Cobalt Carbene Complexes from (Butadiene)zirconocene and (Cyclopentadienyl)cobalt Carbonyls: An Example of a Nonnucleophilic Synthesis of Fischer-Type Carbene Complexes

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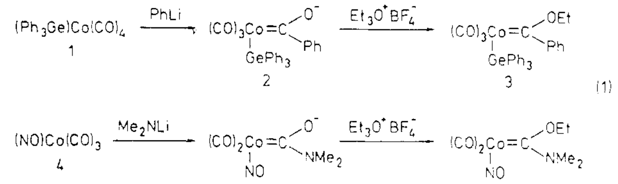
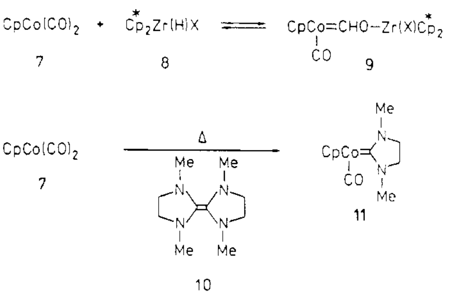
The (s-cis-/s-$trans$-η^4-butadiene)zirconocene equilibrium mixture (**17**/**15** = 55/45) reacts with $CpCo(CO)_2$ at ambient temperature to give the metallacyclic Fischer-type carbene complex $Cp_2\overline{Zr(C_4H_6)(O}C{=})Co(CO)Cp$, **20**. The ($s$-*trans*-diene)metallocene complex reacts much faster with the metal carbonyl than the more nucleophilic (s-cis-C_4H_6)$ZrCp_2$ isomer. The product of this nonnucleophilic carbene complex forming reaction, **20**, was characterized by X-ray diffraction. It crystallizes in the space group $P2_1/c$ with cell constants a = 7.824 (2), b = 15.753 (4), and c = 15.121 (3) Å and β = 99.26 (2)°. Complex **20** is characterized by a rather short Co–C(carbene) bond length of 1.815 (4) Å. At ambient temperature in solution **20** rapidly equilibrates with the starting components Cp_2Zr(butadiene) and $CpCo(CO)_2$. At equilibrium the carbene complex is favored by 85/15. Substitution of a Cl on the Cp ring of the CpCo moiety shifts the equilibrium ratio further to the side of the zirconoxycarbene complex: $(\eta^5\text{-}C_5H_5)_2\overline{Zr\text{-}(C_4H_6)(O}C{=})Co(CO)(\eta^5\text{-}C_5H_4Cl) \rightleftharpoons Cp_2Zr(\text{butadiene}) + (\eta^5\text{-}C_5H_4Cl)Co(CO)_2$ (>98/2).

The method originally developed by Fischer[1] has only in a few cases been successfully applied for the synthesis of mononuclear cobalt carbene complexes.[2] The classical two-step reaction sequence (addition of a nucleophile to the carbon atom of a coordinated CO ligand followed by electrophilic O-alkylation) obviously requires the formation of a sufficiently stabilized acylmetalate intermediate (for examples see eq 1).



(1)

In contrast to the $(CO)_3Co(L)$ moiety, the CpCo(L) fragment is far less suited for anion stabilization. Therefore, it is not surprising that the few known mononuclear carbene complexes employing the CpCo unit have been prepared by different synthetic routes.[3] Bercaw et al. have synthesized zirconoxycarbene complexes from $CpCo(CO)_2$ by using $Cp_2{}^*Zr(H)X$ reagents (X = Cl, F). This reaction sequence, like Fischer's, employs the addition of a nucleophilic reagent to the carbonyl carbon atom. However, this version of the nucleophilic carbonyl–carbene conversion very elegantly circumvents the possible anion stabilization problem by simply reversing the relative order of the nucleophilic and electrophilic reaction steps.[4] The formation of the zirconoxycarbene cobalt complex **9** is reversible, leading to a 70:30 **8**/$CpCo(CO)_2$ equilibrium mixture at ambient temperature. Lappert's synthesis of doubly heteroatom-stabilized carbene complexes by metal induced cleavage of an electron-rich tetramino olefin like **10** represents an example of a truly nonnucleophilic approach[5] toward a solution of this synthetic problem (eq 2).[6]



(2)

We have recently developed a novel procedure for the M–CO → M–carbene conversion[7] making use of the high

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[1] (a) Fischer, E. O.; Maasböl, A. *Angew. Chem.* **1964**, *76*, 645; *Chem. Ber.* **1967**, *100*, 2445. (b) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983.

[2] See, e.g. (a) Fischer, E. O.; Kreissl, F. R.; Winkler, E.; Kreiter, C. G. *Chem. Ber.* **1972**, *105*, 588. (b) Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1970**, *9*, 1691. (c) Carre, F.; Cerveau, G.; Colomer, E.; Corrin, R. J. P.; Young, J. C. *J. Organomet. Chem.* **1979**, *179*, 215. (d) Cerveau, G.; Colomer, E.; Corrin, R. J. P.; Young, J. C. *J. Organomet. Chem.* **1981**, *205*, 31. (e) Yamamoto, Y.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3691.

[3] (a) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278. (b) Macomber, D. W.; Rogers, R. D. *Organometallics* **1985**, *4*, 1485. (c) See however: Barger, P. T.; Bercaw, J. E. *J. Organomet. Chem.* **1980**, *201*, C39.

[4] Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218. Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178.

[5] (a) Lappert, M. F.; Pyl, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2172. (b) Coleman, A. W.; Hitchcock, P. B.; Lappert, M. F.; Maskell, R. K.; Müller, J. *J. Organomet. Chem.* **1983**, *250*, C9.

[6] For interesting different approaches see, e.g.: Singh, M. M.; Angelici, R. J. *Angew. Chem.* **1983**, *95*, 160; *Inorg. Chem.* **1984**, *23*, 2691, 2699. Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1986**, 514. Adams, H.; Bailey, N. A.; Cahill, P.; Rogers, D.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 831. Osborn, V. A.; Parker, C. A.; Winter, M. *J. Chem. Soc., Chem. Commun.* **1986**, 1185.

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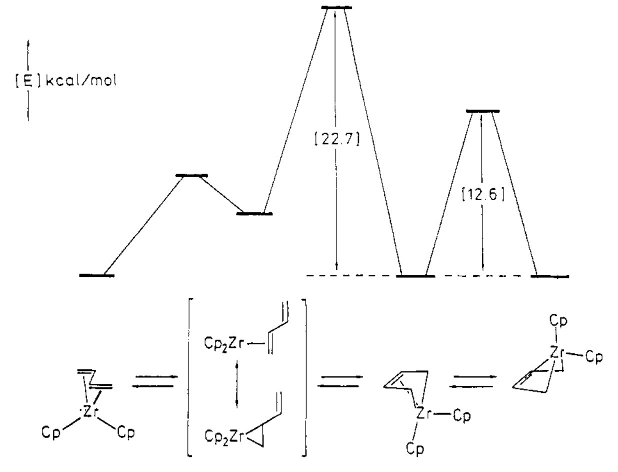
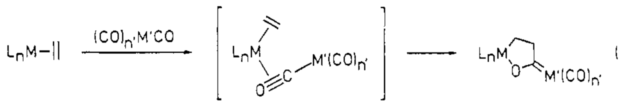
Scheme I. Qualitative Energy Profile of the (Butadiene)zirconocene System of Isomers



15 16 17

reactivity of certain (olefin)metallocene type complexes of titanium, zirconium, and hafnium.[8] These reagents react with a variety of metal carbonyls to yield metallacyclic metaloxycarbene complexes. Here the crucial carbon–carbon coupling process seems to lack the usual nucleophilic reaction characteristics. It presumably occurs during the course of a concerted electrocyclic (6π) ring closure reaction (eq 3).[9]



(3)

12 13 14

So far, reactive (η^2-diene)MCp_2 (M = Zr, Hf),[10] (η^2-aryne)MCp_2 (M = Ti, Zr),[11] and (η^2-ethylene)MCp_2^* (M = Ti)[12] complexes have successfully been used as starting materials for metal carbene synthesis. Our novel method has been employed in metal carbonyl → metal carbene conversions using carbonyl complexes of the transition elements zirconium and hafnium,[13] vanadium and niobium,[14] chromium, molybdenum, and tungsten,[7a,15,17] manganese and rhenium,[16,17] and iron.[7c] We have now used an analogous procedure to prepare (η^5-cyclopentadienyl)cobalt(I) carbene complexes from the reaction of a (cyclopentadienyl)cobalt dicarbonyl with (butadiene)$ZrCp_2$.

Results and Discussion

Synthesis and Spectroscopic Characterization of Cobalt Carbene Complexes. (η^4-Butadiene)zirconocene is unique among the transition-metal conjugated diene complexes as it allows the observation and use of two isoenergetic stable isomers at ambient temperature.[10,18] These isomers differ in the diene ligand geometry and can be described as (*s-trans-* and *s-cis-*η^4-butadiene)$ZrCp_2$, **15** and **17**, respectively. These isomers interconvert rather rapidly at room temperature (**15** → **17**: $\Delta G^\ddagger(10.5\ °C) = 22.7$ kcal/mol). Available evidence suggests that this intramolecular rearrangement process proceeds through a reactive (η^2-butadiene)$ZrCp_2$ intermediate, **16**.[9d,10,19] The energy profile for this process is depicted in Scheme I and is characterized by a rapid equilibration of the (*s-trans-*η^4-diene)metallocene, **15**, with the reactive (η^2-diene)MCp_2 intermediate **16** which in turn is protected from rapid rearrangement to the (*s-cis-*1,3-diene)zirconocene isomer **17** by a rather substantial energy barrier.[20]

The special shape of the diene metallocene energy profile allows an easy distinction between nucleophilic and cycloaddition routes for reactions with added reagents having reactive π systems. Under kinetic control, the preferred consumption of **15** relative to **17** has been taken as a strong indication for a reaction path proceeding through the reactive intermediate **16**. Such reaction characteristics have been observed upon treatment of the diene metallocene system with ketones.[9d] The same reaction path has been shown to be favored in the carbene complex synthesis according to eq 3 starting from (butadiene)$HfCp_2$.[7a] It also seems to be followed in the reaction of (cyclopentadienyl)cobalt dicarbonyl with (butadiene)zirconocene.

The (butadiene)zirconocene system reacts rapidly with $CpCo(CO)_2$ in toluene solution. Under kinetic control starting from a near to 1:1 mixture of the geometric (*s-cis-/s-trans-*C_4H_6)$ZrCp_2$ isomers, it is the (*s-trans-*η^4-butadiene)metallocene that has been shown by ^1H NMR measurements to react predominantly (if not exclusively) with the added cobalt carbonyl complex. In contrast, (*s-cis-*butadiene)$ZrCp_2$ is only consumed at a rate which allows equilibration with the more reactive isomer under the reaction conditions applied.

For a synthesis on a preparative scale we have reacted the (butadiene)zirconocene equilibrium mixture at room temperature (i.e. under conditions where the mutual **15** ⇌ **17** rearrangement is fast) with $CpCo(CO)_2$. Under these conditions rapid CC coupling of the carbonyl carbon atom of a coordinated CO ligand occurs with a terminal carbon center of the diene ligand. However, the expected primary product of the electrocyclic ring-closure reaction, the

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(7) (a) Erker, G.; Dorf, U.; Benn, R.; Reinhardt, R.-D.; Petersen, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 7649. (b) Erker, G.; Dorf, U.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1985**, *97*, 572. (c) Erker, G.; Lecht, R. *J. Organomet. Chem.* **1986**, *311*, 45.

(8) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Wiley: New York, 1986.

(9) For related reactions, see (a) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952. Skibbe, V.; Erker, G. *J. Organomet. Chem.* **1983**, *241*, 15. (b) Grevels, F.-W.; Schulz, D.; Koerner v. Gustorf, E. *Angew. Chem.* **1974**, *86*, 558. Grevels, F.-W.; Feldhoff, U.; Leitich, J.; Krüger, C. *J. Organomet. Chem.* **1976**, *118*, 79. (c) Kropp, K.; Erker, G. *Organometallics* **1982**, *1*, 1246; Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659. (d) Erker, G.; Engle, K.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1982**, *94*, 915, 916. Erker, G.; Engle, K.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1983**, *95*, 506. Erker, G.; Dorf, U. *Angew Chem.* **1983**, *95*, 800.

(10) Erker, G.; Wicher, J.; Engle, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344. Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1.

(11) Dvorak, J.; O'Brien, R. J.; Santo, W. *J. Chem. Soc. D* **1970**, 411. Masai, H.; Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 750. Berkovich, E. G.; Shur, V. B.; Vol'pin, M. E.; Lorenz, B.; Rummel, S.; Wahren, M. *Chem. Ber.* **1980**, *113*, 70; *J. Organomet. Chem.* **1982**, *228*, C36. Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189.

(12) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136.

(13) Dorf, U. Dissertation, University of Bochum, 1985.

(14) (a) Erker, G.; Lecht, R.; Schlund, R.; Krüger C. paper submitted for publication. (b) Erker, G.; Lecht, R., unpublished results.

(15) For corresponding thoriumoxycarbene complexes of these elements see: Erker, G.; Mühlenbernd, T.; Benn, R.; Rufinska, A. *Organometallics* **1986**, *5*, 402.

(16) Erker, G.; Lecht R., unpublished results.

(17) Mashima, K.; Jyodoi, K.; Ohyoshi, A.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1145.

(18) (a) Erker, G.; Engle, K.; Korek, U.; Czisch, P.; Berke, H.; Caubere, P.; Vanderese, P. *Organometallics* **1985**, *4*, 1531. (b) For a closely related system see: Hunter, A. D.; Legzdins, P.; Nurse, C. R.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1985**, *107*, 1791.

(19) Dorf, U.; Engel, K.; Erker, G. *Organometallics* **1983**, *2*, 462.

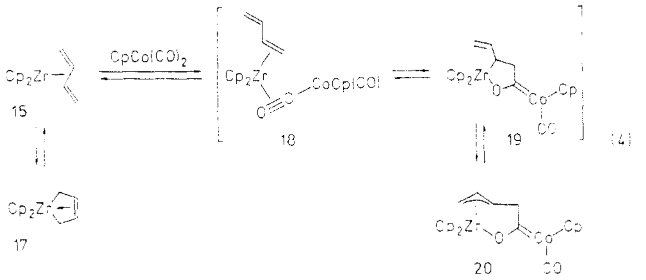
(20) The low barrier of the topomerization (i.e. ring inversion) of the five-membered metallacyclic framework indicates a substantial metal alkyl character for **17**: Krüger, C.; Müller, G.; Erker, G.; Dorf, U.; Engel, K. *Organometallics* **1985**, *4*, 215; and ref 10. See for a comparison: Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858. Hersh, W. H.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5834. Eaton, B.; King, J. A.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 1359, and references cited therein.

Table I. Comparison of Selected $^1H/^{13}C$ NMR Data of 20 and Analogously Structured Metallacyclic (π-Allyl)zirconoxycarbene Complexes $Cp_2\overline{Zr(C_4H_6)(O}C{=})ML_n$ Derived from Different Parent Metal Carbonyl Complexes[a,b]

ML_n	Cp_2Zr	H1a/s	H(2)	H(3)	H(4/4′)	C(carbon)	ref
Co(CO)Cp	5.42, 5.32	1.64, 1.63	4.92	4.56	3.82, 2.28	311.8	c
$Co(CO)(C_5H_4Cl)$	5.36, 5.28	1.59, 1.52	4.89	4.55	3.74, 2.23	311.9	c
$Cr(CO)_5$	5.26, 5.23	1.50, 1.49	4.91	4.53	4.20, 2.66	363.7	7a, 13
$Mo(CO)_5$	5.26, 5.22	1.50, 1.49	4.94	4.63	4.08, 2.54	359.7	7a, 13
$W(CO)_5$	5.24, 5.20	1.51, 1.48	4.94	4.56	4.01, 2.42	343.2	7a, 13
$Fe(CO)_4$	5.27, 5.22	1.52, 1.49	4.94	4.44	4.36, 2.89	344.4	7c
$Fe(CO)_3PPh_3$	5.40, 5.38	1.55, 1.50	5.04	4.72	4.83, 3.25	399.4	7c

[a] Atom numbering scheme as depicted in Figure 1. [b] NMR spectra in benzene-d_6, chemical shifts in ppm relative to Me_4Si, δ scale. [c] This work.

five-membered metallcyclic zirconoxycarbene complex **19**, is not stable under the reaction conditions. The σ-allyl zirconocene complex rapidly rearranges to the more stable metallacyclic π-allyl form **20**. We have isolated the zirconoxycarbene complex **20** of the cobalt carbonyl in about 50% yield by crystallization from toluene/pentane at −30 °C (eq 4).



NMR spectroscopy is a useful diagnostic tool for identifying the metallacyclic carbene complex formed in solution. CC coupling between butadiene carbon center C(4) and a cobalt-bound carbonyl ligand results in the formation of a chiral C-substituted (π-allyl)zirconocene group. For this unit the otherwise often observed allyl ($\pi \rightleftarrows \sigma \rightleftarrows \pi$) isomerization[9d,10] is slow on the NMR time scale. Therefore, the typical π-allyl resonances are observed in the ^1H and ^{13}C NMR spectra of **20** at ambient temperature. Diastereotopic Cp ligands at zirconium give rise to two easily distinguishable resonances in the ^1H (δ 5.42, 5.32) as well as the ^{13}C NMR spectrum. A comparison with analogous metallacylic π-allyl metaloxycarbene complexes derived from a variety of different metal carbonyls reveals that the large chemical shift difference of the protons at C(4) observed for **20** is very characteristic for this type of rigid metallacyclic framework. The carbene ^{13}C resonance is observed at δ 311.8 (Table I).

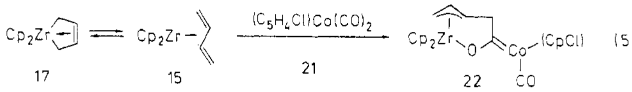
The IR spectrum of **20** reveals that the newly formed zirconoxycarbene ligand acts as a less efficient π acceptor than the remaining carbonyl ligand of the CpCo unit. The C–O stretching frequency in **20** (ν_{CO} = 1932 cm^{-1}) is substantially reduced as compared to the parent $CpCo(CO)_2$ system[3a] (ν_{CO} = 2022, 1960 cm^{-1} in benzene-d_6, compensated).

In solution, the formation of the zirconoxycarbene cobalt complex **20** is reversible. If crystalline **20** is dissolved in toluene-d_8 at ambient temperature, a practically instantaneous equilibration between the carbene complex and its components $CpCo(CO)_2$ and (butadiene)zirconocene is observed. As clearly seen by ^1H NMR spectroscopy reversal of the carbene complex formation by thermally induced CC rupture exclusively leads to the formation of the (*s-trans*-η^4-butadiene)zirconocene isomer **15**. The (*s-cis*-diene)$ZrCp_2$ isomer is only formed in a subsequent reaction which can easily be followed by ^1H NMR knowing the isomerization rate from earlier independent experiments.[10] Starting from pure **20** in toluene solution an equilibrium situation of about 85% zirconoxycarbene complex coexisting with 15% of a $CpCo(CO)_2$/(butadiene)$ZrCp_2$ 1:1 mixture is obtained.

Though far on the side of the carbene complex, this equilibrium might still be too unfavorable to allow a further synthetic use of the zirconoxycarbene complex. We have, therefore, sought for an easily performable way of shifting the reaction equilibrium further to the product side. This result can be achieved readily by the placing of an electron-withdrawing substituent on the η^5-cyclopentadienyl ring of the (cyclopentadienyl)cobalt carbonyl starting material. The replacement of one ring hydrogen by a chlorine substituent is sufficient to shift the equilibrium (within the limits of the standard ^1H NMR analysis) completely to the product side.

(η^5-C_5H_4Cl)$Co(CO)_2$ (**21**) was reacted with an equimolar amount of the (butadiene)$ZrCp_2$ equilibrium mixture in toluene solution at room temperature. After workup the metallacyclic zirconoxycarbene complex **22** was isolated in slightly less than 40% yield. ^1H NMR spectra of solutions of **22** in toluene-d_8 did not reveal any measurable concentration of **21** or **15**/**17** being in equilibrium with the carbene complex **22**.

The incorporation of the chlorine substituent within the cobalt-bound cyclopentadienyl ligand shifts the $Cp_2\overline{Zr(C_4H_6)(O}C{=})Co(CO)(\eta^5\text{-}C_5H_4R)/(\eta^5\text{-}C_5H_4R)Co(CO)_2$ equilibrium ratio from 85/15 (R = H) to >98/2 (R = Cl) (eq 5).



The NMR spectra of **22** are very similar to those of **20** ($^{13}C_{carbene}$(**22**): δ 311.9) except for the fact that the chiral substituted metallacyclic (π-allyl)$ZrCp_2$ structural subunit leads to the observation of two pairs of diastereotopic methine groups of the (η^5-C_5H_4Cl) moiety coordinated to the late transition metal in this mixed metal Fischer-type carbene complex (e.g. ^{13}C: δ 85.20, 85.16, 80.80, 80.72). In the IR spectrum (benzene-d_6 solution, compensated) **22** exhibits a CO band (ν_{CO} = 1935 cm^{-1}) at only a marginally higher wavenumber as compared to the "unsubstituted" analogue **20**.

Molecular Structure of 20. Crystals suited for a solid-state structure analysis were obtained upon recrystallization of **20** from toluene at −30 °C. The molecular structure of $(\eta^5\text{-}C_5H_5)_2\overline{Zr(C_4H_6)(O}C{=})Co(CO)(\eta^5\text{-}C_5H_5)$, **20**, has been determined by X-ray diffraction methods. A perspective view of the molecular configuration of this heterobimetallic compound is illustrated in Figure 1 with the non-hydrogen atom labeling scheme. The principal structural feature associated with **20** is the large zirconacyclic ring, which is formed presumably by carbon–carbon coupling of a coordinated carbonyl from (η^5-C_5H_5)$Co(CO)_2$

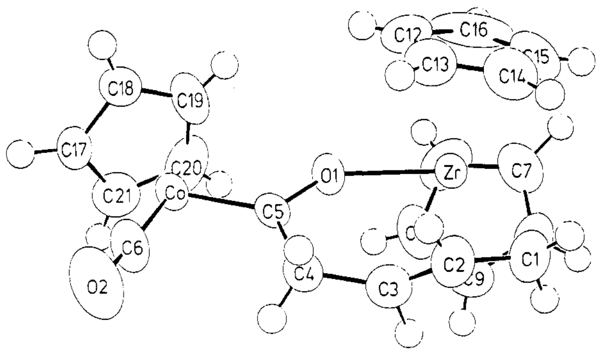


Figure 1. Perspective view of the molecular configuration of $(\eta^5\text{-}C_5H_5)_2Zr(C_4H_6)(OC{=})Co(CO)(\eta^5\text{-}C_5H_5)$ with atom labeling scheme for the non-hydrogen atoms. The thermal ellipsoids are scaled to enclose 50% probability. For clarity the radii of the spheres for the hydrogen atoms have been reduced arbitrarily.

with a coordinatively unsaturated $(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-butadiene})$ species. The resultant ring, shown in Figure 2 with pertinent bond distances and angles, binds to the zirconium atom via a substituted allyl unit and the oxygen of the coupled carbonyl. This mode of interaction is analogous to that previously observed for $(\eta^5\text{-}C_5H_5)_2Zr(C_4H_6)(OC{=})M(CO)_5$ (M = Cr, Mo, and W),[7a,13] which is prepared similarly by the electrocyclic ring-closure reaction of $M(CO)_6$ with (*s-cis*/*s-trans*-η^4-butadiene)zirconocene.

Like these metallacyclic zirconoxycarbene complexes **20** exhibits a characteristically distorted (η^3-allyl) unit bonded to the Cp_2Zr moiety. The pertinent bonding parameters of the $(allyl)ZrCp_2$ fragment in **20** indicate a substantial deviation from a symmetrical π-allyl ligand[21] toward a σ,π type bonding mode. The unsymmetrical nature of this interaction is clearly revealed by the corresponding Zr–C bond distances (Zr–C(1) = 2.423 (5), Zr–C(2) = 2.492 (5), Zr–C(3) = 2.614 (5) Å). Further, the greater interaction of Zr with C(1) and C(2) leads to a lengthening of the terminal C(1)–C(2) bond of 1.403 (7) Å as compared to the internal C(2)–C(3) bond of 1.304 (7) Å, which retains considerable double bond character. The zirconacycle is completed by a syn-oriented C(3)–C(4) linkage (1.477 (6) Å), a rather long C(4)–C(5) bond (1.543 (5) Å), and a C(5)–O(1) bond which still shows substantial double bond character (1.287 (4) Å). The remaining relatively long Zr–O(1) bond of 2.138 (2) Å is consistent with that expected for a Zr–O single bond[22] and is ca. 0.2 Å longer than those found for the seven-membered zirconacyclic products obtained from the corresponding coupling reactions of (butadiene)zirconocene with ketones.[9d,21c] The Zr–O interaction is further accompanied by a smaller Zr–O(1)–C(5) bond angle of 137.2 (2)°. By comparison, the corresponding Zr–O bond distances and Zr–O–C bond angles in $(\eta^5\text{-}C_5H_5)_2Zr(OC(C_6H_5)_2CH_2C(H){=}C(H)CH_2)$[9d] and $(\eta^5\text{-}C_5H_5)_2Zr(OC(i\text{-}C_3H_7)_2CH_2C(H){=}C(H)CH_2)$[21c] are 1.946 (4) Å, 150.5 (4)° and 1.961 (7) Å, 155.2 (7)°, respectively. The absence of any significant degree of multiple bond character for the Zr–O bond in **20** is most likely a consequence of the competitive π donation from the allyl moiety into the remaining equatorially directed metal orbitals of the canted zirconocene fragment.[23]

The Co–C(carbonyl) distances (Co–C(6) = 1.692 (4) and Co–C(5) = 1.815 (4) Å) are consistent with those expected for a Fischer-type carbene complex. However, comparison with $(CO)_3(GePh_3)Co{=}C(C_2H_5)OC_2H_5$ (Co–C(carbene) = 1.913 (11); C(carbene)–O = 1.289 (10) Å),[2d] $Cp(PhS)Co{=}C(C_4H_{10}N_2)$ (Co–C(carbene) = 1.902 (3) Å),[3b] and $(PPh_3)(CO)(NO)Co{=}C(C_5H_{12}N_2)$ (Co–C(carbene) = 1.974 (15) Å)[5b] indicates a pronounced metal to carbon π interaction for **20**. The metal to carbene carbon bond length found here appears to be the shortest so far observed for a Fischer-type cobalt carbene complex. It is in accord with the finding that the four substituents of the "Co–C(5)–π system" are all located in one plane. The maximum deviation of C(4), C(5), O(1), Co, C(6), and the Cp centroid from planarity is 0.15 (1) Å. Of the two geometric isomers possible for this arrangement, only the *E* isomer (exhibiting O(1) and the cobalt bound CO group trans to each other) has been observed in the crystal. The CC coupling produces nearly sp^2 hybridization about C(5) (C(4)–C(5)–O(1) = 111.5 (3), C(4)–C(5)–Co = 126.5 (2), O(1)–C(5)–Co = 122.0 (2)°) and is accompanied by a substantial lengthening of the O(1)–C(5) bond. The O(1)–C(5) bond of 1.287 (4) Å is ca. 0.12 Å longer than the corresponding O(2)–C(6) bond of 1.168 (5) Å of the remaining uncoupled carbonyl.

Conclusions

Fischer-type carbene complexes, $Cp_2Zr(C_4H_6)(OC{=})Co(CO)(\eta^5\text{-}C_5H_4R)$ (R = H, Cl), have been prepared by the coupling reaction of $Cp_2Zr(butadiene)$ with a late-transition-metal complex, $(\eta^5\text{-}C_5H_4R)Co(CO)_2$. Presumably, these complexes are formed in an essentially nonnucleophilic reaction sequence, possibly via carbon–carbon bond formation during the course of a concerted metallacyclic ring-closure reaction that subsequently involves a rapid σ-allyl $\rightleftarrows$ π-allyl interconversion.[24] The effectiveness of this coupling reaction for generating the desired carbene can be significantly enhanced by introducing an electron-withdrawing substituent at the cobalt Cp ligand. In $(\eta^5\text{-}C_5H_4Cl)Co(CO)_2$ the Cl substituent reduces the back-donating ability of the cobalt, as indicated by the increase of the CO stretching frequencies from 2028 and 1967 cm^{-1} in $CpCo(CO)_2$ to 2035 and 1980 cm^{-1} in $(\eta^5\text{-}C_5H_4Cl)Co(CO)_2$. This effect is less pronounced in the corresponding zirconoxycarbene complexes, **20** and **22**. In addition, the zirconoxycarbene group by being a poorer π-acceptor is expected to be less sensitive toward electronic destabilizing/stabilizing effects as compared to the carbonyl ligand. Therefore, the observed pronounced Cp-substituent effect on the product/reactant ratio at equilibrium may reflect a destabilizing effect on the educt rather than a stabilizing effect on the product side of this coupling reaction.

Experimental Section

All reactions were carried out in an inert atmosphere (argon) using Schlenk type glassware. Solvents were dried and freshly

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(21) (a) Brauer, D. J.; Krüger, C. *Organometallics* **1982**, *1*, 204, 207. (b) Highcock, W. J.; Mills, R. M.; Spencer, J. L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1986**, 829. (c) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Akita, M.; Yasuda, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3735. (d) Erker, G.; Berg, K.; Angermund, K.; Krüger, C., paper submitted for publication.

(22) Silver, M. E.; Chun, H. Y.; Fay, R. C. *Inorg. Chem.* **1982**, *21*, 3765. See also Erker, G.; Dorf, U.; Krüger, C.; Tsay, Y.-H. *Organometallics* **1987**, *6*, 680.

(23) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(24) Many examples of rapidly proceeding $\sigma \rightleftarrows \pi$-allyl ligand rearrangements at zirconium are known. See, e.g. Henc, B.; Jolly, P.; Salz, R.; Wilke, G.; Benn, R.; Hoffmann, E. G.; Mynott, R.; Schroth, G.; Seevogel, K.; Sekutowski, A.; Krüger, C. *J. Organomet. Chem.* **1980**, *191*, 425. Benn, R.; Rufinska, A.; Schroth, G. *J. Organomet. Chem.* **1981**, *217*, 91, and references cited therein. Hoffmann, E. G.; Kallweit, R.; Schroth, G.; Seevogel, K.; Stempfle, K.; Wilke, G. *J. Organomet. Chem.* **1975**, *97*, 183. Erker, G.; Berg, K.; Krüger, C.; Müller, G.; Angermund, K.; Benn, R.; Schroth, G. *Angew. Chem.* **1984**, *96*, 445. Erker, G.; Berg, K.; Benn, R.; Schroth, G. *Chem. Ber.* **1985**, *118*, 1383. Erker, G.; Berg, K.; Angermund, K.; Krüger, C., paper submitted for publication. Several additional examples can be found in ref 8.

distilled from potassium/benzophenone, lithium aluminum hydride, or P_4O_{10} (halogenated hydrocarbons) under argon prior to use. Deuteriated solvents benzene-d_6 and toluene-d_8 were treated with sodium/potassium alloy, distilled, and stored under argon. The following spectrometers were used for characterizing the compounds prepared: NMR, Bruker WP 80 FT (^{1}H, 80 MHz), AC-200 FT (^{1}H, 200 MHz, variable temperature), and WH 400 FT (^{1}H, 400 MHz, ^{13}C, 100.6 MHz); IR, Nicolet 7000 FT IR spectrometer. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr. Melting points are uncorrected. $CpCo(CO)_2$, $(\eta^5\text{-}C_5H_4Cl)Co(CO)_2$,[25] and Cp_2Zr(butadiene)[10] were prepared according to literature procedures.

Preparation of $(\eta^5\text{-}C_5H_5)_2Zr(C_4H_6)(OC{=})Co(CO)(\eta^5\text{-}C_5H_5)$ (20). A solution of 1.1 g (6.1 mmol) of $CpCo(CO)_2$ in 10 mL of toluene was added to a solution of 1.2 g (4.4 mmol) of the (*s-cis/s-trans*-η^4-butadiene)$ZrCp_2$ equilibrium mixture in 130 mL of toluene at room temperature over a period of 15 min. The mixture was stirred for 1.5 h. A small amount of an unidentified amorphous dark precipitate was removed by filtration. Then 15 mL of petroleum ether was added and the product **20** crystallized at −30 °C. Two fractions of red crystals were collected to give a combined yield of 1.02 g (51%) of the carbene complex **20** (mp 144 °C). Anal. Calcd for $C_{21}H_{21}O_2CoZr$ (455.57): C, 55.37; H, 4.65. Found: C, 55.44; H, 4.63. ^{1}H NMR (benzene-d_6, 400 MHz, ambient temperature, chemical shifts relative to Me_4Si, δ scale, numbering scheme as given in Figure 1): δ 5.42, 5.32 (s, each 5 H, Cp_2Zr), 4.95 (s, 5 H, CpCo), 1.64, 1.63 (m, 2 H, H1s/a), 2.28, 3.82 (dd each, 2 H, H4/4′), 4.56 (m, 1 H, H3), 4.92 (m, 1 H, H2); coupling constants (Hz), ^2J(H,H), 4.1 (H1s,H1a), −15.6 (H4,H4′); ^3J(H,H): 7.7 (H1s,H2), 14.4 (H1a,2), 15.4 (H2,H3), 10.5 (H3,H4′), 4.8 (H3,H4). ^{13}C NMR: δ 108.7, 108.2 (Cp_2Zr), 84.3 (CpCo), 43.6 (C(1)), 126.0 (C(2)), 112.1 (C(3)), 65.8 (C(4)), 311.8 (C(carbene)), C(CO) not observed. IR (benzene-d_6, compensated): ν 1932.6 cm^{-1}.

X-ray Data Collection and Structural Analysis of 20. A dark reddish orange crystal was wedged into a glass capillary tube under a prepurified N_2 atmosphere and sealed. The sample was transferred to a Picker goniostat that is computer controlled by a Krisel Control diffractometer automation system. Similar procedures to those described elsewhere[26] were employed to determine the lattice parameters for the monoclinic unit cell and the orientation matrix and to collect the X-ray diffraction data. The systematic absences of $\{0k0\}$, $k = 2n + 1$, and $\{h0l\}$, $l = 2n + 1$, uniquely determine the space group as $P2_1/c$ (No. 14, C_{2h}^5). Duplicate reflections, which had been corrected for crystal decay, absorption,[27] and Lorentz-polarization effects were averaged to provide 3248 unique reflections with $F_o^2 > 0$ for the structural analysis. Further details regarding the refined lattice parameters and data collection procedure are summarized in Table II.

Table II. Data for X-ray Diffraction Analysis of $(\eta^5\text{-}C_5H_5)_2Zr(C_4H_6)(OC{=})Co(CO)(\eta^5\text{-}C_5H_5)$

A. Crystal Data	
crystal system	monoclinic
space group	$P2_1/c$ (No. 14, C_{2h}^5)
a, Å	7.824 (2)
b, Å	15.753 (4)
c, Å	15.121 (3)
β, deg	99.26 (2)
V, Å^3	1839.4 (9)
fw, amu	455.57
d(calcd), g/cm^3	1.645
Z	4
μ, cm^{-1}	15.03
B. Data Collection and Analysis Summary	
crystal dimensions, mm	0.30 × 0.35 × 0.75
reflections sampled	$\pm hkl$
2θ range for centered reflections	$30° < 2\theta < 35°$
scan rate	2°/min
scan width, deg	$1.1 + 0.7 \tan\theta$
no. of standard reflections	3
% crystal decay	5%
total no. of measd reflections	3380
no. of unique data used	3248 ($F_o^2 > 0$)
agreement between equiv data	
$R_{av}(F_o)$	0.044
$R_{av}(F_o^2)$	0.072
transmission coefficients	0.60–0.66
P	0.03
discrepancy indices (for 2816 data with $F_o^2 > \sigma(F_o)$)	
$R(F_o)$	0.042
$R(F_o^2)$	0.056
$R_w(F_o^2)$	0.071
σ_1	1.40
no. of variables	310
data to parameter ratio	10.5:1

The initial positions for the Zr and Co atoms were determined from an interpretation of the Harker vectors of an unsharpened three-dimensional Patterson map. A subsequent Fourier summation provided approximate coordinates for the remaining non-hydrogen atoms. A difference Fourier calculation using only low-angle data with $(\sin\theta)/\lambda < 0.40$ Å^{-1} was used to locate all of the hydrogen atoms. Full-matrix least-squares refinement[28-32] (based on F_o^2) with anisotropic temperature factors for the 25 non-hydrogen atoms and isotropic temperature factors for the 21 hydrogen atoms converted with final discrepancy indices of $R(F_o) = 0.042$, $R(F_o^2) = 0.056$, $R_w(F_o^2) = 0.071$ with $\sigma_1 = 1.40$ for the 2816 data with $F_o^2 > \sigma(F_o^2)$. The maximum parameter shift to error ratio for any of the 310 varied parameters did not exceed 0.10 during the last refinement cycle. A final difference Fourier synthesis verified the completeness of the structural analysis.

The values for the refined positional parameters for all of the atoms are provided in Table III. The interatomic distances and bond angles and their estimated standard deviations for the non-hydrogen atoms are given in Table IV. Tables of the refined temperature factors, the carbon–hydrogen distances and angles, the pertinent least-squares planes and torsional angles, and the observed and calculated structure factors for $(\eta^5\text{-}C_5H_5)_2Zr(C_4H_6)(OC{=})Co(CO)(\eta^5\text{-}C_5H_5)$ are available as supplementary material.[33]

NMR Monitored Reaction of Cp_2Zr(butadiene) with $CpCo(CO)_2$. A solution of 40 mg (0.145 mmol) of the (*s-cis/s-trans*-η^4-butadiene)zirconocene equilibrium mixture in 0.8 mL of toluene-d_8 was transferred to a 5 mm diameter NMR tube and cooled to −78 °C. $CpCo(CO)_2$ (26 mg, 0.145 mmol) was added. The sealed tube was kept in the refrigerant until the first ^{1}H NMR spectrum was taken at ambient temperature immediately after mixing of the components and homogenizing of the reaction mixture by shaking the cold NMR tube. The reaction was followed by ^{1}H NMR (AC 200). Over a period of 3.5 h, nine ^{1}H NMR spectra of the changing mixture were recorded. The Cp_2Zr-

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[25] Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 165. Conway, B. G.; Rausch, M. D. *Organometallics* **1985**, *4*, 688.

[26] Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889.

[27] The absorption correction was performed with the use of the general polyhedral-shape routine of the program DTALIB. The distance from the crystal center to each frace and the corresponding orientation angles (ϕ and χ) needed to place each face in diffracting position were provided to define the crystal's shape, size, and orientation with respect to the diffractometer's coordinate system.

[28] The least-squares refinement[29] of the X-ray diffraction data was based upon the minimization of $\sum\omega_i|F_o^2 - S^2F_c^2|^2$, where ω_i is the individual weighting factor and S is the scale factor. The discrepancy indices were calculated from the expressions $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$, $R(F_o^2) = \sum|F_o^2 - F_c^2|/\sum F_o^2$, and $R_w(F_o^2) = [\sum\omega_i|F_o^2 - F_c^2|^2/\sum\omega_i F_o^4]^{1/2}$. The standard deviation of an observation of unit weight, σ_1, equals $[\sum\omega_i|F_o^2 - F_c^2|/(n - p)]^{1/2}$, where n is the number of observations and p is the number of parameters varied during the last refinement cycle.

[29] The values of the atomic scattering factors in all of the structure factor calculations were those of Cromer and Mann[30] for the non-hydrogen atoms and those of Stewart et al.[31] for the hydrogen atoms. Corrections for anomalous dispersion[32] were also included.

[30] Cromer, D. T.; Mann, J. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 231.

[31] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[32] Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891.

[33] The computer programs that were employed during the X-ray structural analysis are described in: Nicholson, G. A.; Petersen, J. L.; McCormick, B. J. *Inorg. Chem.* **1980**, *19*, 195.

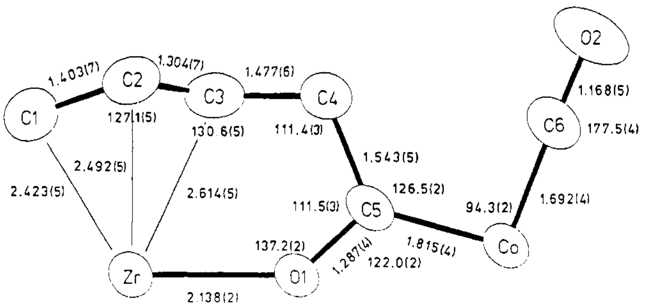

Figure 2. Pertinent interatomic distances and bond angles within the zirconacyclic ring of $(\eta^5\text{-}C_5H_5)_2\overline{Zr(C_4H_6)(O}C{=})Co(CO)(\eta^5\text{-}C_5H_5)$.

Table III. Positional Parameters for $(\eta^5\text{-}C_5H_5)_2\overline{Zr(C_4H_6)(O}C{=})Co(CO)(\eta^5\text{-}C_5H_5)$[a]

atom	*x*	*y*	*z*
Zr	0.16850 (4)	0.19867 (2)	0.00988 (2)
Co	0.40757 (6)	0.45776 (3)	0.15254 (3)
O1	0.2546 (3)	0.3181 (1)	0.0678 (2)
O2	0.7482 (4)	0.4408 (2)	0.2528 (3)
C1	0.3190 (6)	0.0675 (3)	0.0557 (4)
C2	0.4376 (6)	0.1309 (3)	0.0897 (4)
C3	0.4165 (6)	0.1895 (3)	0.1478 (3)
C4	0.5012 (6)	0.2729 (3)	0.1655 (3)
C5	0.3816 (4)	0.3458 (2)	0.1253 (2)
C6	0.6083 (5)	0.4460 (3)	0.2124 (3)
C7	−0.1437 (5)	0.1590 (4)	−0.0139 (4)
C8	−0.0711 (6)	0.1084 (3)	0.0555 (4)
C9	−0.0150 (6)	0.1581 (4)	0.1287 (4)
C10	−0.0531 (6)	0.2395 (4)	0.1074 (4)
C11	−0.1297 (6)	0.2431 (4)	0.0191 (5)
C12	0.2258 (10)	0.2893 (4)	−0.1178 (4)
C13	0.3621 (7)	0.2349 (4)	−0.1021 (3)
C14	0.3077 (9)	0.1557 (4)	−0.1244 (4)
C15	0.1351 (11)	0.1564 (5)	−0.1516 (4)
C16	0.0799 (9)	0.2408 (7)	−0.1489 (4)
C17	0.3748 (6)	0.5901 (2)	0.1564 (3)
C18	0.3545 (6)	0.5638 (3)	0.0673 (3)
C19	0.2174 (7)	0.5070 (3)	0.0548 (4)
C20	0.1530 (6)	0.4992 (3)	0.1359 (5)
C21	0.2488 (6)	0.5515 (3)	0.1982 (4)
H1	0.337 (6)	0.033 (3)	0.015 (3)
H2	0.240 (6)	0.043 (3)	0.100 (3)
H3	0.528 (7)	0.157 (4)	0.061 (4)
H4	0.327 (8)	0.161 (4)	0.196 (4)
H5	0.534 (6)	0.283 (3)	0.228 (4)
H6	0.588 (6)	0.272 (3)	0.138 (3)
H7	−0.199 (6)	0.136 (3)	−0.080 (3)
H8	−0.054 (5)	0.050 (3)	0.056 (3)
H9	0.032 (6)	0.142 (3)	0.183 (3)
H10	−0.029 (6)	0.282 (3)	0.140 (3)
H11	−0.161 (6)	0.286 (3)	−0.006 (3)
H12	0.232 (6)	0.339 (3)	−0.107 (3)
H13	0.480 (7)	0.245 (3)	−0.078 (3)
H14	0.376 (7)	0.101 (4)	−0.122 (4)
H15	0.084 (9)	0.111 (5)	−0.166 (4)
H16	−0.002 (5)	0.248 (3)	−0.160 (3)
H17	0.467 (5)	0.630 (3)	0.183 (3)
H18	0.430 (6)	0.582 (3)	0.027 (3)
H19	0.188 (7)	0.485 (3)	0.002 (3)
H20	0.067 (7)	0.469 (3)	0.147 (3)
H21	0.234 (5)	0.558 (3)	0.257 (3)

[a] The estimated standard deviations in parentheses for this and all subsequent tables refer to the least significant figures.

Table IV. Interatomic Distances (Å) and Bond Angles (deg) for Non-Hydrogen Atoms in $(\eta^5\text{-}C_5H_5)_2\overline{Zr(C_4H_6)(O}C{=})Co(CO)(\eta^5\text{-}C_5H_5)$[a,b]

A. Interatomic Distances			
Zr–C1	2.423 (5)	C1–C2	1.403 (7)
Zr–C2	2.492 (5)	C2–C3	1.304 (7)
Zr–C3	2.614 (5)	C3–C4	1.477 (6)
Zr–O1	2.138 (2)	C4–C5	1.543 (5)
Zr–C7	2.491 (4)	O1–C5	1.287 (4)
Zr–C8	2.536 (5)	Co–C5	1.815 (4)
Zr–C9	2.555 (6)	Co–C6	1.692 (4)
Zr–C10	2.533 (6)	O2–C6	1.168 (5)
Zr–C11	2.461 (5)	Co–C17	2.102 (4)
Zr–C12	2.498 (6)	Co–C18	2.110 (4)
Zr–C13	2.513 (6)	Co–C19	2.072 (5)
Zr–C14	2.546 (7)	Co–C20	2.072 (5)
Zr–C15	2.504 (6)	Co–C21	2.115 (5)
Zr–C16	2.480 (6)	Co–Cp(3)	1.728 (5)
Zr–Cp(1)	2.228 (5)	C14–C15	1.347 (1)
Zr–Cp(2)	2.222 (6)	C15–C16	1.399 (14)
C7–C8	1.367 (7)	C16–C12	1.392 (11)
C8–C9	1.369 (8)	C17–C18	1.393 (6)
C9–C10	1.344 (9)	C18–C19	1.387 (7)
C10–C11	1.373 (9)	C19–C20	1.404 (10)
C11–C7	1.414 (8)	C20–C21	1.378 (8)
C12–C13	1.359 (9)	C21–C17	1.394 (7)
C13–C14	1.344 (9)		
B. Bond Angles			
Cp(1)–Zr–Cp(2)	130.0 (2)	C1–C2–C3	127.1 (5)
Zr–O1–C5	137.2 (2)	C2–C3–C4	130.6 (5)
C11–C7–C8	106.1 (5)	C3–C4–C5	111.4 (3)
C7–C8–C9	109.0 (5)	C4–C5–O1	111.5 (3)
C8–C9–C10	108.8 (5)	C4–C5–Co	126.5 (2)
C9–C10–C11	108.6 (5)	O1–C5–Co	122.0 (2)
C10–C11–C7	107.5 (5)	C5–Co–C6	94.3 (2)
C16–C12–C13	106.9 (6)	Co–C6–O2	177.5 (4)
C12–C13–C14	109.5 (6)	C21–C17–C18	109.3 (4)
C13–C14–C15	109.3 (6)	C17–C18–C19	106.8 (4)
C14–C15–C16	107.3 (7)	C18–C19–C20	108.4 (5)
C15–C16–C12	106.9 (6)	C19–C20–C21	108.3 (5)
		C20–C21–C17	107.3 (5)

[a] Cp(*n*) denotes the centroid of a cyclopentadienyl ring. [b] The esd's for the interatomic distances and bond angles were calculated from the standard errors of the fractional coordinates of the corresponding atomic positions.

$\overline{(C_4H_6)(O}C{=})CoCp(CO) \rightleftharpoons Cp_2Zr(butadiene) + CpCo(CO)_2$ equilibration was similarly followed by ^1H NMR starting from pure **20**.

Preparation of $(\eta^5\text{-}C_5H_5)_2\overline{Zr(C_4H_6)(O}C{=})Co(CO)(\eta^5\text{-}C_5H_4Cl)$ (22). To a solution of 0.82 g (3.0 mmol) of the (*s-cis*/*s-trans*-η^4-butadiene)$ZrCp_2$ equilibrium mixture in 100 mL of toluene were added 0.64 g (3.0 mmol) of $(\eta^5\text{-}C_5H_4Cl)Co(CO)_2$ at room temperature. The mixture was stirred for 2.5 h and then filtered from a small amount of an unidentified dark precipitate. The solution was concentrated in vacuo, petroleum ether was added, and the solution was again concentrated in vacuo (almost to dryness) to give 0.54 g (37%) of **22** (mp 71 °C). ^1H NMR (toluene-d_8, 400 MHz, ambient temperature): δ 5.36, 5.28 (s, 5 H each, Cp_2Zr), 4.94, 4.49 (m, 4 H, $(C_5H_4Cl)Co$), 1.59, 1.52 (m, 2 H, H1s,a), 2.23, 3.74 (dd, 1 H each, H4/4′), 4.55 (m, 1 H, H3), 4.89 (m, 1 H, H2); coupling constants (Hz), ^2J(H,H), 4.0 (H1s, H1a), −16.0 (H4,H4′); ^3J(H,H), 7.7 (H1s, H2), 14.4 (H1a, H2), 15.4 (H2, H3), 10.5 (H3, H4′), 4.8 (H3, H4). ^{13}C NMR: δ 108.8, 108.4 (Cp_2Zr), 85.20, 85.16, 80.80, 80.72 ($(C_5H_4Cl)Co$), 43.9 (C(1)), 126.8 (C(2)), 111.8 (C(3)), 64.9 (C(4)), 311.9 (C(carbene)). IR (benzene-d_6, compensated): ν 1935 cm^{-1}.

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Supplementary Material Available: Tables of temperature factors, hydrogen atom bond distances and angles, and least-squares planes and torsion angles for $(\eta^5\text{-}C_5H_5)_2\overline{Zr(C_4H_6)(O}\text{-}C{=})Co(CO)(\eta^5\text{-}C_5H_5)$ (4 pages); tables of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.