Octacarbonyl dicobalt-catalyzed selective carbonylation of (trimethylsilyl)diazomethane to obtain (trimethylsilyl)ketene

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Abstract

(Trimethylsilyl)diazomethane has been selectively carbonylated to (trimethylsilyl)ketene at 10 °C under atmospheric pressure of carbon monoxide in the presence of octacarbonyl dicobalt as the catalyst. The rate of (trimethylsilyl)ketene formation is first order with respect to both (trimethylsilyl)diazomethane and octacarbonyl dicobalt, and negative first order with respect to carbon monoxide.
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1. Introduction

Diazoalkanes are useful carbene precursors, especially in transition metal-catalyzed synthetic applications [1]. The decomposition of diazoalkanes in the presence of various transition metal complexes is well documented [2–5], but octacarbonyl dicobalt was declared to be ineffective in diazo decomposition [6] based on the observed sluggish ylide generation and cyclopropanation with ethyl diazoacetate at 60 °C [7]. However, it was found that octacarbonyl dicobalt does react with ethyl diazoacetate under ambient conditions in a fast reaction by evolution of N_2 and CO to give mono- and di-ethoxycarbonylcarbene bridged dicobalt carbonyl complexes in high yield [8]. The carbene bridges in these complexes can easily be displaced by CO to regenerate $Co_2(CO)_8$ and to obtain organic products which are derivatives of the highly reactive ethoxycarbonylketene [9] formed by carbene-carbon monoxide coupling.

We found that the less reactive (trimethylsilyl)ketene is selectively formed in a $Co_2(CO)_8$-catalyzed carbonylation of (trimethylsilyl)diazomethane under very mild reaction conditions.

2. Results

In accord with Eq. [1], solutions of (trimethylsilyl)diazomethane (0.10 mol/dm³) in *n*-heptane in the presence of $Co_2(CO)_8$ (0.010 mol/dm³) at 10 °C and in an atmosphere of carbon monoxide give after 4 h reaction time reaction mixtures, containing according to the infrared spectra, (trimethylsilyl)ketene (up to 0.10 mol/dm³) and $Co_2(CO)_8$ (0.010 mol/dm³). No observable pressure change accompanied the reaction.

$$Me_3SiCHN_2 + CO \xrightarrow[10\,°C,\,1\,bar,\,4\,h]{10\,mol\%\,Co_2(CO)_8} N_2 + \underset{100\%\ yield}{Me_3SiCH{=}C{=}O}$$

(1)
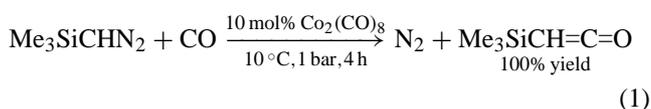
By distillation at atmospheric pressure of the reaction mixture, all the (trimethylsilyl)ketene formed can be separated in form of a colorless *n*-heptane solution. Quantitative gas chromatographic analyses confirmed that the (trimethylsilyl)diazomethane conversions are complete and the (trimethylsilyl)ketene yields are practically 100%.

Monitoring the rate of (trimethylsilyl)ketene formation by measuring the intensity of the ν(CO) band of $Me_3SiCH{=}C{=}O$ at 2116 cm⁻¹ every 2 min, the initial rate was determined. Starting the monitoring at various Me_3SiCHN_2, $Co_2(CO)_8$, and CO concentrations the initial rates of $Me_3SiCH{=}C{=}O$ formation show a first order dependence in

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Table 1
The effect of initial concentrations of Me_3SiCHN_2, $Co_2(CO)_8$, and CO on the initial rate of $Me_3SiCH=C=O$ formation ($r_{Me_3SiCH=C=O}$) and on the observed rate constant ($k_{obs} = r_{Me_3SiCH=C=O} \times [CO]/[Me_3SiCHN_2] \times [Co_2(CO)_8]$) at $10\,^\circ C$ in n-heptane solution

$[Me_3SiCHN_2]_0$ (mol/dm³)	$[Co_2(CO)_8]_0$ (mol/dm³)	$[CO]_0^a$ (mol/dm³)	$10^5 \times r_{Me_3SiCH=C=O}$ (mol/dm³ s)	$10^3 \times k_{obs}$ (s⁻¹)
0.010	0.00985	0.0113	0.42	0.48
0.020	0.00999	0.0114	0.83	0.47
0.040	0.00985	0.0114	1.83	0.53
0.010	0.0196	0.0114	0.81	0.47
0.020	0.00493	0.0114	0.51	0.59
0.020	0.0194	0.0116	1.83	0.54
0.020	0.00938	0.0061	1.67	0.52
0.020	0.00972	0.0171	0.66	0.55
0.020	0.00979	0.0232	0.52	0.58
0.020	0.0380	0.0116	3.17	0.48

[a] The concentration of carbon monoxide was calculated from the partial pressure of CO and the solubility of CO at 1 bar at $10\,^\circ C$ in n-heptane as $0.0119\,mol/dm^3$. This value of CO solubility was obtained by using the known solubility of CO in n-heptane at $25\,^\circ C$ (J.C. Gjaldbaek, Acta Chem. Scand., 6 (1952) 623–633) and the temperature dependence of the solubility of CO in n-hexane (R. Koelliker, H. Thies, J. Chem. Eng. Data 38 (1993) 437–440).

both Me_3SiCHN_2 and $Co_2(CO)_8$ and a negative first order dependence with respect to CO (see Table 1).

In experiments performed at higher than atmospheric pressure of CO, the infrared spectra of the reaction mixtures show, beside the bands of $Me_3SiCH=C=O$ and $Co_2(CO)_8$, the appearance of two additional $\nu(CO)$ bands at 1799 and $1742\,cm^{-1}$, characteristic of 2,3-bis(trimethylsilyl)cyclopropanone [10] and of 2,3,4-tris(trimethylsilyl)cyclobutanone [11], respectively. Applying 50 bar pressure of CO in the catalytic carbonylation of Me_3SiCHN_2, the formation of $Me_3SiCH=C=O$ slows down relative to the known reaction of $Me_3SiCH=C=O$ with Me_3SiCHN_2 which results in the appearance of 2,3-bis(trimethylsilyl)cyclopropanone [10] and 2,3,4-tris(trimethylsilyl)cyclobutanone [11] in the reaction products according to IR and gas chromatographic analysis of the reaction mixture (see Table 2).

The formation of $Me_3SiCH=C=O$ from Me_3SiCHN_2 in the presence of $Co_2(CO)_8$ occurs even in the absence of external CO in the gas phase. Thus, in experiments performed under an atmosphere of argon, up to 5.5 mol $Me_3SiCH=C=O$/mol $Co_2(CO)_8$ were obtained parallel to the corresponding (mainly N_2) gas evolution (Table 3). The course of the gas evolution shows a characteristic "S" shape. After an initial period the gas evolution accelerates and then dies away. A typical example can be seen in Fig. 1.

As can be seen from the data in Table 3 the initial rates of gas evolution show only a small dependence on the initial concentrations of Me_3SiCHN_2.

Table 2
$Me_3SiCH=C=O$, 2,3-bis(trimethylsilyl)cyclopropanone, and 2,3,4-tris(trimethylsilyl)cyclo-butanone formed in 10 h reaction time under 50 bar CO pressure from $1.0\,mol/dm^3$ solutions of Me_3SiCHN_2 in hexane in the presence of 2 mol% $Co_2(CO)_8$ at different temperatures

Temperature (°C)	$Me_3SiCH=C=O$ (%)	2,3-bis(trimethylsilyl)cyclopropanone (%)	2,3,4-tris(trimethylsilyl)cyclobutanone (%)
0	56	25	19
25	4	40	56
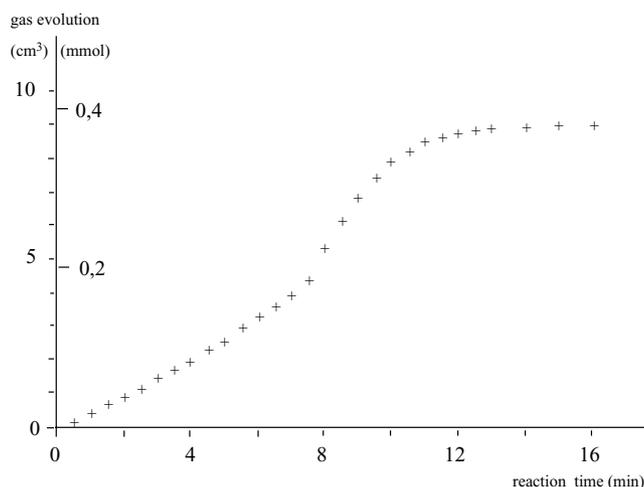
Fig. 1. The course of gas evolution in an experiment started at $10\,^\circ C$ in an atmosphere of argon using 0.40 mmol of Me_3SiCHN_2 and 0.10 mmol of $Co_2(CO)_8$ in $10\,cm^3$ n-heptane solution.

Apart from small amounts of $Co_4(CO)_{12}$ at the end of the gas evolution in experiments using a 1:1 to 6:1 molar ratio of Me_3SiCHN_2:$Co_2(CO)_8$ no other carbonyl cobalt complexes could be detected during and at the end of the reaction, according to the infrared spectra of the reaction mixtures. By raising the Me_3SiCHN_2:$Co_2(CO)_8$ molar ratio from 1:1 to 8:1, less and less of $Co_2(CO)_8$ can be found in the reaction mixtures at the end of the reaction. At the molar ratio of 8:1 or above the final color of the solution is black or colorless with black sediment.

An $0.0050\,mol/dm^3$ solution of $Co_4(CO)_{12}$ in n-heptane at $10\,^\circ C$ in an atmosphere of argon does not show any reaction with Me_3SiCHN_2 at a 1:6 molar ratio in 6 h.

3. Discussion

The facile formation of $Me_3SiCH=C=O$ from the carbene precursor Me_3SiCHN_2 in the presence of $Co_2(CO)_8$

Table 3
Initial rates of gas evolution (r_{gas}), the amounts of gas evolved, the amounts of recovered $Co_2(CO)_8$, the amounts of $Co_4(CO)_{12}$ formed and the yield of $Me_3SiCH=C=O$ at the end of the reaction at $10\,°C$ in reactions of Me_3SiCHN_2 with $Co_2(CO)_8$ under 1 bar argon in experiments with different initial concentrations of Me_3SiCHN_2 in n-heptane solution

$[Me_3SiCHN_2]_0$ (mol/dm^3)	$[Co_2(CO)_8]_0$ (mol/dm^3)	$10^5 \times r_{gas}$ (mol/dm^3 s)	Gas evolved (mol/mol Me_3SiCHN_2)	$Co_2(CO)_8$, recovered (% of Co)	$Co_4(CO)_{12}$, formed (% of Co)	$Me_3SiCH=C=O$, yield (%)
0.01	0.01	2.8	0.94	72	18	81
0.02	0.01	3.0	0.93	52	22	84
0.03	0.01	3.2	0.95	37	15	82
0.04	0.01	3.3	0.95	26	10	81
0.06	0.01	3.6	0.94	5	<5	71
0.08	0.01	4.2	0.74	0	0	68
0.10	0.01	4.1	0.68	0	0	43

proceeds, obviously through a cobalt-mediated diazo decomposition and a consecutive cobalt-mediated carbene/carbon monoxide coupling reaction. In the absence of $Co_2(CO)_8$ no formation of $Me_3SiCH=C=O$ occurs under otherwise identical reaction conditions. A possible mechanism for the $Co_2(CO)_8$-catalyzed $Me_3SiCH=C=O$ formation with the participation of carbon monoxide from the gas phase is depicted in Scheme 1. Octacarbonyl dicobalt serves as the catalyst precursor. The observed negative effect of the CO concentration on the rate of $Me_3SiCH=C=O$ formation suggests that instead of $Co_2(CO)_8$ the coordinatively unsaturated heptacarbonyl dicobalt is involved in the catalytic cycle. Intermediate formation of coordinatively unsaturated $Co_2(CO)_7$ in a small equilibrium concentration from $Co_2(CO)_8$ has frequently been suggested as part of the mechanism in reactions of $Co_2(CO)_8$ where the rate of the reaction was found to be inversely proportional to the concentration of carbon monoxide [12].

The existence of $Co_2(CO)_7$ as a major product of the photochemical decomposition of $Co_2(CO)_8$ in argon matrices has been proved by infrared spectroscopy [13]. This species has no bridging carbonyl groups according to the infrared spectrum. A planar geometry of the four-coordinate cobalt center, with 16 electrons in its valence orbitals, and a trigonal bipyramidal structure of the five-coordinate cobalt
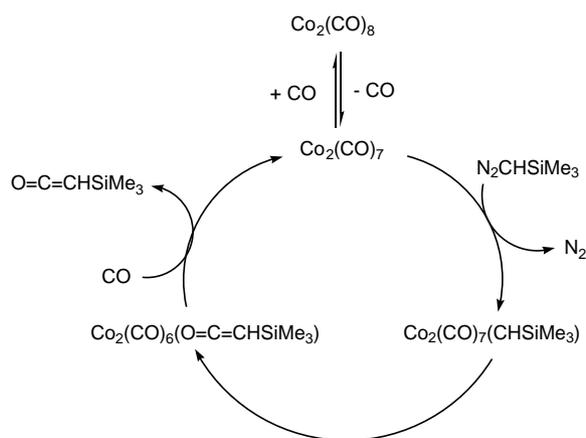
center has been assigned to this complex [13]. Assuming a rate-determining coordination of Me_3SiCHN_2 to the vacant site of $Co_2(CO)_7$ is in accord with the experimentally observed kinetic order in $Co_2(CO)_8$, Me_3SiCHN_2, and CO concentrations. The driving force of this coordination might be the electron density on the carbon atom adjacent to the N_2 group. Once coordinated to cobalt, Me_3SiCHN_2 will lose N_2 rapidly and a cobalt carbenoid, $Co_2(CO)_7(CHSiMe_3)$ might be formed, in which the coupling of the carbene and a CO ligand can take place in a fast reaction forming a coordinated $Me_3SiCH=C=O$ which can be replaced by an external CO to give $Co_2(CO)_7$ for a new catalytic cycle. The assumed intermediate complexes $Co_2(CO)_7(CHSiMe_3)$ and $Co_2(CO)_6(O=C=CHSiMe_3)$ are probably present only in low concentrations not sufficient for detection, because their consecutive transformations are faster than the rate of their formation. However, similar complexes have been described recently. For example, $Co_2(CO)_7(CHCO_2Et)$ was prepared in 82% yield in the reaction of $Co_2(CO)_8$ and ethyl diazoacetate [8], and a ketene complex $Co_2(CO)_7(O=C=CH_2)$ was isolated in 32% yield from a reaction mixture of $Co_2(CO)_8$, CH_2Br_2, and Zn [14].

The observed rate constant of the catalytic formation of $Me_3SiCH=C=O$ at $10\,°C$, $k_{obs} = (0.52 \pm 0.6) \times 10^{-3}\,s^{-1}$ (see Table 1) consists of the equilibrium constant $K = k_1/k_{-1}$ of Eq. (2) and the rate constant k_2 of the rate-determining step Eq. (3) as $k_{obs} = k_2 \times k_1/k_{-1}$.

$$Co_2(CO)_8 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co_2(CO)_7 + CO \qquad (2)$$

$$Co_2(CO)_7 + Me_3SiCHN_2 \overset{k_2}{\rightarrow} Co_2(CO)_7CHSiMe_3 + N_2 \qquad (3)$$
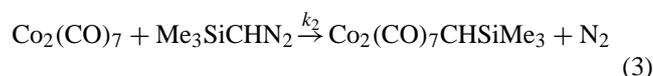
Values of k_1 are known from the observed rates of carbon monoxide ligand exchange in $Co_2(CO)_8$ and free carbon monoxide in the temperature ranges of -20 to $+5\,°C$ [15], 40 to $80\,°C$ [16], and 100 to $180\,°C$ [17]. An extrapolation of the k_1 values from Refs. [15,16] to $10\,°C$ gives $(6.1 \pm 1.6) \times 10^{-3}\,s^{-1}$. Subtracting this value from our $k_{obs} = k_2 \times k_1/k_{-1}$ value of $(0.52 \pm 0.6) \times 10^{-3}\,s^{-1}$, we obtain for the ratio of k_{-1}/k_2 a value of 11.7 ± 5.3, which means that CO competes for the intermediate $Co_2(CO)_7$ 11.7 times more effectively than Me_3SiCHN_2.

$Co_2(CO)_8$

$+ CO \parallel - CO$

$Co_2(CO)_7$

$O=C=CHSiMe_3$

$N_2CHSiMe_3$

N_2

CO

$Co_2(CO)_6(O=C=CHSiMe_3)$

$Co_2(CO)_7(CHSiMe_3)$

Scheme 1.

As can be seen from the data in Table 3 the initial rates of gas evolution (r_{gas}) in experiments started under an argon atmosphere show only a little dependence on the initial concentrations of Me_3SiCHN_2. A reason for this might be that under such experimental conditions the k_1 step in Eq. (2) becomes the bottleneck. From the observed r_{gas} values in Table 3 and the initial concentration of $Co_2(CO)_8$ a k_1 value of $(3.5 \pm 0.7) \times 10^{-3}\,s^{-1}$ can be calculated, which is (very) close to the extrapolated literature value of $(6.1 \pm 1.6) \times 10^{-3}\,s^{-1}$. The other conclusion to be drawn from these experiments is that the formation of $Me_3SiCH=C=O$ from Me_3SiCHN_2 and $Co_2(CO)_8$ under an argon atmosphere can use up all the eight carbon monoxide ligands of $Co_2(CO)_8$ resulting in the formation of metallic cobalt according to Eq. (4).

$$8Me_3SiCHN_2 + Co_2(CO)_8$$
$$\rightarrow 8N_2 + 8Me_3SiCH=C=O + 2Co \qquad (4)$$
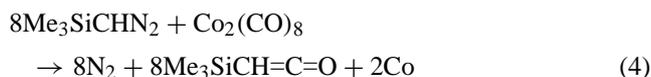
It can be seen from the course of the gas evolution in Fig. 1 that the reaction is faster when the cobalt becomes more and more depleted in CO ligands. The observed fast reactions under argon support the idea that coordinated carbon monoxide and not an external one is the primary source of CO for the $Me_3SiCH=C=O$ product.

4. Experimental

4.1. General comments

Handling of $Co_2(CO)_8$, $Co_4(CO)_{12}$, and Me_3SiCHN_2 was carried out in an atmosphere of dry (P_4O_{10}) and deoxygenated (BTS contact, room temp.) argon or carbon monoxide utilizing standard Schlenk techniques [18]. Solvents were dried and distilled under an atmosphere of argon or carbon monoxide according to standard procedures [19]. IR spectra were recorded on a Thermo Nicolet Avatar 330 FTIR spectrometer using 0.0265, 0.0765, or 0.505 mm CaF_2 solution cells, calibrated by the interference method [20]. Gas chromatographic analyses were performed on a HP 5890 instrument with FID, using a SPB 1 30 m, 0.32 μm column and n-octane or n-hexadecane as an internal standard. Octacarbonyl dicobalt was prepared by a literature procedure [21], and was recrystallized twice in an atmosphere of carbon monoxide, first from CH_2Cl_2 and then from n-heptane. Stock solutions of octacarbonyl dicobalt in n-heptane were prepared under CO at 10 °C or under Ar at 0 °C, and their concentration was checked by cobalt analysis and by quantitative IR analysis. Dodecacarbonyl tetracobalt was prepared from octacarbonyl dicobalt by a literature procedure [22]. All other reagents and solvents were obtained from Sigma-Aldrich. Column chromatography was carried out using silica gel, 200–400 mesh, 60 Å.

4.2. Preparation of solutions of $Me_3SiCH=C=O$ by the $Co_2(CO)_8$-catalyzed carbonylation of Me_3SiCHN_2 in an atmosphere of CO at atmospheric pressure

A solution of $Co_2(CO)_8$ (34.2 mg, 0.1 mmol) and Me_3SiCHN_2 (as 0.50 cm^3 of a 2.0 mol/dm^3 solution in ether, 1.0 mmol) in n-heptane (9.48 cm^3) was stirred in an atmosphere of carbon monoxide at 10 °C for 4 h. IR spectra of the reaction mixture revealed the presence of $Co_2(CO)_8$ in concentrations 0.010 mol/dm^3 and of $Me_3SiCH=C=O$ in 0.10 mol/dm^3 using $\varepsilon_M(1858\,cm^{-1}) = 1857\,cm^2/mmol$ at 30 °C [23], and $\varepsilon_M(2116\,cm^{-1}) = 1377\,cm^2/mmol$ at 30 °C, respectively. Distillation of the reaction mixture at atmospheric pressure in the temperature range 80–94 °C, yielded a colorless fraction (9.2 cm^3) containing 1.0 mmol of $Me_3SiCH=C=O$, according to quantitative IR, and gas chromatographic analyses using 0.493 response factor for $Me_3SiCH=C=O$.

4.3. The carbonylation of (trimethylsilyl)diazomethane under CO pressure in the presence of 2 mol% $Co_2(CO)_8$

A solution of $Co_2(CO)_8$ (13.7 mg, 0.040 mmol) in n-hexane (0.99 cm^3) and Me_3SiCHN_2 (as 1.0 cm^3 of a 2.0 mol/dm^3 solution in hexane, 2.0 mmol) was placed into a glass lined stainless-steel autoclave (total capacity = 12.8 cm^3) in two different compartments in order to prevent their mixing before shaking. The system was pressurized at 25 °C with carbon monoxide to 50 bar, and was shaken for 10 h. IR spectra of the reaction mixture showed the presence of $Co_2(CO)_8$ in 0.019 mol/dm^3 and of $Me_3SiCH=C=O$ in 0.040 mol/dm^3 concentrations, in addition to two very strong $\nu(CO)$ absorptions at 1799 and 1742 cm^{-1} with an intensity ratio of 1:1.4. Flash chromatography on silica gel (160/15 mm column) using methylene chloride as the eluent gave in the second and third 20 cm^3 fractions 2,3,4-tris(trimethylsilyl)cyclobutanone and 2,3-bis(trimethylsilyl)cyclopropanone, respectively.

Stirring a mixture of $Me_3SiCH=C=O$ (0.4 mol/dm^3) and $MeSiCHN_2$ (0.6 mol/dm^3) in n-heptane under argon at 25 °C for 10 h resulted in a 1:1 molar mixture of 2,3-bis(trimethylsilyl)cyclopropanone and 2,3,4-tris(trimethylsilyl)cyclobutanone. Gas chromatographic analysis showed for both compounds the presence of isomers.

4.4. Measurement of the kinetics of the catalytic formation of $Me_3SiCH=C=O$ under CO in the presence of $Co_2(CO)_8$

The reaction was performed in a thermostatted glass reactor (40 cm^3 total volume), equipped with a gas inlet and with a silicon disk port. The gas inlet was connected to a CO-filled constant pressure buffer (4 dm^3 total volume). A stainless-steel canula connected to a 3-port T-valve was immersed close to the bottom of the reactor through the silicon disk. To the two other ports of the valve a Hamilton TLL syringe (2.5 cm^3 volume) and the IR cell (through a PTFE

tubing) were connected. Samples from the reaction mixture for IR analyses were withdrawn through the stainless steel canula, and pumped into the IR cell continuously by using the Hamilton TLL syringe, allowing the liquid sample to return from the IR cell to the reactor through a second PTFE tubing. The solvent and the reactants were added to the CO-filled reactor through the silicon disk using Hamilton TLL syringes. IR spectra were recorded every two minutes. The initial rate of (trimethylsilyl)ketene formation was calculated from the intensity of the $\nu(CO)$ band of $Me_3SiCH=C=O$ at $2116\,cm^{-1}$ ($\varepsilon_M = 1377\,cm^2/mmol$) using the first 5–12 points.

4.5. Measurement of the kinetics of the decomposition of Me_3SiCHN_2 under Ar in the presence of $Co_2(CO)_8$

To a solution of $Co_2(CO)_8$ (0.10 mmol) in *n*-heptane (9.95–9.50 cm^3) in a thermostatted glass reactor (80 cm^3 total volume) connected to a gas burette at 10 °C under an atmosphere of Ar, an aliquot from a cold (10 °C) 2.0 mol/dm^3 stock solution of Me_3SiCHN_2 in hexane (0.050–0.50 cm^3) was injected. The initial rate of the gas evolution was calculated from the first six to eight readings (frequency: 30 s) of the gas burette. At the end of the gas evolution infrared spectra of the reaction mixture were recorded in order to calculate the concentration of $Me_3SiCH=C=O$ at $2116\,cm^{-1}$ ($\varepsilon_M = 1377\,cm^2/mmol$), of $Co_4(CO)_{12}$ at $1866\,cm^{-1}$ ($\varepsilon_M = 10440\,cm^2/mmol$ [24], and $Co_2(CO)_8$ at $1858\,cm^{-1}$ ($\varepsilon_M = 1857\,cm^2/mmol$ at 30 °C [23]). The yield of $Me_3SiCH=C=O$ was twice checked after distillation of the final reaction mixture at atmospheric pressure by quantitative gas chromatographic analysis.

Acknowledgements

References

[1] F. Zaragoza Dörwald, Metal Carbenes in Organic Synthesis, Wiley-VCH, Weinheim, 1999.

[2] S. Patai (Ed.), The Chemistry of Diazonium and Diazo Groups Part II, Wiley, New York, 1978.

[3] H. Zollinger, Diazo Chemistry II. Aliphatic, Inorganic and Organometallic Compounds, VCH, Weinheim, 1995.

[4] W.A. Herrmann, Angew. Chem. 90 (1978) 855–868; Angew. Chem. Int. Ed. Engl. 17 (1978) 800–812.

[5] W.A. Herrmann, Adv. Organomet. Chem. 20 (1982) 159–263.

[6] M.P. Doyle, M.A. McKervey, T. Ye, Modern Catalytic Methods for Organic Synthesis with Diazo Compounds, Wiley, New York, 1998, p. 73.

[7] W.H. Tamblyn, S.R. Hoffman, M.P. Doyle, J. Organomet. Chem. 216 (1981) C64–C68.

[8] R. Tuba, F. Ungváry, J. Mol. Catal. A: Chemical 203 (2003) 59–67.

[9] (a) H. Staudinger, H. Becker, Ber. Dtsch. Chem. Ges. 50 (1927) 1016–1024;
(b) E. Ziegler, H. Sterk, Monatsh. Chem. 98 (1967) 1104–1107;
(c) J. Julien, J.M. Pechine, F. Perez, Tetrahedron Lett. 24 (1983) 5525–5526.

[10] (a) E.N. Fedorenko, G.S. Zaitseva, Y.I. Baukov, I.F. Lutsenko, Zhur. Obshch. Khim. 56 (1986) 2431–2432;
J. Gen. Chem. USSR (Engl. Transl.) 56 (1986) 2150–2152.;
(b) G.S. Zaitseva, A.V. Kisin, E.N. Federenko, V.M. Nosova, L.I. Livantsova, Y.I. Baukov, Zhur. Obshch. Khim. 57 (1987) 2049–2060;
J. Gen. Chem. USSR (Engl. Transl.) 57 (1987) 1836–1845.;
(c) G.S. Zaitseva, I.F. Lutsenko, A.V. Kisin, Y.I. Baukov, J. Lorberth, J. Organomet. Chem. 345 (1988) 253–262.

[11] G.S. Zaitseva, A.V. Kisin, O.P. Novikova, L.I. Livantsova, Y.I. Baukov, Zhur. Obshch. Khim. 58 (1988) 1677–1679;
J. Gen. Chem. USSR (Engl. Transl.) 58 (1988) 1497–1498.

[12] F. Ungváry, Hydroformylation – homogeneous, in: I.T. Horváth (Ed.), Encyclopedia of Catalysis, vol. 3, Wiley, New York, 2003, pp. 734–787.

[13] R.L. Sweany, T.L. Brown, Inorg. Chem. 16 (1977) 421–424.

[14] A. Miyashita, K. Nohira, S. Kaji, H. Nohira, Chem. Lett. (1989) 1983–1986.

[15] (a) F. Basolo, A. Wojcicki, J. Am. Chem. Soc. 83 (1961) 520–528;
(b) S. Bereitschaft, F. Basolo, J. Am. Chem. Soc. 88 (1966) 2702–2706.

[16] D.C. Roe, Organometallics 6 (1987) 942–946.

[17] R.J. Klingler, J.W. Rathke, J. Am. Chem. Soc. 116 (1994) 4772–4785.

[18] D.F. Shriver, The Manipulation of Air-Sensitive Compounds, Krieger, Malabar, FL, 1982.

[19] W.L.F. Armarego, D.D. Perrin, Purification of Laboratory Chemicals, fourth ed., Butterworth-Heinemann, Oxford, 1996.

[20] H.H. Willard, L.L. Merritt Jr., J.A. Dean, F.A. Settle Jr., Instrumental Methods of Analysis, sixth ed., Wadsworth, Belmont, CA, 1981, p. 206.

[21] P. Szabó, L. Markó, G. Bor, Chem. Tech. (Leipzig.) 13 (1961) 549–550.

[22] G. Natta, R. Ercoli, S. Castellano, Chim. Ind. (Milan) 37 (1955) 6–17.

[23] R. Tannenbaum, Diss. ETH Nr 6970, 1980, p. 31.

[24] R. Tannenbaum, Diss. ETH Nr 6970, 1980, p. 32.