of **2a** at −78 °C in a sealed degassed solution of CD_2Cl_2 gave a thermally unstable intermediate identified as the η^5-pentadienoyl complex **7** (Scheme I) from low-temperature ^1H NMR and IR data.[9,10] Warming of **7** gave the hydroxyferrocene **3a** quantitatively.

The structure of **7** is proposed from the following data. After photolysis of a solution of **3a** (CD_2Cl_2, −78 °C) in a sealed degassed NMR tube, the low-temperature (−40 °C) NMR spectra contained new vinyl absorptions centered at δ 6.54 ppm (2 H, m), a cyclopentadienyl absorption at δ 4.29 ppm (5 H, s), a high-field multiplet centered at δ 0.2 ppm (1 H, m), and changes in the complex aromatic resonances. The vinyl and high-field multiplets can be attributed to an ABX spectrum (H_A, δ 6.53 ppm; H_B, δ 6.55 ppm; H_X, δ 0.20 ppm; J_{AB} = 5.6 Hz, J_{AX} = −0.7 Hz, J_{BX} = 8.2 Hz). In order to assign a specific hydrogen to the high-field absorption (and in turn assign the vinyl absorptions), we prepared the labeled butadienyl complex **2a**-d_1 (eq 2). Photolysis of a solution (CD_2Cl_2) of **2a**-d_1 at −78 °C and low-temperature ^1H NMR experiments gave a spectrum consistent with that observed for **7** including the absence of the high-field absorption (H_X). This labeling experiment clearly indicates that the terminal hydrogen of **2a** converts to the terminal hydrogen in the η^5-pentadienoyl complex **7**. In addition, low-temperature IR experiments were also helpful in identifying a second structural feature of **7**. Photolysis of **2a** at −78 °C in CH_2Cl_2 resulted in the disappearance of the terminal carbonyl stretching absorptions with concomitant appearance of a strong 1720 cm^{-1} stretch consistent with the ketene-like moiety present in **7**.[11] In accord with the above NMR data, warming of this solution resulted in loss of the 1720 cm^{-1} stretch with no appearance of new carbonyl absorptions.

A mechanism for the conversion of **2a** to **3a** which incorporates these above observed intermediates is summarized in Scheme I. The sole photochemical process is loss of a terminal carbonyl. Coordination of the terminal alkene moiety generates the η^3-butadienyl intermediate **4**. Carbonyl insertion gives **6**. Rearrangment of **6** gives the η^5-pentadienoyl complex **7**. Formation of a C–C bond via electrocyclic ring closure from **7** followed by keto–enol tautomerization gives product **3a**.

In conclusion, the high-yield conversion of η^1-butadienyl complexes to hydroxyferrocenes appears to be general. Trapping experiments and low temperature spectroscopic data implicate an η^3-butadienyl complex and a pentadienoyl complex as intermediates in the conversion. Further work concerning mechanistic studies and synthetic applications of this cyclization reaction are currently underway.

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Supplementary Material Available: Experimental descriptions and ^1H NMR, ^{13}C NMR, and high-resolution MS data for **2a**, **2b**, **2c**, and **5** and high-resolution MS data for **3a**, **3b**, and **3c** (4 pages). Ordering information given on any current masthead page.

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(9) Approximately 60% conversion to **7** at −78 °C was accomplished with a photolysis time of 4 h. This is indicative of **7** quenching the initial photoreaction. As the hydroxyferrocene product **3a** does not effectively quench the photoreaction, shorter times are needed (cf. ref 8) if the solution is warmed to room temperature occasionally during the reaction. At −40 °C slow conversion of **7** to **3a** is observed in the ^1H NMR. Solubility problems have thwarted our efforts for low-temperature NMR observation of intermediates from photolysis of **2b** and **2c**.

(10) An alkylvinylketene complex would constitute one canonical resonance form for **7**. We thank one reviewer for pointing out that form **7** could better represent the structure of the observed intermediate. Vinylketene complexes have been postulated as intermediates in the Dötz–Wulff cyclization reaction: cf. Fischer, H.; Muhlemeier, J.; Markl, R.; Dötz, K. H. *Chem. Ber.* **1982**, *115*, 1355. Dötz, K. H.; Muhlemeier, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 929.

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Benzyltitanium and -zirconium Cobalt Carbonyls. Preparation and Spectroscopic Characterization

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Summary: Tetrabenzyltitanium (**1a**) and -zirconium (**1b**) react with equimolar $HCo(CO)_4$ (**2**) to give the corresponding tribenzylmetal–cobalt tetracarbonyl (M = Ti, **5a**; M = Zr, **5b**) derivatives. Compounds **5** also can be obtained from $(PhCH_2)_3MX$ (X = Cl, Br) compounds and $[Co(CO)_4]^-$ salts, while complexes **6** are formed from equimolar **5** and **2**. Compounds **5** react with PPh_3 to give the substitution products $(PhCH_2)_3M[Co(CO)_3(PPh_3)]$ (M = Ti, **7a**; M = Zr, **7b**), which also can be obtained from **1a** or **1b** and $HCo(CO)_3(PPh_3)$. The new, very unstable bimetallic complexes **5**, **6**, and **7** were characterized by IR and ^1H NMR spectroscopy.

Transition-metal-assisted or -catalyzed reactions often display a characteristic pattern of products which is typical for the metal. Bimetallic compounds are hoped, believed, or even proved to unify the advantages of the metal components.[2] This goal has been of great interest in the last

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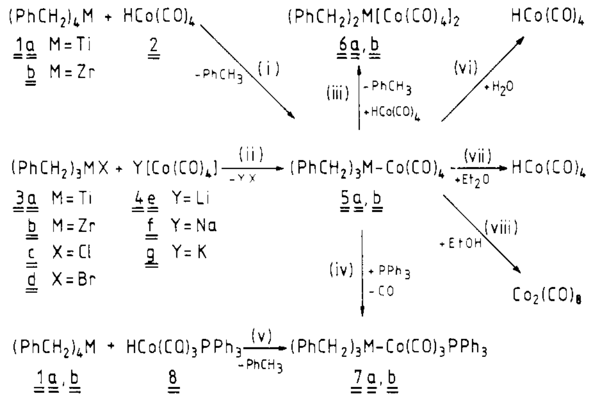
(2) Early/late-transition-metal combination in organic synthesis: (a) Negishi, E.; Van Horn, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 3168. (b) Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254. (c) Schwartz, J.; Loots, M. J.; Kosugi, H. *J. Am. Chem. Soc.* **1980**, *102*, 1333. (d) LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312. (e) Bodnar, T. W.; Cutler, A. R. *Organometallics* **1985**, *4*, 1558. Early suggestions about the importance of these combinations in catalysis: (f) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959; **1976**, *85*, 451. (g) Demitras, G. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 2796. (h) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (i) Wong, K. S.; Labinger, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3652. (j) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665.

0276-7333/89/2308-0558$01.50/0

Scheme I



ᵃFor reaction conditions see in ref 14, (i) through (viii).

decade and has led to interesting results,[3-6] but preparative work was mainly directed toward the most stable representatives, which, however, are not usually the most active catalysts.[7,8]

In low-valent transition-metal complex catalysis group 4[9] alkyls (notably of Ti) and group 9[9] carbonyls (mostly those of Co and Rh) display important catalytic activity. In spite of the outstanding role of these metals, their combination in bimetallic compounds is very rare[10-12] and with the above-mentioned ligands is entirely lacking. This prompts us to report here[13] preliminary results on Ti–Co and Zr–Co compounds bearing exclusively alkyl substituents on the group 4 metal and carbonyl ligands on the cobalt.

The preprative observations are summarized in Scheme I.[14-16] Tetrabenzyltitanium (**1a**) and -zirconium (**1b**) react cleanly with a stoichiometric amount of hydridocobalt tetracarbonyl (**2**) in nonpolar solvents at low temperature (−40 °C) to give the respective bimetallic product **5**. These products were obtained as very unstable red-brown crystals which, however, decomposed when the solvent was removed, even at low temperature. Thus they could be characterized only by spectroscopy and on the basis of their reactions. The formation of **5** and a strictly equivalent amount of toluene was monitored by ^{1}H NMR spectroscopy.

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(8) Reviews: (a) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207. (b) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: Oxford, **1982**; Vol. 6, Chapter 40, p 763. (c) Bruce, M. I. *J. Organomet. Chem.* **1983**, *257*, 417. (d) Bruce, M. I. *J. Organomet. Chem.* **1985**, *283*, 339.

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(14) Conditions of the reactions indicated in Scheme I: (i) **1**:**2** = 1:1; toluene (or toluene-d_8) or toluene/n-hexane (1:1); −40 °C; 2–10 min. The amount of toluene-h_8 formed in this reaction was measured by ^{1}H NMR (anisole internal standard): yield 100 ± 5%. ^{1}H NMR yield: **5a**, 100 ± 5%; **5b**, 90 ± 5%. Side reaction: decomposition of **2** to H_2 (GC, 0–5%) and $Co_2(CO)_8$ (IR 0–5%).[15a] (ii) **3**:**4** = 1:1; toluene or toluene/n-hexane (1:1); −40 °C; 4 h. Yield of **5** varied from 10 to 50%; the latter obtained at **3ac** + **4g**. (iii) **1**:**2** = 1:2 or **5**:**2** = 1:1; conditions as at (i). Yield (^{1}H NMR): **6a**, 85%; **6b**, 75%. (iv) **5**:PPh_3 = 1:1; toluene; 0 °C; 25 min; ^{1}H NMR yield: **7a**, 45%; **7b**, 35% (anisole internal standard). (v) **1**:$HCo(CO)_3PPh_3$ = 1:1; toluene, −40 to +25 °C; 10 min; ^{1}H NMR yield: 95–100% (anisole internal standard). (vi) Protolysis with water: **5**:H_2O = 1:5; toluene or toluene/n-hexane (1:1); −10 °C, 5 min. Yield (ir): ~100%.[15b] (vii) Solvolysis with Et_2O: **5**:Et_2O = 1:5; toluene or toluene/n-hexane (1:1); −10 °C; 5 min. Yield (IR): ~100%.[15b] (viii) Solvolysis with EtOH: **5**:EtOH = 1:5; toluene or toluene/n-hexane (1:1); −10 °C; 5 min. Yield (IR): ~100%.[15a]

(15) Determined by quantitative IR spectroscopy, using published data: [$Co_2(CO)_8$]: (a) Bor, G.; Bêlafi-Rêthy, K. *MÂFKI Közl. (Res. Rep.)* **1965**, *294*, 38. Bor, G.; Dietler, U. K.; Pino, P.; Poë, A. *J. Organomet. Chem.* **1978**, *154*, 301. [$HCo(CO)_4$]: (b) Bor, G.; Pâlyi, G., unpublished results.

(16) Characterization of the new compounds. **5a**: IR (ν(C–O), toluene/n-hexane (1:1)) 2067 s, 2013 m, 1982 vs, 1962 vs cm^{-1}; ^{1}H NMR (toluene-d_8, −40 °C) δ_1 3.34 (s, 6 H, benzyl-CH_2), δ_2 6.58 ([virtual] d, 6 H, ar-ortho-CH), δ_3 6.97 (m, 9 H, ar-meta- + ar-para-CH) Anal. Co:Ti ratio: calcd, 1.00; found, 1.03. **5b**: IR (ν(C–O), toluene/n-hexane (1:1)) 2065 s, 2006 m, 1963 vs, br cm^{-1}; ^{1}H NMR (toluene-d_8, −40 °C) δ_1 2.19 (s, 6 H, benzyl-CH_2), δ_2 6.26 ([virt.] d, 6 H, ar-ortho-CH), δ_3 7.05 (m, 9 H, ar-meta + ar-para-CH). The assignment of the structure is based on close similarities with IR[17] and ^{1}H NMR[18,19] spectra of compounds with analogous structural elements. Anal. Co:Zr ratio: calcd, 1.00; found, 1:01. **6a**: IR (ν(C–O), toluene/n-hexane (1:1)) 2092 w, 2073 m, 2051 s, 2036 vs cm^{-1}; ^{1}H NMR (toluene-d_8, −40 °C) δ_1 4.13 (s, 4 H, benzyl-CH_2), δ_2 6.96 (m, 10 H, ar-CH). Anal. Co:Ti ratio: calcd, 2.00; found, 1.99. **6b**: IR (ν(C–O), toluene/n-hexane (1:1)) 2099 w, 2076 m, 2052 vs, 2034 s cm^{-1}; ^{1}H NMR (toluene-d_8, −40 °C) δ_1 2.44 (s, 4 H, benzyl-CH_2), δ_2 7.00 (m, 10 H, ar-CH). Anal. Co:Zr ratio: calcd, 2.00; found, 1.99. Assignment of the structures is based on similarities with IR[20] and ^{1}H NMR[18,19] spectra of analogous compounds. **7a**: IR (ν(C–O), toluene/n-hexane (1:1)) 1997 m, 1948 s, 1932 vs cm^{-1}; ^{1}H NMR (toluene-d_8, 0 °C) δ_1 3.55 (s, 2 H, benzyl-CH_2), δ_2 6.75 (m, 20 H, ar-CH). Anal. Co:P:Ti ratio: calcd, 1.00:1.00:1.00. Found, 1.00:0.98:1.02. **7b**: IR (ν(C–O), toluene/n-hexane (1:1)) 1996 m, 1937 vs, 1925 vs cm^{-1}; ^{1}H NMR (toluene-d_8, 0 °C) δ_1 2.49 (s, 2 H, benzyl-CH_2), δ_2 7.3 (m, 20 H, ar-CH). Anal. Co:P:Zr ratio: calcd, 1.00:1.00:1.00; found, 1.00:0.93:0.98.

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The structure of compounds **5** can be deduced from the spectra. The IR ν(C–O) band patterns correspond to an $XCo(CO)_4$ (trigonal bipyramidal, with bulky axial X) type[17] complex. The quantitative[19] ^{1}H NMR provides proof for the signals for the M–Co bond,[18d,22] and the ortho/meta + para band separation hints at an η^4-type coordination of the benzyl groups[18] as in the starting compounds **1**.

Synthesis (i) utilizes the well-documented binuclear reductive elimination[23] route. Compounds **5** also could be synthetized by the salt elimination route (ii). This and reactions (iii)–(iv) can be regarded as further indirect proof for the structure of compounds **5**.

Perbenzyls **1** react with 2 molar equiv of **2** or compounds **5** with equimolar **2** to give the bis(tetracarbonylcobalt)-dibenzylmetal derivatives **6a** and **6b** (reaction (i) + (iii) or (iii) in scheme 1). The second cobalt carbonyl moiety can be introduced smoothly under very mild conditions,[14] but no sign of MCo_3 or MCo_4 products was observed using an up to tenfold excess of **2** or more forcing conditions.

Compounds **6** again were very unstable and could be characterized only by spectroscopic methods. The stoichiometry was determined by using quantitative IR[15] and ^{1}H NMR[19] which was facilitated by the fact that almost no byproducts (only some H_2 and $Co_2(CO)_8$) were formed. the IR spectra hint at a nearly linear array[20] of the CoMCo moiety in these complexes. Since the ortho-H signals in the ^{1}H NMR spectra of **6a** and **6b** are shifted into the rest of the aromatic resonance, no statement about the coordination type of the benzyl groups can be made.

^{1}H NMR analysis of solutions containing both of the corresponding **5**/**6** pairs enables us to gain information about the relative thermal stability of these compounds. Slowly warming such solutions from −40 to +25 °C within ~20 min results in decomposition of half of **5** and all of **6**. The rest of **5** disappears within 10–15 min at 25 °C.

Toluene solutions of complexes **5a** and **5b** react with PPh_3 at 0 °C yielding phosphine-substituted products **7a** and **7b** within a few minutes. These complexes could be obtained independently from tetrabenzyls **1a** and **1b** and $HCo(CO)_3PPh_3$ (**8**). Complexes **7a**,**b** also were very unstable and thus were characterized by IR and ^{1}H NMR spectroscopy[16,24] and elemental analysis. The formation (reaction (iv))[25] and spectroscopic behavior[26] of compounds **7** represent an additional piece of evidence for the supposed structure of compounds **5**.

The solvolytic reactions (vi)–(viii) are of two types. In protolyses[24] (vi) and (viii) the known oxophilic[25] nature of the group 4 metal leads to **2** as the primary product in both cases (and $Co_2(CO)_8$ is regarded only as a secondary product in (viii)). Solvolysis (vii) is expected to take a different reaction course. This is now under investigation, together with the metal-containing products of these reactions.

Beyond the chemical and spectroscopic evidence for the covalent bimetallic structure of compounds **5**, **6**, and **7**, comparison of the spectroscopic behavior of these complexes with literature data on more less associated ion pairs,[29,30a-c] CO-bridged complexes,[30d-g] or oligomeric species[30g] enables us to exclude these possibilities.

Our efforts to learn more about the very sensitive bimetallic complexes reported here are continuing.

Acknowledgment. Thanks are due to Prof. L. Markó (Veszprém) and Dr. V. Galamb (Tiszavasvári) for discussions. Cooperation in the spectroscopic and GC measurements by Drs. S. Iglewski, I. Ötvös, and Ms. K. Nagy-Perge is acknowledged. This research was in part supported by the Grant No. OTKA-1749 (1987–1989) of the Hungarian Academy of Sciences (G.P.).

Registry No. **1a**, 17520-19-3; **1b**, 24356-01-2; **2**, 16842-03-8; **3**, 18889-27-5; **4g**, 14878-26-3; **5a**, 117984-39-1; **5b**, 117984-40-4; **6a**, 117984-41-5; **6b**, 117984-42-6; **7a**, 117984-43-7; **7b**, 117984-44-8; **8**, 19537-79-2; $CO_2(CO)_8$, 10210-68-1.

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(19) Absolute signal intensities are given, determined by the anisole internal standard.

(20) {$Xe[CoCO)_4]_2$; X = Cl, Br; E = Ga, In}: ref 17 f. {$R_2E[Co(CO)_4]_2$; R = alkyl, aryl, Cl, Br; E = Si, Ge, Sn}: ref 17f,i. {$Hg[Co(CO)_4]_2$}: (a) Bor, G. *Spectrochim. Acta* **1963**, *19*, 2065. (b) Bor, G. *Inorg. Chim. Acta* **1969**, *3*, 196.

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