[μ_2-(*O*-Acylhydroxycarbene)]dicobalt Hexacarbonyls by Carbon-to-Oxygen Acyl−Acyl Coupling

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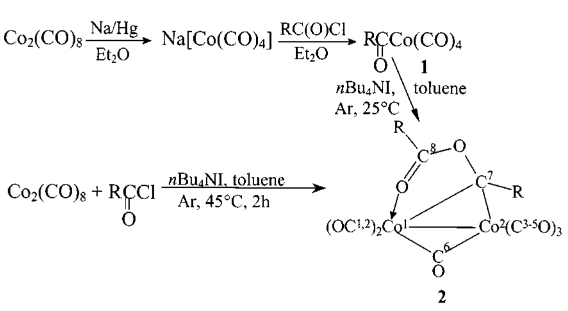
The acylcobalt tetracarbonyls [RC(O)Co(CO)$_4$] (**1**) undergo self-acylation in the presence of *n*Bu$_4$NI, in toluene at room temp., to yield the dinuclear μ_2-acylhydroxycarbene-type complexes [{RC(O)}$_2$Co$_2$(CO)$_6$] (**2**). Complex **2**, with R = *t*Bu, was also characterised by X-ray diffraction.

Introduction

The acylcobalt tetracarbonyls[1] (**1**) have been identified as intermediates of industrially important C−C bond-forming reactions.[2] Since the discovery of the favourable influence of tertiary phosphanes in hydroformylation[3] several reactions of complexes **1** with nucleophiles (Lewis bases) have been studied,[1] although reactions with electrophiles have not been studied so often.[1,4] Here we report on the electrophilic reaction of the acyl oxygen of compounds **1**.



Scheme 1

Results and Discussion

We observed (Scheme 1) that the acylcobalt tetracarbonyls[1] [RC(O)Co(CO)$_4$] (**1**) undergo self-acylation (a kind of Tishchenko reaction[5]) in toluene solution in the presence of *n*Bu$_4$NI, under mild conditions, yielding the dinuclear complexes [{RC(O)}$_2$Co$_2$(CO)$_6$] (**2**). A one-pot synthesis starting from [Co$_2$(CO)$_8$], RC(O)Cl and *n*Bu$_4$NI under similar conditions was also found to give **2** as the only cobalt carbonyl. Complexes **2** were characterised by elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy and single crystal X-ray diffraction of one representative compound (**2c**) (Figure 1).

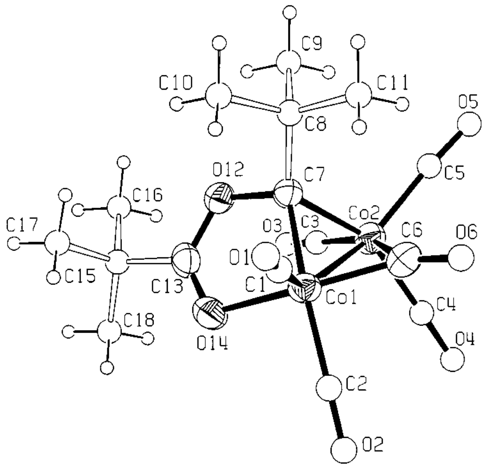


Figure 1. ORTEP drawing of the molecular structure of **2c**; selected bond lengths (pm) and angles (deg.): Co−Co 241.5(1), Co−C(O)$_t$ (av.) 180.9, Co−C(O)$_{br}$ (av.) 191.7, Co−C(7) (av.) 198.7, Co(1)−O(14) 202.6(4), Co(1)−C(13) 273.4(4), C(13)−O(14) 123.0(6), C(13)−O(12) 131.4(6), C(7)−O(12) 146.9(6); Co(1)−C(7)−Co(2) 74.8(3), Co(1)−C(6)−Co(2) 78.0(4), C(7)−O(12)−C(13) 116.6(6), C(8)−C(7)−O(12) 103.6(6)

The spectra show close analogies with other [(μ_2-L′)(μ_2-L′′)Co(CO)$_5$L′′′] complexes.[4,6] The X-ray crystal structure shows a Co$_2$(CO)$_6$ skeleton with the acylhydroxy carbene and a carbonyl ligand in bridging positions and an O-to-

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Co coordination of the oxygen in the "acylating" acyl group. The overall structure of complexes **2** is a new type of cobalt carbonyl, showing some analogy to that of the "lactone" complexes $[(\mu_2\text{-butenolide})(\mu_2\text{-CO})Co_2(CO)_6]$.[7] Such an O-to-Co coordination is a very rare phenomenon[8] with low-valent cobalt carbonyls. The relative orientation of the bridging carbonyl and the ester groups indicates a quantitative stereoselectivity of the formation of complexes **2**.[9] The preparative and structural results can be rationalized by supposing I^- coordination to (a part of) the acylcobalt carbonyls, which could increase the charge separation and thus facilitate the formation of the acyl electrophile, followed by the organization of the dinuclear structure of **2** (Scheme 2). This picture could give an insight into the mechanism of action of ionic additives in Co-catalysed CO chemistry.[10] I^- coordination to low-valent cobalt carbonyls has been documented previously.[11] The μ_2-hydroxycarbene ligand in complexes **2** might bear some relevance to the as-yet not fully explored question of the mechanism of the Fischer−Tropsch reaction.[12]

$$RC(O)Co(CO)_4 + (nBu_4N)I \rightleftharpoons (nBu_4N)[RC(O)Co(CO)_3(I)] + CO$$

$$\begin{aligned} &RC(O)Co(CO)_4 + [RC(O)Co(CO)_3(I)]^- \longrightarrow \\ &\quad\longrightarrow \{\mu_2,O\text{-}\eta^1\text{-}[RC(O)]_2\}(\mu_2\text{-CO})Co_2(CO)_5 + CO + I^- \end{aligned}$$

Scheme 2

Experimental Section

All experiments were performed using standard Schlenk techniques, with carefully deoxygenated, dry gases and solvents.

Preparation of Complex 2c: Dicobalt octacarbonyl (684 mg, 2 mmol) and *n*-tetrabutylammonium iodide(960 mg, 2.6 mmol) were placed into a thermostated reaction vessel under Ar. Toluene (15 mL) was then added and the mixture was stirred for 10 min. at 25 °C. After this period *t*BuC(O)Cl (640 mg, 5.3 mmol) was added. The temperature was then raised to 45 °C and the solution was stirred for an additional 2 h. After this period the solution was left to cool to room temp., filtered, the filtrate was dried at reduced pressure (room temp.) and an oily product (1551 mg, 82%) was obtained which contained **2c** as the only cobalt carbonyl (IR). This crude product was dissolved in 3 mL *n*-hexane and the solution cooled to −78 °C to give brownish yellow [m.p. 73.5 °C (dec.)] crystals (278 mg, 15%). Occasionally the recrystallization was repeated using 0.5−1.5 mL of *n*-hexane. The product is very soluble in all solvents which did not react with **2c**, hence the low yields of crystalline product.

2c could also be prepared from 1 mmol of **1c** {obtained from $Na[Co(CO)_4]$ (195 mg, 1 mmol) and pivaloyl chloride (121 mg, 1 mmol) in 15 mL Et_2O} and pivaloyl chloride (60 mg, 0.5 mmol) in toluene (15 mL), at room temp., under Ar atmosphere after 2 h stirring. Yield: 60−70% (IR). − $C_{16}H_{18}Co_2O_8$ (456.18): calcd. C 42.13, H 3.98, Co 25.84; found C 42.3, H 4.1, Co 25.7. MW calcd. 456.18; found (m.s.) 456.

Spectroscopic Characterisation of Compounds 2 $[\{RC(O)\}_2Co_2(CO)_6]$ (for carbon position see Scheme 1)

2a (R = Me): IR (*n*-hexane): $\nu(C-O)_t$: 2088.0 s, 2052.3 vs, 2020.4 vs, 2013.4 vs, 2006.1 s; $\nu(C-O)_{br}$: 1830.1 ms; $\nu(C-O)_{org.}$: 1640 w cm^{-1}. − ^{1}H NMR (400.13 MHz, C_6D_6, 300 K, TMS): δ = 1.24 [s, 3 H, C*H*$_3$-C(8)], 2.20 [s, 3 H, C*H*$_3$-C(7)]. − ^{13}C NMR (100.62 MHz, C_6D_6, 300 K, TMS): δ = 19.3 [*C*H$_3$-C(8)], 23.3 [*C*H$_3$-C(7)], 179.5 [*C*(7)], 181.5 [*C*(8)], 199.3 [(*C*O)$_2$-Co(1)], 201.0 [(*C*O)$_3$-Co(2)], 229.1 [*C*(6)].
2b (R = *i*Pr): IR (*n*-hexane): $\nu(C-O)_t$: 2084.5 s, 2048.5 vs, 2016.5 vs, 2009.0 s, 2004.5 s; $\nu(C-O)_{br}$: 1837.5 s; $\nu(C-O)_{org.}$: 1623 w cm^{-1}. − ^{1}H NMR (400.13 MHz, C_6D_6, 300 K, TMS): δ = 1.19 [d, ^3J(H,H) = 7.60 Hz, 6 H, (C*H*$_3$)$_2$-CH-C(7)], 1.25 [d, ^3J(H,H) = 6.80 Hz, 6 H, (C*H*$_3$)$_2$-CH-C(8)], 2.26 [m, ^3J(H,H) = 6.80 Hz, 1 H, C*H*-C(8)], 2.39 [m, ^3J(H,H) = 7.60 Hz, 1 H, C*H*-C(7)]. − ^{13}C NMR (100.62 MHz, C_6D_6, 300 K, TMS): δ = 24.6, [(*C*H$_3$)$_2$-CH-C(8)] 25.0 [(C*H*$_3$)$_2$-CH-C(7)], 34.1 [*C*H-C(8)], 50.8 [*C*H-C(7)], 187.5 [*C*(8)], 198.0 [*C*(7)], 200.5 [(*C*O)$_2$-Co(1)], 201.5 [(*C*O)$_3$-Co(2)], 229.9 [*C*(6)].
2c (R = *t*Bu): IR (n-hexane): $\nu(C-O)_t$: 2083.5 s, 2047.5 vs, 2014.0 vs, 2008.0 s, 2003.5 s; $\nu(C-O)_{br}$: 1830.1 ms; $\nu(C-O)_{org.}$: 1640 w cm^{-1}. − ^{1}H NMR (400.13 MHz, C_6D_6, 300 K, TMS): δ = 0.95 [s, 9 H, C*H*$_3$-C-C(8)] 1.23 [s, 9H C*H*$_3$-C-C(7)]. − ^{13}C NMR (100.62 MHz, C_6D_6, 300 K, TMS): δ = 27.6 [(*C*H$_3$)$_3$-C-C(8)], 31.6 [(*C*H$_3$)$_3$-C-C(7)], 39.4 [*C*-C(8)], 51.1 [*C*-C(7)], 188.9 [*C*(8)], 200.6 [(*C*O)$_2$-Co(1)], 201.8 [(*C*O)$_3$-Co(2)], 206.7 [*C*(7)], 230.0 [*C*(6)].

A full list of spectra is available as Supporting Information.

Crystal Structure of 2c: Crystal dimensions 0.30 × 0.20 × 0.15 mm, triclinic, space group $P\bar{1}$, $a = 8.759(2)$, $b = 9.305(1)$, $c = 12.794(2)$ Å, $\alpha = 86.35(2)$, $\beta = 88.35(4)$, $\gamma = 73.12(4)°$, $V = 995.7(3)$ Å^3, $Z = 2$, $\rho_{calcd.} = 1.521$ g/cm^3 $\mu = 13.394$mm^{-1}, θ range 3.46−75.00°, $F(000) = 464$, 241 parameters and 12 restraints were refined for 4058 [$R(int) = 0.0109$] independent reflections with $I > 2\sigma(I)$ to $R1 = 0.0915$, $wR2 = 0.1078$ and GOF = 0.91.
Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133917. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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