N–N bond distances stand for a non-negligible representation of the tetrazadiene-Rh^{I} form.

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 the same way by the steric bulk provided by the phenyl groups of the tripod ligand, which encircle it with the planes almost aligned in the direction of the bond (Figure 2, bottom). Presumably, the bent arrangement of the imido ligand in **3** and **4** and the reduced bulkiness of the aryl versus adamantyl groups permit access to a wider array of substrates at the rhodium–imido bond.

Moreover, the bulkiness of the PhBP$_3$ ligand along with that of the adamantyl group on the nitrogen atom prevent the formation of a dimer of the type [{Rh(PhBP$_3$)(μ-NR)}$_2$]. Further, even for the smaller C$_6$F$_5$ 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 the Supporting Information), thus corroborating that 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 bond distance whereby the metal ion is confined in a pseudo-tetrahedral environment.[22] These characteristics are a consequence of a special Rh=N bond consisting primarily of 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 the nitrogen atom 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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[1] For recent leading references, see: a) J. L. Roizen, M. E. Harvey, J. Du Bois, *Acc. Chem. Res.* **2012**, *45*, 911 – 922; b) Q. Nguyen, K. Sun, T. G. Driver, *J. Am. Chem. Soc.* **2012**, *134*, 7262 – 7265; c) S. Wiese, J. L. McAfee, D. R. Pahls, C. L. McMullin, T. R. Cundari, T. H. Warren, *J. Am. Chem. Soc.* **2012**, *134*, 10114 – 10121; d) T. A. Ramirez, B. Zhao, Y, Shi, *Chem. Soc. Rev.* **2012**, *41*, 931 – 942; e) C. A. Laskowski, A. J. M. Miller, G. L. Hillhouse, T. R. Cundari, *J. Am. Chem. Soc.* **2011**, *133*, 771 – 773; f) F. Collet, C. Lescot, P. Dauban, *Chem. Soc. Rev.* **2011**, *40*, 1926 – 1936; g) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417 – 424; h) Y. M. Badiei, A. Dinescu, X. Dai, R. M. Palomino, F. W. Heinemann, T. R. Cundari, T. H. Warren, *Angew. Chem.* **2008**, *120*, 10109 – 10112; *Angew. Chem. Int. Ed.* **2008**, *47*, 9961 – 9964; i) P. Müller, C. Fruit, *Chem. Rev.* **2003**, *103*, 2905 – 2920; j) L. Maestre, W. M. C. Sameera, M. M. Díaz-Requejo, F. Maseras, P. J. Pérez, *J. Am. Chem. Soc.* **2013**, *135*, 1338 – 1348; k) A. I. Olivos Suarez, H. Jiang, X. P. Zhang, B. de Bruin, *Dalton Trans.* **2011**, *40*, 5697 – 5705.

[2] J. F. Berry, *Comments Inorg. Chem.* **2009**, *30*, 28 – 66.

[3] a) E. R. King, E. T. Hennessy, T. A. Betley, *J. Am. Chem. Soc.* **2011**, *133*, 4917 – 4923; b) E. T. Hennessy, T. A. Betley, *Science* **2013**, *340*, 591 – 595; c) A. I. Olivos Suarez, V. Lyaskovskyy, J. N. H. Reek, J. I. van der Vlugt, B. de Bruin, *Angew. Chem.* **2013**, *125*, 12740 – 12760; *Angew. Chem. Int. Ed.* **2013**, *52*, 12510 – 12529; d) V. Lyaskovskyy, A. I. Olivos Suárez, H. Lu, H. Jiang, X. P. Zhang, B. de Bruin, *J. Am. Chem. Soc.* **2011**, *133*, 12264 – 12273.

[4] a) C. T. Saouma, J. C. Peters, *Coord. Chem. Rev.* **2011**, *255*, 920 – 937; b) I. H. Wasbotten, A. Ghosh, *Inorg. Chem.* **2007**, *46*, 7890 – 7898; c) W. A. Nugent, J. M. Mayer, *Metal-Ligand Multiple Bonds*, Wiley, New York, **1988**.

[5] a) D. M. Jenkins, T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2002**, *124*, 11238 – 11239; b) T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2003**, *125*, 10782 – 10783; c) X. Dai, P. Kapoor, T. H. Warren, *J. Am. Chem. Soc.* **2004**, *126*, 4798 – 4799; d) X. Hu, K. Meyer, *J. Am. Chem. Soc.* **2004**, *126*, 16322 – 16323; e) D. T. Shay, G. P. A. Yap, L. N. Zakharov, A. L. Rheingold, K. H. Theopold, *Angew. Chem.* **2005**, *117*, 1532 – 1534; *Angew. Chem. Int. Ed.* **2005**, *44*, 1508 – 1510; f) R. E. Cowley, R. P. Bontchev, J. Sorrell, O. Sarracino, Y. Feng, H. Wang, J. M. Smith, *J. Am. Chem. Soc.* **2007**, *129*, 2424 – 2425; g) C. Jones, C. Schulten, R. P. Rose, A. Stasch, S. Aldridge, W. D. Woodul, K. S. Murray, B. Moubaraki, M. Brynda, G. La Macchia, L. Gagliardi, *Angew. Chem.* **2009**, *121*, 7542 – 7546; *Angew. Chem. Int. Ed.* **2009**, *48*, 7406 – 7410; h) E. R. King, G. T. Sazama, T. A. Betley, *J. Am. Chem. Soc.* **2012**, *134*, 17858 – 717861.

[6] a) D. J. Mindiola, G. L. Hillhouse, *J. Am. Chem. Soc.* **2001**, *123*, 4623 – 4624; b) R. Waterman, G. L. Hillhouse, *J. Am. Chem. Soc.* **2003**, *125*, 13350 – 13351; c) E. Kogut, H. L. Wiencko, L. Zhang, D. E. Cordeau, T. H. Warren, *J. Am. Chem. Soc.* **2005**, *127*, 11248 – 11249; d) R. Waterman, G. L. Hillhouse, *J. Am. Chem. Soc.* **2008**, *130*, 12628 – 12629; e) N. D. Harrold, R. Waterman,

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G. L. Hillhouse, T. R. Cundari, *J. Am. Chem. Soc.* **2009**, *131*, 12872 – 12873; f) V. M. Iluc, A. J. M. Miller, J. S. Anderson, M. J. Monreal, M. P. Mehn, G. L. Hillhouse, *J. Am. Chem. Soc.* **2011**, *133*, 13055 – 13063.

[7] D. S. Glueck, J. Wu, F. J. Hollander, R. G. Bergman, *J. Am. Chem. Soc.* **1991**, *113*, 2041 – 2054.

[8] A transient terminal nitrido complex of rhodium, characterized spectroscopically, is the single example of multiple Rh = N bonds. M. G. Scheibel, Y. Wu, A. C. Stückl, L. Krause, E. Carl, D. Stalke, B. de Bruin, S. Schneider, *J. Am. Chem. Soc.* **2013**, *135*, 17719 – 17722.

[9] A. A. Danopoulos, G. Wilkinson, T. K. N. Sweet, B. Hursthouse, *J. Chem. Soc. Dalton Trans.* **1996**, 3771 – 3778.

[10] a) C. Tejel, M. A. Ciriano, S. Jiménez, V. Passarelli, J. A. López, *Inorg. Chem.* **2008**, *47*, 10220 – 10222; b) K. Ishiwata, S. Kuwata, T. Ikariya, *J. Am. Chem. Soc.* **2009**, *131*, 5001 – 5009; c) S. Takemoto, S. Otsuki, Y. Hashimoto, K. Kamikawa, H. Matsuzaka, *J. Am. Chem. Soc.* **2008**, *130*, 8904 – 8905.

[11] M. J. McGlinchey, F. G. A. Stone, *Chem. Commun.* **1970**, 1265 – 1265.

[12] a) P. R. Sharp, *J. Chem. Soc. Dalton Trans.* **2000**, 2647 – 2657; b) for a comprehensive list of references on the bimetallic Group 9 – 11 complexes featuring bridging imido ligands, see: R. E. Cowley, N. J. DeYonker, N. A. Eckert, T. R. Cundari, S. DeBeer, E. Bill, X. Ottenwaelder, C. Flaschenriem, P. L. Holland, *Inorg. Chem.* **2010**, *49*, 6172 – 6187.

[13] a) C. Tejel, M. A. Ciriano, M. Bordonaba, L. A. Oro, C. Graiff, A. Tiripicchio, *Chem. Eur. J.* **2004**, *10*, 708 – 715; b) C. Tejel, M. Bordonaba, M. A. Ciriano, F. J. Lahoz, L. A. Oro, *Chem. Commun.* **1999**, 2387 – 2388; c) C. Tejel, Y. M. Shi, M. A. Ciriano, A. J. Edwards, F. J. Lahoz, J. Modrego, L. A. Oro, *J. Am. Chem. Soc.* **1997**, *119*, 6678 – 6679; d) C. Tejel, Y. M. Shi, M. A. Ciriano, A. J. Edwards, F. J. Lahoz, L. A. Oro, *Angew. Chem.* **1996**, *108*, 1614 – 1616; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1516 – 1518; e) C. Tejel, Y. M. Shi, M. A. Ciriano, A. J. Edwards, F. J. Lahoz, L. A. Oro, *Angew. Chem.* **1996**, *108*, 707 – 709; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 633 – 634.

[14] C. Tejel, A. M. Geer, S. Jiménez, J. A. López, M. A. Ciriano, *Organometallics* **2012**, *31*, 2895 – 2906.

[15] CCDC 953092 (**2**) and 953741 (**6**) 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.

[16] C. Tejel, M. A. Ciriano, M. Bordonaba, J. A. López, F. J. Lahoz, L. A. Oro, *Chem. Eur. J.* **2002**, *8*, 3128 – 3138.

[17] The angle Rh-N-C is very soft. Thus, an opening to 180° for **4a** is associated to a low energy change of 0.3 kcal mol^{-1} (see the Supporting Information).

[18] a) L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, **1960**; b) B. F. Wicker, H. Fan, A. K. Hickey, M. G. Crestani, J. Scott, M. Pink, D. J. Mindiola, *J. Am. Chem. Soc.* **2012**, *134*, 20081 – 20096.

[19] S. Jiménez, J. A. López, M. A. Ciriano, C. Tejel, A. Martínez, R. A. Sánchez-Delgado, *Organometallics* **2009**, *28*, 3193 – 3202.

[20] a) D. J. Mindiola, G. L. Hillhouse, *Chem. Commun.* **2002**, 1840 – 1841; b) S. D. Brown, T. A. Betley, J. C. Peters, *J. Am. Chem. Soc.* **2003**, *125*, 322 – 323; c) C. A. Laskowski, G. L. Hillhouse, *Organometallics* **2009**, *28*, 6114 – 6120.

[21] R. E. Cowley, E. Bill, F. Neese, W. W. Brennessel, P. L. Holland, *Inorg. Chem.* **2009**, *48*, 4828 – 4836, and references therein.

[22] A. M. Geer, A. Julián, J. A. López, M. A. Ciriano, C. Tejel, *Chem. Eur. J.* **2014**, *20*, 2732 – 2736.

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Communications

Multiple Bonds

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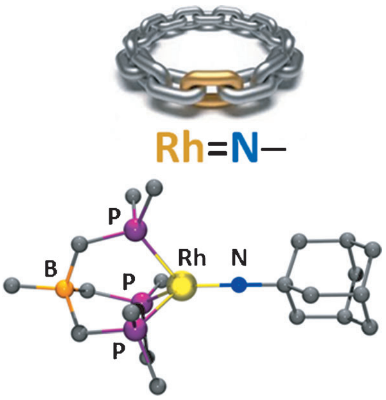
Terminal Imido Rhodium Complexes



A missing link: Terminal imido rhodium complexes with a Rh=N multiple bond have been prepared, thus providing compounds which have been elusive to synthesis. Preliminary studies indicate rhodium imides are somewhat ambiphilic and can therefore undergo protonation at the nitrogen atom, as well as hydrogenation at the Rh=N bond. These systems also engage in nitrene-group transfer and cycloaddition reactions.

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