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Metal-Assisted Aldol-Type Condensation of Two Acetimino Ligands To Give a 4-Imino-2-methylpentan-2-amino Rhodium(III) Complex

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Summary: The intramolecular aldol-like condensation of two acetimino ligands has been observed for the first time to occur in $[Rh(Cp^*)Cl(NH{=}CMe_2)_2]ClO_4$ *(***1·**ClO_4*), under catalytic or stoichiometric reaction conditions, to give* $[Rh(Cp^*)Cl\{N,N\text{-}NH{=}C(Me)CH_2C(Me)_2NH_2\}]X$ *(***2·***X, X = Cl,* ClO_4*). The crystal structures of* **1·**ClO_4 *and* **2·***Cl have been determined.*

Acetimine is among the products resulting from the condensation of acetone and ammonia.[1] However, as it decomposes after short periods of storage[2] and it is difficult to isolate[3] and handle, few complexes with this ligand have been reported; none of them were prepared using acetimine itself or a general method.[4,5] We have prepared $[Ag(NH{=}CMe_2)_2]ClO_4$ and are exploring its potential application as a general reagent for the synthesis of acetimino metal complexes.[6] Thus, its reaction with $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$ (2:1; $Cp^* = \eta^5\text{-}C_5Me_5$) gave the first acetimino Rh(III) complex, $[Rh(Cp^*)Cl(NH{=}CMe_2)_2]ClO_4$ (**1·**ClO_4) (Scheme 1). An attempt to prepare $[Rh(Cp^*)Cl_2(NH{=}CMe_2)]$ by reacting **1·**ClO_4 with PPNCl (1:1) unexpectedly produced the complex [Rh(Cp*)Cl(imam)]Cl (**2·**Cl; imam = κ^2-*N*,*N*-4-imino-2-methylpentan-2-amino) (Scheme 1). The homologous perchlorate salt $[Rh(Cp^*)Cl(imam)]ClO_4$ (**2·**ClO_4) was obtained in almost quantitative yield from **2·**Cl and $AgClO_4$ (1:1, acetone, 30 min) or, more surprisingly, by stirring **1·**ClO_4 under a CO atmosphere (1.8 bar, acetone, room temperature, 24 h), or by treating it with a catalytic amount of $Ph_2C{=}NH$ (1:0.1, acetone, 24 h). The complex **2·**ClO_4 is the major product in the reactions of **1·**ClO_4 with $AsPh_3$ (1:1, acetone, 24 h) and with a catalytic amount of SMe_2 (1:0.1, acetone, 24 h) or on heating it to 70 °C in solution (CH_2Cl_2 or acetone, in a Carius tube) for 24 h (Scheme 1). However, no condensation of the acetimine ligands takes place when **1·**ClO_4 is stirred in acetone for 24 h at room temperature or reacted with PPh_3, XyNC, or $[Ag(NH{=}CMe_2)_2]ClO_4$ (1:1).

Metal complexes of the imam ligand are very scarce indeed, and only nine of them (including the Br^-, NO_3^-, and ClO_4^- salts of the $[Ni(imam)_2]^{2+}$ cation) have been fully characterized by their X-ray crystal structures.[7] They were obtained by reacting various ammine complexes of Co(III)[8] or Ni(II) with acetone,[9,10] by treating $Cu(NO_3)_2$[10] or Pd(II) complexes[5] with acetone and ammonia, or by reacting Ru(III) complexes[11] with ammonium thiobenzoate and acetone or with ammonia and

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(1) Bradbury, R. B.; Hancox, N. C.; Hatt, H. H. *J. Chem. Soc.* **1947**, 1394. Murayama, K.; Morimura, S.; Amakasu, O.; Toda, T.; Yamao, E. *Chem. Abstr.* **1969**, *70*, 324. Murayama, K.; Morimura, S.; Amakasu, O.; Toda, T.; Yamao, E. *Nippon Kagaku Zasshi* **1969**, *90*, 296.

(2) Findeisen, K.; Heitzer, H.; Dehnicke, K. *Synthesis* **1981**, 702.

(3) Verardo, G.; Giumanini, A. G.; Strazzolini, P.; Poiana, M. *Synth. Commun.* **1988**, *18*, 1501.

(4) Vicente, J.; Chicote, M.-T.; Abrisqueta, M.-D.; Guerrero, R.; Jones, P. G. *Angew. Chem., Int. Ed.* **1997**, *36*, 1203. Vicente, J.; Chicote, M. T.; Guerrero, R.; Saura-Llamas, I. M.; Jones, P. G.; Ramírez de Arellano, M. C. *Chem. Eur. J.* **2001**, *7*, 638. Sellmann, D.; Thallmair, E. *J. Organomet. Chem.* **1979**, *164*, 337. Harman, W. D.; Taube, H. *Inorg. Chem.* **1988**, *27*, 3261. Rappert, T.; Yamamoto, A. *Chem. Lett.* **1994**, 2211. Fischer, E. O.; Knauss, L. *Chem. Ber.* **1970**, *103*, 1262. Czarkie, D.; Shvo, Y. *J. Organomet. Chem.* **1970**, *280*, 123. Wong, K.-Y.; Che, C.-M.; Li, C.-K.; Chiu, C.-K.; Zhou, Z.-Y.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1992**, 754. Adcock, P. A.; Keene, F. R.; Smythe, R. S.; Snow, M. R. *Inorg. Chem.* **1984**, *23*, 2336. Yeh, W. Y.; Ting, C. S.; Peng, S. M.; Lee, G. H. *Organometallics* **1995**, *14*, 1417. Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2000**, *19*, 5454. KIingebiel, W.; Noltemeyer, M.; Schmidt, H.-G.; Schmidt-Bäse, D. *Chem. Ber./Recl.* **1997**, *130*, 753. Aresta, M.; Quaranta, E.; Dibenedetto, A.; Giannoccaro, P.; Tommasi, I.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1997**, *16*, 834. King, R. B.; Douglas, W. M. *Inorg. Chem.* **1974**, *13*, 1339. Forniés, J.; Casas, J. M.; Martín, A.; Rueda, A. J. *Organometallics* **2002**, *21*, 4560.

(5) Ruiz, J.; Rodríguez, V.; Cutillas, N.; López, G. *Organometallics* **2002**, *21*, 4912.

(6) Vicente, J.; Chicote, M. T.; Guerrero, R.; Vicente-Hernández, I.; Jones, P. G. *Inorg. Chem.* **2003**, *42*, 7644.

(7) CCDC CSD version 5.25, December 2004.

(8) Alzuet, G.; Ferrer, S.; Casanova, J.; Borrás, J.; Castiñeiras, A. *Inorg. Chim. Acta* **1993**, *205*, 79. Fairlie, D. P.; Turner, M.; Byriel, K. A.; McKeon, J. A.; Jackson, W. G. *Inorg. Chim. Acta* **1999**, *290*, 133.

(9) Rose, N. J.; Elder, M. S.; Busch, D. H. *Inorg. Chem.* **1967**, *6*, 1924.

(10) Hanic, F.; Serator, M. *Chem. Zvesti* **1964**, *18*, 572.

(11) Gould, R. O.; Stephenson, T. A.; Thomson, M. A. *J. Chem. Soc., Dalton Trans.* **1978**, 769.

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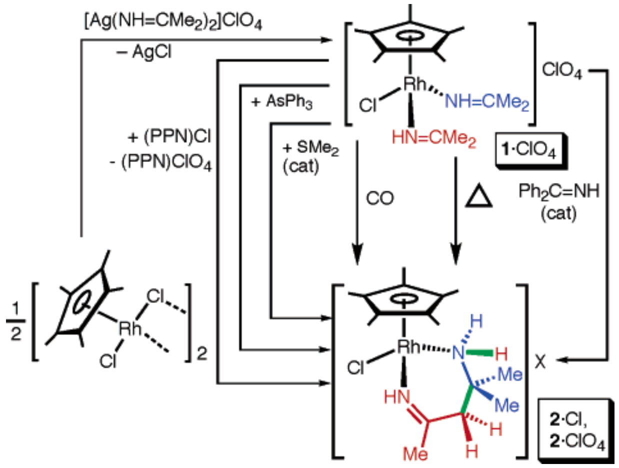
Scheme 1



mesityl oxide. It was suggested that the imam ligand forms by the condensation of two NH_3 ligands and two Me_2CO molecules or one of mesityl oxide in a template type reaction.[8,11,12] Surprisingly, the formation of the Pd(imam) complexes was explained[5] on the assumption that the imam ligand forms in equilibrium with other species in ammonia/acetone mixtures. However, no experimental or bibliographic evidence was given to support the existence of free imam in such mixtures.

The formation of complexes **2**·Cl and **2**·ClO_4 evidences for the first time that the imam ligand can form by an intramolecular aldol-type self-condensation of two acetimino ligands, promoted by gentle heating or by the addition of various ligands. A process involving the attack of free acetimine (generated by a replacement or dissociation process) at an acetimino ligand can be ruled out, since the reactions of **1**·ClO_4 with PPh_3, XyNC, and $[Ag(NH{=}CMe_2)_2]ClO_4$ (1:1) gave the corresponding mono- or triacetimino products (by NMR), respectively, while no complex with the imam ligand could be detected, despite the presence of free acetimine in such reaction mixtures.

On the assumption that the same mechanism applies to all the reactions of **1** with L to give **2**, the ability of CO to promote the condensation process allows us to conclude that the role of the added ligand is not that of the base usually required as the catalyst in aldol condensations. However, it is evident that the coordination of L can modify both the electronic properties of the metal (changing the coordination mode of Cp* from η^5 to η^3 (**A** in Scheme 2), among other effects) and/or the geometry of the complex (change in coordination number or relative disposition of the ligands, particularly the two acetimines). The latter seems to be the most important effect, since (i) condensation occurs also in the absence of added L upon gentle heating of **1**·ClO_4 and (ii) the nature of the ligands capable of effecting condensation ranges from σ and π donor (Cl^-, SMe_2) to π acceptor/weak σ donor (CO).

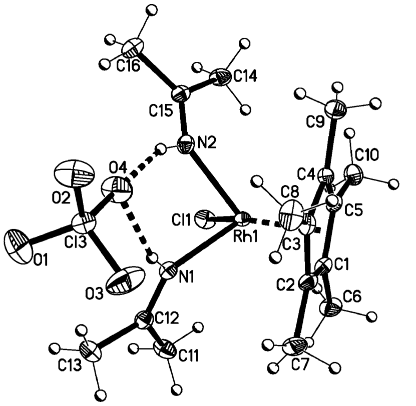
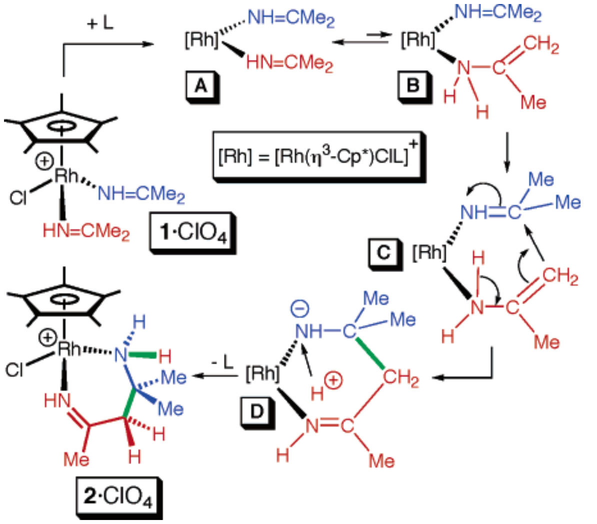


Figure 1. Ellipsoid representation of complex **1**·ClO_4 (50% probability level).

Scheme 2



Scheme 2 shows a reasonable proposal for this rearrangement involving the imine−enamine tautomerization of one of the ligands (**A** → **B**), which, along with the modified geometrical and/or electronic properties of the complex, could help the C−C coupling (**C**) to give the imino−imido intermediate (**D**) and a proton that would migrate to the negatively charged imido nitrogen, the final step being the dissociation of L to give **2**·ClO_4. Note that (i) the condensation involves the formation of a new C−C bond and the transfer of one proton between two nitrogen atoms without the need of an external base, (ii) the added ligands responsible for the condensation act catalytically, (iii) the changes necessary to effect condensation in **1**·ClO_4 can be achieved by gentle heating, and (iv) any ligand capable of replacing one of the acetimino ligands in **1**·ClO_4, such as PPh_3 or XyNC, precludes the synthesis of **2**.

The crystal structures of **1**·ClO_4 and **2**·Cl have been determined**.** The structure of **1**·ClO_4 involves two independent $[Rh(Cp^*)Cl(NH{=}CMe_2)_2]^+$ cations displaying only small differences in bond distances and angles (one of them is represented in Figure 1). Both cations, $[Rh(Cp^*)Cl(NH{=}CMe_2)_2]^+$ and $[Rh(Cp^*)Cl(imam)]^+$ (Figure 2), exhibit a pseudoctahedral “three-legged piano stool” geometry with the Cp* group occupying three *fac* coordination sites.

The bond distances and angles are normal, and the Cp*Rh(III) moieties do not display special features.[7]

In the complex **2**·Cl the six-membered RhN_2C_3 chelate ring adopts a conformation with the C3 and the C4 atoms respectively lying 0.27 Å below and 0.57 Å above the plane of the other four atoms. Hydrogen bonds of the types N−H···O (**1**) and N−H···Cl (**2**) are present in both complexes, leading to a layer structure.

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(12) Curtis, N. F. *Coord. Chem. Rev.* **1968**, *3*, 3.

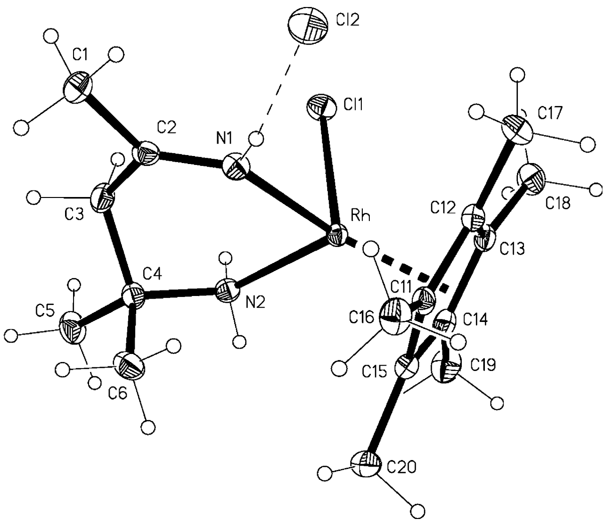

Figure 2. Ellipsoid representation of complex **2**·Cl (50% probability level).

In conclusion, we have prepared the first Rh(III) complexes with acetimino or imam [κ^2-*N,N*-NH=C(Me)-CH$_2$C(Me$_2$)NH$_2$] ligands. Although the imam ligand is present in a few complexes, this is the first time that it has been shown to form from an unprecedented intramolecular metal-assisted aldol-type condensation of two acetimino ligands. The process occurs under various reaction conditions, including by the catalytic addition of some ligands or by mild heating. A reasonable reaction pathway is proposed on the basis of experimental data. The potential of acetimino complexes as a source of interesting new reactions is underlined.

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Supporting Information Available: Text giving experimental details of the preparation of **1**·ClO$_4$, **2**·Cl, and **2**·ClO$_4$ and CIF files giving X-ray crystallographic CIF data for **1**·ClO$_4$ and **2**·Cl. This material is available free of charge via the Internet at http://pubs.acs.org.

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