Synthesis of a Stable N-Hetero - Rh I -Metallacyclic Silanone

Shintaro Takahashi, Kazuki Nakaya, María Frutos, Antoine Baceiredo, Nathalie Saffon-merceron, Stéphane Massou, Norio Nakata, Daisuke Hashizume, Vicenç Branchadell, Tsuyoshi Tsuyoshi Kato

► To cite this version:

Shintaro Takahashi, Kazuki Nakaya, María Frutos, Antoine Baceiredo, Nathalie Saffon-merceron, et al.. Synthesis of a Stable N-Hetero - Rh I -Metallacyclic Silanone. *Angewandte Chemie International Edition*, 2020, 59 (37), pp.15937-15941. 10.1002/anie.202006088 . hal-03028308

HAL Id: hal-03028308

<https://hal.science/hal-03028308>

Submitted on 27 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Synthesis of A Stable *N*-Hetero-*Rh*^I-Metallacyclic Silanone

Shintaro Takahashi, Kazuki Nakaya, María Frutos Pastor, Antoine Baceiredo, Nathalie Saffon-Merceron, Stéphane Massou, Norio Nakata, Daisuke Hashizume, Vicenç Branchadell, Tsuyoshi Kato*

Abstract: A novel *N*-hetero-*Rh*^I-metallacyclic silanone **2** has been synthesized. The silanone **2**, showing an extremely large dimerization energy ($\Delta G = +86.2$ kcal/mol), displays considerable stability and persists in solution up to 60 °C. Above 120 °C, an intramolecular *C*_{sp3}-H insertion occurs slowly over a period of two weeks leading to the bicyclic silanol **5**. The exceptional stability of **2**, related to the unusual electronic and steric effects of *Rh*^I-substituent, should allow for a more profound study and understanding of these new species. Furthermore, the metallacyclic silanone **2** presents two reactive centers (Si=O and *Rh*), which can be involved depending upon the nature of reagents. Of particular interest, the reaction with *H*₂ starts with the hydrogenation of *Rh*^I centre leading to the corresponding *Rh*^{III}-dihydride complex **7** and it undergoes a *cis/trans*-isomerization via a particular mechanism, demonstrating that addition-elimination processes can also happen for silanones just like their carbon analogues!

Silanones are generally highly reactive transient species and are observable only under specific conditions such as in argon matrix at low temperature,^[1] in the gas phase^[2] or on the solid surface.^[3] Particularly, the dimerization and oligomerization of silanones,

producing stable Si-O σ-bonded compounds, are strongly exothermic and barrierless processes. The poor stability of silanones is the obvious bottleneck to advance a more profound study of their reactivity. Recently, various silanones stabilized as donor- or donor/acceptor- complexes, have been synthesized and were demonstrated to be useful stable silanone sources.^[4-8] These efficient stabilization methods also allowed to isolate SiO₂ as stable donor-acceptor complexes.^[9] Nevertheless, not surprisingly, the study of their reactivity is considerably restricted, which hampers profound exploration of their potentials in synthesis. However, the synthesis of stable "base-free" silanones remains a difficult task. Indeed, although the recent studies demonstrated that bulky or/and strongly σ- or/and π-donating substituents efficiently stabilize silanones **I-V** enough to be isolated in the crystalline form,^[10-14] most of them remain unstable in solution at room temperature. To the best of our knowledge, only two silanones, such as the chromium-substituted cationic silanone **I**^[10] and cyclic dialkylsilanone **V**,^[14] are stable in solution at RT. However, even silanone **V**, protected by extremely bulky substituents, dimerizes above 60 °C. As a consequence, up to date, their reactivity exploration is still largely limited to reactions taking place at room temperature.^[15] Here we report the synthesis of a *N*-hetero-*Rh*^I-metallacyclic silanone **2** which presents a remarkable persistence in solution, and therefore allows reactions requiring thermal activation such as C(sp³)-H and H-H bond activations.

[*] Dr. M. Frutos Pastor, Dr. A. Baceiredo, Dr. T. Kato
Laboratoire Hétérochimie Fondamentale et Appliquée
(UMR 5069), Université de Toulouse, CNRS, 118 route de
Narbonne, F-31062 Toulouse (France)
Fax: (+33) 5-6155-8204
E-mail: kato@chimie.ups-tlse.fr
Homepage: http://hfa.ups-tlse.fr (Equipe - ECOIH)

Dr. N. Saffon-Merceron, Dr. S. Massou
Institut de Chimie de Toulouse (FR 2599), Université de
Toulouse, CNRS, 118 route de Narbonne, F-31062
Toulouse (France)

K. Nakaya, S. Takahashi, Dr. N. Nakata
Department of Chemistry, Graduate School of Science and
Engineering, Saitama University
Shimo-okubo, Sakura-ku, Saitama 338-8570 (Japan)

Dr. D. Hashizume
RIKEN Center for Emergent Matter Science (CEMS), 2-1
Hirosawa, Wako, Saitama 351-0198 (Japan)

Prof. V. Branchadell
Departament de Química
Universitat Autònoma de Barcelona
08193 Bellaterra (Spain)

[**] We are grateful to the CNRS (IEA-SiM), the Spanish MINECO (grant CTQ2016-77978-R), the CNRS-JSPS Bilateral Open Partnership Joint Research Projects (SANDTEC-PICS, no. I2017650) and Marelli corporation (Marelli next-generation scholarship) for financial support of this work. We also thank Dr. K. Sugamata (College of Science, Rikkyo University) for the measurement of HRMS.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

We have recently reported the synthesis of an isolable *N*-hetero-*Rh*^I-metallacyclic silylene (*R*' = Ph)^[16] with a limited stability ($t_{1/2}$ = 2 h, at 50 °C).^[17] The silylene **1** with cyclohexyl groups (*R*' = Cy) on the phosphorus atoms shows an improved stability, and no degradation was observed in toluene at 60 °C for several hours (decomposition at 110 °C, $t_{1/2}$ = 8 h).

Scheme 1. Synthesis of cyclic (amino)(rhodium) silanone **2**

The silylene **1** readily reacts with N₂O at -40 °C to give the corresponding silanone **2** (Scheme 1), which was isolated as highly air sensitive orange crystals from a saturated pentane solution at RT (yield 83 %). Silanone **2** is stable in C₆D₆ solution, and no detectable degradation was observed after a week at 60 °C. In the ²⁹Si-NMR spectrum, a signal with a high multiplicity (dddd) appears at significantly low field (δ = 81.5 ppm, ¹J_{SiRh} = 83.1 Hz, ²J_{SiP} = 30.2, 44.8 and 170.1 Hz) compared to those of donor-stabilized silanones (-55 to -91 ppm),^[4-8] but in the same region as observed for three-coordinated silanones **II** - **IV** stabilized by π -donating substituents (28.8 – 71.3 ppm).^[11,12,13] Nevertheless, this signal is considerably up-field shifted relative to those observed for other three-coordinated silanones without π -donor substituents such as chromium-substituted cationic silanone **I** (170 ppm)^[10] and cyclic dialkyl silanone **V** (129 ppm).^[14] The ³¹P-NMR spectrum displays three signals of an AMM'X pattern with large rhodium-phosphorus coupling constants [P_A: dddd, δ = 72.0 ppm, ¹J_{PRh} = 110.2 Hz, P_B: dddd, δ = 56.2 ppm, ¹J_{PRh} = 125.6 Hz, P_C: dddd, δ = 101.5 ppm, ¹J_{PRh} = 151.0 Hz]. This spectral pattern, showing a large *trans*-coupling constant (²J_{PA-PB} = 324.4 Hz) and two small *cis*-coupling constants (²J_{PA-PC} = 26.0 Hz and ²J_{PB-PC} = 23.7 Hz), is typical for square planar Rh^I complexes, suggesting a classical geometry around the Rh^I-center in **2**, instead of the unusual distorted tetrahedral geometry observed for silylene **1**.^[18]

Figure 1. Molecular structure (left) and space filling representations (right) of silanone **2**. Thermal ellipsoids represent 30 % probability. H and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-O 1.540(3), N1-Si1 1.775(3), Rh-Si1 2.237(1), Rh-P1 2.310(1), Rh-P2 2.315(1), Rh-P3 2.362(1), P1-C1 1.776(4), C1-C2 1.359(5), C2-N1 1.376(4), O-Si1-N1 106.8(2), O-Si1-Rh 129.0(1), N1-Si1-Rh 122.7(2), Si1-Rh-P1 92.1(1), P2-Rh-P3 84.4(1), Rh-P1-C1 116.9(1), P1-C1-C2 130.9(3), C1-C2-N1 130.1(3), C2-N1-Si1 124.8(2), θ_{Rh} = 30.0°, Σ_{Si} = 358.39°. θ_{Rh} : dihedral torsion angle between two planes, Rh-Si1-P1 and Rh-P2-P3. (θ_{Rh} = 0°: square planar, θ_{Rh} = 90°: tetrahedral)

The molecular structure of silanone **2**^[19] reveals a planar geometry around the three-coordinated silicon atom ($\Sigma_{Si} = 358.39^\circ$) and a short Si=O bond length [1.540 (3) Å] which is longer than those of chromium-substituted silanone **I** (1.526 Å)^[10] and of dialkylsilanone **V** (1.518 Å)^[14] but is similar to those observed for other π -donor substituted silanones **II** - **IV** (1.533 - 1.543 Å).^[11,12,13] The N1-Si1 bond length [1.775 (3) Å] is almost identical to that of silylene **1** (1.771 - 1.781 Å). Although the Si1-Rh bond [2.237 (1) Å] is slightly elongated compared to those of **1** (2.141 - 2.174 Å), it is still shorter than classical Si(sp²)-Rh^I bonds (2.30 - 2.35 Å),^[20] which suggests a remaining Rh-Si π -interaction. The X-ray structure of silanone **2** also demonstrates that, after the oxidation of silicon centre, **2** reveals a square planar geometry around the metal centre [θ_{Rh} = 30.07° for **2** (Figure 1), θ_{Rh} = 63.38 – 76.88° for **1**^[25]], in good agreement with the ³¹P-NMR data. The space-filling

representation of **2** clearly shows a Si=O moiety sterically well-shielded by substituents (Figure 1 right). Thanks to the square planar geometry, the steric shields of cyclohexyl groups reach to the space around (even beyond) the terminal O atom of silanone. This long-range steric protection by the particular substituent system probably explains the exceptional thermal stability of **2** (Figure 1, right).

To gain more insight into the electronic structure of silanone **2**, DFT calculations have been performed at the M06/6-31G(d) level of theory. The optimized structure of **2** agrees quite well with the experimentally observed one (Si-O: 1.556 Å, Si-N: 1.791 Å, Si-Rh: 2.286 Å, θ_{Rh} = 33.4°).

Figure 2. Calculated NBO charges and bond orders (in parenthesis) of acetone, dimethylsilanone, ylide-substituted silanone **II**, bora-ylide substituted silanone **IV** and **2** as well as dimerization energies (ΔG) of **2** and its simpler model **2-simple**. WBI: Wiberg bond index.

NBO analysis of **2** clearly indicates that the Si-Rh bond has a decreasing bond order (WBI: 0.58) relative to the corresponding silylene **1** (WBI: 0.82), while the Si-N bond order remains almost unchanged (WBI: 0.46 for **2** and 0.45 for **1**, Figure 2), suggesting a reducing π -donation from the square planar Rh^I substituent toward the Si centre compared to that in **1**. Nevertheless, the positive charge on the Si atom of silanone is particularly small (+1.69), which is even smaller than that calculated for the silanone **IV** with a strongly π - and σ -donating bora-ylide substituent (+1.94). This is probably due to an extremely strong σ -donating effect of the square planar Rh^I atom. Contrarily, the tetrahedral Rh^I substituent in the silylene **1** was predicted to present a strong σ -accepting character.^[16] It is also well known that σ -donating substituents efficiently stabilize a trigonal planar geometry of Si atom.^[12,13,22] These probably explain the adaptation of square planar geometry of Rh^I atom (weak π -donation and strong σ -donation) rather than tetrahedral one (strong π -donation and strong σ -acceptation). It should be noted that the silanone **2** with a tetrahedral Rh^I group is not a minimum on the energy surface. The calculations also indicate the disfavored dimerization of **2** showing a strongly endergonic nature of the process (ΔG = +86.2 kcal/mol), which is in good agreement with the experimentally observed high thermal stability of **2**. It is worth noting that the dimerization of related persistent silanones **II** and **IV** are thermodynamically favored processes (ΔG = -30 and -16 kcal/mol respectively).^[11,13] In marked contrast, for a model **2'** with smaller substituents (Me groups on the P and N atoms and aryl group instead of Cy, *t*Bu and *i*Pr groups respectively, Figure 2), the dimerization is strongly exergonic (ΔG = -64.8 kcal/mol). Therefore, the exceptional stability of **2** is principally due to the efficient kinetic protection by the bulky substituents. However, this value is much smaller than that calculated for Me₂Si=O (ΔG = -95 kcal/mol),

suggesting considerable thermodynamic stabilization provided by the electronic effect of N- and Rh(I)-based substituents.

The highest occupied molecular orbital (HOMO, -4.83 eV) corresponds to the $d(z^2)$ orbital of Rh atom. As expected, due to the presence of electron-donating Rh-substituents, the energies of n_O (HOMO-4 and -7: -5.99 and -6.20 eV) and $\pi_{Si=O}$ (HOMO-10: -6.99 eV) bond orbitals are significantly higher than those of $Me_2Si=O$ [HOMO(n_O): -9.56 eV, HOMO-1($\pi_{Si=O}$): -10.27 eV]. In contrast, the lowest unoccupied orbital (LUMO), corresponding to the $\pi^*_{Si=O}$ orbital mixed with the rhodium d-orbital (-0.78 eV) is similar to that of $Me_2Si=O$ [LUMO($\pi^*_{Si=O}$): -0.89 eV]. These results are in good agreement with the high reactivity of silanone **2**.

Scheme 2. Reactions of (amino)(rhodium) silanone **2**

Silanone **2** shows a typical reactivity toward H_2O and H_3SiPh , with a polarized O-H and Si-H σ -bonds, to immediately afford at RT the corresponding 1,2-adducts **3** and **4**, respectively (Scheme 2). More interestingly, at 120 °C, an intramolecular C(sp^3)-H insertion involving a t-butyl group gives the bicyclic silanol **5**. Due to the high thermal stability of **2**, the reaction is particularly slow and takes two weeks to reach complete conversion. Both reactions are diastereoselective, probably due to the unsymmetrical environment around the Si=O moiety related to the distorted square planar geometry around the Rh atom in **2**. In contrast to these reactions at the Si=O function, the reaction of **2** with CO takes place at the Rh centre to form the corresponding carbonyl complex **6**. This has been clearly indicated by the ^{29}Si -NMR signal for the unreacted silanone fragment ($\delta = 102$ ppm) as well as the appearance of a new carbonyl carbon signal in a typical region in ^{13}C -NMR ($\delta = 206$ ppm, $J_{RhC} = 56.3$ Hz).

Scheme 3. Hydrogenation of silanone **2**

Silanone **2** also reacts with H_2 via an oxidative addition to the Rh center at room temperature, affording the corresponding Rh^{III} -dihydride-substituted silanone **7** as a mixture of *cis/trans*-isomers (*cis* : *trans* = 1 : 2, Scheme 3). The oxidative addition of H_2 is reversible at room temperature as indicated by the H_2 -pressure-dependent ratio between **2** and **7**, and the constant ratio of *cis/trans*-isomers of **7** at different pressures. The complete conversion to **7** was achieved under 3 bar of H_2 -pressure, and the initial Rh^I -substituted silanone **2** was completely recovered after removal of

H_2 -pressure. Although all attempts to isolate **7** failed, its formation as a mixture of two isomers is supported by a multi-nuclear NMR analysis showing particularly large *trans*-coupling constants of two nuclei on the Rh atom such as J_{HP} (124 Hz)^[22] for **7-cis** and J_{HH} (12.6 Hz)^[23] and J_{SiP} (176 Hz)^[24] for **7-trans**. As expected, for both isomers, the large coupling constants between two apical phosphorous atoms are also observed ($J_{PP(trans)} = 372$ Hz for **7-cis** and 373 Hz for **7-trans**). The remaining silanone functions are also confirmed by their ^{29}Si -NMR signals appearing in the typical region (117.8 ppm for **7-cis** and 65.4 ppm for **7-trans**). Under the H_2 pressure (3bars), the Rh^{III} -substituted silanones **7** are stable at room temperature, while, at 60 °C, they evolve further via a hydrogenation of silanone moiety to give the corresponding silanol **8**. The formation of **8** was confirmed by an X-ray diffraction analysis.

To understand better the reaction of **2** with H_2 , we performed DFT calculations with a simplified model **2'** (Figure 3). The calculations indicate slightly exergonic nature of the first hydrogenation reaction to form the Rh^{III} -substituted silanone **7'-cis** ($\Delta G_{2' \rightarrow 7'cis} = 3.6$ kcal/mol) and its low energy barrier ($\Delta G_{2' \rightarrow 7'cis}^\ddagger = 11.1$ kcal/mol), which is in good agreement with the experimentally observed reversibility of the reaction at room temperature. The calculations also indicate that the *cis/trans* isomerization of H_2Rh^{III} complex **7'-cis** starts with the 1,2-migration of hydrogen from the Rh to the Si atom to form a zwitter-ionic intermediate **9'-cis**. The successive conformational transformation of **9'-cis** into **9'-trans**, changing the side of H-Rh bond relative to the H-Si bond, proceeds through the formation of μ -hydride ($O=Si \leftarrow H-Rh$) complex as intermediate.^[21] Then, the reverse 1,2-hydrogen migration from Si to Rh centre affords the corresponding *trans*-isomer **7'-trans**.^[26] All transformations in the *cis/trans* isomerization process cost little energy and the *trans*-isomer is only slightly more stable than the *cis*-isomer, which explains the formation of **7-trans** as the major isomer. Despite the intervention of transition metal moiety, this *cis/trans*-isomerization (hydride attack on the silanone to form a silanolate intermediate **9** / elimination-readdition of Rh to change sides of Rh-H bond / reverse hydrogen migration to reform the silanone)^[21] demonstrates that the addition-elimination process, which is one of the most important reactions of the carbonyl group, can also happen for silanones.^[27]

Figure 3. Calculated reaction pathways for the hydrogenation of **2'** and calculated Gibbs energies ΔG (kcal/mol) for each step of the reaction. In parenthesis are calculated reaction barriers $\Delta G^\ddagger$ (kcal/mol).

Concerning the mechanism of the hydrogenation of silanone **2** into silanol **8**, three possibilities can be considered: 1) direct

hydrogenation of Rh^I-substituted silanone **2**, 2) direct hydrogenation of H₂Rh^{III}-substituted silanone **7** followed by a dehydrogenation at Rh^{III} centre, 3) isomerization of H₂Rh^{III}-substituted silanone **7** via hydrogen migrations. The first two possibilities were excluded by the excessively high energy barriers calculated for these processes ($\Delta G_{2 \rightarrow 8}^\ddagger = 31.6$ kcal/mol and $\Delta G_{7 \rightarrow \text{cis-}8}^\ddagger = 34.2$ kcal/mol). The hydrogenation process by the isomerization of H₂Rh^{III}-substituted silanone **7** proceeds in three steps: 1) the Rh $\rightarrow$ Si hydrogen migration to generate the twitter-ionic intermediate **9-cis**, 2) the isomerization of **9'-cis** to **9'-trans**, 3) Rh $\rightarrow$ O hydrogen migration to give **7'-trans**. All steps cost low energy ($\Delta G^\ddagger = 4.6 - 20.7$ kcal/mol). The most costly step is the last one, the Rh $\rightarrow$ O hydrogen migration, while the reaction barrier ($\Delta G_{9 \rightarrow 8}^\ddagger = 20.7$ kcal/mol) is much smaller than those calculated for the direct H₂ addition processes. In addition, the moderately elevated reaction barrier is in good agreement with the experimental conditions requiring a slight thermal activation (60 °C) for the reaction to occur. These results demonstrate that the hydrogenation of silanone **2** proceeds indirectly, the Rh substituent acting as an activator of H₂. In addition, in contrast to the diastereoselective reactions of **2** with H₂O and PhSiH₃, the hydrogenation affords silanol **8** as a mixture of two diastereomers (major : minor = 85 : 15), which also supports the proposed indirect hydrogenation mechanism and the rapid cis/trans isomerization of Rh-hydrogenated intermediate **7**.

A novel stable *N*-hetero-Rh^I-metallacyclic silanone **2**, has been successfully synthesized. The silanone **2**, showing an extremely large dimerization energy ($\Delta G = +86.2$ kcal/mol), displays considerable stability and persists in solution up to 60 °C, while it slowly isomerizes at 120 °C via an intramolecular insertion into C(sp³)-H bond. The exceptional stability of silanone **2**, related to the unusual electronic and steric effects of the Rh^I-substituent (strong σ - and π -donations and long-range steric protection), should allow for a more profound study and understanding of silanone derivatives. Furthermore, the Rh-metallacyclic silanone **2** presents two reactive centers (Si=O and Rh), which can be involved depending upon the nature of reagents. Notably, the reaction with H₂, resulting in the hydrogenation of silanone moiety, proceeds via cooperative involvement of both sites, and it starts with the reaction at Rh^I centre. Of particular interest, the resulting silanone **7** presenting a hexa-coordinate Rh^{III}-dihydride moiety, undergoes a *cis/trans*-isomerization via a particular mechanism, demonstrating that the addition-eliminations processes, which are classical carbonyl reactivities, can also be observed with silanones. More detailed investigations on the reactivity of this new stable silanone **2** are under active investigation.

Received: ((will be filled in by Received: ((will be filled in by the editorial staff))

Published online on ((will be filled in by the editorial staff))

Keywords: stable silanone · stable silylene · NHSi · metallacycles · rhodium complex

- [1] a) H. Schnöckel, *Z. Anorg. Allg. Chem.* **1980**, 460, 37; b) C. A. Arrington, R. West, J. Michl, *J. Am. Chem. Soc.* **1983**, 105, 6176; c) R. Withnall, L. Andrews, *J. Am. Chem. Soc.* **1985**, 107, 2567; d) V. N. Khabashesku, Z. A. Kerzina, E. G. Baskir, A. K. Maltsev, O. M. Nefedov, *J. Organomet. Chem.* **1988**, 347, 277; e) V. N. Khabashesku, Z. A. Kerzina, K. N. Kudin, O. M. Nefedov, *J. Organomet. Chem.* **1998**, 566, 45; f) M. M. Linden, H. P. Reisenauer, D. Gerbig, M. Karni, A. Schäfer, T. Müller, Y. Apeloig, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2015**, 54, 12404.
- [2] R. J. Glinski, J. L. Gole, D. A. Dixon, *J. Am. Chem. Soc.* **1985**, 107, 5891.
- [3] V. A. Radtsiga, L. N. Senchenyab, *Russ. Chem. Bull.* **1996**, 45, 1849.
- [4] a) S. Yao, M. Brym, C. van Willen, M. Driess, *Angew. Chem. Int. Ed.* **2007**, 46, 4159; b) S. Yao, Y. Xiong, M. Brym, M. Driess, *J. Am. Chem. Soc.* **2007**, 129, 7268; c) Y. Xiong, S. Yao, M. Driess, *J. Am. Chem. Soc.* **2009**, 131, 7562; d) S. Yao, Y. Xiong, M. Driess, *Chem. Eur. J.* **2010**, 16, 1281; e) Y. Xiong, S. Yao, R. Miller, M. Kaupp, M. Driess, *Nat. Chem.* **2010**, 2, 577; f) Y. Xiong, S. Yao, R. Miller, M. Kaupp, M. Driess, *J. Am. Chem. Soc.* **2010**, 132, 6912; g) Y. Xiong, S. Yao, M. Driess, *Dalton Trans.* **2010**, 39, 9282; h) Y. Xiong, S. Yao, M. Driess, *Angew. Chem. Int. Ed.* **2010**, 49, 6642; i) J. D. Epping, S. Yao, M. Karni, Y. Apeloig, M. Driess, *J. Am. Chem. Soc.* **2010**, 132, 5443; j) K. Hansen, T. Szilvási, B. Blom, E. Irran, M. Driess, *Chem. Eur. J.* **2015**, 21, 18930.
- [5] a) R. S. Ghadwal, R. Azhakar, H. W. Roesky, K. Prçpper, B. Ditttrich, S. Klein, G. Frenking, *J. Am. Chem. Soc.* **2011**, 133, 17552; b) R. S. Ghadwal, R. Azhakar, H. W. Roesky, K. Prçpper, B. Ditttrich, C. Goedecke, G. Frenking, *Chem. Commun.* **2012**, 48, 8186.
- [6] a) T. Muraoka, K. Abe, Y. Haga, T. Nakamura, K. Ueno, *J. Am. Chem. Soc.* **2011**, 133, 15365; b) T. Muraoka, K. Abe, H. Kimura, Y. Haga, K. Ueno, Y. Sunada, *Dalton Trans.* **2014**, 43, 16610.
- [7] a) R. Rodriguez, T. Troadec, D. Gau, N. Saffon-Merceron, D. Hashizume, K. Miqueu, J.-M. Sotiropoulos, A. Baceiredo, T. Kato, *Angew. Chem. Int. Ed.* **2013**, 52, 4426; b) R. Rodriguez, D. Gau, T. Troadec, N. Saffon-Merceron, V. Branchadell, A. Baceiredo, T. Kato, *Angew. Chem. Int. Ed.* **2013**, 52, 8980; c) T. Troadec, M. Lopez Reyes, R. Rodriguez, A. Baceiredo, N. Saffon-Merceron, V. Branchadell, T. Kato, *J. Am. Chem. Soc.* **2016**, 138, 2965; d) M. Lopez-Reyes, T. Troadec, R. Rodriguez, A. Baceiredo, N. Saffon-Merceron, V. Branchadell, T. Kato, *Chem. Eur. J.* **2016**, 22, 10247.
- [8] For a recent review of silanones and their heavier Group 14 congeners, see: Y. Xiong, S. Yao, M. Driess, *Angew. Chem. Int. Ed.* **2013**, 52, 4302.
- [9] R. Rodriguez, D. Gau, J. Saouli, A. Baceiredo, N. Saffon-Merceron, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2017**, 56, 3935.
- [10] A. C. Filippou, B. Baars, O. Chernov, Y. N. Lebedev, G. Schnakenburg, *Angew. Chem. Int. Ed.* **2014**, 53, 565.
- [11] I. Alvarado-Beltran, A. Rosas-Sánchez, A. Baceiredo, N. Saffon-Merceron, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2017**, 56, 10481.
- [12] D. Wendel, D. Reiter, A. Porzelt, P. J. Altmann, S. Inoue, B. Rieger, *J. Am. Chem. Soc.* **2017**, 139, 17193.
- [13] A. Rosas-Sánchez, I. Alvarado-Beltran, A. Baceiredo, N. Saffon-Merceron, S. Massou, D. Hashizume, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2017**, 56, 15916.
- [14] R. Kobayashi, S. Ishida, T. Iwamoto, *Angew. Chem. Int. Ed.* **2019**, 58, 9425.
- [15] Sila-Wittig reactions of silanone: D. Reiter, P. Frisch, T. Szilvasi, S. Inoue, *J. Am. Chem. Soc.* **2019**, 141, 16991.
- [16] S. Takahashi, E. Bellan, A. Baceiredo, N. Saffon-Merceron, S. Massou, N. Nakata, D. Hashizume, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2019**, 58, 10310.
- [17] Such an insertion reaction involving the phenyl group of DPPE is quite common for binuclear transition metal complexes with a reactive metal centre at the β -position of phosphorus atoms of DPPE: a) G. Bruno, G. De Munno, G. Tresoldi, S. Lo Schiavo, P. Piraino, *Inorg. Chem.* **1992**, 31, 1538; b) W.-Y. Wong, F.-L. Ting, W.-L. Lam, *Eur. J. Inorg. Chem.* **2002**, 2103; c) A. Rahaman, F. R. Alam, S. Ghosh, D. A. Tocher, M. Haukka, S. E. Kabir, E. Nordlander, G. Hogarth, *J. Organomet. Chem.* **2014**, 751, 326.
- [18] The crystal structure clearly demonstrated the distorted tetrahedral geometry around Rh atom of silylene **1** ($\theta_{Rh} = 63.28-76.88^\circ$). See the supporting information for details.
- [19] CCDC-1998336 (**B**), CCDC-1998337 (**1**), CCDC-1998338 (**2**), CCDC-1998339 (**3**), CCDC-1998340 (**4**), CCDC-1998341 (**5**) and CCDC-1998342 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>.
- [20] Si(sp²)-Rh bonds: a) E. Neumann, A. Pfaltz, *Organometallics* **2005**, 24, 2008; b) A. Rosas-Sánchez, I. Alvarado-Beltran, A. Baceiredo,

- N. Massou, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2017**, *56*, 10549.
- [21] See the supporting information for details.
- [22] a) A. Sekiguchi, T. Fukawa, M. Nakamoto, V. Ya. Lee, M. Ichinohe, *J. Am. Chem. Soc.* **2002**, *124*, 9865. b) A. Sekiguchi, S. Inoue, M. Ichinohe, Y. Arai, *J. Am. Chem. Soc.* **2004**, *126*, 9626.
- [23] a) W. A. Herrmann, C. Kocher, *Angew. Chem. Int. Ed.* **1997**, *36*, 2162; b) C. Heinemann, T. Müller, Y. Apeloig, H. Schwarz, *J. Am. Chem. Soc.* **1996**, *118*, 2023.
- [24] No detectable $^2J_{\text{HH}}$ coupling was observed for the **7-cis**.
- [25] J. L. McBee, J. Escalada, T. Don Tilley, *J. Am. Chem. Soc.* 2009, *131*, 12703.
- [26] A similar mechanism of cis-trans isomerization was reported for the a pincer-type carbonyl-Ir complex, proceeding through the reversible hydride migrations between Ir and C=O ligand: T. T. Lekich, B. Gary, S. M. Bellows, T. R. Cundari, L. M. Guard, M. Heinekey, *Dalton Trans.* **2018**, *47*, 16119.
- [27] The formation of silanone by the elimination of KBr from the corresponding silanolate ion is known: S. Ishida, T. Abe, F. Hirakawa, T. Kosai, K. Sato, M. Kira, T. Iwamoto, *Chem. Eur. J.* **2015**, *21*, 15100.
-

((Catch Phrase))

S. Takahashi, K. Nakaya, A. Baceiredo,
N. Saffon-Merceron, S. Massou, N.
Nakata, D. Hashizume, V. Branchadell,
T. Kato _____ **Page – Page**

A Stable *N*-Hetero-*Rh*^I-Metallacyclic
Silanone

A novel *N*-hetero-*Rh*^I-metallacyclic silanone has been synthesized. This silanone, showing an extremely large dimerization energy ($\Delta G = +86.2$ kcal/mol), is stable in solution at 60 °C and only slowly isomerizes at 120 °C, via an intramolecular C(sp³)-H bond insertion. This *Rh*^I-substituted silanone can react either on both sites, the Si=O function or the *Rh* center, depending on the type of reagents. Of particular interest, the reaction with H₂, resulting in the hydrogenation of silanone moiety, proceeds via cooperative involvement of both sites.