

of **2a** at -78°C in a sealed degassed solution of CD_2Cl_2 gave a thermally unstable intermediate identified as the η^5 -pentadienyl 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 -pentadienyl 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**. Rearrangement of **6** gives the η^5 -pentadienyl 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 pentadienyl complex as intermediates in the conversion. Further work concerning mechanistic studies and synthetic applications of this cyclization reaction are currently underway.

Acknowledgment. We thank Dr. J. Lay, Jr., at the National Center for Toxicological Research, Jefferson, AR, for the high-resolution mass spectroscopic data. N.T.A.

(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.; Muhlemaier, J.; Markl, R.; Dötz, K. H. *Chem. Ber.* 1982, 115, 1355. Dötz, K. H.; Muhlemaier, J. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 929.

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would like to thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for funding of this research.

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.

Benzyltitanium and -zirconium Cobalt Carbonyls. Preparation and Spectroscopic Characterization

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Received April 22, 1988

Summary: Tetrabenzyltitanium (**1a**) and -zirconium (**1b**) react with equimolar $\text{HCo}(\text{CO})_4$ (**2**) to give the corresponding tribenzylmetal-cobalt tetracarbonyl ($\text{M} = \text{Ti}$, **5a**; $\text{M} = \text{Zr}$, **5b**) derivatives. Compounds **5** also can be obtained from $(\text{PhCH}_2)_3\text{MX}$ ($\text{X} = \text{Cl}, \text{Br}$) compounds and $[\text{Co}(\text{CO})_4]^-$ salts, while complexes **6** are formed from equimolar **5** and **2**. Compounds **5** react with PPh_3 to give the substitution products $(\text{PhCH}_2)_3\text{M}[\text{Co}(\text{CO})_3(\text{PPh}_3)]$ ($\text{M} = \text{Ti}$, **7a**; $\text{M} = \text{Zr}$, **7b**), which also can be obtained from **1a** or **1b** and $\text{HCo}(\text{CO})_3(\text{PPh}_3)$. 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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The structure of compounds **5** can be deduced from the spectra. The IR $\nu(\text{C-O})$ band patterns correspond to an $\text{XCo}(\text{CO})_4$ (trigonal bipyramidal, with bulky axial X) type¹⁷ complex. The quantitative¹⁹ ^1H 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 groups¹⁸ as in the starting compounds **1**.

Synthesis (i) utilizes the well-documented binuclear reductive elimination²³ route. Compounds **5** also could be synthesized 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 IR¹⁵ and ^1H NMR¹⁹ which was facilitated by the fact that almost no byproducts (only some H_2 and $\text{Co}_2(\text{CO})_8$) were formed. The IR spectra hint at a nearly linear array²⁰ of the CoMCo moiety in these complexes. Since the ortho-H signals in the ^1H 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.

^1H 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 $+25^\circ\text{C}$ 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 $\text{HCo}(\text{CO})_3\text{PPh}_3$ (**8**). Complexes **7a,b** also were very

unstable and thus were characterized by IR and ^1H NMR spectroscopy^{16,24} and elemental analysis. The formation (reaction (iv))²⁵ and spectroscopic behavior²⁶ 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 protolyses²⁴ (vi) and (viii) the known oxophilic²⁵ nature of the group 4 metal leads to **2** as the primary product in both cases (and $\text{Co}_2(\text{CO})_8$ 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; $\text{Co}_2(\text{CO})_8$, 10210-68-1.

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