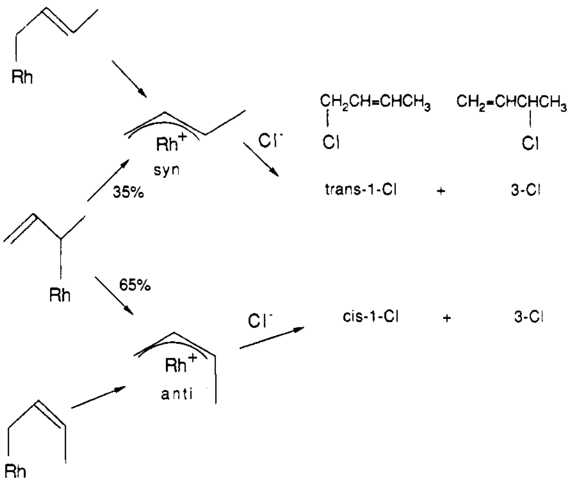
Scheme I



The regiochemical distribution of products (3-Cl/1-Cl) from $CH_3CH(COCl)CH{=}CH_2$ is consistent with that predicted from 3-Cl/1-Cl ratios from *trans*-$CH_3CH{=}CHCH_2COCl$ (50/1, via the *syn*-(η^3-1-methylallyl)Rh intermediate) and *cis*-$CH_3CH{=}CHCH_2COCl$ (2/1, via the *anti*-(η^3-1-methylallyl)Rh intermediate): $CH_3CH(COCl)CH{=}CH_2$ forms approximately 35/65 *syn-/anti*-(η^3-1-methylallyl)Rh intermediates to give the observed 3-Cl/1-Cl ratio of 3.5/1 (Scheme I).[23] Although we do not have the clear experimental cis/trans ratio in the 1-Cl product, the observation of more cis 1-Cl product is certainly consistent with the analysis.[23]

In summary, we have provided conclusive evidence that there cannot be any rearranged (η^1-allyl)Rh intermediates during the reaction in which the regiochemistry of chlorine is lost in the formation of allyl chlorides from β,γ-unsaturated acid chlorides. The observed 1,3-scrambling of chlorine is best explained by Cl^- attacks at the 1- and 3-positions of an (η^3-allyl)Rh^+ intermediate[24] to form the 1- and 3-chloro products. This conclusion may shed some light on the general question of (η^3-allyl)M vs (η^1-allyl)M as reactive intermediates in similar reactions of other (allyl)M systems. In addition, these results provide clear evidence that the formation of RCl from the decarbonylations of RCOCl in the so-called "reductive elimination" step is not a simple coupling of R,Cl from Rh, as has been indicated in a number of literature reports.[16b,29]

Acknowledgment is made to the University of Rochester for financial support and Johnson Matthey, Inc., for a generous loan of $RhCl_3$.

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[23] The 50/1 ratio of 3-Cl/trans-1-Cl products from *trans*-$CH_3CH{=}CHCH_2COCl$ must be the product distribution from the *syn*-(η^3-1-methylallyl)Rh^+ intermediate. Similarly, the 2/1 ratio of 3-Cl/cis-1-Cl products from *cis*-$CH_3CH{=}CHCH_2COCl$ must be the product distribution from the *anti*-(η^3-1-methylallyl)Rh^+ intermediate. However, $CH_3CH(COCl)CH{=}CH_2$ can form both *syn*- and *anti*-(η^3-1-methylallyl)Rh^+ intermediates. Partition between *syn*- and *anti*-(η^3-1-methylallyl)Rh^+ intermediates must lead to a product distribution between 50/1 and 2/1. It can be calculated that decarbonylations of $CH_3CH(COCl)CH{=}CH_2$ via 35/65 *syn-/anti*-(η^3-1-methylallyl)Rh^+ intermediates (35% is the upper limit for the syn intermediate) will give the observed 3.5/1 ratio of 3-Cl/1-Cl products. In addition, the cis/trans ratio in $CH_3CH{=}CHCH_2Cl$ should be approximately 31/1.

[24] The formation of a (η^3-allyl)Rh^+ intermediate in the rate-determining step suggests a way to understand the reactivity sequence we have observed. The rate of the product formation from decarbonylations of RCOCl follows the sequence

R = allyl > benzyl > methoxymethyl ≫ methyl ≫ vinyl, aryl[8,9,25]

Thus for allyl, benzyl, and methoxymethyl (substrates having electron pairs at β-positions), the ionization of chloride is much faster because of the participation and assistance of the electron pair. This proposal is also consistent with the fairly large negative entropy of activation (−12.2 eu) observed for the benzyl chloride formation step in the decarbonylation of phenylacetyl chloride.[9b] For methyl, vinyl, and aryl (substrates not having electron pairs at β-positions), the ionization of chloride is much slower. The formation of methyl chloride is faster than that of vinyl or aryl chlorides because the last two are poor substrates for nucleophilic substitutions.[26]

[25] Liu, T.-Z. Ph.D. Thesis, University of Rochester, 1989.

[26] (a) As reported in ref 8a, the rate of decomposition of $RhCl_2(CO)(styryl)(PPh_3)_2$ in the presence of excess PPh_3 is proportional to $k_2[PPh_3]/(k_{-1}[Cl^-] + k_2[PPh_3])$, where k_{-1} is the rate constant of Cl^- returning to $(Rh-R)^+$ at Rh and k_2 is the rate constant of nucleophilic attack by PPh_3 at carbon to form the decarbonylation product. In the absence of other nucleophiles, this term becomes $k_2/(k_{-1} + k_2)$. Vinyl and aryl are poor substrates for substitution reactions, so that k_2 is much smaller than k_2 for substitutions at methyl. Therefore, the overall rate of formation of methyl chloride is much greater than that of vinyl or aryl chloride. (b) Nucleophilic attacks of halide at the α-carbon in alkyl ligands in cationic metal complexes (preformed by oxidation of the corresponding neutral complexes) have been well-established in the literature.[27,28] Thus, it seems that nucleophilic substitutions of chloride at the α-carbon in metal–R complexes is common in cleavages of metal–carbon bond.

[27] (a) Sanderson, L. J.; Baird, M. C. *J. Organomet. Chem.* **1986**, *307*, C1–C4. (b) Rogers, W. N.; Page, J. N.; Baird, M. C. *Inorg. Chem.* **1981**, *20*, 3521–3528.

[28] Magnuson, R. H.; Halpern, J. *J. Chem. Soc., Chem. Commun.* **1978**, 44–46.

[29] Weinberg, E. L.; Baird, M. C. *J. Organomet. Chem.* **1979**, *179*, C61–C64.

Organometallic Clusters with Face-Capping Arene Ligands. 3.† [(β,α,1,2-η)-1-Vinylnaphthalene]cyclopentadienylcobalt and [μ_2-(1–3-η:4–6-η)-1,6-Diphenylhexatriene]bis(cyclopentadienylcobalt)(*Co*–*Co*): Model Compounds for Intermediates in the Synthesis of $(CpCo)_3[\mu_3\text{-}(\eta^2{:}\eta^2{:}\eta^2)\text{-arene}]$ Clusters

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Summary: Reaction of 1-phenylbuta-1,3-diene (**3a**), 1,4-diphenylbuta-1,3-diene (**3b**), and 1,6-diphenylhexa-1,3,5-triene (**5**) with $CpCo(C_2H_4)_2$ (**2**) results in the complexes $CpCo(\eta^4\text{-}CHR{=}CHCH{=}CHR')$ (R = H, R′ = Ph, **4a**; R = R′ = Ph, **4b**; R = Ph, R′ = CH=CHPh, **6**). **6** reacts further with **2** to give $(CpCo)_2[\mu_2$-(1–3-η:4–6-η)-1,6-diphenylhexatriene] (**7**) with a *syn*-$(CpCo)_2$[bis(enyl)] structure. From 1-vinylnaphthalene and **2** CpCo[(β,α,1,2-η)-1-vinylnaphthalene] (**11**) is obtained. **7** and **11** are model compounds for mono- and dinuclear intermediates in the synthesis of $(CpCo)_3[\mu_3\text{-}(\eta^2{:}\eta^2{:}\eta^2)\text{-arene}]$ clusters.

We have recently published a simple high yield synthetic route to a novel class of transition-metal clusters with face-capping arene ligands.[1] The compounds $(CpCo)_3[\mu_3\text{-}(\eta^2{:}\eta^2{:}\eta^2)\text{-arene}]$ [arene = α- and β-methylstyrene (**1a**,**b**), *o*-, *m*-, and *p*-methyl-β-methylstyrene (**1c**–**e**), stilbene (**1f**),

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† Part 2 of this series: Wadepohl, H.; Zhu, L. *J. Organomet. Chem.*, in press.

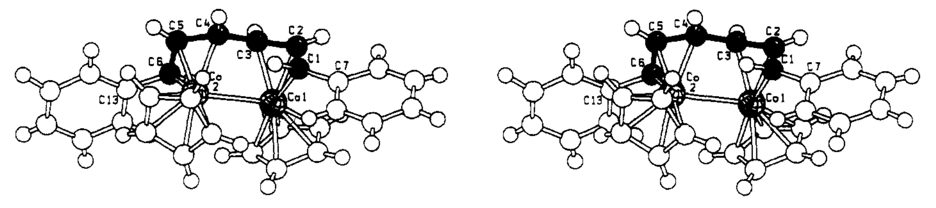
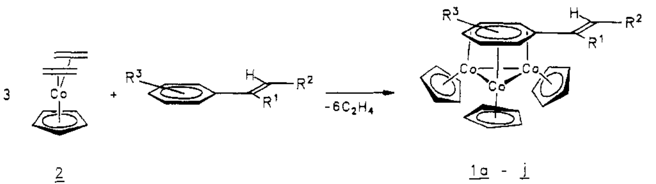


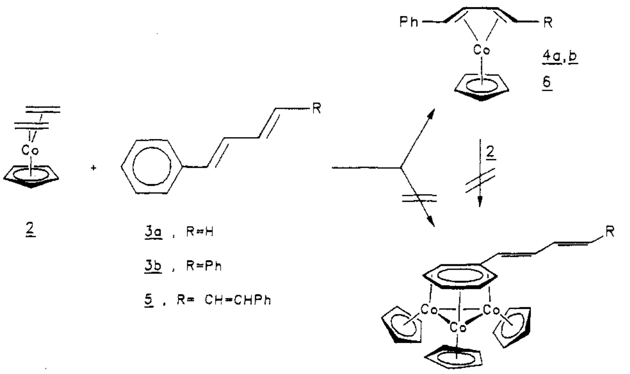
Figure 1. Molecular structure of **7**. Important bond lengths (A) and angles (deg) with estimated standard deviations in parentheses: Co1–Co2, 2.631 (1); Co1–C1, 2.091 (3); Co1–C2, 1.960 (4), Co1–C3, 2.026 (3); Co2–C4, 2.040 (3); Co2–C5, 1.963 (3); Co2–C6, 2.084 (3); C1–C2, 1.418 (5); C2–C3, 1.408 (5); C3–C4, 1.453 (5); C4–C5, 1.408 (5); C5–C6, 1.404 (5); Co1–C19···C23, 2.059 (4)···2.088 (5); Co2–C24···C28, 2.068 (3)···2.112 (4); C7–C1–C2, 124.6 (2); C1–C2–C3, 118.9 (2); C2–C3–C4, 122.4 (3); C3–C4–C5, 124.9 (3); C4–C5–C6, 119.9 (3); C5–C6–C13, 123.7 (3).

p-methoxystilbene (**1g**), 1,1-diphenylethene (**1h**), *p*-methylstyrene (**1i**), *p*-methoxystyrene (**1j**)] were prepared from $CpCo(C_2H_4)_2$ (**2**) and the corresponding ring and/or side chain substituted vinylbenzene ligands.[1] Allylbenzenes can be used in place of the latter and are catalytically isomerized to the propen-1-yl derivatives in a preequilibrium at ambient temperature. The double bond in the α-position to the arene ring is crucial for the formation of the μ_3-arene clusters, although it can easily be hydrogenated once the cluster has been formed.



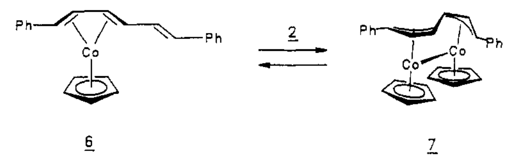
2 1a - j

From phenyl-substituted conjugated dienes and trienes we failed to obtain μ_3-arene complexes. Instead, the reaction of the butadienes (*E*)-PhCH=CHCH=CH$_2$ (**3a**) and (*E*,*E*)-PhCH=CHCH=CHPh (**3b**) with **2** led to the formation of the red η^4-butadiene complexes **4a**,**b** in high yields.[2] With excess **2** $H(CpCo)_4(\mu_3\text{-}CCH_3)$,[3] the thermal decomposition product of **2**, was formed in addition to **4**.



2 3a , R=H
3b , R=Ph
5 , R= CH=CHPh

4a,**b** were characterized by spectroscopic methods[4] and present no significant differences from other CpCo(η^4-butadiene) complexes.[5] Reaction of **2** and (*E*,*E*,*E*)-1,6-diphenyl-hexa-1,3,5-triene (**5**) in 1:1 stoichiometry gave the brown (1–4-η)-hexa-1,3,5-triene complex **6**.[6,7] Complex **6** cleanly reacted further with **2** to yield the dark red dinuclear $(CpCo)_2(\mu\text{-}Ph(CH)_6Ph)$ (**7**).[8] **7** could also be isolated from the reaction of **5** with 2 molar equiv of **2**.



6 7

NMR spectroscopic data[9] unambigously establish a symmetrically bridged structure in solution. The crystal structure[10] shows a twisted Ph(CH)$_6$Ph ligand[11] functioning as a six-electron donor via two η^3-enyl units (Figure 1). The μ_2-(η^3:η^3) coordination of the hexatriene is reflected

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(1) (a) Wadepohl, H.; Büchner, K.; Pritzkow, H. *Angew. Chem.* **1987**, *99*, 1294; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1259. (b) Wadepohl, H.; Büchner, K.; Pritzkow, H. XIII International Conference on Organometallic Chemistry, Torino, 1988, Abstract 159.

(2) Preparation of **4a**: in a typical experiment, 730 mg (4.06 mmol) of **2** and 530 mg (4.08 mmol) of **3a** were stirred in petroleum ether (bp 40–60 °C) at room temperature. After 4 h, the solvent was removed in vacuo and the deep red residue chromatographed on Al_2O_3/5% H_2O with petroleum ether/toluene (1:1): yield 820 mg (79%); mp 64 °C. Anal. Calcd for $C_{15}H_{15}Co$: C, 70.87, H, 5.95. Found: C, 70.52; H, 5.83. Preparation of **4b**: **4b** was obtained as a red powder from 1.07 g (5.94 mmol) **2** and 1.23 g (5.94 mmol) **3b** under the same conditions and recrystallized from petroleum ether (bp 40–60 °C): yield 1.37 g (70%); mp 202–204 °C.

(3) (a) Stella, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *New J. Chem.* **1988**, *12*, 621. (b) Wadepohl, H.; Pritzkow, H. *Polyhedron* **1989**, *8*, 1939.

(4) **4a**: ^{1}H NMR (200.1 MHz, C_6D_6) δ 7.24–6.99 (m, arene-H), 5.34 (dd, *J*(HH) = 4.8, 8.9 Hz, 1 H, H-2), 4.88 (m, 1 H, H-3), 4.36 (s, 5 H, Cp), 1.82 (ddd, *J*(HH) = 6.7, 1.7, 0.8 Hz, 1 H, H-4(exo)), 1.15 (dd, *J*(HH) = 8.9, 0.9 Hz, 1 H, H-1), –0.04 (ddd, *J*(HH) = 9.4, 1.7, 0.8 Hz, 1 H, H-4(endo)); $^{13}C\{^1H\}$ NMR (*J*-modulated spin echo, 50.3 MHz, C_6D_6) δ 146.4 (arene-C(ipso)), 128.8, 126.2, 124.6 (arene-CH), 81.1 (Cp), 78.1, 76.4 (C-2, C-3), 50.5 (C-1), 31.4 (CH_2). **4b**: ^{1}H NMR (200.1 MHz, C_6D_6) δ 7.30–7.01 (m, arene-H), 5.33 (m, 2 H, H-2/3), 4.15 (s, 5 H, Cp), 1.47 (m, 2 H, H-1/4); $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, multiplicity determination with DEPT spectra) δ 146.1 (arene-C(ipso)), 128.9, 126.4, 124.8 (arene-CH), 82.6 (Cp), 75.7 (C-2/3), 50.4 (C-1/4); MS (70 eV) *m/z* 330 (100%, M$^+$), 265 (15, $\{M - Cp\}^+$), 239 (10, $\{M - C_7H_7\}^+$), 202 (10, $\{M - C_{10}H_8\}^+$), 187 (5, $\{Cp_2Co - 2H\}^+$), 136 (10), 124 (30, $\{CpCo\}^+$).

(5) (a) Yamazaki, H.; Yasufuku, K.; Wakatsuki, Y. *Organometallics* **1983**, *2*, 726. (b) Binger, P.; Martin, T. R.; Benn, R.; Rufińska, A.; Schroth, G. *Z. Naturforsch.* **1984**, *39B*, 993.

(6) Preparation of **6**: a mixture of 650 mg (3.61 mmol) of **2** and 740 mg (3.19 mmol) of **5** in 60 mL of petroleum ether (bp 40–60 °C) was stirred at room temperature for 4 h. The brown precipitate was filtered off and recrystallized several times from toluene/petroleum ether (bp 40–60 °C): yield 820 mg (72%); mp 196 °C. Anal. Calcd for $C_{23}H_{21}Co$: C, 77.52; H, 5.94. Found: C, 77.89; H, 5.91.

(7) **6**: ^{1}H NMR (200.1 MHz, C_6D_6, assignment by $^1H^1H$ double resonance) δ 7.36–7.01 (arene-H), 6.57 (d, *J*(HH) = 15.8 Hz, H-6), 6.05 (dd, *J*(HH) = 15.7, 10.2 Hz, 1 H, H-5), 5.25 (dd, *J*(HH) = 4.8, 8.8 Hz, 1 H, H-2), 4.99 (dd, *J*(HH) = 4.9, 8.5 Hz, 1 H, H-3), 4.28 (s, 5 H, Cp), 1.48 (d, *J*(HH) = 8.7 Hz, 1 H, H-1), 1.48 (m, 1 H, H-4); $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6) δ 146.1, 139.2, 137.9, 136.9, 134.0, 133.1, 129.6, 129.1, 128.9, 128.3, 127.8, 126.8, 126.3, 125.7, 124.8 (arene-C, olefin-C), 82.1 (Cp), 77.5, 75.9 (C-2, C-3), 52.3, 50.4 (C-1, C-4); MS *m/z* 356 (15%, M$^+$), 289 (14), 232 (100, **5**$^+$), 153 (11), 141 (31), 128 (22), 117 (11), 115 (20), 91 (50, $\{C_7H_7\}^+$).

(8) Preparation of **7**: 940 mg (5.22 mmol) of **2** and 450 mg (1.94 mmol) of **5** were heated in 100 mL of petroleum ether (bp 40–60 °C) at 30 °C. A brown precipitate present after 1 h was identified as **6**. Further heating to 60 °C (1 h) resulted in a red solution and dark red precipitate. After 2 more hours at 60 °C the solid was filtered off and recrystallized from petroleum ether: yield 630 mg (68%), mp 158–160 °C. Anal. Calcd for $C_{28}H_{26}Co_2$: C, 70.01, H, 5.46. Found: C, 69.75; H, 5.37.

(9) **7**: ^{1}H NMR (200.1 MHz, C_6D_6) δ 7.55–7.04 (m, arene-H), 5.55 (m, 2 H, H-2/5), 4.53 (s, 10 H, Cp), 3.51 (m, 2 H, H-1/6), 2.24 (m, 2 H, H-3/4). A simulation of the $(AMX)_2$ spin system of the protons H-1 to H-6 with *J*(12) = *J*(56) = 11.3 Hz, *J*(23) = *J*(45) = 4.6 Hz, *J*(34) = 3.5 Hz, and all ^nJ(HH) $\approx$ 0 Hz (for $n > 3$) gave satisfactory agreement with the observed spectrum; ^{13}C NMR (50.3 MHz, C_6D_6) δ 146.4 (s, arene-C(ipso)), 129.3 (d, arene-C), 125.4 (d, arene-C), 124.5 (dt, arene-C), 81.2 (dquint, Cp), 76.8 (d, C-2/5), 51.3 and 40.8 (d, C-1/6,C-3/4); MS (70 eV) *m/z* 480 (2%, M$^+$), 356 (100, **6**$^+$), 291 (11), 290 (24), 289 (97, $\{7 - Cp_2Co - 2H\}^+$), 265 (14, $\{5 - C_7H_7\}^+$), 213 (14), 212 (13), 189 (12, $\{Cp_2Co\}^+$), 141 (11), 128 (11), 124 (34, $\{CpCo\}^+$), 115 (16), 91 (20, $\{C_7H_7\}^+$), 59 (34, Co$^+$).

Scheme I

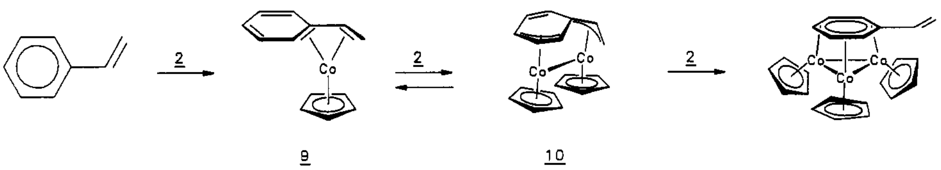


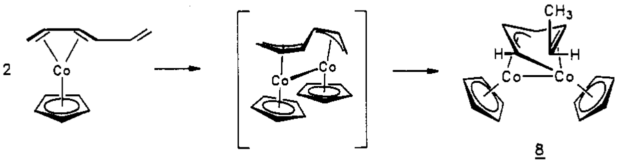
Table I. Details of the Crystal Structure Determination of [μ_2-(1–3-η:4–6-η)-1,6-Diphenylhexatriene)bis(cyclopentadienylcobalt)(*Co–Co*) (7)[a]

mol formula	$C_{28}H_{26}Co_2$
cryst size, mm	0.20 × 0.25 × 0.55
habitus	needle
cryst system	monoclinic
space group	$P2_1/a$
a, Å	7.375 (5)
b, Å	28.205 (17)
c, Å	10.385 (6)
β, deg	90.14 (5)
V, Å^3	2160
Z	4
M_r	480.38
d_{calcd}, g cm^{-1}	1.48
F_{000}	992
μ(Mo Kα), cm^{-1}	15.5
X-radiatn	Mo Kα; graphite monochromator
$2\theta_{min}$, $2\theta_{max}$, deg	3, 52
hkl range	±9,34,12
reflctns measd	4348
unique	4348
obsd	2956 [$I \geq 2\sigma(I)$]
abs correctn	numerical
T_{min},T_{max}	0.685, 0.751
parameters refined	375
R values	$R = 0.035$; $R_w = 0.026$ ($w = \sigma^{-2}(F)$)

[a] All calculations were performed by using SHELX-76 (Sheldrick, G. M. *SHELX-76 Program for Crystal Structure Determination*; Cambridge University, Cambridge, England, 1976). Scattering factors were those given by Cromer and Mann (Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1986**, *24*, 321).

in the carbon–carbon bond lengths along the chain: the central C3–C4 bond (1.45 Å) is significantly longer than the "allylic" bonds C2–C1/3 and C5–C4/6 (d(C–C)$_{mean}$ = 1.41 Å). A metal–metal bond (d(Co–Co) = 2.631 Å)[12] connects the CpCo moieties in syn positions with respect to the hexacarbon chain. Disregarding the phenyl groups the molecule very nearly has C_2 symmetry.

The analogous unsubstituted hexatriene complex was previously postulated[13] as an unstable intermediate in the formation of (CpCo)$_2$[μ_2-(1-σ:4,5-η:1–3-η)-hexa-2,4-diene-1,1-diyl] (8), a product of vinyl CH activation and 1,6-hydrogen shift of the former. In contrast, the highly substituted (CpCo)$_2$[μ_2-(1–3-η^3:4–6-η^3)-1,6-bis(alkoxycarbonyl)-2,3,4,5-tetraphenylhexa-1,3,5-triene], along with "flyover" type products (resulting from CH activation), was isolated from the reaction of CpCo(PPh$_3$)(PhC$_2$Ph) with alkyl diazoacetates.[14] A 1,6-anti,anti configuration (corresponding to a (Z,E,Z)-hexatriene) was assigned to the former on the basis of ^{1}H NMR data. Two other possible hypothetical isomers with 1,6-syn,syn and 1,6-syn,anti configurations of the bridging ligands ((E,E,E) and (E,E,Z)-hexatrienes) were suspected to have vinylic CH bonds directed to a cobalt atom, which supposedly made these complexes unstable with respect to CH activation.[14] In contrast, there are no close contacts between any hexatriene hydrogens and the cobalt atoms in the solid-state structure of 7, which has a 1,6-syn,syn (E,E,E) configuration of the hexatriene ligand.



In contrast to the synthesis of the first μ_3-arene cluster, namely, [(CO)$_3$Os]$_3$[μ_3-(η^2:η^2:η^2)-benzene],[15] where the μ_3-benzene was generated from a cluster-bound cyclohexadienyl ligand, the metal backbone of (CpCo)$_3$[μ_3-(η^2:η^2:η^2)-arene] (1) is assembled from mononuclear units at the template of the vinylbenzene. This reaction must proceed in a stepwise manner. We consider **9** and **10** as the likely candidates for the mono- and dinuclear intermediates (Scheme I).[16]

Loss of aromaticity and ring strain render **10** too unstable to be isolated. Consequently, its equilibrium concentration will be low. However, complex **7** can be regarded as a model compound for the dinuclear intermediate **10**. The hexacarbon chain, which is coordinated to a (CpCo)$_2$ backbone in μ-(η^3:η^3) fashion, is common for both **7** and **10**. Synfacial arrangement of the metal atoms, as it is forced by the metal–metal bond, is necessary for the formation of the μ_3-arene cluster **1** from **10**. An alternative μ-(β,α,1,2-η^4:3–6-η^4) coordination mode of the vinylbenzene in the dinuclear intermediate should result in an antifacial arrangement of the two metals, which then, in the course of further reaction with **2**, cannot form a trinuclear cluster.[17] In our model system, the equilibrium between **6** + **2** and **7** was established by the degradation of **7** with ethylene.[18]

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(10) Single crystals of 7 were obtained from petroleum ether at 20 °C. Crystal data for $C_{28}H_{28}Co_2$: monoclinic, space group $P2_1/a$; a = 7.375 (5), b = 28.205 (17), c = 10.385 (6) Å; β = 90.14 (5)°; = 2160 Å^3; Z = 4, μ = 15.5 cm^{-1}. Of the 4348 unique reflections collected (Stoe/Siemens four-circle diffractometer, Mo Kα, graphite monochromator, ω scan, 3° ≤ 2θ ≤ 52°) 2956 were considered observed ($I \geq 2\sigma(I)$, numerical absorption correction). The structure was solved with the heavy-atom method and refined by blocked matrix least squares (375 parameters, Co and C anisotropic, H isotropic): R = 0.035 and R_w = 0.026 ($w = \sigma^{-2}(F)$) (SHELX-76).

(11) Torsional angles along the μ_2-(η^3:η^3)-C$_6$ chain are as follows C7C1C2C3, 170.8°; C1C2C3C4, 35.8°; C2C3C4C5, −160.2°; C3C4C5C6, 33.3°; C4C5C6C13, 167.1°. In solution the twisted conformation of the bridging ligand is maintained: NOE difference spectra showed effects between the resonances for H-1/6 and H-2/5, H-1/6 and H-3/4, and H-2/5 and H-3/4 indicating spatial proximity of protons H-1 and H-2, H-1 and H-4, H-2 and H-3, and H-3 and H-6.

(12) The Co–Co bond is longer than those in hydrocarbyl-bridged "flyover" complexes but still within the range found in other bridged dicobalt complexes: Nesmeyanov, A. N.; Rybinskaya, M. I.; Rybin, L. V.; Kaganovich, V. S. *J. Organomet. Chem.* **1973**, *47*, 1. Holten, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. *Chem. Rev.* **1983**, *83*, 135 and references cited therein.

(13) King, J. A., Jr.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1983**, *105*, 4846.

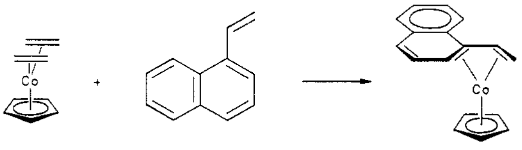
(14) Hong, P.; Aoki, K.; Yamazaki, H. *J. Organomet. Chem.* **1978**, *150*, 279.

(15) Gomez-Sal, M. P.; Johnson, B. F. G.; Lewis, J.; Paithby, P. R.; Wright, A. H. *J. Chem. Soc. Chem. Commun.* **1985**, 1682.

(16) For the sake of clarity, styrene is used in Scheme 1. However, in contrast to many ring or side chain substituted derivatives, from styrene and 2 only mononuclear products were obtained: Wadepohl, H.; Büchner, K., to be submitted for publication.

(17) "Envelope flip" isomerization of CpCo(η^4-diene) complexes was shown to involve exchange of exo and endo substituents at C1 and C4: Eaton, B.; King, J. A., Jr.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 1359. In a cyclic system, this path is not available.

A model compound for the postulated mononuclear intermediate 8 was obtained from 1-vinylnaphthalene and 2.[19] The green product was identified as CpCo[(β,α,1,2-η^4)-1-vinylnaphthalene] (11) on the basis of its NMR spectra[20] and preliminary X-ray crystallographic data.[21]



2

11

The β,α,1,2-η^4 and β,α,1,2-η^4:3–6-η^4 coordination modes are quite common in $(CO)_3Fe$(vinylbenzene) chemistry.[22] However, CpCo complexes like 8 or 11 are rare,[5,23] and to our knowledge, no $(CO)_3Fe$ analogues of 7 or 10, with a transoid μ-(η^3:η^3)-bis(enyl) coordination, have been reported.[24] This may be an explanation for the failure to synthesize $[(CO)_3Fe]_3(\mu_3\text{-arene})$ clusters, the $Fe_3(CO)_9$ analogues of 1.

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Registry No. 2, 69393-67-5; 3a, 16939-57-4; 3b, 538-81-8; 4a, 123074-39-5; 4b, 123074-38-4; 5, 17329-15-6; 6, 123074-40-8; 7, 123074-41-9; 11, 123074-42-0; Co, 7440-48-4; 1-vinylnaphthalene, 826-74-4.

Supplementary Material Available: Listings of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters (9 pages); a listing of observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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(18) Reaction of 7 with 1 bar of ethylene (petroleum ether (bp 40–60 °C), room temperature, 4 h) resulted in the formation of 6. 6, along with $H(CpCo)_4(CCH_3)$, was also obtained from the reaction of 7 (hexanes, 60 °C) with 2.

(19) Preparation of 11: 1.26 g (7.0 mmol) of 2 and 0.40 g (2.6 mmol) of 1-vinylnaphthalene were stirred in 60 mL of petroleum ether (bp 40–60 °C) at room temperature. After 3 h a dark gray solid was removed by filtration and a further 0.40 g of 1-vinylnaphthalene was added to the solution that was heated at 60 °C for 5 more hours. Cooling overnight to −20 °C resulted in the formation of dark green crystals that were separated from the mother liquor, washed with cold (−30 °C) petroleum ether, and dried in vacuo: yield 450 mg (31%) of dark green needles; slow decomposition at room temperature.

(20) 11: ^{1}H NMR (200.1 MHz, C_6D_6) δ 8.27–7.35 (m, H-5, H-6, H-7, H-8), 6.93 (m, 1 H, H-4), 6.78 (m, 1 H, H-3), 6.11 (m, 1 H, H-α), 4.16 (s, 5 H, Cp), 1.91 (d, J(HH) = 5.2 Hz, 1 H, H-β(exo)), 1.56 (d, J(HH) = 5.2 Hz, 1 H, H-2), −0.38 (d, J(HH) = 8.6 Hz, 1 H, H-β(endo); ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, multiplicity determination with DEPT spectra) δ 137.7 (d), 127.6 (d), 127.1 (d), 126.4 (d), 123.5 (d), 122.5 (d), 90.7 (s, C-1), 80.6 (d, Cp), 66.8 (d, C-α), 49.7 (d, C-2), 29.9 (t, C-β), the quaternary carbons 9 and 10 were not detected; MS (70 eV) m/z 278 (100, M^+), 211 (10), 189 (13, $\{Cp_2Co\}^+$), 154 (19, $\{M - CpCo\}^+$), 139 (6), 124 (65, $\{CpCo\}^+$), 59 (13, Co^+).

(21) Pritzkow, H., unpublished results.

(22) King, R. B. In *The Organic Chemistry of Iron*; Koerner v. Gustorf, E. A., Grevels, F.-W., Fischler, I., Eds.; Academic Press: New York, 1981; Vol. 2, and references cited therein.

(23) Lehmkuhl, H.; Nehl, H.; Benn, R.; Mynott, R. *Angew. Chem.* **1986**, *98*, 628; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 646.

(24) The isomeric (η^3:η^3-tetramethylenethane)$Fe_2(CO)_6$(*Fe–Fe*) is well-known,[22] as is the cisoid [(1–3-η:4–6-η)-cycloheptatriene)]$Fe_2(CO)_6$(*Fe–Fe*): Cotton, F. A.; DeBoer, B. G.; Marks, T. J. *J. Am. Chem. Soc.* **1971**, *93*, 5069. A mononuclear compound, $(CO)_2Fe$(dehydro-β-ionone), with a transoid η^3:η^3-hexatriene ligand has been reported: Franck-Neumann, M.; Heitz, M. P., Martina, D.; De Cian, A. *Tetrahedron Lett.* **1983**, *24*, 1611.

Book Reviews

Carbon Dioxide Activation by Metal Complexes. By Arno Behr. VCH Verlagsgesellschaft, Weinheim (FRG). 1988. 161 pages. $98.00. ISBN 0895-73826-0.

This book consists of four chapters surveying the organometallic chemistry of carbon dioxide. It has a subject index and is comprehensively documented with 800 references. Following two brief introductory chapters, the text is comprised of two major chapters: one (chapter 3) entitled “Stoichiometric Reactions of Carbon Dioxide on Transition Metal Centers” and a second (chapter 4) dealing with “Catalytic Reactions of Carbon Dioxide at Transition Metal Centers”.

Chapter 3 includes subheadings on the coordination chemistry of CO_2, insertion reactions of CO_2 with M–H, M–O, M–N, and M–C bonds, and oxidative coupling of cycloalkenes, cycloalkanes, monoenes, and 1,3-dienes with CO_2. This compendium is very representative of our current understanding of these processes. Nevertheless, most of what is covered in the text is extensively reviewed in the literature, as one might expect for a rapidly growing, topical research area. There is however much original information in this section, e.g., infrared, ^{1}H, ^{13}C, and ^{31}P NMR, and mass spectral data.

The final chapter (Chapter 4) deals with catalytic reactions of carbon dioxide with hydrogen, heterocycles, hydrocarbons, monoenes, 1,3-dienes, and butadiene. In this section many model catalytic processes are presented where the yield of products are very low. This can be a bit misleading to the casual reader.

Overall I found the book to be well produced and illustrated. The cost appears excessive for 160 pages. Notwithstanding, it is a book which should be in all libraries and on the shelves of those researchers and teachers interested in this *important* area of organometallic chemistry. Unfortunately, I purchased a copy of it prior to receiving one for review!

The direction of electron flow as indicated by the arrows on the illustration on the book’s cover are counterintuitive for the oxidative coupling of an alkene or alkyne to carbon dioxide.

Donald J. Darensbourg, *Texas A&M University*