O-Silylation of Acylcobalt Tetracarbonyls: Synthesis of a New Type of Dinuclear μ_2-Hydroxycarbene Cobalt Carbonyl Derivatives

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O-Silylation of acylcobalt tetracarbonyls, $RC(O)Co(CO)_4$, gives the dinuclear carbene complexes $[\{\mu_2\text{-}RC(OSiR'_3)\}(\mu_2\text{-}CO)Co_2(CO)_6]$, of which one derivative (R = Me, R′ = Ph) was characterized by X-ray diffraction.

Lewis acid promotion of carbonylations[1] adds an interesting dimension to the reactivity of acylmetal carbonyls towards electrophiles, providing new synthetic possibilities, which apparently have not received proper attention up till now. We attempted to explore this aspect by silylation of acylcobalt tetracarbonyls **1**, compounds which were identified as key intermediates of important catalytic reaction cycles.[2] The preliminary results of this study are reported, as summarized in Scheme 1.

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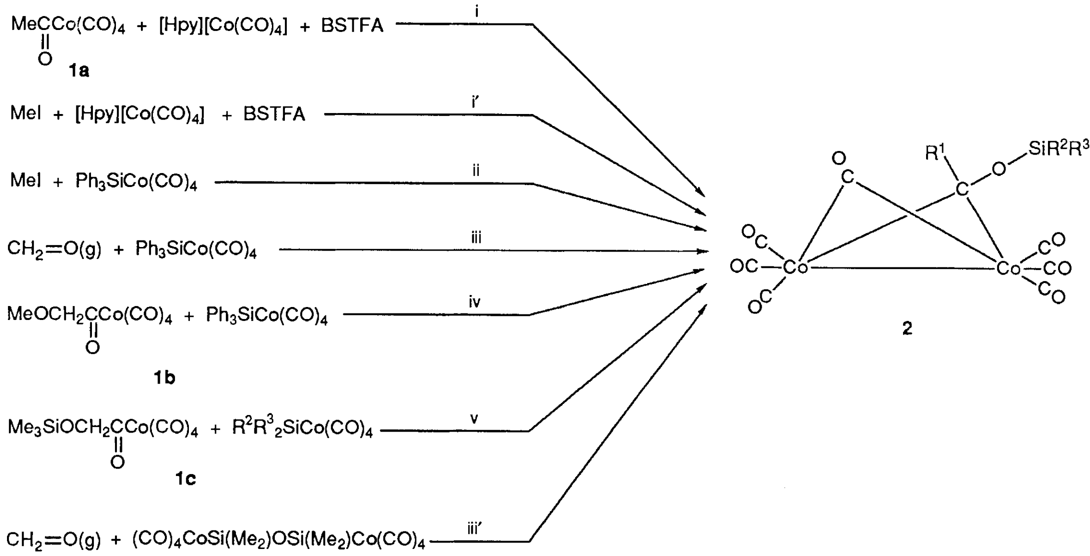

2 a R^1 = Me, R^2 = R^3 = Me
b R^1 = Me, R^2 = R^3 = Ph
c R^1 = CH_2OMe, R^2 = R^3 = Ph
d R^1 = CH_2OSiMe_3, R^2 = R^3 = Me
e R^1 = CH_2OSiMe_3, R^2 = R^3 = Ph
f R^1 = CH_2OSiPh_3, R^2 = R^3 = Ph
g R^1 + R^2 = $CH_2OSi(Me_2)O$, R^3 = Me

Scheme 1 *Reagents and conditions*: i = i′, CH_2Cl_2, −5 °C, Ar; ii, pyridine (catalyst), CH_2Cl_2, room temp., Ar; iii = iii′, PBu_3-(catalyst), *hν*, toluene, room temp., Ar; iv, PBu_3 (catalyst), n-hexane, room temp., Ar; v, PBu_3(catalyst), toluene, room temp., Ar or CO

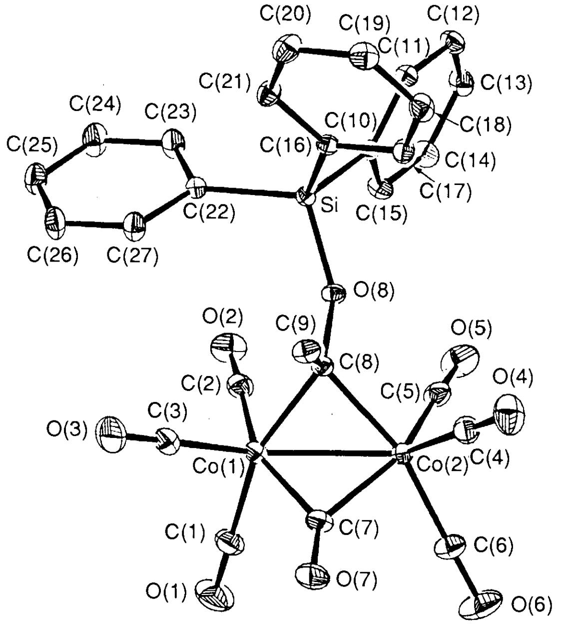

Fig. 1 ORTEP drawing (30% probability ellipsoids) of $[\{\mu_2\text{-MeC}(OSiPh'_3)(\mu_2\text{-CO})Co_2(CO)_6]$ **2b**, view perpendicularly to the Co–Co vector. For sake of clarity the hydrogen atoms have been omitted. Some significant bond lengths are: Co(1)–Co(2) 244.6(1), Co(1)–C(7) 192.9(2), Co(2)–C(7) 191.9(2), Co(1)–C(8) 201.8(2), Co(2)–C(8)-202.1(2), C(8)–O(8) 138.4(2), O(8)–Si 165.9(1) pm.

Acetyl(tetracarbonyl)cobalt **1a** reacts with the silylating agent bis(trimethylsilyl)trifluoroacetamide (BSTFA) and excess of $[Co(CO)_4]^-$ under mild conditions (reaction i) to give the silylated bridging hydroxycarbene derivative **2a**. This complex represents a new class of dicobalt carbene complexes.[3]

Some alternative ways of obtaining compounds of the type **2** were also found in course of this study. Thus, compounds **2a** and **2b** could be obtained by one-pot reactions i and i′.

The relevance of hydroxycarbene complexes to suggested mechanisms of CO hydrogenation[4] prompted us to attempt the synthesis of **2** type compounds from a simple molecule, which was suspected of being an intermediate of this reaction: formaldehyde. In fact formaldehyde gave derivatives **2e** and **2g** under mild conditions: reactions iii and iii′. Additional **2** derivatives containing the $-CH_2-$moiety could be obtained from the formaldehyde-derived[5] precursors **1b** and **1c** (reactions iv and v).

The structure of compounds **2** was established by analyses, analogies of the ν(C–O) band pattern to that of other dinuclear cobalt carbonyls[3,6] and the X-ray diffraction structure determination‡ of a representative (**2b**: Fig. 1). The spectra of compounds **2** indicate that the configuration around the bridgehead carbene atom is in all complexes similar to that shown in Fig. 1; however, low intensity bands in some cases in the IR spectra hint at the possibility of the formation of the other isomer as well (Scheme 1)§.

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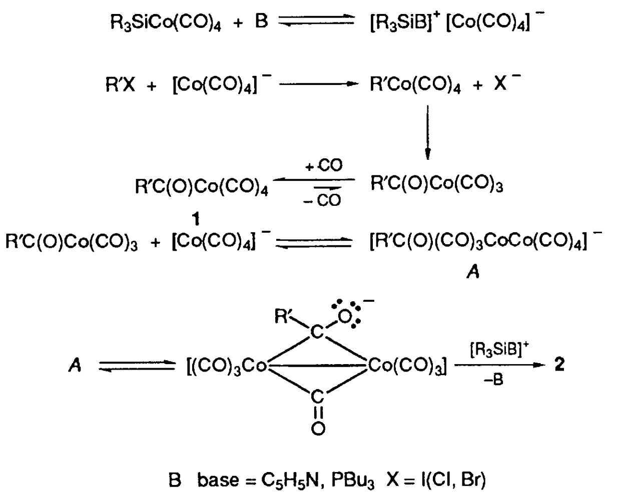
‡ *Crystal data* for **2b**: $C_{27}H_{18}Co_2O_8Si$; M = 616.39, triclinic, space group $P\bar{1}$, No. 2, a = 830.1(3), b = 9415(2), c = 1928.8(2) pm, α = 85.21(2), β = 82.23(3), γ = 67.65(3)°, U = 1380.5(5) Å^3, F(000) = 624, Z = 2, D_c = 1,483 g cm^{-3}, Mo-Kα radiation, λ = 0.7103 Å, μ(Mo-Kα) = 12.9 cm^{-1}. Intensities were measured with a CAD4 automatic diffractometer at room temperature with θ ranging from 3 to 25° on a crystal sealed in a Lindemann capillary; data were corrected for absorption (max–min relative transmission factors 1.00–0.90), Lorentz-polarization effects and decay (6%). 3837 reflections with $I > 3\sigma(I)$ were used in the structure refinements. The hydrogen atoms were located from difference Fourier maps and refined with B = 6 Å^2. The final R value 0.024 (R_w = 0.032). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Examples of characterization of compounds **2**: **2b** Satisfactory elemental analyses were obtained; m.p. 96–99 °C (decomp.); IR (n-pentane) $\nu(C\text{-}O)_t$ 2090.5m, 2058.8vs, 2038.6s, 2024.0s, 2014w, $\nu_{max}(C\text{-}O)_{br}$ 1839.1 ms cm^{-1}; ^1H NMR (C_6D_6) δ 2.25 (s, 3H, CH_3), 6.9–7.8 (m, 15H, C_6H_5); ^{13}C NMR (δ, C_7D_8) 49.7, 128.0; 130.8, 135.6, 137.5, 184.6, 204.0; MS (70 eV) highest fragment m/z 604 $[C(OSiPh_3)CH_3]_2^+$.

2c Satisfactory elemental analyses were obtained, IR (n-hexane) $\nu(C\text{-}O)_t$ 2100m, 2097sh, 2061vs, 2059sh, 2041vs, 2028vs,br, 2018s, 2004sh, $\nu_{max}(C\text{-}O)_{br}$ 1856w, 1836s. ^1H NMR (C_6D_6) δ 2.12 (s, 3H, CH_3), 3.32 (s, 2H, CH_2) 6.1–7.7 (m, 15H, C_6H_5).



B base = C_5H_5N, PBu_3 X = I(Cl, Br)

Scheme 2

The overall structure of compound **2b** resembles that of bridged $Co_2(CO)_8$[7a] and of other dinuclear cobalt carbonyls with two bridging ligands[3b,7b]. The Co–Co distance falls within the range (238.8[3b] to 259.4)[8] observed for supported cobalt–cobalt single bonds. The Co–C(carbene) distances (*ca.* 201.8 pm) are comparable with those in other dicobalt carbene complexes.[3b,7b] The dihedral angle between the two Co–(μC)–Co planes is surprisingly narrow in **2b** (110.9°) with respect to $Co_2(CO)_8$ (*ca.* 128.3°).[7a] The very large C(carbene)–O–Si bond angle [140.4(1)°] is consistent with recently reported structural features of alkoxysilane compounds.[9]

A plausible mechanistic picture (Scheme 2) could involve the intermediacy of the anionic dinuclear complex *A*, which gains support from its similarity to the reported $[RC(O)\text{-}Co(Y)(CO)_3]^-$ (Y = I[10] or CO_2R[10a,11]) type complex or analogous Mn and Re[12] derivatives [*A*: Y = $Co(CO)_4$].

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References

1 *e.g.* C. P. Horwitz and D. F. Shriver, *Adv. Organomet. Chem.*, 1984, **23**, 219; L. T. Lee and H. Alper, submitted for publication.
2 *Catalysis in C_1 Chemistry*, ed. W. Keim, Riedel, Dordrecht, 1983; V. Galamb and G. Pályi, *Coord. Chem. Rev.*, 1984, **59**, 203; H. des Abbayes, *Isr. J. Chem.*, 1985, **26**, 249.
3 Others were obtained from the carbonylation and isomerisation of acetylenes. (*a*) H. W. Sternberg, J. G. Shukys, C. Delle Donne, R. Markby, R. A. Friedel and I. Wender, *J. Am. Chem. Soc.*, 1959, **81**, 2339; (*b*) I. T. Horváth, G. Pályi, L. Markó and G. D. Andreetti, *J. Chem. Soc., Chem. Commun.*, 1979, 1054; *Inorg. Chem.*, 1983, **22**, 1049.
4 G. Henrici-Olivé and S. Olivé, *The Chemistry of the Catalysed Hydrogenation of Carbon Monoxide*, Springer, Berlin, 1984; C. K. Roofer-De Poorter, *Chem. Rev.*, 1981, **81**, 447.
5 A. Sisak, E. Sámpar-Szerencsés, V. Galamb, L. Németh, F. Ungáry and G. Pályi, *Organometallics*, 1989, **8**, 1096.
6 G. Bor, *Chem. Ber.*, 1963, **96**, 2644; G. Pályi, G. Váradi, A. Vizi-Orosz and L. Markó, *J. Organomet. Chem.*, 1975, **90**, 93; G. Váradi, I. Vecsei, A. Vizi-Orosz, G. Pályi and A. G. Massey, *J. Organomet. Chem.*, 1976, **114**, 213.
7 (*a*) P. C. Leung and P. Coppens, *Acta Crystallogr., Sect. B*, 1983, **39**, 535; G. G. Sumner, H. P. Klug and L. E. Alexander, *Acta Crystallogr.*, 1964, **17**, 732; (*b*) O. S. Mills and G. Robinson, *Inorg. Chim. Acta*, 1967, **1**, 61.
8 A. S. Foust, C. F. Campana, J. D. Sinclair and L. F. Dahl, *Inorg. Chem.*, 1979, **18**, 3047.
9 S. Shambayti, J. F. Blake, S. G. Wierschke, P. L. Jorgensen and S. L. Schreiber, *J. Am. Chem. Soc.*, 1990, **112**, 697.
10 (*a*) M. Tasi and G. Pályi, *Organometallics*, 1985, **4**, 1523; (*b*) M. Röper and C. Krüger, *J. Organomet. Chem.*, 1988, **339**, 159.
11 F. Haász, T. Bartik, V. Galamb and G. Pályi, *Organometallics*, 1990, **9**, 2773.
12 C. P. Casey, C. R. Cyr, R. L. Anderson and D. F. Marten, *J. Am. Chem. Soc.*, 1975, **97**, 3053.