Journal of Organometallic Chemistry, *450* (1993) 137–143

JOM 23251

Carbonylation of 2-bornenyl(methyl)zirconocene

Gerhard Erker, Ralf Noe and Markus Albrecht

Organisch-Chemisches Institut der Universität Münster, Corrensstr. 40, W-4400 Münster (Germany)

Arnold L. Rheingold

Department of Chemistry, University of Delaware, Newark, DE 19716 (USA)

(Received August 24, 1992)

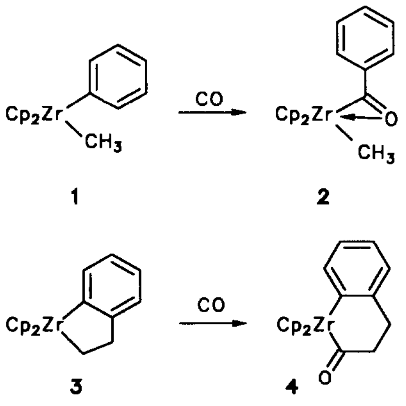
Abstract

The reaction of methylzirconocenechloride with 2-bornenyllithium yields (2-bornenyl)methylzirconocene (**10a**). Carbonylation of **10a** takes place exclusively by CO-insertion into the Zr–C(sp^2) bond to give $Cp_2ZrMe(\eta^2\text{-}OC\text{-}C_{10}H_{15})$ (**16a**). The corresponding hafnium complex **10b** reacts analogously to give **16b**. Complex **16a** was characterized by X-ray diffraction, and found to contain an η^2-acyl ligand bonded to zirconium in the thermodynamically favored "O-inside" arrangement with the following bonding parameters: d Zr–C(acyl) = 2.192(7) Å, d Zr–O(acyl) = 2.258(6) Å, d C=O = 1.246(9) Å, angles O(acyl)–Zr–C(acyl) = 32.5(2)°, Zr–C(acyl)–O(acyl) = 76.7(4)°.

1. Introduction

The insertion of carbon monoxide into transition metal to carbon σ-bonds is a fundamental organometallic reaction of great importance in many transformations of organic substrates catalyzed by metal complexes or mediated by the action of stoichiometric metal-containing reagents [1]. Mechanistically the "carbonyl insertion" reaction is in fact a 1,2-hydrocarbyl migration to a coordinated carbonyl ligand. For this step the migratory aptitude of σ-hydrocarbyl groups has been known experimentally for some systems. However, due to the complexity of the reaction paths followed it has not been possible to achieve this for many synthetically relevant metal complexes. Such systems often have mechanisms in which the σ-hydrocarbyl migration to coordinated CO is not the product-determining step [2]. In mechanistically interesting and sometimes synthetically important, competitive situations this may eventually result in some rather unexpected changes in the observed product selectivities. A typical example of this is the carbonylation of aryl(alkyl)zirconocene complexes; carbonyl insertion into the Zr–C(sp^2) bond is observed exclusively in the acyclic case (*e.g.* **1** → **2** in Scheme 1), whereas only the Zr–C(sp^3) bond undergoes CO insertion when an analogous metallacyclic starting material is employed (**3** → **4**) [3].

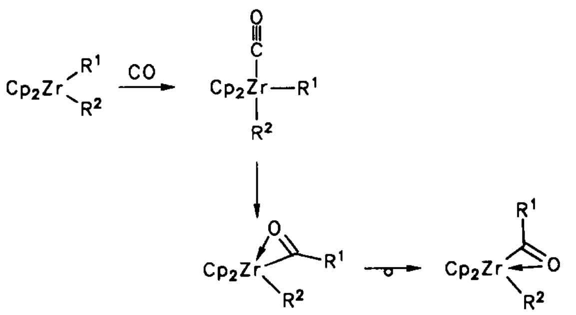
This crossover in carbonylation selectivity is a consequence of the specific reaction path followed in the carbonylation of these d^0-configured 16-electron early transition metal metallocene complexes. For several examples it has been established both theoretically and experimentally that CO adds to the $Cp_2ZrR^1R^2$ species in the σ-ligand plane from a lateral position to give an "O-outside" (acyl)metallocene complex, which may subsequently isomerize [4]. Thus, it is the carbonyl addition in this particular mechanistic scheme that



Scheme 1.

Correspondence to: Professor G. Erker.

0022-328X/93/$6.00



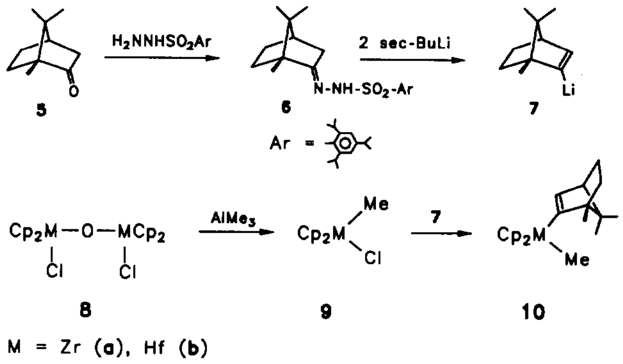
Scheme 2.

determines the selectivity of the product formation and not the intrinsic migratory aptitude of the σ-hydrocarbyl ligands involved.

Carbonyl insertion reactions exhibiting a sequential mechanistic pathway such as depicted in Scheme 2 are thus not expected to show selectivity patterns governed by the general σ-hydrocarbyl migratory aptitudes. For assessing selectivities in these rather special carbonylation reactions one apparently has to learn about the influence of various types of σ-hydrocarbyl ligands on the regioselective primary carbonyl addition step, the lateral preference of which is eventually preserved in the (η^2-acyl)metallocene predominantly formed in such an intramolecular competition in the carbonylation reaction. Group 4 alkenyl(alkyl)metallocene complexes would be especially interesting substrates in this respect since they allow competition between CO insertion into a Zr–C(sp^2) and a Zr–C(sp^3) σ-bond. Unfortunately, many alkenyl(alkyl)metallocenes are rather labile due to intramolecular (alkyne)metallocene formation [5] or intermolecular ligand coupling [6]. We have found that the use of the strained and bulky 2-bornenyl ligand improves the thermal stability of such d^0-/16-electron alkenyl(alkyl)metallocene complexes, and this has enabled us to investigate experimentally the favored carbonylation pathway in such systems.

2. Results and discussion

The σ-2-bornenyl ligand system was prepared from (+) camphor (**5**). Treatment with H_2NNHSO_2Ar (Ar = 2,4,6-triisopropylphenyl) gave the arylsulfonylhydrazone (**6**), which was converted by the Shapiro reaction under rigorously anhydrous conditions to give 2-bornenyllithium (**7**) [7]. The alkenyllithium reagent **7** was then treated with methylzirconocenechloride (**9a**) [8] in 1 : 1 stoichiometry to yield (2-bornenyl)methylzirconocene (**10a**), isolated in 94% yield. (2-Bornenyl)methylhafnocene (**10b**) was synthesized analogously.



The σ-alkenyl ligand in **10a** shows an olefinic ^{1}H NMR resonance at δ 5.45. The ^{13}C NMR signals of the Zr–C=CH moiety are δ 206.0 and 134.3. The =CH ^{13}C NMR resonance shows a ^1J(CH) coupling constant of 163 Hz. These NMR data can be compared with those for the relatively few examples of (alkenyl)zirconocene complexes whose structures are known from X-ray diffraction studies. These fall into two categories with regard to the bonding at the β-alkenyl carbon center. As can be seen from the selected data given in Table 1, it looks as if the (2-bornenyl)metallocene complexes do not possess the β C–H · · · M agostic interactions that are often present in such metal complexes with a

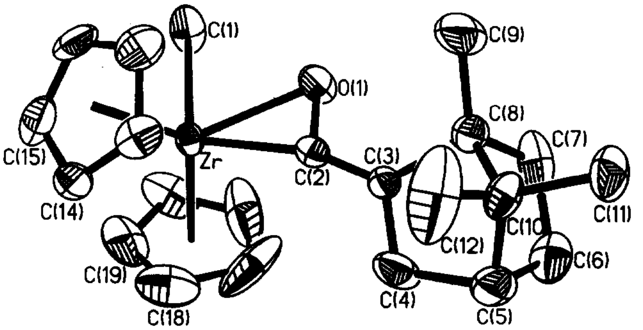


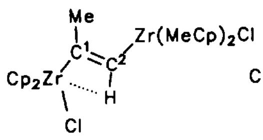
Fig. 1. A view of the molecular structure of the (η^2-acyl)zirconocene complex **16a**.

TABLE 1. Selected spectroscopic data for (alkenyl)zirconocene complexes $Cp_2MX(-C^1R{=}C^2HR')$

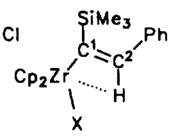
Compound	$\delta C^1 = (^{13}C)$	$\delta = C^2H$ ($^{13}C^a$, ^1H)	IR ν (C=C)	Ref.
10a	206.0	134.3 (163) 5.45	1600	[b]
10b	215.5	138.9 (163) 5.46	1597	[b]
11	215.4	124.1 (112) 8.33	1550	[9]
12a	206.8	113.3 (123) 8.59	–	[10]
12b	204.5	109.4 (120) 8.41	–	[10]
12c	198.7	104.1 (111) 7.85	–	[10]
13	205.4	143.9 (141) 7.90	–	[11]

[a] ^1J(CH) in parentheses. [b] This work.

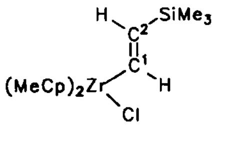
similar substitution pattern at the alkenyl unit [9–11]. The complexes for which a β-alkenyl CH $\cdots$ metal agostic interaction was demonstrated by X-ray diffraction all exhibit rather small $^1J(C^2\text{–}H)$ coupling constants of between 112 and 123 Hz at the distal alkenyl terminus. In contrast, the corresponding ^1J(CH) coupling constant for complexes **10** is very different, *viz.* 163 Hz. We conclude that there is probably an ordinary σ-alkenyl ligand present in complexes **10** which is only bonded to the early transition metal center through the alkenyl carbon center C^1 by an ordinary metal-to-carbon σ-bond.



11



12

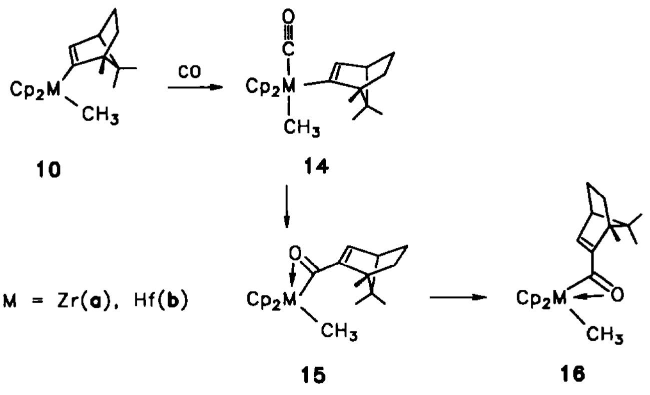


13

X = Cl(a),Br(b),I(c)

Complexes **10** must be regarded as coordinatively-unsaturated 16-electron bis(hydrocarbyl)metallocene complexes. As expected they react readily with carbon monoxide. At ambient temperature (σ-2-bornenyl)-methylzirconocene (**10**) takes up one molar equivalent of CO. Within the detection limits of the NMR analysis only a single reaction product is formed. The formation of this product is quantitative under the reaction conditions used. After the usual work-up and recrystallization this carbonylation product (**16a**) was isolated in 52% yield as an orange crystalline material.

Complex **16a** features the ^{13}C NMR signals of the alkenyl moiety at δ 161.0 [=CH, ^1J(CH) = 168 Hz] and 150.5 [C=]. The olefinic hydrogen ^{1}H NMR resonance is at δ 7.05. There are four ^{1}H/^{13}C NMR methyl resonances, at δ 1.28, 0.78, 0.62, 0.60/19.7 (^1J(CH) = 125 Hz), 18.8(125), 14.4(118), and 12.0(125). It is apparent that insertion of CO has only taken place into the Zr–C(sp^2) bond of the zirconium–(σ-2-bornenyl)linkage. We did not observe any indication of the presence of a zirconium-bound acetyl ligand in the carbonylation products obtained at various temperatures (−70°C to room temperature) starting from the alkenyl(methyl)metallocene complexes **10a** or **10b**.



Scheme 3.

The ^{13}C NMR spectrum of the carbonylation product **16a** shows an acyl–ligand resonance at δ 304.6. This is in a range [δ 390–250] typically observed for (η^2-acyl)metal complexes [4,12], *i.e.* for a situation where both the carbonyl carbon and the carbonyl oxygen center are bonded to the transition metal. The IR ν(C=O) of **16a** at 1569 cm^{-1} is compatible with the presence of a η^2-acyl functional group, although the η^1- and η^2-acetyl bands seem to overlap considerably in the IR spectra [13].

Complex **16a** was characterized by X-ray diffraction. It contains a bent metallocene unit with a Cp(centroid)–Zr–Cp(centroid) angle of 130.2°. In the Cp–Zr–Cp bisecting σ-plane there are a methyl group [d Zr–C(1) = 2.327(9) Å] and a η^2-acyl ligand. The CO insertion has thus taken place into the Zr–C(sp^2) bond of the zirconium bound alkene ligand of the starting material **10a**. The added carbon monoxide has formed a C(sp^2)–C(sp^2) linkage to the 2-bornenyl moiety [d C(2)–C(3) = 1.452(11) Å, angle C(2), C(3), C(4) = 122.1(8)°]. The remaining C=C double bond within the bornenyl system has a carbon–carbon distance of d C(3)–C(4) = 1.332(13) Å.

The characteristic structural feature of complex **16a** is the η^2-coordinated acyl group. Coordination of this unit to zirconium takes place through both the carbonyl carbon and carbonyl oxygen atoms. The resulting Zr,C,O three-membered ring system lies in the main

TABLE 2. Selected structural data of (η^2-acyl)zirconocene complexes [a]

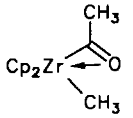
	Zr–C$_{acyl}$	Zr–O$_{acyl}$	C=O	Zr,C,O	Zr,O,C	C,Zr,O	Ref.
16a	2.192(7)	2.258(6)	1.246(9)	76.7(4)	70.8(4)	32.5(2)	[b]
17	2.197(6)	2.290(4)	1.211(8)	78.6(4)	70.2(4)	31.2(2)	[14]
18	2.183(3)	2.248(1)	1.244(3)	76.6(2)	70.9(1)	32.6(1)	[15]
19	2.189(3)	2.306(2)	1.226(3)	79.5(2)	69.0(2)	31.5(1)	[11]
20	2.192(4)	2.192(3)	1.302(5)	72.8(2)	72.7(2)	34.5(1)	[16]

[a] Bond lengths in Å and bond angles in degrees. [b] This work.

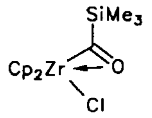
plane of the bent metallocene containing the σ-ligands. The Zr–O(acyl) bond is somewhat larger than the Zr–C(acyl) bond, as is often observed for (η^2-acyl)-zirconium complexes (see Table 2; complex **20** represents an exception to this rule, probably owing to its pronounced metallaoxirane character). The length of the C=O bond of the η^2-acyl moiety in complex **16a** is within the usual range for a carbon-to-oxygen double bond. Comparison with representative examples (Table 2) again reveals that this is a typical structural feature of (η^2-acyl)zirconocene complexes. The observed rather short Zr–C(acyl) distance in **16a** (and in analogous examples, see Table 2) is noteworthy. It probably indicates the presence of some Zr–C=O π-interaction normal to the σ-plane. A similar π-conjugation has recently been observed in dimetallic (η^2-alkene)zirconocene type complexes [17].

(η^2-Acyl)bis(cyclopentadienyl)zirconium(IV) systems can principally give rise to two stereoisomers. Both have the η^2-acyl ligand lying in the Cp–Zr–Cp bisecting major plane but differ in the relative orientation of the carbonyl oxygen to the remaining σ-ligand. The acyl group can be bonded with the oxygen adjacent to this ligand, and thus occupy the central position in the σ-ligand plane at the open side of the bent metallocene wedge ("O-inside" position), or it may be separated from the additional σ-ligand by the carbonyl carbon atom and have the carbonyl oxygen atom oriented laterally ("O-outside" position) [4]. The X-ray crystal structure analysis of complex **16a** shows that the isolated product has the carbon oxygen bonded in the central position, and the η^2-acyl group at zirconium is oriented in the "O-inside" arrangement, which is usually the thermodynamically favored of the two (η^2-acyl)zirconocene isomers [18].

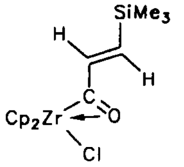
The carbonylation reactions of both the zirconium and hafnium complexes **10a,b** are highly regioselective. Within the detection limits of the analytical methods used we observed only carbonyl insertion into the metal–C(sp^2) linkage. In both cases the adjacent M–CH$_3$ bond remains untouched. As discussed above, this is probably not a consequence of the higher migratory aptitude of the C(sp^2) center in the actual hydrocarbyl migration to the coordinated carbonyl ligand. In terms of the assumed mechanism of the carbonylation reactions at the zirconocene backbone (see Scheme 2) the observed product selectivity is probably related to a high preference for lateral CO addition at zirconium at the coordination site adjacent to the alkenyl ligand. We conclude that this pathway seems to be favored even when the bulky 2-bornenyl ligand is employed.



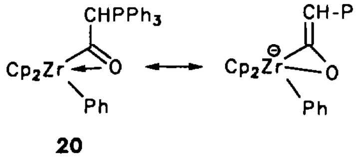
17



18



19



20

3. Experimental details

Organometallic compounds were prepared and handled under argon using Schlenk-type glassware or a glovebox. Solvents were dried and distilled prior to use. The following instruments were used for characterization: Bruker AC 200 P NMR spectrometer (^{1}H: 200 MHz; ^{13}C: 50 MHz), Nicolet 5DXC FT IR spectrometer, Gallenkamp melting point apparatus and Du Pont DSC 910, and Voss Heraeus CHNO rapid analyzer for elemental analysis. Camphor(2,4,6-triisopropylphenyl) sulfonylhydrazone **6** [7], methylzirconocenechloride **9a**, and methylhafnocenechloride **9b** [8] were prepared by published procedures.

3.1. Bornenyl(methyl)zirconocene (10a)

To a solution of 2.24 g (5.18 mmol) of camphor-(2,4,6-triisopropylphenyl)sulfonylhydrazone (**6**) in 80 ml of tetrahydrofuran was added dropwise at −78°C 8.0 ml (10.4 mmol) of a solution of sec-butyllithium in cyclohexane/n-hexane 92/8. After 1 h the mixture was warmed to 0°C, nitrogen being evolved. The mixture was recooled to −78°C, a solution of 1.41 g (5.18 mmol) methylzirconocenechloride (**9a**) in 20 ml tetrahydrofuran was added, and the mixture stirred for an additional hour. The mixture was allowed to warm to ambient temperature, the precipitate was filtered off, the solvent removed *in vacuo*, and 1.81 g (94%) of a yellow oil (**10a**) was isolated; this solidified over several weeks, m.p. 41°C (DSC). Anal. Found: C, 65.52; H, 7.79. $C_{21}H_{28}Zr$ (371.7) calc.: C, 67.86; H, 7.59%. ^{1}H NMR (benzene-d_6): δ 5.80 (s, 10H, Cp-H), 5.45 (d, ^3J 3.1, 1H, =CH), 2.16 (m, 1H, bridgehead CH), 1.87–1.74/1.55–1.18 (m, 4H, -CH_2- CH_2-), 1.02/0.97/0.80 (each: s, 3H, CH_3), 0.12 H(s, 3H, Zr-CH_3). ^{13}C NMR (benzene-d_6): δ 206.0 (Zr-C=), 134.3 (=CH, ^1J(CH) 163 Hz), 110.4/109.6 (Cp-C, 172 Hz), 60.7/56.6 ($C_{\text{quart.}}$), 54.1 (bridgehead CH, 145 Hz), 32.4 (Zr-CH$_3$, 118 Hz), 31.9 (130 Hz), 25.4 (each: CH$_2$, 131 Hz), 20.7/20.4/16.7 (each: CH$_3$, 123 Hz). IR (KBr): $\tilde{\nu}$

3091, 3023, 2988, 2945, 2918, 2862, 1798, 1701, 1600 (C=C), 1442, 1380, 1100, 1016, 800, 790, 744, 451 cm^{-1}.

3.2. *Bornenyl(methyl)hafnocene (**10b**)*

As in the preparation of **10a**, 1.08 g (2.50 mmol) arenesulfonylhydrazone (**6**) in 30 ml of tetrahydrofuran was treated with 3.9 ml of a solution of sec.-butyllithium (5.07 mmol) and the mixture treated with 896 mg (2.50 mmol) of methylhafnocene chloride (**9b**) to give 1.10 g (96%) of **10b** as a yellow oil, which partly solidified within weeks. Anal. Found: C, 54.03, H, 6.76. $C_{21}H_{28}Hf$ (458.9) calc.: C, 54.96; H, 6.15%. ^1H NMR (benzene-d_6): δ 5.76 (s, 10H, Cp–*H*), 5.46 (d, ^3J 3.0, 1H, =C*H*), 2.15 (m, 1H, bridgehead C*H*), 1.87–1.73/1.55–0.85 (m, 4H, CH_2–CH_2), 1.05/0.94/0.80 (each: s, 3H, CH_3), −0.09 (s, 3H, Hf–CH_3). ^{13}C NMR (benzene-d_6): δ 215.5 (Zr–C=), 138.9 (=*C*H, ^1J(CH) 163 Hz), 110.1/109.3 (Cp–*C*, 172 Hz), 61.1/56.6 ($C_{\text{quart.}}$), 54.3 (bridgehead *C*H, 140 Hz), 39.7 (Hf–CH_3, 115 Hz), 32.2/25.3 (each: CH_2), 20.7/20.5 (each: CH_3, 124 Hz), 16.8 (CH_3, 123 Hz). IR (KBr): $\tilde{\nu}$ 3100, 3037, 2960, 2929, 2866, 1597 (C=C), 1460, 1444, 1381, 1363, 1262, 1100, 1018, 803 cm^{-1}.

3.3. *Carbonylation of **10a***

A solution of **10a** (195 mg, 0.52 mmol) in 5 ml of pentane/CH_2Cl_2 (5 : 1) was treated for 2 h with carbon monoxide. Within minutes the color changed from yellow to orange. The concentrated solution was cooled to −30°C to give 110 mg (52%) of orange crystals of **16a** that were of suitable quality for an X-ray diffraction study, m.p. 141°C (DSC). Anal. Found: C, 64.50; H, 7.14. $C_{22}H_{28}OZr$ (339.7) calc.: C, 66.11; H, 7.14%. ^1H NMR (benzene-d_6): δ 7.05 (d, ^3J 3.4, 1H, =C*H*), 5.48/5.43 (each: s, 5H, Cp–*H*), 2.32 (m, 1H, bridgehead C*H*), 1.80–1.38/1.24–1.12/1.02–0.80 (m, CH_2–CH_2), 1.28/0.78/0.62/0.60 (each: s, 3H, CH_3). ^{13}C NMR (benzene-d_6) δ 304.6 (*C*=O), 161.0 (=*C*H, ^1J(CH) 168 Hz), 150.5 (=*C*–), 106.3 (Cp–*C*, 172 Hz), 57.5/54.2 ($C_{\text{quart.}}$), 53.7 (bridgehead *C*H, 149 Hz), 31.5 (133 Hz)/24.5 (134 Hz, both –CH_2–), 19.7 (CH_3, 125 Hz), 18.8 (CH_3, 125 Hz), 14.4 (Zr–CH_3, 118 Hz), 12.0 (CH_3, 125 Hz). IR (KBr): $\tilde{\nu}$ 3108, 2979, 2963, 2952, 2926, 2869, 2803, 1569 (C=O), 1482, 1263, 1104, 1017, 796 cm^{-1}.

3.4. *X-Ray crystallography of complex **16a***

A suitable crystal was mounted on a glass fiber with epoxy cement. Details of the data collection and refinement parameters are listed in Table 3. The unit-cell parameters were obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). The systematic absences in the diffraction data uniquely established the space group as $P2_12_12$. No correction for absorption was required (low μ, well-shaped crystal).

TABLE 3. Details of X-ray crystal structure analysis of **16a**, data collection, and structure solution

Crystal parameters	
Formula	$C_{22}H_{28}OZr$
Crystal system	orthorhombic
Space group	$P2_12_12$
a(Å)	13.687(6)
b(Å)	21.647(9)
c(Å)	6.816(2)
V(Å^3)	2019.8(13)
Z	4
$d_{\text{calc.}}$ (g cm^{-3})	1.312
μ (cm^{-1})	5.49
Size (mm)	0.26×0.36×0.47
Color	yellow
T (K)	299
Data collection	
Diffractometer	Siemens P4
Radiation	Mo Kα (λ 0.71073 Å)
Monochromator	graphite
Scan limits (°)	4 ≤ 2θ ≤ 54
Reflections collected	4720
Independent reflections	4414
Independent reflections, $F_o^2 \geqslant n\sigma F_o^2$	2809
Standard reflections	3 std/ 197 rflns
Decay	< 1%
Refinement	
$R(F)$ (%)	5.87
$R_w(F)$ (%)	6.85
GOF	1.00
Data/parameter	12.9
Δ/σ	0.001
$\Delta(\rho)$(e Å^{-3})	1.66

The structure was solved by direct methods, which located the Zr atom. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. All hydrogen atoms were included in calculated positions and refined isotropically (d(CH) = 0.960 Å, $U = 1.2U$ for attached C). All non-hydrogen atoms were refined with anisotropic thermal parameters. Positional parameters are listed in Table 4 and selected bond distances and angles in Table 5. All software and values of the scattering factors were from the SHELXTL PLUS (4.2) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Further details of the crystal structure investigation of compound **16a** are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD-56576, the names of the authors, and the journal citation.

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Zr	1537(1)	8624(1)	6244	36(1)
O(1)	1531(6)	8038(2)	8986(9)	62(2)
C(1)	1386(9)	9390(4)	8620(15)	73(4)
C(2)	1669(6)	7700(3)	7534(11)	38(3)
C(3)	1741(6)	7034(3)	7745(11)	37(3)
C(4)	2215(9)	6685(4)	6449(16)	69(4)
C(5)	2329(9)	6037(5)	7308(16)	70(4)
C(6)	3048(7)	6142(5)	9065(19)	75(4)
C(7)	2478(8)	6514(6)	10474(17)	79(5)
C(8)	1488(8)	6620(3)	9494(12)	46(3)
C(9)	681(10)	6840(5)	10772(19)	107(6)
C(10)	1343(6)	5994(3)	8422(15)	50(3)
C(11)	1272(7)	5440(4)	9832(15)	69(4)
C(12)	469(10)	5985(6)	7040(23)	131(8)
C(13)	108(7)	8060(5)	4742(15)	59(4)
C(14)	452(7)	8471(4)	3298(13)	54(3)
C(15)	271(8)	9067(5)	3962(20)	74(4)
C(16)	−174(8)	9038(6)	5749(16)	73(5)
C(17)	−272(7)	8420(5)	6288(23)	77(4)
C(18)	2798(10)	8537(8)	3587(25)	99(6)
C(19)	2687(9)	9134(7)	3867(23)	93(5)
C(20)	2989(10)	9305(8)	5655(19)	94(6)
C(21)	3357(10)	8792(10)	6481(27)	136(9)
C(22)	3234(12)	8292(7)	5335(40)	160(13)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.5. Carbonylation of **10a** at −78°C

A (yellow) solution of 30 mg of **10a** in 0.5 ml of toluene-d_8 was treated at −78°C with CO *via* a capillary for 2 h in an NMR-tube. Complex **16a** was the only product formed; ^{1}H-NMR (210 K): 6.81 (d, ^3J 3.2, 1H, =C–H), 5.40/5.34 (each: 5H, Cp–H), 2.10 (m, 1H, bridgehead CH), 1.7–1.3/0.9–0.75 (m, CH_2–CH_2), 1.32/0.74/0.71/0.55 (each: 3H, CH_3).

TABLE 5. Selected bond distances (Å) and angles (°) for **16a**

Zr–Cnt(1) [a]	2.225(11)	Zr–Cnt(2)	2.233(14)
Zr–C(1)	2.327(9)	Zr–O(1)	2.258(6)
Zr–C(2)	2.192(7)	C(2)–C(3)	1.452(11)
C(2)–O(1)	1.246(9)	C(3)–C(4)	1.332(13)
C(3)–C(8)	1.532(11)	C(4)–C(5)	1.528(14)
C(5)–C(6)	1.567(16)	C(5)–C(10)	1.550(15)
C(6)–C(7)	1.476(16)	C(7)–C(8)	1.527(15)
C(8)–C(9)	1.486(16)	C(8)–C(10)	1.552(11)
C(10)–C(11)	1.540(13)	C(10)–C(12)	1.523(17)
Cnt(1)–Zr–Cnt(2)	130.2(4)	Cnt(1)–Zr–C(1)	103.6(4)
Cnt(2)–Zr–C(1)	102.6(4)	Cnt(1)–Zr–O(1)	110.7(3)
Cnt(2)–Zr–O(1)	115.1(4)	Cnt(1)–Zr–C(2)	103.8(4)
Cnt(2)–Zr–C(2)	104.2(4)	C(1)–Zr–C(2)	112.2(3)
O(1)–Zr–C(2)	32.5(2)	O(1)–Zr–C(1)	79.8(3)
O(1)–C(2)–C(3)	121.0(7)	Zr–C(2)–O(1)	76.7(4)
Zr–C(2)–C(3)	162.0(6)	C(2)–C(3)–C(4)	122.1(8)
C(2)–C(3)–C(8)	130.1(7)	C(4)–C(3)–C(8)	107.1(7)
C(3)–C(4)–C(5)	108.4(9)	C(4)–C(5)–C(6)	103.0(8)
C(5)–C(6)–C(7)	104.1(8)	C(6)–C(7)–C(8)	105.4(9)
C(3)–C(8)–C(7)	103.2(8)	C(5)–C(10)–C(8)	93.8(7)

[a] Cnt(1) = centroid of atoms C(13) to C(17); Cnt(2) = centroid of atoms (C18) to C(22).

3.6. Carbonylation of **10b**

Carbonylation of 185 mg (0.40 mmol) of **10b** dissolved in 15 ml of toluene was carried out at ambient temperature for 2 h. The solvent was then removed and the orange product dried *in vacuo* to give 175 mg (92%) of **16b**, m.p. 104°C (DSC). The product was only characterized spectroscopically. ^{1}H NMR (benzene-d_6): δ 7.04 (d, ^3J 3.4, =CH), 5.43/5.39 (each: s, 5H, Cp–H), 2.31 (m, 1H, bridgehead CH), 1.80–1.65/1.53–1.42/1.20–0.90 (m, –CH_2–CH_2), 1.28/0.78/0.62/0.52 (each: s, 3H, CH_3). ^{13}C NMR (benzene-d_6): δ 314.6 (C=O), 160.7 (=CH, 168 Hz), 150.8 (=C–), 105.8 (Cp–C, 172 Hz), 57.5/54.3 ($C_{\text{quart.}}$), 53.6 (bridgehead CH, 145 Hz), 31.5 (133 Hz)/24.5 (134 Hz, each: –CH$_2$–), 19.7 (CH$_3$, 125 Hz), 18.8 (CH$_3$, 125 Hz), 17.3 (Hf–CH$_3$, 116 Hz), 12.1 (CH$_3$, 125 Hz), IR (KBr): $\tilde{\nu}$ 3100, 2979, 2962, 2925, 2871, 2810, 1569 (C=O), 1473, 1459, 1263, 1104, 1018, 801 cm^{-1}.

Acknowledgments

Financial support from the Fond der Chemischen Industrie, the Volkswagen-Stiftung, the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, and the Alfried Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged.

References

1 E. L. Muetterties and J. Stein, *Chem. Rev., 79* (1979) 479; C. K. Rofer-de Poorter, *Chem. Rev., 81* (1981) 447; J. Falbe (ed.), *New Syntheses with Carbon Monoxide*, Springer-Verlag, Heidelberg, 1980; A. Mortreux and F. Petit (eds.), *Industrial Applications of Homogeneous Catalysis*, Reidel, Dordrecht, 1988; W. Keim, *J. Organomet. Chem., 372* (1989) 15 and references cited therein; D. F. Shriver and M. J. Sailor, *Acc. Chem. Res., 21* (1988) 374 and references cited therein; P. L. Pauson, Cyclopentenone Formation from Alkyne–Cobalt Complexes in: A. de Meijere, H. tom Dieck (eds.), *Organometallics in Organic Synthesis*, Springer-Verlag, Berlin Heidelberg, 1988.

2 K. Noack and F. Calderazzo, *J. Organomet. Chem., 10* (1967) 101; A. Wojcicki, *Adv. Organomet. Chem., 11* (1973) 87; J. M. Manriquez, D. R. McAlister, R. D. Sanner and J. E. Bercaw, *J. Am. Chem. Soc., 100* (1978) 2716; P. T. Wolczanski and J. E. Bercaw, *Acc. Chem. Res., 13* (1980) 121; P. Hofmann, P. Stauffert, M. Frede and K. Tatsumi, *Chem. Ber., 122* (1989) 1559; D. M. Roddick and J. E. Bercaw, *Chem. Ber., 122* (1989) 1579; N. Koga and K. Morokuma, *Chem. Rev., 91* (1991) 823.

3 G. Erker and F. Rosenfeldt, *J. Organomet. Chem., 188* (1980) C1; G. Erker and K. Kropp, *J. Organomet. Chem., 194* (1980) 45.

4 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc., 98* (1976) 1729; K. Tatsumi, A. Nakamura, P. Hofmann, P. Stauffert and R. Hoffmann, *J. Am. Chem. Soc., 107* (1985) 4440; P. Hofmann,

P. Stauffert, K. Tatsumi, A. Nakamura and R. Hoffmann, *Organometallics, 4* (1985) 404; G. Erker and F. Rosenfeldt, *Angew. Chem., 90* (1978) 640; *Angew. Chem., Int. Ed. Engl., 17* (1978) 605; see also: G. Erker, U. Dorf, J. L. Atwood and W. E. Hunter, *J. Am. Chem. Soc., 108* (1986) 2251; G. Erker, R. Schlund and C. Krüger, *J. Chem. Soc., Chem. Commun.*, (1986) 1403; G. Erker, C. Krüger and R. Schlund, *Z. Naturforsch., 42b* (1987) 1009.

5 S. L. Buchwald, R. T. Lum and J. C. Dewan, *J. Am. Chem. Soc., 108* (1986) 7441; S. L. Buchwald, B. T. Watson and J. C. Huffmann, *J. Am. Chem. Soc., 109* (1987) 2544; T. Takahashi, D. R. Swanson and E.-I. Negishi, *Chem. Lett.*, (1987) 623; S. L. Buchwald and R. B. Nielsen, *Chem. Rev., 88* (1988) 1047 and references cited therein; P. Binger, P. Müller, R. Benn, A. Rufińska, B. Gabor, C. Krüger and P. Betz, *Chem. Ber., 122* (1989) 1035; S. L. Buchwald and R. B. Nielsen, *J. Am. Chem. Soc., 111* (1989) 2870.

6 P. Czisch, G. Erker, H.-G. Korth and R. Sustmann, *Organometallics, 3* (1984) 945.

7 A. R. Chamberlin, E. L. Liotta and F. T. Bond, *Org. Synth., 61* (1981) 141; G. Erker and A. A. H. van der Zeijden, *Angew. Chem., 102* (1990) 543; *Angew. Chem., Int. Ed. Engl., 29* (1990) 512, and references cited theirein.

8 P. C. Wailes and H. Weigold, *J. Organomet. Chem., 24* (1970) 405; J. R. Surtees, *J. Chem. Soc., Chem. Commun.*, (1965) 567.

9 G. Erker, W. Frömberg, K. Angermund, R. Schlund and C. Krüger, *J. Chem. Soc., Chem. Commun.*, (1986) 372.

10 G. Erker, R. Zwettler, C. Krüger, R. Schlund, I. Hyla-Kryspin and R. Gleiter, *J. Organomet. Chem., 346* (1988) C 15; I. Hyla-Kryspin, R. Gleiter, C. Krüger, R. Zwettler and G. Erker, *Organometallics, 9* (1990) 517; G. Erker, R. Zwettler, C. Krüger, I. Hyla-Kryspin and R. Gleiter, *Organometallics, 9* (1990) 524.

11 G. Erker, R. Schlund and C. Krüger, *Organometallics, 8* (1989) 2349.

12 F. R. Kreißl, W. J. Sieber, M. Wolfgruber and J. Riede, *Angew. Chem., 96* (1984) 618; *Angew. Chem., Int. Ed. Engl., 23* (1984) 640; P. V. Bonnesen, P. K. L. Yau and W. H. Hersh, *Organometallics, 6* (1987) 1587; H. I. Hayen, H. G. Alt and R. D. Rogers, *J. Organomet. Chem., 323* (1987) 339; S. Cai, D. M. Hoffman, D. Lappas, H.-G. Woo and J. C. Huffman, *Organometallics, 6* (1987) 2273; see also ref. [15].

13 G. Fachinetti, C. Floriani and H. Stoeckli-Evans, *J. Chem. Soc., Dalton Trans.*, (1977) 2297; W.-K. Wong, W. Tam, C. E. Strouse and J. A. Gladysz, *J. Chem. Soc., Chem. Commun.*, (1979) 530; J. A. Marsella, K. G. Moloy and K. G. Caulton, *J. Organomet. Chem., 201* (1980) 389; J. Schiemann and E. Weiss, *J. Organomet. Chem., 255* (1983) 179; K. G. Moloy and T. J. Marks, *J. Am. Chem. Soc., 106* (1984) 7051; G. S. Bristow, M. F. Lappert, T. R. Martin, J. L. Atwood and W. E. Hunter, *J. Chem. Soc., Dalton Trans.*, (1984) 399; S. Rosenberg, S. P. Lockledge and G. L. Geoffroy, *Organometallics, 5* (1986) 2517; A. R. Hermes and G. S. Girolami, *Organometallics, 7* (1988) 394; G. Cardaci, G. Bellachioma and P. Zanazzi, *Organometallics, 7* (1988) 172.

14 G. Fachinetti, G. Fochi and C. Floriani, *J. Chem. Soc., Dalton Trans.*, (1977) 1946.

15 B. K. Campion, J. Falk and T. D. Tilley, *J. Am. Chem. Soc., 109* (1987) 2049; see also: D. M. Roddick, R. H. Heyn and T. D. Tilley, *Organometallics, 8* (1989) 324.

16 G. Erker, U. Korek, R. Schlund and C. Krüger, *J. Organomet. Chem., 364* (1989) 133.

17 G. Erker, R. Zwettler, C. Krüger, R. Noe and S. Werner, *J. Am. Chem. Soc., 112* (1990) 9620; G. Erker, M. Albrecht, C. Krüger and S. Werner, *Organometallics, 10* (1991) 3791; G. Erker, *Comments Inorg. Chem., 13* (1992) 111.

18 For related examples containing other metals see *e.g.*: E. C. Guzman, G. Wilkinson, J. L. Atwood, R. D. Rogers, W. E. Hunter and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, (1978) 465; W. R. Roper, G. E. Taylor, J. M. Waters and L. J. Wright, *J. Organomet. Chem., 182* (1979) C46; U. Franke and E. Weiss, *J. Organomet. Chem., 165* (1979) 329; P. J. Fagan, J. M. Manriquez, T. J. Marks, V. W. Day, S. H. Vollmer and C. S. Day, *J. Am. Chem. Soc., 102* (1980) 5393; R. E. Cramer, R. B. Maynard, J. C. Paw and J. W. Gilje, *Organometallics, 1* (1982) 869; M. D. Curtis, K.-B. Shiu and W. M. Butler, *Organometallics, 2* (1983) 1475; F. Y. Petillon, J.-L. Le Quéré, F. Le Floch-Pérénnou, J.-E. Guerchais, M.-B. Gomes de Lima, L. J. Manojlović-Muir, K. W. Muir and D. W. A. Sharp, *J. Organomet. Chem., 255* (1984) 231; J. F. Harrod, A. Malek, F. D. Rochon and R. Melanson, *Organometallics, 6* (1987) 2117; M. M. Kubicki, R. Kergoat, H. Scordia, L. C. Gomes de Lima, J. E. Guerchais and P. L'Haridon, *J. Organomet. Chem., 340* (1988) 41; D. L. Reger, S. A. Klaeren, J. E. Babin and R. D. Adams, *Organometallics, 7* (1988) 181; see also refs. [12] and [13] and L. D. Durfee and I. P. Rothwell, *Chem. Rev., 88* (1988) 1059 and references cited therein.