Unprecedented formation of methylsilylcarbonates from iridium-catalyzed reduction of CO2 with hydro silanes†

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The iridium complex \(\text{[Ir(\mu-\text{CF}_3\text{SO}_3)(\kappa^2-\text{NSiMe}_2)_2]}_2 (3)\) (\(\text{NSiMe}_2 = \text{4-methylpyridine}-2\)-yloxyd iethylsilyl) has been prepared by reaction of \(\text{[Ir(\mu-\text{Cl})(\kappa^2-\text{NSiMe}_2)_2]}_2 (1)\) with two equivalents of \(\text{AgCF}_3\text{SO}_3\). The solid structure of 3 evidenced its dinuclear nature, being a rare example of an iridium species with triflate groups acting as bridges. The 3-catalyzed reduction of \(\text{CO}_2\) with \(\text{HSiMe(OSiMe}_3)_2\) affords a mixture of the corresponding silylformate and methoxysilane together with the silyl carbonate \(\text{CH}_3\text{OCO}_2\text{SiMe}(\text{OSiMe}_3)_2 (4a)\). This is the first time that the formation of silyl carbonates has been observed from the catalytic reduction of \(\text{CO}_2\) with silanes. Analogous behaviour has been observed when \(\text{HSiMe}_2\text{Ph}\) and \(\text{HSiMePh}_2\) were used as reductants.

Introduction

The catalytic reaction of \(\text{CO}_2\) with silicon-hydrides has proven to be an effective and thermodynamically favoured methodology for its reduction to formate, formaldehyde, methanol or methane (Scheme 1).1,2

However, to the best of our knowledge the formation of methylsilylcarbonates, \(\text{MeOCO}_2\text{SiR}_3\) (Fig. 1), as products of the catalytic reduction of \(\text{CO}_2\) with silicon-hydrides has not been reported so far.

On the other hand, hydro siloxanes are obtained in large scale as side products of the silicone industry and therefore, the development of catalytic processes effective for the selective reduction of \(\text{CO}_2\) based on hydro siloxanes, instead of hydro silanes, as reductants is of great interest.3 In this context, in recent years we have focused our research on the application of iridium species as catalysts for the reduction of \(\text{CO}_2\) with \(\text{1,1,1,3,5,5,5-heptamethyltrisiloxane, HSiMe(OSiMe}_3)_2\).5,6

Recently, we have described the synthesis and catalytic behavior of the iridium(III) complexes \(\text{[Ir(\mu-\text{Cl})(\kappa^2-\text{NSiMe}_2)_2]}_2 (1)\) and \(\text{[Ir(CF}_3\text{CO}_2)(\kappa^2-\text{NSiMe}_2)_2]}_2 (2)\) (\(\text{NSiMe}_2 = \{4\text{-methylpyridine}-2\)-yloxyd iethylsilyl) (Scheme 2). Species 2 catalyzed the selective reduction of \(\text{CO}_2\), depending on the reaction conditions, to silylformate or methoxysilane with \(\text{HSiMe(OSiMe}_3)_2\).6 As a continuation of our studies on the chemistry of iridium complexes with pyridine-2-yloxyI-silyl ligands, we have found that the triflate derivative \(\text{[Ir(\mu-\text{CF}_3\text{SO}_3)(\kappa^2-\text{NSiMe}_2)_2]}_2 (3)\) (Scheme 2) catalyzes the reaction of \(\text{CO}_2\) (3 bar) with \(\text{HSiMe(OSiMe}_3)_2\) to give a mixture of the corresponding silylformate and methoxysilane along with a new compound that has been characterized by multinuclear NMR spectroscopy as \(\text{CH}_3\text{OCO}_2\text{SiMe(OSiMe}_3)_2 (4a)\). To the best of our knowledge, this is the first time that the formation of silyl carbonates from the catalytic reduction of \(\text{CO}_2\) with silanes has been observed. The results from these studies are described below.

Scheme 1 Products from the catalytic reduction of \(\text{CO}_2\) with silicon-hydrides reported so far.

Fig. 1 Methylsilylcarbonates.
Results and discussion

Synthesis and characterization of the catalyst precursor

The reaction of complex 1 with two equivalents of AgCF₃SO₃ leads to the formation of [Ir(μ-CF₃SO₃)](κ²-NSiMe₂)₂ (3), which has been isolated as a white solid in 89% yield. The solid structure of complex 3 evidenced its dinuclear nature (Fig. 2). As far as we know, 3 is the first example of an iridium species with triflate groups acting as bridges. The molecule exhibits a crystallographic inversion center, with half the molecule as the independent part. Each metal atom shows an octahedral geometry like that found for the independent part. Each metal atom shows an octahedral structure of complex 3 evidenced its dinuclear nature (Fig. 2). As far as we know, 3 is the first example of an iridium species with triflate groups acting as bridges. The molecule exhibits a crystallographic inversion center, with half the molecule as the independent part. Each metal atom shows an octahedral geometry like that found for the independent part. Each metal atom shows an octahedral geometry like that found for the independent part.

3-Catalyzed reduction of ¹³CO₂ with silicon hydrides

Preliminary studies on the 3-catalyzed reaction of CO₂ (3 bar) with HSiMe(OSiMe₃)₂ at 298 K showed that 24 hours are required to achieve the conversion of 94% of the starting hydrosiloxane into a mixture of the corresponding silylformate (53.0%) and methoxysilane (21.4%) along with a new compound (25.6%) (TOF = 3.9 h⁻¹). This behavior differs from that previously reported for 3, which under the same reaction conditions catalyzed the full conversion of HSiMe(OSiMe₃)₂ into silylformate (93.0%) and methoxysilane (7.0%) in 3.5 h (TOF = 28.6 h⁻¹). Therefore, complex 2 is not only more active but also more selective than 3.

To determine the nature of the new species observed when 3 is used as catalyst for the hydroisilylation of CO₂, we decided to study this reaction using isotopically labeled ¹³CO₂. Thus, ¹H and ¹³C NMR studies of the 3-catalyzed (1.0 mol%) reaction of ¹³CO₂ (2.7 bar, 323 K, C₆D₆) with HSiMe(OSiMe₃)₂ were performed. These experiments evidenced, since early reaction stages, the presence of a mixture of ¹³CH₃O⁻¹³CO₂⁻SiMe(OSiMe₃)₂ (4a), together with the corresponding silylformate, H⁻¹³CO₂SiMe(OSiMe₃)₂ (5a), and the methoxysilane, ¹³CH₂OSiMe(OSiMe₃)₂ (6a) (Table 1).

The most characteristic resonance in the ¹H NMR spectra of 4a is a doublet of doublets centered at δ 3.33 ppm (J_C–H = 146.9 Hz; J_C–H = 4.1 Hz) corresponding to the ¹³CH₃O protons of the starting hydrosiloxane and expressed in mol%.

Table 1: Results from 3-catalyzed reduction of ¹³CO₂ (2.7 bar) with HSiMe(OSiMe₃)₂

| Entry | T (K) | 4a (%) | 5a (%) | 6a (%) | Conversion (%) | Time (h) |
|-------|-------|--------|--------|--------|----------------|---------|
| 1     | 323   | 26.7   | 65.2   | 8.1    | 70             | 3       |
| 2     | 323   | 18.8   | 70.0   | 11.2   | 98             | 12      |
| 3     | 323   | 19.0   | 70.0   | 11.0   | 98             | 24      |
| 4     | 358   | 11.7   | 68.7   | 19.6   | 100            | 24      |
| 5     | 358   | 8.5    | 68.0   | 23.5   | 100            | 48      |
| 6'    | 323   | 0      | 0      | 0      | 0              | 24      |

* General conditions: 3 (1.0 mol%) in 0.5 mL of dry C₆D₆. Calculated by ¹H NMR and expressed in mol%. Calculated by ¹H NMR relative to the starting hydrosiloxane and expressed in mol%. After 24 h at 323 K. Control experiment without iodid catalyst (Fig. S24 see ESI).
The formation of methoxy-silanes from the catalytic reduction of CO$_2$ with hydrosilanes has been so far explained by reaction of bis(silyl)acetalts with the corresponding hydrosilanes (Scheme 3, Path B).\textsuperscript{6,7} Indeed, since it has been observed that at 323 K only traces of 4a are transformed into 6a (Table 1 entry 3) it is reasonable to assume that under these conditions 6a is formed by reactions of the bis(silyl)acetal 13CH$_2$[OSiMe(OSiMe$_3$)$_2$]$_2$ (7a) with HSiMe(OSiMe$_3$)$_2$. In agreement with this we have observed the presence of traces of 7a in the NMR spectra of this reaction (ESI†). However, after 24 h of reaction 98% of the starting hydrosiloxane was consumed and therefore, under these conditions, the formation of 6a at 358 K can only be explained by thermal decomposition of 4a (Scheme 3, Path B).

Analogous behavior has been observed when HSiMe$_2$Ph and HSiMe$_3$Ph$_2$ were used as reducing agents. Thus, the formation of the mixtures of methyl-silyl-carbonate 13CH$_3$O–13CO$_2$SiR$_3$ (SiR$_3$ = SiMe$_2$Ph, 4b; SiMePh$_2$, 4c) and the corresponding silylformate and methoxysilane from the 3-catalyzed reduction of 13CO$_2$ with HSiR$_3$ (SiR$_3$ = SiMe$_2$Ph, SiMePh$_2$) was also observed (ESI†).

It should be mentioned, that the formation of the methylsilyl-carbonates was not observed along the 2-catalyzed reduction of CO$_2$ with HSiMe(OSiMe$_3$)$_2$.\textsuperscript{6} In this context, even though species 2 and 3 seem very similar, their reactivity against silanes is very different. Thus, while complex 3 is stable in presence of one equivalent of HSiMe(OSiMe$_3$)$_2$ at 323 K, the trifluoroacetate ligand in 2 is reduced to give the corresponding silyl ether CF$_3$CH$_2$OSiR$_3$.\textsuperscript{6} Therefore, it is reasonable to think that the stability of the triflate ligand could play a role stabilizing reaction intermediates, which could open new paths of reaction, no accessible in 2-catalyzed CO$_2$ hydrosilylation reactions.

At this point the question arises, how methylsilylcarbontes are formed from the 3-catalyzed hydrosilylation of CO$_2$. A plausible mechanism proposal is shown in Scheme 4. The formation of methycarbonates has been explained by insertion of CO$_2$ into the Ir–O bond of iridium–OCH$_3$ species.\textsuperscript{8} Therefore, we propose that the reaction of an iridium-methoxy intermediate (A in Scheme 4) with CO$_2$ could lead to the methylcarbontes species B, which by reaction with HSiR$_3$ would afford the corresponding methylsilylcarbonate and the Ir–H species C. The next step, is the reaction of C with CO$_2$ to give the iridium-formate intermediate D, which according to our previous results has been found to be a thermodynamically favoured

(Fig. 3). This resonance shows a direct C–H bond correlation in the 1H–13C HSQC spectra with a doublet resonance centered at $\delta$ 54.1 ppm ($J_{C-H} = 1.7$ Hz), assigned to the 13CH$_3$O carbon in the 13C APT NMR spectra, and also a C–H bond correlation in the 1H–13C HMBC spectra with a doublet resonance that appeared centered at $\delta$ 153.0 ppm ($J_{C-H} = 1.8$ Hz), assigned to the 13CO$_3$ carbon in the 13C APT NMR spectra. These data compare well with those reported for alkyl-silyl-carbonates and support the structure proposed for 4a in Table 1 (see ESI†).

Under the above described reaction conditions the slow consumption of HSiMe(OSiMe$_3$)$_2$ was observed (Table 1, entries 1 and 2). Thus, after 12 h the reaction is complete and 1H and 13C NMR spectra evidenced the consumption of all the starting 13CO$_2$ and of the 98% of HSiMe(OSiMe$_3$)$_2$ to give a mixture of 4a (18.8 mol%), 5a (70.0 mol%) and 6a (11.2 mol%) (Table 1, entry 2). Heating this sample for another 12 h at 323 K did not evidence changes in the composition of the mixture (Table 1, entry 3). Interestingly, increasing the temperature at 358 K the slow transformation of 4a into 6a occurs (Table 1 entries 4 and 5), in addition, the formation of 13CO$_2$ was observed. This outcome agrees with the known thermal behavior of alkyl-silyl-carbonates, ROCO$_2$SiR$_3$,\textsuperscript{3} which thermally decompose to give the corresponding methoxysilane and CO$_2$ (Scheme 3, Path A).

Scheme 3 Reaction paths for the formation of methoxysilanes from the 3-catalyzed hydrosilylation of CO$_2$.

Scheme 4 Plausible mechanism proposal for the formation of methyl-silyl-carbonates from the 3-catalyzed hydrosilylation of CO$_2$. 

Fig. 3 CH$_3$O-region of the 1H NMR spectra in C$_6$D$_6$ of the 3-catalyzed reaction of 13CO$_2$ (2.7 bar) with HSiMe(OSiMe$_3$)$_2$ at 323 K.
process. Finally, the reaction of the iridium–formate D with excess of silane could regenerate A closing the catalytic cycle.

Experimental

General considerations

All manipulations were carried out under an argon atmosphere by Schlenk-type techniques or in a glovebox MBraun Unilab. Organic solvents were dried by standard procedures and distilled under argon prior to use or obtained oxygen- and water-free from a solvent purification system (Innovative Technologies). $^1$H, $^{13}$C, $^{29}$Si and $^{19}$F NMR spectra were obtained on a Bruker AV-300, AV-400 or AV-500 spectrometer. Chemical shifts ($\delta$), reported in ppm, are referenced to the residual solvent peaks and coupling constants ($\textit{J}$) are reported in Hz.

Synthesis of 3. Toluene (10 mL) was added to a light-coloured Schlenk containing $[\text{Ir}(\mu-\text{Cl})(\text{C}_2\text{NSiMe}_2)_2]$ (1) (300 mg, 0.268 mmol) and silver triethylsilane (151 mg, 0.590 mmol). The mixture was stirred at room temperature for 5 hours and then filtered through Celite. Solvent was removed under reduced pressure and the solid was washed with pentane (3 × 8 mL) to afford a white solid. Yield: 320 mg (89%). $^1$H NMR (300 MHz, $\text{C}_6\text{D}_6$, 298 K): $\delta$ 8.73 (d, $J_{\text{H-H}}$ = 6.2 Hz, 2H, py), 6.32 (s, 2H, py), 6.02 (s, $J_{\text{H-H}}$ = 6.2 Hz, 2H, py), 1.51 (s, 6H, Me-py), 0.72 (s, 6H, Si–Me), 0.41 (s, 6H, Si–Me). $^{13}$C NMR (75 MHz, $\text{C}_6\text{D}_6$, 298 K):$J_{\text{C-C}}$ = 153.0 (d, 2$J_{\text{C-C}}$ = 1.7 Hz, CH$_3$O), 148.7 (s, py), 118.4 (s, py), 111.9 (s, py), 106.0 (s, CH$_3$-py), 3.8 (s, CH$_3$-Si), 2.4 (s, CH$_3$-Si). $^{29}$Si($^1$H) NMR (118 MHz, $\text{C}_6\text{D}_6$, 298 K): $\delta$ 38.2 (Ir–Si). $^{19}$F NMR (282 MHz, $\text{C}_6\text{D}_6$, 298 K): $\delta$ −76.97 (s, CF$_3$SO$_3$). High resolution mass spectrometry (ESI$^+$): calcd. $m/z$ = 525.1006; found $m/z$ = 525.1004 (M$^+$−CF$_3$SO$_3$).

3-Catalyzed (1.0 mol%) reaction of 13CO$_2$ with HSiR$_3$.

A young cap NMR tube was charged with 3 (2.83 mg, 0.0021 mmol), 0.42 mmol of the corresponding silane (114 µL, HSiMe(OSiMe)$_2$), 64.4 µL, HSiMe$_2$Ph; 83.7 µL, HSiMe$_3$P) and 0.5 mL of $\text{C}_6\text{D}_6$. Argon gas was evacuated by three freeze-pump-thaw cycles. Then the tube was pressurized with 13CO$_2$ (2.7 bar), heated at 323 K and monitored by NMR spectroscopy.

Selected data for 4a. $^1$H NMR plus HSQC and HMQC ($^1$H–$^1$H; $^1$H–$^{13}$C) (300 MHz, $\text{C}_6\text{D}_6$, 298 K): $\delta$ 3.33 (dd, $J_{\text{H-C}}$ = 146.9 Hz, $J_{\text{H-C}}$ = 4.1 Hz, 3H, CH$_3$OCCO$_2$), $^{13}$C($^1$H) plus HSQC and HMBD $^1$H–$^{13}$C (75 MHz, $\text{C}_6\text{D}_6$, 298 K): $\delta$ 153.0 (d, $J_{\text{C-C}}$ = 1.7 Hz, CO$_2$). Selected data for 4b: $^1$H NMR plus HSQC $^1$H–$^{13}$C (300 MHz, $\text{C}_6\text{D}_6$, 298 K): $\delta$ 3.30 (dd, $J_{\text{H-C}}$ = 147.1 Hz, $J_{\text{H-C}}$ = 4.1 Hz, 3H, CH$_3$OCCO$_2$), $^{13}$C($^1$H) plus HSQC and HMBD $^1$H–$^{13}$C (75 MHz, $\text{C}_6\text{D}_6$, 298 K): $\delta$ 154.1 (d, $J_{\text{C-C}}$ = 1.7 Hz, CO$_2$). Selected data for 4c: $^1$H NMR plus HSQC $^1$H–$^{13}$C (300 MHz, $\text{C}_6\text{D}_6$, 298 K): $\delta$ 3.23 (dd, $J_{\text{H-C}}$ = 147.1 Hz, $J_{\text{H-C}}$ = 4.1 Hz, 3H, CH$_3$OCCO$_2$), $^{13}$C($^1$H) plus HSQC and HMBD $^1$H–$^{13}$C (75 MHz, $\text{C}_6\text{D}_6$, 298 K): $\delta$ 153.9 (d, $J_{\text{C-C}}$ = 1.8 Hz, CO$_2$), 54.3 (d, $J_{\text{C-C}}$ = 1.8 Hz, CH$_3$O).

Crystal structure determination of complex 3. Single crystal X-ray diffraction data were collected at 100(2) K with graphite-monochromated Mo Kα radiation (λ = 0.71072 Å) using narrow frame rotation (Δω = 0.3°) on a Bruker Smart APEX diffractometer. Measured intensities were integrated and corrected for absorption effects with SAINT+ and SADABS.

Conclusions

In conclusion, the use of triethylsilane, instead of trifluoroacetate, as ancillary ligand in the chemistry of Ir-(-SiMe$_2$)$_2$ species allows the preparation of 3, which is a rare example of a dinuclear iridium complex with trifluoroacetate ligands acting as bridges. $^1$H NMR studies of the 3-catalyzed reduction of CO$_2$ with hydroxilanes evidenced the unprecedented formation of methylsilylcarbonyl as reaction products, together with the corresponding silylformate and methoxysilane.

The results of this investigation show that the formation of methoxysilanes during the catalytic reduction of CO$_2$ with silanes, which traditionally has been explained by the catalytic reaction of bis(silyl)acetals with silanes, could also be consequence of thermal decomposition of the corresponding methylsilylcarbonylate.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 (a) J. Chen, M. McGraw and E.Y.-X. Chen, ChemSusChem, 2019, 12, 4543–4569; (b) F. J. Fernández-Alvarez and L. A. Oro, ChemCatChem, 2018, 10, 4783–4796; (c) C. Chauvier and T. Cantat, ACS Catal., 2017, 7, 2107–2115; (d) F. J. Fernández-Alvarez, A. M. Aitani and L. A. Oro, Catal. Sci. Technol., 2014, 4, 611–624.

2 For examples of transition-metal free catalyzed processes see: K. Motokura, C. Nakagawa, R. A. Pramudita and...
Y. Manaka, ACS Sustainable Chem. Eng., 2019, 7, 11056–11061; and references therein.

3 (a) Y. Yamamoto and D. S. Tarbell, J. Org. Chem., 1971, 36, 2954–2956; (b) M. Paul, J. Dunougès, R. Calas and E. Frainnet, J. Organomet. Chem., 1972, 38, 267–274; (c) Y. Yamamoto, D. S. Tarbell, J. R. Fehlner and B. M. Pope, J. Org. Chem., 1973, 38, 2521–2525; (d) R. Tacke, M. Link, A. Bentlage-Felten and H. Zileh, Z. Naturforsch., 1985, 40b, 942–947; (e) H. Yildirimyan and G. Gattow, Z. Anorg. Allg. Chem., 1985, 521, 135–144.

4 D. Addis, S. Das, K. Junge and M. Beller, Angew. Chem., Int. Ed., 2011, 50, 6004–6011.

5 (a) R. Lalrempuia, M. Iglesias, V. Polo, P. J. Sanz Miguel, F. J. Fernández-Alvarez, J. J. Pérez-Torrente and L. A. Oro, Angew. Chem., Int. Ed., 2012, 51, 12824–12827; (b) E. A. Jaseer, M. N. Akhtar, M. Osman, A. Al-Shammar, H. B. Oladipo, K. Garcés, F. J. Fernández-Alvarez, S. Al-Khattaf and L. A. Oro, Catal. Sci. Technol., 2015, 5, 274–279; (c) A. Julián, E. A. Jaseer, K. Garcés, F. J. Fernández-Alvarez, P. García-Orduña, F. J. Lahoz and L. A. Oro, Catal. Sci. Technol., 2016, 6, 4410–4417; (d) A. Julián, J. Guzmán, E. A. Jaseer, F. J. Fernández-Alvarez, R. Royo, V. Polo, P. García-Orduña, F. J. Lahoz and L. A. Oro, Chem.–Eur. J., 2017, 23, 11898–11907; (e) A. I. Ojeda-Amador, J. Munarriz, P. Alamán-Valtierra, V. Polo, R. Puerta-Oteo, M. V. Jiménez, F. J. Fernández-Alvarez and J. J. Pérez-Torrente, ChemCatChem, 2019, 11, 5524–5535.

6 J. Guzmán, P. García-Orduña, V. Polo, F. J. Lahoz, L. A. Oro and F. J. Fernández-Alvarez, Catal. Sci. Technol., 2019, 9, 2858–2867.

7 (a) T. C. Eisenschmid and R. Eisenberg, Organometallics, 1989, 8, 1822–1824; (b) S. N. Riduan, Y. Zhang and J. Y. Ying, Angew. Chem., Int. Ed., 2009, 48, 3322–3325; (c) S. N. Riduan, J. Y. Ying and Y. Zhang, ChemCatChem, 2013, 5, 1490–1496; (d) D. S. Morris, C. Weetman, J. T. C. Wennmacher, M. Cokoja, M. Drees, F. E. Kühn and J. B. Love, Catal. Sci. Technol., 2017, 7, 2838–2845; (e) D. Specklin, F. Hild, C. Fliedel, C. Gourlaouen, L. F. Veiro and S. Dagorne, Chem.–Eur. J., 2017, 23, 15908–15912; (f) M. Saleh, D. R. Powell and R. J. Wehmschulte, Organometallics, 2017, 36, 4810–4815.

8 N. Hazari and J. E. Heimann, Inorg. Chem., 2017, 56, 13655–13678.

9 SAINT+, version 6.01: Area-Detector Integration Software, Bruker AXS, Madison, 2001.

10 (a) SADABS (Version 2016/02), Bruker AXSMadison; (b) L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, J. Appl. Crystallogr., 2015, 48, 3–10.

11 (a) G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 1990, 46, 467–473; (b) G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112–122.

12 G. M. Sheldrick, Acta Crystallogr., Sect. C: Struct. Chem., 2015, 71, 3–8.

13 L. J. Farrugia, J. Appl. Crystallogr., 2012, 45, 849–854.

14 P. van der Sluis and A. L. Spek, Acta Crystallogr., Sect. A: Found. Crystallogr., 1990, 46, 194–201.