

## Formation of a Bridging-Imido d<sup>6</sup> Rhodium Compound by Nitrene Capture. Insertion and Cycloaddition Reactions

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The first d<sup>6</sup> rhodium imido complex,  $[(C_5Me_5)Rh(\mu-NSO_2C_6H_4Me-p)]_2$  (**2**), has been obtained from the reaction of  $[(C_5Me_5)Rh(C_2H_4)_2]$  with chloramine-T. Carbon monoxide inserts into the N–Rh bonds in **2** to give the dinuclear ureylene complex  $[(C_5Me_5)Rh(\mu-((Ts)N-CO-N(Ts))Rh(CO)(C_5Me_5))]$ , while the azide  $C_6F_5N_3$  adds to **2** to give the mononuclear tetrazeno complex  $[(C_5Me_5)Rh\{\mu-(p-MeC_6H_4SO_2)N_4(C_6F_5)\}]$ .

Imido complexes of the late transition metals (groups 9 and 10) are rare. Such complexes are of interest as intermediates in imido group transfer reactions, and they may play relevant roles in catalytic C–N bond formation reactions.<sup>1</sup> This practical and fundamental significance has encouraged several groups to search for suitable and reproducible synthetic methods for this class of compounds. While iridium and ruthenium imides, such as  $[(C_5Me_5)Ir\equiv N^tBu]^2$  and  $[(\eta^6\text{-benzene})Ru\equiv NAr]$  (Ar = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>),<sup>3</sup> remained for some time as isolated examples of late-transition-metal terminal imides, several groups have recently described imido complexes of the first-row metals cobalt<sup>4</sup> and nickel,<sup>5</sup> which show an interesting reactivity.<sup>6</sup> In marked contrast, the imido chemistry of the second-row metal

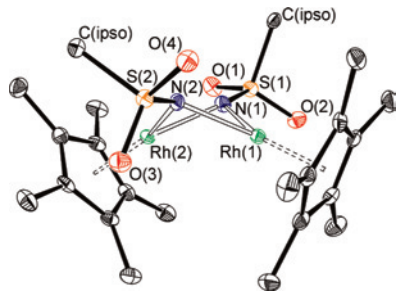
rhodium has been developed rather more slowly. At present, just two families of d<sup>8</sup>-rhodium imido complexes are known, namely, dinuclear dppm-bridged amido/imido tautomers<sup>7</sup> and polynuclear complexes based on triply bridging “ $\mu_3\text{-NC}_6\text{H}_4\text{Me}$ ” imido ligands,<sup>8</sup> along with an early compound reported by McGlinchey and Stone,<sup>9</sup> and a novel dinuclear d<sup>7</sup>-rhodium complex just reported.<sup>10</sup> For a long time, d<sup>6</sup> rhodium imido compounds have been obstinately elusive, although evidence for the complex  $[(C_5Me_5)RhNR]$  (R = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) as a transient intermediate species was given by Danopoulos and Wilkinson.<sup>11</sup> Here we report our preliminary results on the successful synthesis and full characterization of the first d<sup>6</sup> rhodium imido complex and some exploratory reactions that open this chemistry, inaccessible up to now.

Treatment of the yellow complex  $[(C_5Me_5)Rh(C_2H_4)_2]$  (**1**) with chloramine-T ( $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{NCl}^-\text{Na}^+$ ) in dichlo-

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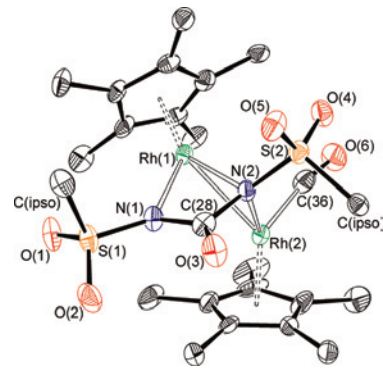


**Figure 1.** Molecular structure of **2** (only the C(ipso) of the *p*-tolyl groups is shown). Selected bond distances (Å): Rh(1)–N(1), 2.006(3); Rh(1)–N(2), 2.006(3); Rh(2)–N(1), 1.992(3); Rh(2)–N(2), 2.017(3); S(1)–N(1), 1.584(3), S(2)–N(2), 1.581(3). Sum of the bond angles around N (deg): N(1), 354.6; N(2), 344.8.

romethane renders sodium chloride and a navy-blue solution, from which the dinuclear imido compound  $[(C_5Me_5)Rh(\mu-NTs)]_2$  (**2**; Ts = *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>) was easily isolated as a navy-blue solid in good yield. Chloramine-T has been used recently as a nitrene source in green chemistry for alkene aziridination and alkane tosylamidation,<sup>12</sup> but it is a very unusual reagent in organometallic chemistry. In this area, (sulfonylimido) metal species remain sparse.<sup>13</sup>

Quite surprisingly, complex **2** was found to be an air- and moisture-stable compound, and single crystals were grown by slow evaporation of a hexane solution of **2** in air without special precautions. Apparently, the electron-withdrawing sulfonyl group rather than alkyl or aryl on the imido nitrogen in **2** could be one of the reasons for the unusual stability of this complex. In the structure of **2** (Figure 1), two *p*-tosylimido ligands bridge two (C<sub>5</sub>Me<sub>5</sub>)Rh moieties, making a folded four-membered “Rh<sub>2</sub>N<sub>2</sub>” ring with a relatively short Rh–Rh separation, 2.7992(4) Å. The metric parameters in **2** fall in the range of those found in the related bis(imido)-bridged diiridium complexes, and the structure was found to be quite similar to that of the recently reported iridium counterpart  $[(C_5Me_5)Ir(\mu-NTs)]_2$ .<sup>14</sup>

Because steric factors, modulated by thermodynamic considerations,<sup>15</sup> can control the mononuclear/dinuclear nature of imido complexes, as proven by Burrell and Steedman in ruthenium chemistry,<sup>3</sup> we tried to obtain an imido mononuclear d<sup>6</sup> rhodium complex by using the complex  $[(C_5H_3^tBu_2)Rh(C_2H_4)_2]$  (**3**) with a bulky Cp ring. A new imidorhodium(III) complex (**4**) resulted from the reaction of **3** with chloramine-T, although it was further identified as the dinuclear complex  $[(C_5H_3^tBu_2)Rh(\mu-NTs)]_2$  (**4**) with a structure similar to that of **2** (see the Supporting Information). The preparation of **4** provides, on the other hand, a second example of a d<sup>6</sup> rhodium imido



**Figure 2.** Molecular structure of **5** (only the C(ipso) of the *p*-tolyl groups is shown). Selected bond distances (Å): Rh(1)–N(1), 2.135(6); Rh(1)–N(2), 2.141(6); Rh(2)–N(2), 2.116(6); N(1)–C(28), 1.371(9); N(2)–C(28), 1.455(9); C(28)–O(3), 1.208(8); S(1)–N(1), 1.619(6); S(2)–N(2), 1.654(6). Sum of the bond angles around N (deg): N(1), 354.9; N(2), 336.9 (Rh(2) is excluded).

compound. Attempts to obtain mononuclear imido complexes by bridge splitting reactions of **2** with conventional two-electron donors, such as pyridine, triphenylphosphane, or acetonitrile, were unsuccessful.

Preliminary studies on the reactivity of the novel compound **2** indicate an ambivalent character, acting as a mono- or dinuclear compound depending on the substrate. Thus, treatment of **2** in dichloromethane with carbon monoxide under atmospheric pressure results in a color change from navy blue to deep green with the formation of the complex  $[(C_5Me_5)Rh(\mu-(TsN-CO-NTs)Rh(CO)(C_5Me_5)]$  (**5**) in 10 min. Complex **5** was isolated as a dark-green crystalline solid in good yield, and it was fully characterized. Its structure is shown in Figure 2.

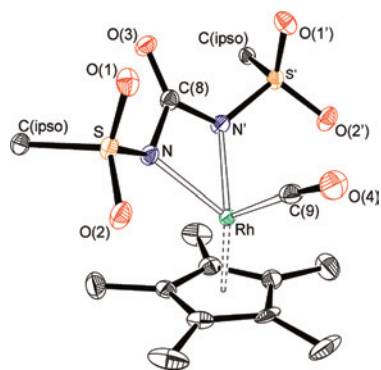
Complex **5** is a result of the incorporation of two molecules of carbon monoxide into the dinuclear complex **2**. One of them becomes coordinated to Rh(2) as a terminal ligand, while the other develops two N–C bonds with the former imido nitrogen atoms to build the ureylene moiety. The newly formed dianionic carbonylbis(*p*-tosylazanido) ligand is bonded to the metals in a nonsymmetrical way, chelating one of the rhodium atoms [Rh(1)] through both nitrogen atoms and bridging both metals via N(2). Electron counting of **5** (34 v.e.) and the quite short Rh–Rh distance [2.6919(8) Å] are consistent with a Rh–Rh bond in the molecule.

Prolonged exposure of a green solution of **5** to carbon monoxide produces cleavage of the complex into the orange rhodium(III) compound  $[(C_5Me_5)Rh(CO)(TsN-CO-NTs)]$  (**6**) and the well-known complex  $[(C_5Me_5)Rh(CO)_2]$ . Complex **6** retains the chelating symmetrically bonded *N,N'*-bis(tosyl)-ureato ligand plus a carbonyl ligand, as shown in the structure of **6** (Figure 3).

A rational sequence of reactions yielding complexes **5** and **6** is shown in Scheme 1. Most probably, the reaction of **2** with carbon monoxide starts with the coordination of this molecule to one of the metals to give the intermediate **A**. In **A**, the carbon monoxide ligand inserts into one Rh–N(imido) bond to form **B**, which contains a carbonyl(*p*-tosyl)azanido ligand bridging the two rhodium atoms.

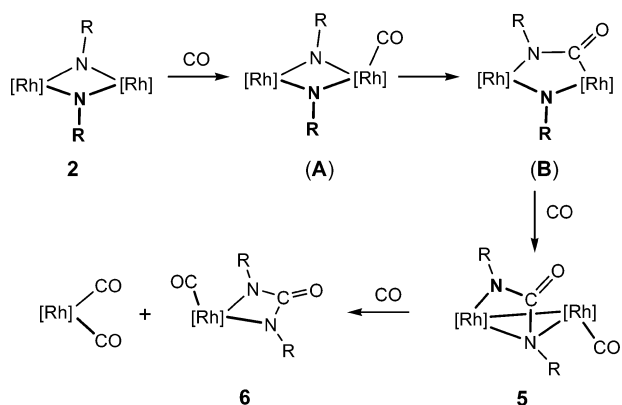
This ligand could be reductively eliminated as a neutral isocyanate, but it is not. Instead, coordination of a second

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**Figure 3.** Molecular structure of **6** (only the C(ipso) of the *p*-tolyl groups is shown). Selected bond distances (Å): Rh–N, 2.113(2); N–C(8), 1.398(4); C(8)–O(3), 1.212(5); S–N, 1.628(3).

**Scheme 1.** Proposed Pathway for the Reaction of **2** with Carbon Monoxide To Give Complex **5** ([Rh] = (C<sub>5</sub>Me<sub>5</sub>)Rh, R = *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)



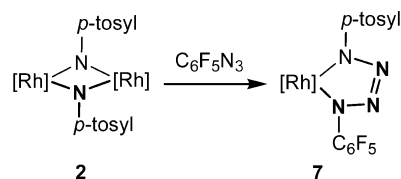
carbon monoxide molecule to the intermediate **B** promotes migration of the C(O)–Rh bond to the close imido nitrogen to form the ureylene fragment, as found in the isolated complex **5**. This last step represents a reductive elimination resulting in the product, the rhodium(II) complex. In this context, formation of the ureylene fragment is the result of a dinuclear reactivity in which both metals cooperate to coordinate and insert carbon monoxide into two N(imido)–Rh bonds. The formation of these two new N–C bonds is facilitated by the bis(imido) molecular core, which makes the dinuclear elimination step feasible. The slow addition of carbon monoxide to **5** simply cleaves the metal–metal bond, splitting the molecule unsymmetrically into the rhodium(III) complex **6**, which keeps the *N,N'*-bis(tosyl)ureato ligand, and a rhodium(I) complex.

Isolation of complexes with a ureato ligand from reactions of imido complexes with carbon monoxide is unprecedented in imido metal chemistry. Typically, these reactions lead to free or coordinated isocyanates<sup>2,16,17</sup> and, in some instances,

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**Scheme 2.** Formation of the Unsymmetrical Tetrazene Complex **7**



to dimetallacycloimide complexes.<sup>17</sup> However, the few reported ways to ureato complexes from imido complexes are their reactions with isocyanates,<sup>11,18</sup> which could explain the formation of ureas in the reductively catalyzed carbonylation of nitroaromatics.<sup>19</sup>

On the other hand, complex **2** reacts easily with the organic azide C<sub>6</sub>F<sub>5</sub>N<sub>3</sub> in toluene to give the red complex [(C<sub>5</sub>Me<sub>5</sub>)Rh{(p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)N<sub>4</sub>(C<sub>6</sub>F<sub>5</sub>)}] (**7**), which contains a chelating and unsymmetrical *N,N'*-diaryltetraazenediido ligand. The tetrazenide complex **7** was isolated as a crystalline red solid in good yield, and it was fully characterized in solution and in the solid state (see Supporting Information). Because a single isomer was observed in the product, the tetrazenide ligand results from a regioselective addition of pentafluorophenylazide to the *p*-tosylimido ligand in such a way that the substituted nitrogen atoms are bonded to the metal (Scheme 2). This is a typical result of a [3 + 2] cycloaddition reaction of organic azides with mononuclear imido complexes, previously reported for osmium,<sup>18a</sup> iridium,<sup>11</sup> and zirconium complexes,<sup>20</sup> which would indicate that **2** behaves as a mononuclear imido complex for cycloaddition reactions.

In conclusion, imidorhodium complexes, other than polynuclear ones, with a d<sup>6</sup> metal configuration can be prepared. The Rh–N bond is highly reactive in insertion and cycloaddition reactions with appropriate substrates. These findings provide an opening for the chemistry of these long elusive compounds to be studied further.

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**Supporting Information Available:** X-ray crystallographic data in CIF format, experimental procedures for the preparation and characterization of the new complexes (elemental analyses, NMR spectra, and mass spectra), crystal data, and full ORTEP representations for **2** and **4–7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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