

Surface organometallic chemistry: Facile μ_2 -carbene to μ_3 -carbyne transformation of organocobalt carbonyls on silica surface

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Abstract

μ_2 -[ROC(O)C(R)]- μ_2 -(CO)Co₂(CO)₅ (R = Me, *i*Pr, *t*Bu, Ph) bridging carbene-type dinuclear cobalt carbonyls (**1**) undergo a facile surface-mediated clusterification while chromatographed on silica gel, yielding [μ_3 -RC(O)OC]Co₃(CO)₉ (**2a**) complexes. These latter are then transformed to the corresponding (μ_3 -RC)Co₃(CO)₉ (**2b**) derivatives by silica-mediated decarboxylation. The X-ray diffraction structure of **2a** (R = *t*Bu) was determined and that of **2b** (R = Ph) was confirmed.

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1. Introduction

Organometallic reactions in the “two dimensional” space [1] of the surface of inorganic oxides became a versatile synthetic tool in the last decade [2,3], leading sometimes to unexpected new products or to unusually high selectivity and yields [3,4].

We report here on the aggregation of some organocobalt carbonyls to generate cluster structures of higher nuclearity, mediated by the silica surface.

2. Results and discussion

2.1. Surface reactions

The recently reported new class of cobalt carbonyls, [RC(O)]₂Co₂(CO)₆ (**1**) [5] is formed by self-acylation of acylcobalt carbonyls [6] in apolar solvents. These latter complexes are rather stable either in solution or in solid state. We have shown now that during attempts to purify of complexes **1** by TLC or column-chromatography on silica gel these complexes undergo an unexpected transformation of the μ_2 -carbene dicobalt skeleton of **1** to species of higher nuclearity. This surface-mediated clusterification [3], yields two trinuclear μ_3 -carbyne type cobalt carbonyl complexes (**2a** and **2b**). Additional experiments starting from

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complexes **2a** have shown that complexes **2b** are generated by decarboxylation of the former ester-type species. Even if the trinuclear complexes **2** are known [7,8], the surprising very easy clusterification process was confirmed by the X-ray structure determination of both types **2a** and **2b**. Beyond this direct structural evidence, the products were characterised by elemental analyses as well as by infrared and ^1H and ^{13}C NMR spectra [8].

Fact the μ_2 -carbene \rightarrow μ_3 -carbyne transformation mediated by the silica surface reported here might be considered analogous to the proton-induced transformation of the μ_2 -butenolidedicobalt heptacarbonyls [9] to the corresponding $[(\mu_3\text{-R}'\text{OC(O)CR}=\text{CH-C})\text{Co}_3(\text{CO})_9]$ ($\text{R}, \text{R}' = \text{H}$ or alkyl) methylidyne derivatives [10] which occurs in solution. As a matter of fact, a similar rearrangement was claimed to occur as a possible step of the Fischer–Tropsch surface chemistry [11].

In the light of our results, the easy formation of $\text{H}_3\text{CCC(O)}_3(\text{CO})_9$ and $(\mu_3\text{-MesC})\text{Co}_3(\text{CO})_9$ ($\text{Mes} = 2,4,6$ -trimethylphenyl) from acetyl chloride and $\text{Co}_2(\text{CO})_8$ or from mesitoyl chloride and $[\text{Co}(\text{CO})_4]^-$, respectively, which was reported earlier to occur in solution [12] may proceed also through the same $\mathbf{1} \rightarrow \mathbf{2a} \rightarrow \mathbf{2b}$ path, under the effect of some proton acidity produced from the acetyl or mesitoyl chloride.

The easy decarboxylation of the ester-type complexes **2a** is an additional example of a similar chemical process such as the decarbonylation of $[\mu_3\text{-RC(O)C}]\text{Co}_3(\text{CO})_9$ type ketones, observed by Seyferth's group [13] as well as the decarboxylation of the $\text{ROC(O)Co}(\text{CO})_4$ type "esters", observed by us a decade ago [14]. It is worth noting also that the production of the ester-type complex such as, $[\mu_3\text{-CH}_3\text{C(O)OC}]\text{Co}_3(\text{CO})_9$ (**2a**, $\text{R} = \text{Me}$), requires a complex synthesis involving the acylation of the lithium salt $(\mu_3\text{-LiOC})\text{Co}_3(\text{CO})_9$ by acetyl chloride [8a].

The surface processes of clusterification and decarboxylation reported in this paper provide an additional and new piece of evidence to the role of the silica surface in the rich surface organometallic chemistry occurring in the "two dimensional" phase of the surface of a material (silica) regarded in the past as one of the most inert supports for catalysis or chromatography [15]. In fact, these reactions do not occur so easily and under so mild conditions when working in solution.

A control experiment (suggested by one of the Referees of the present paper) have shown, that the observed transformations occur also in oxidative (air) or in Ar atmosphere, but while the silica surface results quantitative conversion in ca. 40 min, these treatments require several hours to achieve a comparable degree of clusterification. The clusterification proceeds faster under air atmosphere than under Ar and it seems to be inhibited by CO atmosphere.

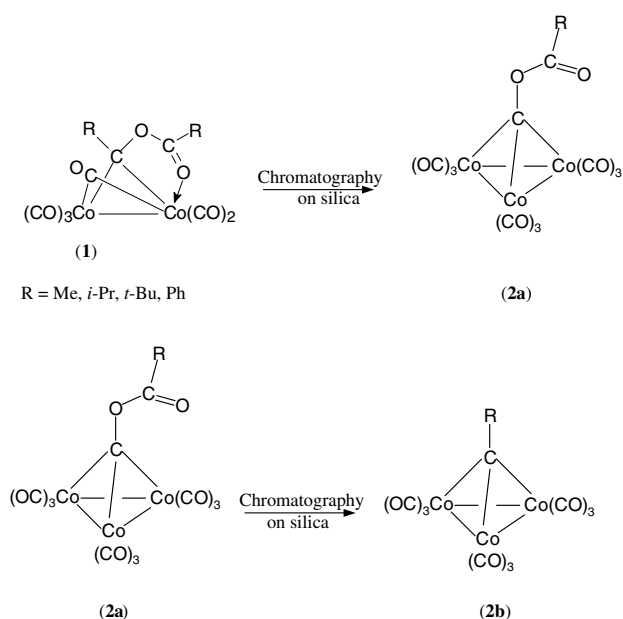
2.2. Structures

The silica surface-promoted clusterification and decarboxylation reactions (shown in Scheme 1) observed in course of the present work, prompted us to confirm, by X-ray diffraction, the aggregation process to generate both **2a** and **2b**, even if some of these products, obtained by other preparative ways, were already characterized by diffraction studies [8]. The X-ray structures of **2a**, $\text{R} = \text{Me}$ [8a] as well as of **2b**, $\text{R} = \text{Me}$ [8e] and $\text{R} = \text{Ph}$ [8g,8h] were reported in earlier communications. We obtained crystals of suitable quality for X-ray diffraction experiments for the **2a** ($\text{R} = t\text{Bu}$) and **2b** ($\text{R} = \text{Ph}$) derivatives. Since the structure of the latter complex was known, we report here only the structure of the ester derivative **2a** ($\text{R} = t\text{Bu}$), while the X-ray details of the structure of **2b** ($\text{R} = \text{Ph}$) is described in the Additional Supporting Material.

In fact details of the X-ray structure determination of complexes **2a** ($\text{R} = t\text{Bu}$) and **2b** ($\text{R} = \text{Ph}$) are deposited in the Cambridge Crystallographic Data Bank under numbers: CCDC 279416 and CCDC 279417.

Both structures, first of all, prove beyond doubt the clusterification and decarboxylation processes occurring on the silica surface and depicted in Scheme 1. In addition, some features of structure of **2a** ($\text{R} = t\text{Bu}$) are interesting also on their own right.

The structure of **2a** ($\text{R} = t\text{Bu}$) consists of an equilateral triangle of Co atoms, each of which is bonded to three carbonyl groups (Fig. 1). A $t\text{BuCC(O)OC}$ group caps a face of the Co_3 triangle; the C–O bond is nearly perpendicular to the Co_3 plane, the dihedral angle between the C19 and O10 line and the normal to the Co_3



Scheme 1.

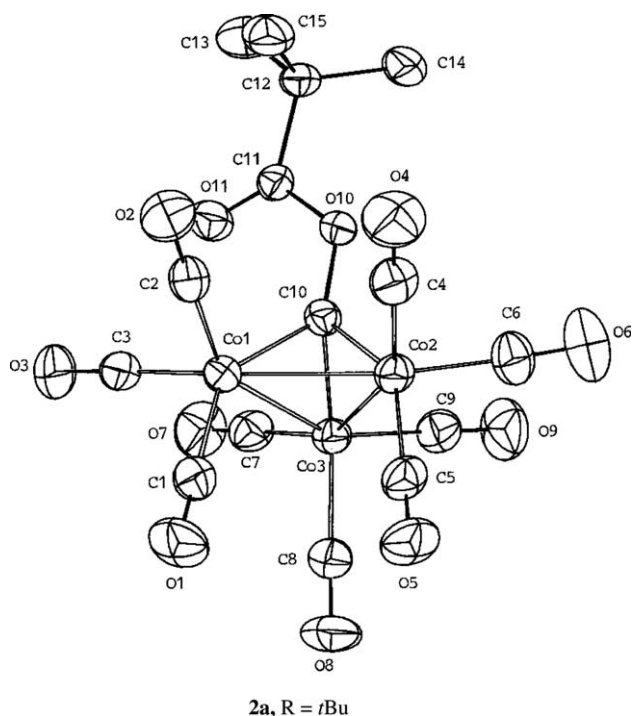


Fig. 1. ORTEP drawing of the structure of complex **2a**, R = *t*Bu. Some selected interatomic distances (Å) and bond angles (°) are: Co–C10 (av.) 1.883; C10–O10 1.372(4); C11–O10 1.376(5); C11–O11 1.182(5); Co–Co–C10 (av.) 48.9; Co–C10–Co (av.) 82.4; Co1–C10–O10 132.9(3); Co2–C10–O10 123.2(3); Co3–C10–O10 134.7(3); O10–C11–O11 122.8(4); O10–C11–C12 122.8(4); O11–C11–C12 126.8(4).

plane being 7.4(2)°. The group of atoms C10, O10, C11, O11 is almost planar [maximum deviation 0.048(5) Å for C11] and it is nearly perpendicular to the Co₃ plane [dihedral angle 86.6(1)°]. The Co–C10 bond distances are very close to those found for **2a** (R = Me) [8a] and in L_XM–O–CCO₃(CO)₉ (M = B, Ti, Zr, L_X = Br₂NEt₂, (C₅H₅)₂, (acac)₂) [16] type complexes. The O10–C10 and O10–C11 bond distances are not significantly different and are close to a O–C single bond. The C11–O11 bond distance corresponds to a double bond. The O11 oxygen atom is not involved in coordination, the minimum contact distance being 3.48 Å with Co1. The C10 carbon atom is *cis* with respect to the O11 oxygen atom as indicated by the torsion angle O11–C11–O10–C10 which is –9.2(6), probably as a result of some steric hindrance due to the *t*-butyl group. All the other bond distances and angles are as expected.

The X-ray structure of complex **2b** (R = Ph) is in excellent agreement with the published results [8g,8h].

3. Conclusion

In this work, we have produced clear evidence that the silica surface may induce under very mild conditions, a facile process of cluster aggregation or decarboxylation, which usually requires in solution the presence

of strong acidity [9,10] or a thermal treatment [13,14], although it is known that the acidity of surface silanol groups is very weak [15]. In conclusion, our work is an interesting additional observation which confirms the role of the silica surface as an unusual reaction medium in the growing area of organometallic chemistry for synthetic purposes mediated by the surface of an inorganic oxide [3].

4. Experimental

All compounds used were of commercial origin, except complexes **1**, which were prepared according to the published procedure [5].

Experiments were performed under exclusion of air using standard inert techniques [17].

Spectroscopic measurements were performed with the following instruments: IR spectra were recorded with a Bruker FT-IR IFS 113V spectrometer, ¹H and ¹³C NMR experiments were performed with a Bruker AMX-400 instruments.

Details of X-ray structure determinations will be given below.

4.1. Transformation of complexes **1** into complexes **2** on silica

Compounds **1** (~0.4 g) were chromatographed on silica (TLC: Aldrich, 20 cm × 20 cm × 250 μm, particle size 5–17 μm, pore size 60 Å; column: Aldrich, 150 × 23 mm, particle size 70–230 mesh, *n*-hexane eluent). Compounds **2** were formed, together with minor amounts of Co₄(CO)₁₂ and some insoluble (probably ionic) products as the only cobalt carbonyls, accompanied by rests of non-converted **1**. The formation of compound **2b** from **2a** was proved by chromatography of pure **2a** on silica, where only **2b** was formed. The chromatographic treatment allowed also the separation of complexes **2a** and **2b**. These were then characterized by IR, ¹H and ¹³C NMR spectroscopy, elementary analysis and X-ray diffraction for **2a** (R = *t*Bu) and **2b** (R = Ph). The order of elution: **2b** (violet), **1** (unreacted, yellow/brown) and **2a** (violet). This procedure yielded almost quantitatively the *sum* of the products **2a** and **2b**, but the ratio of these complexes was fairly variable, depending also on the length of the column or on the rate of chromatography (longer column or slower chromatography favoured **2b**).

Following the advice of one of the referees of the present paper, we performed some control experiments about the relative facility (rate) of the above-described transformation. Five portions (100 mg each) complex **1** (R = *t*Bu) were dissolved in 20 ml portions of *n*-hexane and treated as follows: (a) chromatographed on a 20 cm × 40 mm silica (as above) column which lasted ca.

20 min, (b) left to stand in open Schlenk vessel under air, at r.t., (c) left to stand in open Schlenk vessel, but with air current bubbled through the solution, (d) left to stand in Ar atmosphere, changing the Ar in the Schlenk vessel each 30 min and (e) left to stand under CO atmosphere, changing the CO atmosphere in each 30 min. These solutions were analysed time-to-time by IR spectroscopy in the 2200–1600 cm^{-1} range. From the spectroscopic analysis, it could be concluded that these treatments ((a)–(e)) resulted: (a) ca. 50% conversion after the first and ca. 100% conversion after the second chromatography (total 40 min), (b) ca. 30% conversion after 4 h, quantitative conversion after 24 h (but derivative **2a** was detected only after 4 h), (c) quantitative conversion after 6 h, (d) ca. 30% conversion after 6 h and (e) practically no change after 24 h.

4.2. Spectroscopic characterization of complexes **2a** and **2b**

4.2.1. *R* = Me, **2a**

IR ($\nu(\text{C}-\text{O})$, *n*-hexane, cm^{-1}): 2103 m, 2051 vs, 2038 s, 2018 m, 1768 m; ^1H NMR (400.13 MHz, CDCl_3 , 300 K, TMS): δ (ppm) = 3.42 (s, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CDCl_3 , 300 K, TMS): δ (ppm) = 45.2 (CH_3), 168.4 ($\text{CH}_3-\text{C}(\text{O})\text{O}$), 200.0 (CO_{coord}), 308.3 (CH_3-C).

4.2.2. *R* = Me, **2b**

IR ($\nu(\text{C}-\text{O})$, *n*-hexane, cm^{-1}): 2102.4 m, 2052.0 vs, 2038.2 s, 2018.0 m; ^1H NMR (400.13 MHz, CDCl_3 , 300 K, TMS): δ (ppm) = 3.66 (s, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CDCl_3 , 300 K, TMS): δ (ppm) = 45.2 (CH_3), 200.0 (CO_{coord}), 292.3 ($\text{C}-\text{CH}_3$).

4.2.3. *R* = *i*Pr, **2a**

IR ($\nu(\text{C}-\text{O})$, *n*-hexane): 2100 w, 2058 vs, 2042 s, 2023 m; ^1H NMR (400.13 MHz, CDCl_3 , 300 K, TMS): δ (ppm) = 1.25 (d, $J_{\text{HH}} = 6.90$ Hz, 6H, CH_3), 4.15 (m, $J_{\text{HH}} = 6.90$ Hz, 1H, CH); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CDCl_3 , 300 K, TMS): δ (ppm) = 23.6 (CH_3), 68.0 (CH), 167.6 ($\text{CH}-\text{C}(\text{O})\text{O}-\text{C}$), 199.4 (CO_{coord}), 306.0 ($\text{CH}-\text{C}(\text{O})\text{O}-\text{C}$).

4.2.4. *R* = *i*Pr, **2b**

IR ($\nu(\text{C}-\text{O})$, *n*-hexane, cm^{-1}): 2102.2 m, 2051.1 vs, 2037.9 s, 2017.1 m; ^1H NMR (400.13 MHz, CDCl_3 , 300 K, TMS): δ (ppm) = 1.50 (d, $J_{\text{HH}} = 6.60$ Hz, 6H, CH_3), 3.76 (m, $J_{\text{HH}} = 6.60$ Hz, 1H, CH); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CDCl_3 , 300 K, TMS): δ (ppm) = 29.2 (CH_3), 55.6 (CH), 200.2 (CO_{coord}), 292.3 ($\text{C}-\text{CH}(\text{CH}_3)_2$).

4.2.5. *R* = *t*Bu, **2a**

IR ($\nu(\text{C}-\text{O})$, *n*-hexane): 2107 m, 2059 vs, 2041 s, 2022 m, 1980 vw $\nu(^{13}\text{C}-\text{O})$, 1764 w; ^1H NMR (400.13 MHz,

CDCl_3 , 300 K, TMS): δ (ppm) = 1.07 (s, 9H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CDCl_3 , 300 K, TMS): δ (ppm) = 29.6 ($(\text{CH}_3)_3$), 39.8 ($\text{COC}(\text{O})-\text{C}-(\text{CH}_3)_3$), 173.8 ($\text{CO}-\text{C}(\text{O})-\text{C}-(\text{CH}_3)_3$), 199.4 (CO_{coord}), 293.4 ($\text{CO}-\text{C}(\text{O})-\text{C}-(\text{CH}_3)_3$).

4.2.6. *R* = *t*Bu, **2b**

IR ($\nu(\text{C}-\text{O})$, *n*-hexane): 2101 m, 2050 vs, 2037 s, 2017 m; ^1H NMR (400.13 MHz, CDCl_3 , 300 K, TMS): δ (ppm) = 1.26 (s, 9H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CDCl_3 , 300 K, TMS): δ (ppm) = 29.6 ($(\text{CH}_3)_3$), 56.5 ($\text{C}-\text{C}-(\text{CH}_3)_3$), 200.4 (CO_{coord}), 289.3 ($\text{C}-\text{C}-(\text{CH}_3)_3$).

4.2.7. *R* = Ph, **2a**

IR ($\nu(\text{C}-\text{O})$, *n*-hexane): 2108 w, 2061 vs, 2042 s, 2031 w, 1747 m; ^1H NMR (400.13 MHz, CDCl_3 , 300 K, TMS): δ (ppm) = 7.52–7.55, 7.70–7.72 (m, 5H, C_6H_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CDCl_3 , 300 K): decomposed during data acquisition.

4.2.8. *R* = Ph, **2a**

IR ($\nu(\text{C}-\text{O})$, *n*-hexane): 2102 w, 2056 vs, 2040 s, 2022 w, 1981 sh $\nu(^{13}\text{C}-\text{O})$; ^1H NMR (400.13 MHz, CDCl_3 , 300 K, TMS): δ (ppm) = 7.27–7.32, 7.48–7.55 (m, 5H, C_6H_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CDCl_3 , 300 K, TMS): δ (ppm) = 127.9–158.2 (C_6H_5), 199.8 (CO_{coord}), 283.5 ($\text{C}_6\text{H}_5-\text{C}$).

4.2.9. *R* = Ph, **1**

IR ($\nu(\text{C}-\text{O})$, *n*-hexane): 2087 m, 2061 vs, sh, 2025 m, 2013 m, 1834 w; ^1H NMR (400.13 MHz, CDCl_3 , 300 K, TMS): δ (ppm) = 7.06–8.17 (m, 10H, C_6H_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, CDCl_3 , 300 K, TMS): 123.8–137.8 (C_6H_5), 176.5 ($\text{C}_6\text{H}_5-\text{C}(\text{OC}(\text{O}))-\text{CO}_2$), 188.9 ($-\text{C}(\text{O}-\text{C}(\text{O}))-\text{CO}_2$), 196.8 ($\text{CO}-\text{Co}$), 200.2 ($\text{CO}-\text{Co}$), 232.1 ($\text{CO}_{\text{bridge}}$).

4.3. X-ray structural determination

4.3.1. *R* = *t*Bu, **2a**

Philips PW1100 diffractometer, SHELX-86 program, Gould 32/77 computer. Crystal dimensions 0.24 × 0.45 × 0.48 mm, triclinic, space group $P\bar{1}$, $a = 10.116(1)$ Å, $b = 12.852(1)$ Å, $c = 9.046(1)$ Å, $\alpha = 107.51(1)^\circ$, $\beta = 104.62(1)^\circ$, $\gamma = 68.04(1)^\circ$, $V = 1027.1(2)$ Å³, $Z = 2$, $\rho_{\text{calcd.}} = 1.753$ g cm^{-3} , $\mu = 24.4$ cm^{-1} , 2θ range 5–60°, $F(000) = 536$, unique total data: 3626, unique obsd. Data (NO) 2742, no. of variables (NV) 262, NO/NV = 10.5, $R = \sum|\Delta F|/\sum|F_0| = 0.031$. Radiation used: graphite monochromated Mo K α ($\lambda = 0.7107$ Å). Unit cell parameters were obtained by least-squares analysis of the setting angles of 25 carefully centred reflections chosen from diverse regions of reciprocal space.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2005.07.061](https://doi.org/10.1016/j.jorganchem.2005.07.061).

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