Strained and Reactive Donor/Acceptor-Supported Metalla-Silanone

Shintaro Takahashi, Manuel Ramos Enriquez, Ekaterina Bellan, Antoine Baceiredo, Nathalie Saffon-Merceron, Norio Nakata, Daisuke Hashizume, Vicenç Branchadell, Tsuyoshi Kato*

Abstract: A novel stable donor/acceptor-supported Mn(I)-metallasilanone **3** was synthesized. The intramolecular silanone-Mn(I) interaction induces a highly strained three-membered cyclic structure, leading to an exceptionally high reactivity of **3** as a donor/acceptor complex of silanone. Indeed, metallasilanone **3** readily reacts with various small molecules such as H₂ or ethylene gas in mild conditions.

In contrast to the ubiquitous carbonyl function, the heavier silicon analogue, silanones **I**, are generally highly reactive transient species^[1] which were observed either in low-temperature argon matrices^[2] or in the gas phase^[3] and were evidenced by trapping reactions.^[4] Silanones present a strongly polarized Si=O double bond (Si^{δ+}-O^{δ-}) with a considerably large bond energy difference between SiO- π - and - σ -bonds,^[5] and therefore, they easily oligomerize to give polysiloxanes.^[6] Even though some recent studies have demonstrated that bulky or/and strongly σ - or/and π -donating substituents efficiently stabilize silanones, the synthesis of stable silanones **I** remains a great challenge and, to date, only a limited number of isolable silanones are available.^[7-12]

A drastic improvement in the stability was achieved by Driess's group, using donor (**II**)^[13] or donor/acceptor (**III**)^[14] systems.^[15-19] Thanks to that, several stable and easy-to-manipulate silanone derivatives have been prepared.^[15-19] Particularly, the formation of donor/acceptor complexes **III**, which blocks both nucleophilic O and electrophilic Si centers, is very efficient. This was clearly demonstrated by the formation of chloro-substituted silanone as an air-stable molecule^[20] as well as the isolation of SiO₂ as a stable monomeric species.^[21] Nevertheless, not surprisingly, such a stabilization considerably reduces the reactivity thus limiting their synthetic potential.^[22] A solution of this issue would be the introduction of the Lewis acidic component (A) as a Si-substituent, that would allow the formation of an intramolecular Si=O $\rightarrow$ A interaction. Because of the high strain of the resulting three membered ring, complexes **IV** should present an enhanced reactivity. To date, only two stable transition-metal substituted silanones **V** have been described by Filippou's group^[7] and by us.^[8] Particularly, the cyclic Rh^I-substituted silanone shows a unique reactivity associated with the two reactive centers (Si=O and Rh). However, in both cases, the desired intramolecular interaction to form a strained silanone-metal complex (type **IV**) was not observed.

[*] Dr. M. Ramos Enriquez, Dr. E. Bellan, 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
Institut de Chimie de Toulouse (FR 2599), Université de Toulouse, CNRS, 118 route de Narbonne, F-31062 Toulouse (France)

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 (SANDETEC-PICS, no. I2017650) and Marelli corporation (Marelli next-generation scholarship) for financial support of this work.

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

Here, we would like to report the synthesis of Mn^I-substituted silanone **3** showing an original intramolecular silanone-Mn interaction. Contrary to poorly reactive donor/acceptor-stabilized silanones (**III**), this highly strained cyclic silanone complex **3** is particularly reactive and is able to achieve the H₂-splitting at room temperature.

Scheme 1. Synthesis of Mn^I-substituted silanone **3**

As a precursor of cyclic silanone complexes, the Mn^I-silylidene complex **2** was readily synthesized by the stoichiometric reaction of phosphine-stabilized chloro-silylene **1** with NaMn(CO)₅ in toluene at 80 °C (Scheme 1). Complex **2** was isolated as a highly air-sensitive dark purple powder in 86 % yield. In the ²⁹Si-NMR spectrum, a broad doublet signal appears at significantly down field

($\delta = 182$ ppm, $^1J_{\text{SiP}} = 52.6$ Hz), but with an upfield shift compared to previously reported NHC-stabilized transition metal silylidene complexes **VI**^[23] (M = Cr, Mo, W) (230 to 279 ppm) and the recently reported stable silylene-Mn complexes **VII** (285 to 364 ppm).^[24] The ^{31}P -NMR spectrum displays a singlet signal at 31.9 ppm, which is significantly upfield shifted compared with that of the phosphine-stabilized silylene **1** (75.0 ppm). In the ^{13}C -NMR spectrum, the four carbonyl ligands appear as a broad signal at 226 ppm, probably due to the rapid isomerization through the pseudo rotation of $\text{Mn}(\text{CO})_4$ moiety at RT. The structure of **2** reveals a planar Si1 center ($\Sigma^\circ_{\text{Si}} = 360^\circ$) and a Si-Mn bond (2.163 Å) considerably shorter than Si-Mn single bonds (ca 2.35 Å), but similar to that observed for silylene-Mn complexes **VII** (2.188 Å), and in agreement with the Si=M double character of transition-metal substituted silylidene complexes.

Figure 1. Molecular structures of **2** (left) and **3** (right). Thermal ellipsoids represent 30 % probability. H and disordered atoms and solvent molecules (**3**) are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2**: Si1-Mn 2.163(3), N1-Si1 1.749(9), Si1-P 2.320(4), Mn-C (average) 1.822, C-O (average) 1.132, N1-Si1-P 88.7(3), N1-Si1-Mn 136.5(3), Mn-Si1-P 134.8(2), C3-Mn-C4 172.5(6), C5-Mn-C6 101.5(10), Si1-Mn-C3 83.5(4), Si1-Mn-C4 89.7(4), Si1-Mn-C5 129.3(4), Si1-Mn-C6 129.2(10), $\Sigma^\circ_{\text{Si}} = 360.0$. **3**: Mn-Si1 2.268(1), Si1-O1 1.592(2), O1-Mn 2.147(2), N1-Si1 1.791(2), Si1-P 2.310(1), Mn-C (average) 1.820, C-O (average) 1.142, O1-Si1-Mn 64.85(8), Si1-O1-Mn 72.99(8), O1-Mn-Si1 42.16(6), N1-Si1-P 89.90(8), N1-Si1-Mn 133.72(9), Mn-Si1-P 132.77(4), Si1-Mn-C3 90.58(10), Si1-Mn-C4 87.26(11), Si1-Mn-C5 143.61(11), Si1-Mn-C6 118.19(13), C3-Mn-C4 174.84(16), C5-Mn-C6 98.19(17). ($\Sigma^\circ_{\text{Si(N,P,Mn)}} = 356.39$)

In contrast to other double-bonded silicon species or silylene-Mn complexes **VII**, which are generally highly reactive, silylidene complex **2** is moderately reactive, and no reaction was observed with H_2 , ethylene, CO_2 , and 2,3-dimethylbutadiene. However, complex **2** readily reacts with N_2O at -40°C to afford the corresponding three-membered cyclic donor/acceptor-supported silanone **3** (Scheme 1), which was isolated as extremely air-sensitive yellow crystals from a concentrated THF solution at -50°C (yield 42 %). Silanone **3** was obtained as a 70 : 30 mixture of two diastereomers as indicated by two sets of signals systematically observed in all NMR spectra. In the ^{31}P -NMR spectrum, two singlet signals (major: 40.6 ppm, minor: 40.7 ppm) appeared in the same region to those of silylidene complex **2** (40.4 ppm). In contrast, ^{29}Si -NMR signals for the Mn-substituted Si atom are significantly upfield shifted (major: -6.0 ppm, $^1J_{\text{SiP}} = 29.9$ Hz, minor: -3.4 ppm, $^1J_{\text{SiP}} = 30.0$ Hz), which is in good agreement with a three-membered ring containing a silicon atom. In contrast to the case of silylidene complex **2**, ^{13}C -NMR displays well-defined four singlet signals corresponding to the carbonyl ligands in the typical region (214.9 - 223.3 ppm) for each diastereomer of **3**.

The X-ray diffraction analysis of **3**^[25] reveals a three-membered cyclic donor/acceptor-silanone structure with two intramolecular coordination interactions $\text{P} \rightarrow \text{Si}=\text{O} \rightarrow \text{Mn}$. The Si1-O1 bond length (1.592 (2) Å), considerably elongated compared to Si=O double bonds (1.535 - 1.549 Å), is at the upper limit of those observed for donor/acceptor-supported silanones **III** (1.538 - 1.587 Å), but is still shorter than Si-O single bonds (1.65 Å), suggesting a weak and strongly polarized Si=O multiple-bond character. Indeed, the second order perturbation theory analysis indicates that one of the three lone pairs on O atom of silanone function is delocalized to the Si atom resulting in a relatively strong donor-acceptor interaction (99.6 kcal/mol). The Wiberg bond index and the Meyer bond order for the Si=O fragment are calculated to be 0.752 and 1.520 respectively.^[26] Probably due to the ring strain, O1-Mn bond distance (2.147 (2) Å) is elongated from those of five-membered cyclic one **8** (2.077 Å) (vide-infra) and other related $\text{R}_2\text{C}=\text{O} \rightarrow \text{MnR}(\text{CO})_4$ complexes (2.55-2.069 Å).^[27] The Si1-Mn bond (2.268 Å) is shorter than single bonds observed for $\text{R}_3\text{Si-Mn(L)}(\text{CO})_4$ complexes (2.35 - 2.50 Å)^[28] but is similar to those observed for the previously reported base-stabilized silylene-Mn^I complexes (2.279 - 2.281 Å).^[29]

Figure 2. Calculated frontier molecular orbitals of **3** at the M06/6-31G(d) level (isosurface level = ± 0.05 e/(a.u.)³). In parenthesis are calculated energy levels in eV.

To gain more insight into the electronic structure of metallasilanone **3**, DFT calculations have been performed at the M06/6-31G(d) level of theory. The optimized structure of **3** agrees quite well with the experimental one (Si-Mn: 2.248 Å, Si-O: 1.606 Å, O-Mn: 2.135 Å, O-Si-Mn: 64.80°). The highest occupied molecular orbital (HOMO, -5.58 eV) corresponds to the Si-Mn σ -bond and the lowest unoccupied bond orbital (LUMO, -1.22 eV) mainly consists of a combination of two anti-bonding σ^* -orbitals at Si and P atoms ($\sigma^*_{\text{Si-O}}$ and $\sigma^*_{\text{P-N}}$). A labile character of $\text{Si}=\text{O} \rightarrow \text{Mn}$ interaction in **3** is suggested by the considerably low-lying $\sigma^*_{\text{O-Mn}}$ orbital (LUMO+1, -1.05 eV, Figure 3a) as well as the relatively high-lying O-Mn σ -bond orbital (or n_{O} orbital directing to Mn center: HOMO-10, -8.50 eV, Figure 3c) which is close in energy to the $\pi_{\text{Si-O}}$ orbital (HOMO-9, -7.97 eV, Figure 3b). This is particularly different from the donor/acceptor-supported silanones of type **III**, with a stronger silanone-Lewis acid interaction.

Thanks to an original donor/acceptor system, silanone complex **3** is perfectly stable at room temperature. However, the addition of

other ligands such as Ph_3P or CO (5 bars), probably inducing a dissociation of silanone from the Mn centre, immediately destabilizes **3**, affording a complex mixture of compounds.

Scheme 2. Reactions of Mn^{I} -substituted silanone **3**

Figure 3. Molecular structures of **6** (left) and **7** (right). Thermal ellipsoids represent 30 % probability. H and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **6**: Si1-Mn 2.305(1), N1-Si1 1.807(1), Si1-O1 1.737(1), O1-P 1.554(1), Mn-C (average) 1.815, C-O (average) 1.147, N1-Si1-Mn 127.89(5), Mn-Si1-O1 110.50(4), N1-Si1-O1 99.17(6), Si1-O1-P 128.94(8), Si1-Mn-C3 95.68(7), Si1-Mn-C5 91.09(7), Si1-Mn-C6 164.72(8), C3-Mn-C4 157.36(10), C5-Mn-C6 97.52(11). **7**: Si1-Mn 2.276(1), Si1-O1 1.689(3), N1-Si1 1.816(3), Si1-P 2.392(1), Mn-C (average) 1.815, C-O (average) 1.149, Mn-Si1-O1 118.40(13), N1-Si1-P 88.39(10), Si-Mn-C3 89.37(13), Si1-Mn-C5 102.30(15), C3-Mn-C4 175.42(18), C5-Mn(1)-C6 103.8(2).

Based on the MO analysis, the silanone-Mn interaction would be expected labile, and indeed, complex **3**, behaving as a metal based Lewis pair (O: Lewis base and Mn: Lewis acid), quickly reacts under 3 bar of CO_2 at room temperature yielding the CO_3 -bridged silylene-manganese complex **4**, via an insertion of CO_2 into the O-Mn bond (Scheme 2). The concept of frustrated Lewis pair has been extended to systems containing transition metals which include not only molecular FLP complexes^[30, 31] but also solid metals with FLP sites on their surface.^[32] Furthermore, complex **3** cleaves, at RT, the Si-H bond of $\text{Ph}_3\text{Si-H}$ to afford the corresponding silyloxy silylene-manganese hydride complex **5**. A typical high-field signal ($\delta = -9.82$ ppm, $^3J_{\text{HP}} = 19.6$ Hz) in the ^1H NMR spectrum is in good agreement with the formation of a manganese hydride.^[33] Of particular interest, the highly strained silanone complex **3** is capable to achieve the H_2 -splitting at room temperature. However, unlike previous reactions, there is no H_2 -adduct formed, but a phosphine oxide-supported hydrosilylene complex **6** was obtained in 56 % yield. This silylene-(tetracarbonyl) $\text{Mn}(\text{I})$ hydride complex **6** has been fully characterized by spectroscopic methods and X-ray diffraction analysis (Figure 3-left).^[25]

To understand better the reaction of **3** with H_2 , we performed DFT calculations with a simplified model **3'** with methyl groups instead of *t*Bu and *i*Pr groups (Figure 4). These calculations indicate that, similarly to the reaction with Ph_3SiH , the reaction starts with the Lewis pair type H-H bond cleavage to form a H_2 -adduct **7'** as an intermediate. This process proceeds through the replacement of Si=O on the Mn center by H_2 to form a dihydrogen-Mn complex intermediate (**Int-1**). Although the formation of **Int-1** is thermodynamically unfavorable ($\Delta G_{3' \rightarrow \text{Int-1}} = +6.8$ kcal/mol), the following H_2 -bond cleavage process costs little energy ($\Delta G_{\text{Int-1} \rightarrow 7'} = 0.4$ kcal/mol) and is exergonic ($\Delta G_{3' \rightarrow 7'} = -25.6$ kcal/mol). Then, the isomerization of **7'** proceeds by a dissociation of phosphine ligand from the Si center and its insertion into the OH bond (**7'**→**Int-4**) followed by a P→Si hydride migration (**Int-4**→**6'**) afford the experimentally obtained complex **6'**. In the overall process, the rate-limiting step is the replacement of silanone on the Mn center by H_2 to generate **Int-1** ($\Delta G_{3' \rightarrow \text{Int-1}}^{\ddagger} = +19.6$ kcal/mol), which is consistent with the fact that no intermediate has been experimentally observed.

Figure 4. Calculated reaction pathways for the hydrogenation of **3'** and calculated relative Gibbs energies ΔG (kcal/mol) of each intermediate and product **6'** from that of **3'**+ H_2 . In parenthesis are calculated reaction barriers $\Delta G^{\ddagger}$ (kcal/mol).

In order to confirm this hypothesis, we considered the synthesis of the hydroxysilylene-Mn(I) complex **7**^[7, 34] via the 1,2-addition of H_2O on the Si=Mn bond of Mn^{I} -silylidene complex **2** (Scheme 3). The reaction proceeds immediately at room temperature leading to the formation of the 1,2-adduct **7**, which, as predicted, slowly isomerizes to give **6**. Nevertheless, complex **7** was found to be stable at -30 °C, and was characterized by NMR spectroscopy. Furthermore, single crystals of complex **7** were grown from a concentrated THF solution at -50 °C and its molecular structure was confirmed by X-ray diffraction study (Figure 3-right).^[25]

Scheme 3. Reactions of Mn^{I} -substituted silanone **3** with H_2O

Of particular interest, the reaction of **3** with ethylene proceeds differently leading to the ethylene-insertion into Si-Mn bond, instead of O-Mn bond, to afford a five-membered cyclic donor-acceptor silanone complex **8** (Scheme 4). The reaction probably starts with the displacement of silanone ligand by ethylene on the Mn center to generate the olefin-Mn(I) complex **9** (Scheme 4), which evolves further by the migratory insertion of ethylene into Si-Mn bond to give the experimentally obtained complex **8**.

Scheme 4. Reaction of silanone-complex **3** with ethylene.

In conclusion, we have successfully synthesized the donor/acceptor-supported Mn(I)-metalla-silanone **3**, which presents a highly strained small cyclic structure formed by the intramolecular silanone-Mn(I) interaction. Thanks to the high ring strain, the interaction Si=O→Mn is labile, leading to an exceptionally high reactivity of Mn^I-substituted silanone **3**, which readily reacts, as a metal-based Lewis Pair, with various small molecules in mild conditions. Further study on the reactivity of this new type of silanone complex and its applications 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 · Lewis pair · metallacycles · manganese complex

- [1] a) C. Friedel, J. M. Crafts, *Ann. Chim. Phys.* **1866**, 9, 5; b) F. S. Kipping, L. L. Lloyd, *J. Chem. Soc. Trans.* **1901**, 79, 449; c) R. Robison, F. S. Kipping, *J. Chem. Soc. Trans.* **1908**, 93, 439.
- [2] 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.
- [3] R. J. Glinski, J. L. Gole, D. A. Dixon, *J. Am. Chem. Soc.* **1985**, 107, 5891.
- [4] a) N. Takeda, N. Tokitoh, R. Okazaki, *Chem. Lett.* **2000**, 244; b) S. Tsutsui, H. Tanaka, E. Kwon, S. Matsumoto, K. Sakamoto, *J. Organomet. Chem.* **2006**, 691, 1341.
- [5] a) H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase, M. Goto, *J. Am. Chem. Soc.* **1998**, 120, 11096; b) J. Kapp, M. Remko, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1996**, 118, 5745; c) V. G. Avakyan, V. F. Sidorkin, E. F. Belogolova, S. L. Guselnikov, L. E. Guselnikov, *Organometallics* **2006**, 25, 6007.
- [6] a) T. Kudo, S. Nagase, *J. Am. Chem. Soc.* **1985**, 107, 2589; b) A. K. Jissy, S. K. Meena, A. Datta, *RSC Adv.* **2013**, 3, 24321; c) T. Kudo, S. Nagase, *J. Phys. Chem.* **1984**, 88, 2833.
- [7] A. C. Filippou, B. Baars, O. Chernov, Y. N. Lebedev, G. Schnakenburg, *Angew. Chem. Int. Ed.* **2014**, 53, 565.
- [8] I. Alvarado-Beltran, A. Rosas-Sánchez, A. Baceiredo, N. Saffon-Merceron, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2017**, 56, 10481.
- [9] D. Wendel, D. Reiter, A. Porzelt, P. J. Altmann, S. Inoue, B. Rieger, *J. Am. Chem. Soc.* **2017**, 139, 17193.
- [10] 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.
- [11] R. Kobayashi, S. Ishida, T. Iwamoto, *Angew. Chem. Int. Ed.* **2019**, 58, 9425.
- [12] S. Takahashi, K. Nakaya, M. Frutos, A. Baceiredo, N. Saffon-Merceron, S. Massou, N. Nakata, D. Hashizume, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2020**, 59, 15937.
- [13] S. Yao, Y. Xiong, M. Brym, M. Driess, *J. Am. Chem. Soc.* **2009**, 131, 7563.
- [14] S. Yao, M. Brym, C. v. Wüllen, M. Driess, *Angew. Chem. Int. Ed.* **2007**, 46, 4159.
- [15] a) S. Yao, Y. Xiong, M. Brym, M. Driess, *J. Am. Chem. Soc.* **2007**, 129, 7268; b) Y. Xiong, S. Yao, M. Driess, *J. Am. Chem. Soc.* **2009**, 131, 7562; c) S. Yao, Y. Xiong, M. Driess, *Chem. Eur. J.* **2010**, 16, 1281; d) Y. Xiong, S. Yao, R. Miller, M. Kaupp, M. Driess, *Nat. Chem.* **2010**, 2, 577; e) Y. Xiong, S. Yao, R. Miller, M. Kaupp, M. Driess, *J. Am. Chem. Soc.* **2010**, 132, 6912; f) Y. Xiong, S. Yao, M. Driess, *Dalton Trans.* **2010**, 39, 9282; g) Y. Xiong, S. Yao, M. Driess, *Angew. Chem. Int. Ed.* **2010**, 49, 6642; h) J. D. Epping, S. Yao, M. Karni, Y. Apeloig, M. Driess, *J. Am. Chem. Soc.* **2010**, 132, 5443; i) K. Hansen, T. Szilvási, B. Blom, E. Irran, M. Driess, *Chem. Eur. J.* **2015**, 21, 18930.
- [16] R. S. Ghadwal, R. Azhakar, H. W. Roesky, K. Prçpper, B. Dittrich, S. Klein, G. Frenking, *J. Am. Chem. Soc.* **2011**, 133, 17552.
- [17] T. Muraoka, K. Abe, Y. Haga, T. Nakamura, K. Ueno, *J. Am. Chem. Soc.* **2011**, 133, 15365.
- [18] 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.
- [19] For review on stable silanones: a) D. Franz, S. Inoue, *Dalton Trans.* **2016**, 45, 9385; b) Y. Xiong, S. Yao, M. Driess, *Angew. Chem. Int. Ed.* **2013**, 52, 4302; c) Y. K. Loh, S. Aldridge, *Angew. Chem. Int. Ed.* **2020**, 59, 2.
- [20] R. Rodriguez, D. Gau, J. Saouli, A. Baceiredo, N. Saffon-Merceron, V. Branchadell, T. Kato, *Angew. Chem. Int. Ed.* **2017**, 56, 3935.
- [21] Donor/acceptor-supported silanones stable in air: R. S. Ghadwal, R. Azhakar, H. W. Roesky, K. Prçpper, B. Dittrich, C. Goedecke, G. Frenking, *Chem. Commun.* **2012**, 48, 8186.
- [22] Poorly reactivity of silanones supported by a base and a transition metal: T. Muraoka, K. Abe, H. Kimura, Y. Haga, K. Ueno, Y. Sunada, *Dalton Trans.* **2014**, 43, 16610.
- [23] a) A. C. Filippou, O. Chernov, K. W. Stumpf, G. Schnakenburg, *Angew. Chem. Int. Ed.* **2010**, 49, 3296; b) A. C. Filippou, O. Chernov, G. Schnakenburg, *Chem. Eur. J.* **2011**, 17, 13574; c) G. Dgbek, F. Hanusch, D. Munz, S. Inoue, *Angew. Chem. Int. Ed.* **2020**, 59, 5823.
- [24] a) J. S. Price, D. J. H. Emslie, J. F. Britten, *Angew. Chem. Int. Ed.* **2017**, 56, 6223; b) J. S. Price, D. J. H. Emslie, *Chem. Sci.* **2019**, 10, 10853.
- [25] CCDC-2077038 (2), CCDC-2077039 (3), CCDC-2077040 (4), CCDC-2077041 (5), CCDC-2077042 (6), CCDC-2077043 (7) and CCDC-1998344 (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/>
- [26] a) K.B. Wiberg, *Tetrahedron* **1968**, 24, 1083; b) I. Mayer, *Chem. Phys. Lett.* **1983**, 97, 270.
- [27] H.-J. Haupt, G. Lohmann, U. Florke, *Z. Anorg. Allg. Chem.* **1985**, 526, 103; b) P. De Shong, D. R. Sidler, P. J. Rybczynski, G. A. Slough, A. L. Rheingold, *J. Am. Chem. Soc.* **1988**, 110, 2575; c) J. M. Cooney, L. H. P. Gommans, L. Main, B. K. Nicholson, *J. Organomet. Chem.* **1988**, 349, 17.
- [28] a) X. Yang, C. Wang, *Angew. Chem. Int. Ed.* **2018**, 57, 923; b) T. Komuro, S. Okawara, K. Furuyama, H. Tobita, *Chem. Lett.* **2012**, 41,

- 774; c) J. M. Higgins, A. L. Schmitt, I. A. Guzei, S. Jin, *J. Am. Chem. Soc.* **2008**, *130*, 16086; d) M. C. Couldwell, J. Simpson, *J. Chem. Soc., Dalton Trans.* **1976**, 714.
- [29] R. Azhakar, S. P. Sarish, H. W. Roesky, J. Hey, D. Stalke, *Inorg. Chem.* **2011**, *50*, 5039.
- [30] Review on Transition metal FLP: S. R. Flynn, D. F. Wass, *ACS Catal.* **2013**, *3*, 2574.
- [31] Mn-based FLP: R. Buhaibeh, O. A. Filippov, A. Bruneau-Voisine, J. Willot, C. Duhayon, D. A. Valyaev, N. Lugan, Y. Canac, J.-B. Sortais, *Angew. Chem. Int. Ed.* **2019**, *58*, 6727.
- [32] a) K. K. Ghuman, T. E. Wood, L. B. Hoch, C. A. Mims, G. A. Ozin, C. V. Singh, *Phys. Chem. Chem. Phys.* **2015**, *17*, 14623; b) K. K. Ghuman, L. B. Hoch, P. Szymanski, J. Y. Y. Loh, N. P. Kherani, M. A. El-Sayed, G. A. Ozin, C. V. Singh, *J. Am. Chem. Soc.* **2016**, *138*, 1206; c) M. Ghoussoub, S. Yadav, K. K. Ghuman, G. A. Ozin, C. V. Singh, *ACS Catal.* **2016**, *6*, 7109; d) S. Zhang, Z.-Q. Huang, Y. Ma, W. Gao, J. Li, F. Cao, L. Li, C.-R. Chang, Y. Qu, *Nat. Commun.* **2017**, *8*, 15266; e) Z.-Q. Huang, L.-P. Liu, S. Qi, S. Zhang, Y. Qu, C.-R. Chang, *ACS Catal.* **2018**, *8*, 546; f) L. Wang, T. Yan, R. Song, W. Sun, Y. Dong, J. Guo, Z. Zhang, X. Wang, G. A. Ozin, *Angew. Chem. Int. Ed.* **2019**, *58*, 9501; g) T. Yan, N. Li, L. Wang, W. Ran, P. N. Duchesne, L. Wan, N. T. Nguyen, L. Wang, M. Xia, G. A. Ozin, *Nat. Commun.* **2020**, *11*, 6095.
- [33] J. Turner, J. A. B. Abdalla, J. I. Bates, R. Tirfoin, M. J. Kelly, N. Phillips, S. Aldridge, *Chem. Sci.*, **2013**, *4*, 4245.
- [34] Other hydroxysilylene-transition metal complexes: a) A. Meltzer, C. Präsang, M. Driess, *J. Am. Chem. Soc.* **2009**, *131*, 7232.

((Catch Phrase))

S. Takahashi, M. Ramos Enriquez, E. Bellan, A. B., N. Saffon-Merceron, N. Nakata, D. Hashizume, V. Branchadell, T. Kato _____ **Page – Page**

Strained and Reactive Donor/Acceptor-Supported Metalla-Silane

A new stable donor/acceptor-supported Mn(I)-metallasilane was synthesized. This silane complex is highly strained because of its incorporation in a small cyclic structure formed by the intramolecular silane-Mn(I) interaction. Thanks to the high ring strain, the interaction Si=O→Mn is labile, leading to an exceptionally high reactivity with various small molecules such as H₂ or ethylene gas in mild conditions.