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Early/late bimetallic complexes: MCo_2 ($M = Ti$, Zr) derivatives [☆]

Tamás Bartik[a], Harald Windisch[a,1], Angela Sorkau[b], Karl-Heinz Thiele[b], Christian Kriebel[c,1], Anke Herfurth[c,1], C. Matthias Tschoerner[c,1], Claudia Zucchi[c], Gyula Pályi[c,*]

[a] *Institute of Organic Chemistry, University of Veszprém, H-8200 Veszprém, Hungary*
[b] *Department of Chemistry, Martin Luther University, D-06217 Merseburg, Germany*
[c] *Department of Chemistry, University of Modena, Via Campi 183, I-41100 Modena, Italy*

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Abstract

$(\eta^5\text{-}C_5H_5)_2M[Co(CO)_4]_2$ ($M = Ti$, Zr) complexes were prepared by alkane elimination from the corresponding metallocene diorganyls and $HCo(CO)_4$ or by salt elimination from metallocene dihalides and $Na[Co(CO)_4]$. $(Ph_2N)_2Ti[Co(CO)_4]_2$ was obtained from $(Ph_2N)_4Ti$ and $HCo(CO)_4$.

Keywords: Titanium complexes; Zirconium complexes; Cobalt complexes; Bimetallic complexes

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1. Introduction

Intermetallic compounds with two different transition metals are hoped to provide a key to molecular level tailoring of multifunctional catalysts [1,2]. If so, the combinations of metals with the most possible different electronic structures would be desirable. This was our aim when we started [3,4] our work [5] on compounds containing unsupported bonds between Group 4 metals ($M = Ti$, Zr, Hf) and the Group 9[2] cobalt. We attempted to construct such molecules with M–Co bond(s) where both M and Co are in ligand environments which are characteristic for catalytically active forms.

The σ-hydrocarbyl-M derivatives of the $Co(CO)_4$ fragment were reported recently [5]. Now we report on new results of combinations where the Group 4 metal bears π-donor ligands, as in derivatives of the corresponding metallocenes. A similar behaviour was expected for the Ph_2N ligand; thus we also report here on one of its derivatives.

2. Experimental

All operations were performed using the Schlenk technique [6] with carefully deoxygenated, dried and CO_2-free solvents. Starting materials were of commercial origin with the exception of $(C_5H_5)_2TiCl_2$, $(C_5H_5)_2ZrCl_2$ [7], $(Ph_2N)_4Ti$, $Cp_2Zr(NPh_2)Cl$ [8], $Na[Co(CO)_4]$ [9], $H[Co(CO)_4]$ [10] and $Co_2(CO)_8$ [11], which were prepared according to published procedures.

IR spectra were obtained with Specord IR [illegible] (Carl Zeiss, Jena) and Bruker FT-IR IFS 113V instruments. ^1H NMR spectra were recorded on a Bruker WP80SY (FT, 80 MHz) spectrometer. Mass spectra were registered on a Joel B 300 instrument equipped with the direct inlet system JMA 2000 B. Gas chromatographic measurements were performed using a Hewlett-Packard 5830 A instrument with etched (HCl) glass capillary columns [12]. Thermogravimetric analyses were performed with a Derivatograph 3427 SK (MOM, Budapest) instrument.

In addition to routine elemental analyses the concentration of the following substances was determined by quantitative IR spectroscopy: $Co_2(CO)_8$ [13], $HCo(CO)_4$ [14] and $[Co(CO)_4]^\cdot$ [15] using published extinction data. Stock solutions of $HCo(CO)_4$ were also analysed by acidimetric titration [16].

[☆] This paper is dedicated to György Bor, pioneer of metal carbonyl chemistry in Central Europe, on the occasion of his 70th birthday.

[*] Corresponding author.

[1] On the leave from the Martin Luther University, Halle-Wittenberg, Germany.

[2] The IUPAC/ACS notation is used for groups of the periodic table: Groups IA and IIA become Groups 1 and 2 and the d transition elements comprise Groups 3–12, while the p elements comprise Groups 13–18.

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*2.1. Preparation of bis(η^5-cyclopentadienyl)titanium-bis(tetracarbonyl-cobalt) (**6a**)*

2.1.1. Method A (salt elimination)

Sodium tetracarbonyl cobaltate, 388 mg (2 mmol) was prepared by Na/Hg reduction of $Co_2(CO)_8$ [9] in Et_2O. The solvent was evaporated (r.t., reduced pressure) and to this residue $(C_5H_5)_2TiCl_2$, 249 mg (1 mmol), suspended in 10 ml of toluene was added at once under Ar atmosphere and r.t.. The reaction mixture was then stirred for 15 h; the progress of the reaction was followed by analysing samples by IR spectroscopy. Already after an hour a white precipitate (NaCl) was formed. After 10–12 h the only observable band system in the ν(C–O) spectrum was that of **6a**. The product was then isolated by recrystallisation from a mixture of toluene/n-hexane (1:10) at −78 °C. Yield 406 mg (78%).

2.1.2. Method B (alkane elimination)

Dibenzyltitanocene, $Cp_2Ti(CH_2Ph)_2$, 270 mg (0.75 mmol), was dissolved in 30 ml of toluene/n-hexane (1:1). To this solution, while stirring at r.t. under Ar atmosphere, 2 ml of a 0.4 mol/l solution of $HCo(CO)_4$ in n-hexane and 2 ml of toluene were added at once. The reaction mixture was then stirred for 20 h at r.t., while from time-to-time samples were taken for IR spectroscopic analyses. After this period the dominant band system in the ν(C–O) spectrum was of **6a** (together with minor amounts, 5–10% of $Co_2(CO)_8$ [13]). Then the solvent and the (eventual) remaining $HCo(CO)_4$ were evaporated at reduced pressure, the residue was extracted by 25 ml of toluene/n-hexane (1:10) and the product was obtained by crystallisation at −78 °C as a brown crystalline material. Yield 359 mg (92%). Similar results were obtained with Cp_2TiPh_2 as the starting material.

Complex **6b** (violet crystals) was prepared by both Methods A (from Cp_2ZrCl_2, ^1H NMR spectroscopic yield 80±5%) and B (from $Cp_2Zr(CH_2Ph)_2$, yield not measured; or Cp_2ZrPh_2, isolated yield 62%). The reaction of $Cp_2Zr(NPh_2)Cl$ with $Na[Co(CO)_4]$ was performed according to Method A. The yield of $Cp_2Zr[Co(CO)_4]_2$ was not determined; on the basis of the IR intensities it was ~50% with respect to starting Zr.

Compound **7** (black oil) was obtained by Method B (yield 90±5%, ^1H NMR).

2.2. Characterisation of new compounds

*2.2.1. $Cp_2Ti[Co(CO)_4]_2$ (**6a**)*

Anal. Found: C, 41.4; H, 2.0; Co, 22.4; Ti, 9.1. Calc. for $C_{18}Co_2H_{10}O_8Ti$: C, 41.58; H, 1.94; Co, 22.67; Ti, 9.21%.

IR (n-hexane (cm^{-1})): 2087m, 2041sh, 2033vs, 2021s, 1990w; (n-hexane/toluene, 10:1): 2088m, 2041sh, 2035vs, 2023s, 1990mw; (nujol mull; bands corresponding to nujol omitted): 3104m ν(C–H) symm., 2088vs, 2040vs, 2030vs, 2016vs ν(C–O), 1448s C–C skeletal, symm., 1132w ring def. symm., 1030m C–H def., antisymm., 1016m (?), 870w, 845w C–H def., antisymm., 816s CH def. symm., 406m Ti–Cp skeletal.

^1H NMR (toluene-d$_8$, 80 MHz, δ (ppm), HMDSO) 5.78 (s, br, 10H, C_5H_5).

Thermogravimetry: (flat) inflections at 360 °C (−43%, ~8 CO), 570 °C (−12.5%, ~C_5H_5), 800 °C (−12.5%, ~C_5H_5). In preparations of **6a** according to reaction (ii) (Scheme 1) from **3b** the amount of RH (toluene) formed was determined by GLC: 81% (with respect to starting **3b**). MS (peak mass, intensity, tentative assignment): 296 (3) $(C_5H_5)_2TiCo_2{}^+$; 280 (4) $(C_5H_3)(C_4H_3)TiCo_2{}^+$; 266 (2) $(C_4H_2)_2TiCo_2{}^+$; 208 (10) $(C_5H_5)_2Ti(H)_2(CO)^+$; 207 (18) $(C_5H_5)_2Ti(H)(CO)^+$/$(C_5H_4)Co(CO)_3{}^+$; 206 (68) $(C_5H_5)_2Ti(CO)^+$; 189 (55) $(C_5H_5)_2Co^+$; 124 (22) $C_5H_5Co^+$; 113 (2) $(C_5H_5)_2Ti^+$; 95 (10) ?; 66 (76) $C_5H_6{}^+$; 65 (54) C_5H_5; 59 (18) Co^+; 40 (20) $C_3H_4{}^+$; 39 (22) $C_3H_3{}^+$; 38 (32) $C_3H_2{}^+$; 28 (100) CO^+. $T_{dec.}$ 89 °C.

*2.2.2. $Cp_2Zr[Co(CO)_4]_2$ (**6b**)*

Anal. Found: C, 38.1; H, 2.1; Co, 20.8. Calc. for $C_{18}Co_2H_{10}O_8Zr$: C, 38.38; H, 1.79; Co, 20.92%.

IR (n-hexane (cm^{-1})): 2087w, 2031vs, 2017s, 1991w; (n-hexane/toluene, 10:1): 2088m, 2032vs, 2021s, 199w.

^1H NMR (toluene-d$_8$, 80 MHz, δ (ppm), HMDSO): 5.8 ((virtual) t, 10H, C_5H_5).

^{13}C NMR (C_6D_6, δ (ppm)): 114.0 (C_5H_5), ~196 (br, CO).

Thermogravimetry: (flat) inflections at 240 °C (−39.8%, ~ 8 CO), 420 °C (−11.5%, ~C_5H_5), 860 °C (−11.5%, ~C_5H_5). In preparations of **6b** according to reaction (ii) (Scheme 1) from **4b** the amount of RH (toluene) was measured by quantitative ^1H NMR spectroscopy (anisol internal standard): 100±5% (with respect to starting **4b**). MS (peak mass, intensity, tentative assignment): 392 (5) $(C_5H_5)_2ZrCo(CO)_4{}^+$; 306 (2) $(C_5H_4)_2ZrCo(CO)^+$; 279 (20) $(C_5H_5)(C_4H_4)ZrCo^+$; 207 (12) $(C_5H_4)Co(CO)_3{}^+$; 204 (6) $(C_5H_4)(C_4H)Zr^+$; 202 (4) $Co_2(CO)_3{}^+$; 194 (10) $(C_5H_4)(C_3H_3)Zr^+$; 193 (12) $(C_5H_4)(C_3H_2)Zr^+$; 189 (100) $(C_5H_5)_2Co^+$; 179 (10) $(C_5H_4)Co(CO)_2{}^+$; 178 (6) $(C_5H_3)Co(CO)_2{}^+$; 156 (4) $(C_5H_5)Zr^+$; 152 (8) $(C_5H_5)Co(CO)^+$; 128 (12) $(C_3H_5)Co(CO)^+$/$(C_3H)Zr^+$; 124 (62) $(C_5H_5)Co^+$; 115 (18) $Co(CO)_2{}^+$/C_2Zr^+; 91 (3) Zr^+; 66 (68) $C_5H_6{}^+$; 65 (35) $C_5H_5{}^+$; 63 (8) $C_5H_3{}^+$; 59 (27) Co^+; 51 (5) $C_4H_3{}^+$; 40 (18) $C_3H_4{}^+$; 39 (20) $C_3H_3{}^+$; 28 (62) CO^+. $T_{dec.}$ 139 °C.

*2.2.3. $(Ph_2N)_2Ti[Co(CO)_4]_2$ (**7**)*

Anal. Found: C, 52.9; H, 2.9; N, 3.6; Co, 16.0. Calc. for $C_{32}H_{20}O_8N_2Co_2Ti$: C, 52.92; H, 2.78; N, 3.6; Co, 16.23%.

IR (n-hexane (cm^{-1})): 2092w, 2040vs, 2026s.

^{1}H NMR (C_6D_6, 80 MHz, δ (ppm), HMDSO): 6.9 (m, 8H, ar-*ortho*-C*H*) 7.2 (m, 12H ar-*meta*-+ar-*para*-C*H*).

2.3. Protolytic experiments

Complex **6a**, 52 mg (0.1 mmol), was placed into a thermostatted reaction vessel equipped by a gas volumetric burette. To this sample methanol, 2 ml (74 mmol), was added at once. The reaction mixture was then stirred by external magnetic stirring for 15 min at 20 °C and then analysed. No remarkable volume change of the gas phase was observed. The alcoholic phase showed the formation of 0.088 mmol $HCo(CO)_4$ (88%) by quantitative IR analysis. A 1 ml sample was drawn dry, the residue was taken up by THF-d_8 and the ^{1}H NMR spectrum was obtained: 3.72 (s, 6H, CH_3), 5.5–6.3 (m, 10H, C_5H_5), which can be attributed to $Cp_2Ti(OCH_3)_2$ [17].

Experiments were performed similarly (in toluene solvent) using HCl gas (consumed quantity was not measured), H_2O, EtOH and PhOH reacting these with both complexes **6a** and **6b**. The two **6** derivatives react similarly. The products were identified by their known spectra: $HCo(CO)_4$, [14], $Cp_2M(OR)_2$ (R = Me, Et, Ph) and Cp_2MCl_2 (M = Ti, Zr) [17–19]. In the hydrolysis experiments white precipitates were obtained, which were tentatively assigned to $Cp_2M(OH)_2$ complexes (^{1}H NMR (C_6D_6): Ti: 2.7 (s, br, 2H, O*H*), 5.99 (s, 10H, C_5*H*$_5$); Zr: (C_6D_6) 2.8–3.1 (br, 2H, O*H*) 6.1 (m, 10H, C_5*H*$_5$); in both cases the higher field signals can also be assigned to H_2O in hydrated oligomeric oxydes) on the basis of the literature data [20]. The hydroxides could not be isolated and some doubts about their identity are not unfounded [3].

Complex **7** was treated similarly but its reactivity was different. $HCo(CO)_4$ [14] forms only with excess H_2O and PhOH or HCl (not measured). In the case of PhOH and HCl the Ti-containing products were identified by spectroscopy $Ti(OPh)_4$ [21] and $TiCl_4$ [22]. Hydrolysis yields a white voluminous precipitate which was assigned to $TiO_2 \cdot xH_2O$ [23]. On the other hand with MeOH, EtOH, n-PrOH, n-BuOH, t-BuOH and n-PentOH only the IR spectrum of $[Co(CO)_4]^-$ [24] was observed. We formulate tentatively the product as $[(RO)_3Ti(ROH)_x][Co(CO)_4]$ [5b, 25]. The IR spectrum expected for eventual $[Ph_2NH_2][Co(CO)_4]$ [5b] was not observed.

2.4. Thermolysis in solution

A 5 ml sample of a 0.016 molar solution of complex **6b** in toluene was placed into a thermostatted reaction vessel equipped with a gas burette and external magnetic stirring. The solution while being stirred was slowly heated. Decomposition was observed at 80 ± 2 °C. The decomposition was characterised by the volume change, ~2 mol CO/mol complex **6b** (since the vapour pressure of toluene at 80 °C cannot be neglected [26] the result of volume change was corrected by a comparative experiment under identical conditions without complex **6b**), and the disappearance of the IR bands of the complex **6b**, accompanied by the emergence of a new band system. The reaction mixture was then chromatographed on silica. One yellow band could be eluted. This substance was characterised as $CpCo(CO)_2$; IR (ν(C–O), n-hexane): 2031s, 1070s [27], ^{1}H NMR (toluene-d_8): 4.30 (s, 5H, C_5H_5). The Zr-containing fraction could not be eluted.

Complex **6a** shows a similar behaviour, yielding also a (unidentified) grey precipitate. A toluene solution of complex **7** did not show signs of decomposition until 100 °C.

2.5. Reaction with PRR'$_2$ compounds

To a solution of complex **7** (3 ml, 0.02 M, in toluene 3 ml) a 6 ml sample of a 0.02 M solution of the PRR'$_2$ ligand (Co:P = 1:1) was added at once, at room temperature. Gas evolution (CO) was observed. The solution was stirred for 30 min and then analysed by IR spectroscopy. In all cases (**6a**, **6b** and **7**) the only identified metal carbonyl product was $Co_2(CO)_6(PR_3)_2$. IR ν(C–O) (cm^{-1}) spectra were as follows: R = R' = Et (toluene) 1944 (lit. CS_2: 1946.2 [28]); R = R' = iPr (toluene) 1943; R = Ph R' = Et (toluene) 1949 (lit. CS_2: 1950.2 [28]); R = R' = Ph (KBr pellet) 1943 (lit. KBr: 1950 [29]), (nujol mull) 1943 (lit. nujol: 1946.3 [30]); R = R' = OEt (toluene) 1965; R = R' = OC_6H_4-*o*-Ph (toluene) 1984; R = R' = OPh (toluene) 1978 (lit. $CHCl_3$: 1979 [31]). The Ti-containing fraction (brown precipitate) appears to be a complex mixture of products which could not be identified.

3. Results and discussion

The synthetic results are summarised in Scheme 1. Both the salt elimination and the hydride elimination routes could be used under mild conditions, with good yields. One particular feature of these reactions should be pointed out: all efforts (using reactant M:Co ratios from 1:0.5 to 1:1.5) to prepare asymmetric derivatives such as $Cp_2M(R)[Co(CO)_4]$ failed; such intermediates could not be detected even by spectroscopic analysis of the reaction mixtures. This tendency is particularly surprising for the amide starting compound $(Ph_2N)_4Ti$, since monocobalt derivatives of alkylic $(R_2N)_4Ti$ compounds (R = Me, Et) could be prepared without difficulty [5b].

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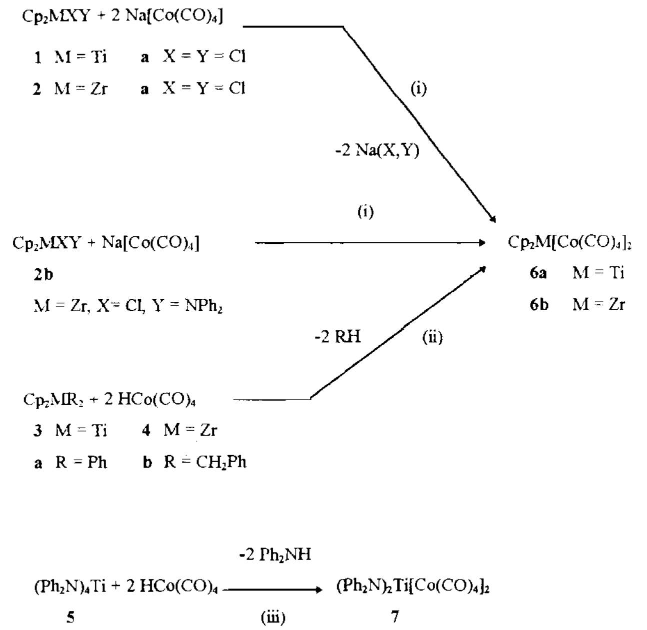
[3] As it was pointed out justly by one of the Referees of this paper.



Scheme 1.

An additional proof for the strong tendency to form dicobalt derivatives was obtained by using $Cp_2Zr(NPh_2)Cl$ as the starting material in an ion-metathesis (A) type reaction, which yielded only **6b** as the metal carbonyl product, most probably according to the following disproportionation.

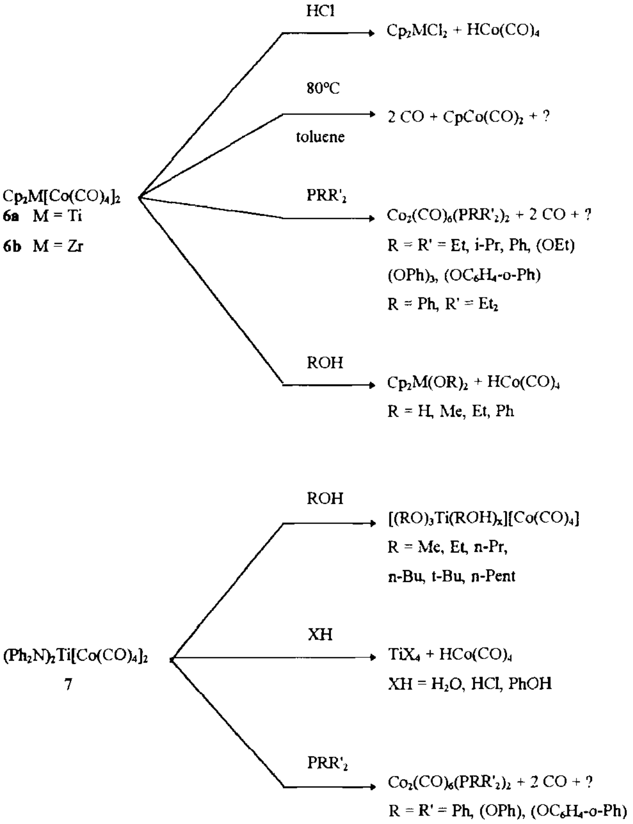
$$2Cp_2Zr(NPh_2)Cl + 2Na[Co(CO)_4] \longrightarrow$$

$$2[Cp_2Zr(NPh_2)Co(CO)_4] \longrightarrow$$

$$\underset{\mathbf{6b}}{Cp_2Zr[Co(CO)_4]_2} + Cp_2Zr(NPh_2)_2$$

The structure of products **6** and **7** is based on analyses, stoichiometry of the preparation, reactions and spectra (see Section 2).

Information from the analytical, thermoanalytical and ^1H NMR spectra is straightforward. IR ν(C–O) spectra can be compared with several IR studies on $RCo(CO)_4$ or $X[Co(CO)_4]_2$ compounds [32] where in some cases X-ray structures are also available [33]. The IR spectra of compounds **6** and **7** are more similar to those of the $RCo(CO)_4$ type than to those of the $X[Co(CO)_4]_2$ type. This kind of behaviour indicates the absence of significant coupling between the two $Co(CO)_4$ fragments, similarly to other $TiCo_2$ or $ZrCo_2$ complexes [5] but unlike the linear $Hg[Co(CO)_4]_2$ [34] or the angular $Me_2Ge[Co(CO)_4]_2$ [32c, 35]. This interesting difference should also be analysed theoretically as soon as structural data become available. The reactivity of complexes **6** and **7** follow fairly similar patterns (Scheme 2). These complexes are more stable than their σ-hydrocarbyl analogs such as $(PhCH_2)_2M[Co(CO)_4]_2$ (M = Ti, Zr [5]) which is quite understandable if the M–Co bond is supposed to contain, beyond the σ component, also a π (or δ) type component [5b,36]. Protolytic fission of the M–Co bond identifies M as a partially positive and Co as a partially negative charged centre in agreement with earlier findings. Reaction with tertiary phosphorus ligands follows a path different from other M–Co derivatives [5]: apparently the substitution of a CO ligand on the Co atom results in a fast (most probably homolytic) fission of the M–Co bond and yields $Co_2(CO)_6(PR_3)_2$ derivatives.



Scheme 2.

The cyclopentadienyl transfer from Ti or Zr to cobalt, yielding $CpCo(CO)_2$ [26] is in line with the much higher d-electron density available on the late transition metal than on the early one, or in other words with the expected more hard character of Group 4 and more soft character of Group 9.

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