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# *Articles*

## Isolable Zirconium(IV) Carbonyl Complexes. Synthesis and Characterization of $(C_5R_5)_2Zr(\eta^2\text{-}COCH_3)(CO)^+$ Species (R = Me, H)

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The synthesis and characterization of the first isolable terminal carbonyl complex of Zr(IV) is described. The reaction of $(C_5R_5)_2Zr(CH_3)(\mu\text{-}CH_3)B(C_6F_5)_3$ with CO yields the $\eta^2$-acyl carbonyl complexes $[(C_5R_5)_2Zr(\eta^2\text{-}COCH_3)(CO)][CH_3B(C_6F_5)_3]$ (**2**, R = Me; **3**, R = H). Complex **2** exists as a 9/1 mixture of "O-outside" (**2a**) and "O-inside" (**2b**) isomers which differ in the orientation of the $\eta^2$-acyl ligand. Analogous O-outside (**3a**) and O-inside (**3b**) isomers are observed for **3**, but the isomer preference is reversed (**3a**/**3b** = 1/5). The $\nu_{CO}$ values for the O-inside isomers **2b** (2152 cm$^{-1}$) and **3b** (2176 cm$^{-1}$) are higher than the free CO value, indicating that the Zr–CO bond is primarily $\sigma$-donor in character. The $\nu_{CO}$ values for the O-outside isomers **2a** (2105 cm$^{-1}$) and **3a** (2123 cm$^{-1}$) are slightly lower than the free CO value, as a result of overlap of a filled Zr–acyl bonding orbital and a CO $\pi^*$ orbital (i.e. $\sigma \rightarrow \pi^*$ back-bonding). **2a** can be isolated as a thermally stable solid; however, in $CH_2Cl_2$ solution both **2** and **3** lose CO under vacuum. **2a** has been characterized by single crystal X-ray diffraction: $a$ = 16.951(5) Å, $b$ = 10.642(4) Å, $c$ = 22.217(6) Å, $V$ = 4008(4) Å$^3$, $Z$ = 4 in space group, $Pca2_1$. Consistent with the $\nu_{CO}$ values, the C–O distance (1.13(1) Å) in the nearly linear carbonyl ligand (Zr–C–O angle 175.1(7)°) is not significantly perturbed from that in free CO. The Zr–$C_{CO}$ distance (2.25(1) Å) is consistent with the absence of significant Zr–C $\pi$-bonding.

### Introduction

Metal carbonyl chemistry is dominated by low valent metal CO complexes ($d^2$–$d^8$) in which $d \rightarrow \pi^*$ back-bonding contributes significantly to the M–CO bond strengths.[1] However, CO complexes of poorly back-bonding late transition metal ions, including Ag(I),[2] Au(I),[3] Pd(II), and Pt(II),[4,5] have also been prepared, in some cases only very recently. These "nonclassical" CO complexes typically exhibit $\nu_{CO}$ values which are higher than that of free CO (2143 cm$^{-1}$ gas phase), indicating that the M–CO bonds are primarily $\sigma$-donor in character, and that $d \rightarrow \pi^*$ back-bonding is minimal or absent.[6] Representative examples include $Ag(CO)B(OTeF_5)_4$ ($\nu_{CO}$ 2204 cm$^{-1}$) and *cis*-$PtCl_2(CO)_2$ ($\nu_{CO}$ 2179, 2136 cm$^{-1}$ in $C_2H_2Cl_4$).[7] The bonding in these complexes is comparable to that in CO adducts of main group Lewis acids, e.g. $H_3B$–CO ($\nu_{CO}$ 2165 cm$^{-1}$)[8] and $SnCl_2$–CO ($\nu_{CO}$ 2176 cm$^{-1}$).[9]

Electrophilic, high-oxidation state early transition metal species also might be expected to coordinate CO in a $\sigma$-donor only mode. However, despite the fact that $d^0$ early transition metal compounds play a key role in CO activation chemistry,[10] $d^0$ early metal carbonyl complexes are very rare. Known examples include the thermally unstable hydride and alkyl complexes $Cp^*_2M(H)_2(CO)$ ($Cp^* = C_5Me_5$; M = Zr, Hf; $\nu_{CO}$ 2044, 2036 cm$^{-1}$)[11] and $Cp_2Zr\{\eta^2\text{-}CH(Me)(6\text{-ethylpyrid-2-yl})\text{-}C,N\}(CO)^+$ ($\nu_{CO}$ 2095 cm$^{-1}$),[12] and an insoluble Ti(IV) species $\{[Cp_2Ti(CO)]_2\text{-}(\mu\text{-}(NC)_2C{=}C(CN)_2\}^{2+}TCNE^{2-}$ ($\nu_{CO}$ 2055 cm$^{-1}$).[13] The surprising *lowering* of the $\nu_{CO}$ values of these $d^0$ complexes below the free CO value has been ascribed to overlap of filled M—L $\sigma$ bonding orbitals with a CO $\pi^*$ orbital, i.e.

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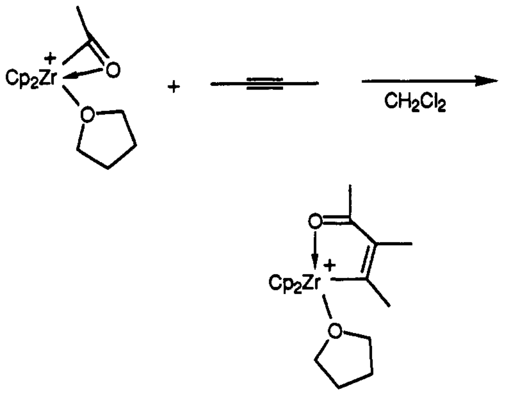
$\sigma \rightarrow \pi^*$ back-bonding.[14] For comparison, $\nu_{CO}$ values for related $d^1$ metal carbonyl species are in the same range, e.g. $Cp_2Ti(CO)Cl$ (2068 cm$^{-1}$),[15] $Cp_2Ti(C_6F_5)(CO)$ (2060 cm$^{-1}$), and $Cp^*{}_2Ti(CO)Cl$ (2000 cm$^{-1}$),[16] while values for $d^2$ species are considerably lower, e.g. $Cp^*{}_2Zr(CO)_2$ (1945, 1852 cm$^{-1}$) and $Cp^*{}_2Hf(CO)_2$ (1940, 1844 cm$^{-1}$).[17] Several other group 4 metal carbonyl compounds exist which have significant M(IV) character. X-ray diffraction and spectroscopic studies of $Cp_2Ti(CO)(PhCCPh)$ ($\nu_{CO}$ 1995 cm$^{-1}$) indicate that this species has substantial Ti(IV) metallacyclopropene character.[18] Similarly, reasonable M(IV) resonance structures can be written for the carbonyl aldehyde complexes $Cp^*{}_2M(CO)(\eta^2\text{-}O{=}CHCH_2CHMe_2)$ (M = Zr, Hf; $\nu_{CO}$ 1940, 1930 cm$^{-1}$),[19] although the $\nu_{CO}$ values are lower.[20] In general, these high valent group 4 metal CO complexes are labile and reactive, due to the lack of conventional $d \rightarrow \pi^*$ back-bonding and the correspondingly weak M—CO bonds, and the presence of alkyl or hydride ligands which undergo facile CO insertion. Studies of these systems are of fundamental importance for understanding how electrophilic metal centers activate unsaturated substrates and for designing new reactive electrophilic metal species.

During studies of the carbonylation chemistry of cationic $(C_5R_5)_2Zr(R)(L)^+$ complexes,[21,22] we discovered a family of surprisingly robust Zr(IV) terminal CO complexes. In this paper we describe synthetic, spectroscopic, and crystallographic studies of these novel species.

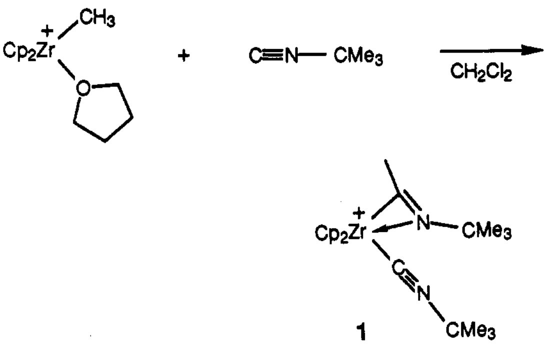
## Results and Discussion

**CO Inhibition of $Cp_2Zr(\eta^2\text{-}COR)(L)^+$ Alkyne Insertion Reactions.** We recently discovered that cationic Zr acyl complexes $[Cp_2Zr(\eta^2\text{-}COR)(THF)][BPh_4]$ undergo facile insertions of alkynes to afford chelated $\beta$-ketovinyl complexes.[23] During the course of this work, we made the surprising observation that added CO strongly inhibits these reactions. For example, $[Cp_2Zr(\eta^2\text{-}COCH_3)(THF)][BPh_4]$ reacts readily with 2-butyne in the absence of CO ($CD_2Cl_2$, 23 °C, 5 h) to yield $[Cp_2Zr\{\eta^2\text{-}C(CH_3){=}C(CH_3){=}C(CH_3)(COCH_3)\text{-}C,O\}(THF)][BPh_4]$ (100%, eq 1). However, in the presence of 1 atm of CO, only trace amounts of this product are formed after 24 h under otherwise identical conditions. One possible explanation for this dramatic inhibition is that CO competes with 2-butyne for the coordination site on Zr; i.e. that formation of a CO adduct $Cp_2Zr(\eta^2\text{-}COCH_3)(CO)^+$ is favored over formation of the 2-butyne adduct $Cp_2Zr(\eta^2\text{-}COCH_3)(2\text{-}butyne)^+$ which leads to the insertion product. Accordingly, we have investigated the synthesis of Zr(IV) carbonyl complexes of this type.



(1)

**Synthesis of $[Cp_2Zr\{\eta^2\text{-}C({=}N^tBu)(CH_3)\}(CN^tBu)][BPh_4]$.** In an initial effort to assess the possibility that $Cp_2Zr(\eta^2\text{-}COR)^+$ species can coordinate CO, we investigated the chemistry of related Zr(IV) isocyanide complexes. Isocyanides are stronger $\sigma$-donor ligands than CO,[24] and Bochmann had previously prepared several cationic Ti(IV) isocyanide complexes, including $[Cp_2Ti\{\eta^2\text{-}C({=}N^tBu)(CH_3)\}(CN^tBu)][BPh_4]$, which was characterized by X-ray diffraction and is a direct analogue of $Cp_2Zr(\eta^2\text{-}COCH_3)(CO)^+$.[25] The cationic methyl complex $Cp_2Zr(CH_3)(THF)^+$ (as the $BPh_4^-$ salt) reacts rapidly with *tert*-butyl isocyanide to yield the iminoacyl isocyanide complex $Cp_2Zr\{\eta^2\text{-}C({=}N^tBu)(CH_3)\}(CN^tBu)^+$ (**1**, eq 2). The low field $ZrC({=}N^tBu)$ $^{13}C$ NMR resonance ($\delta$ 226.4) for **1** is consistent with the $\eta^2$-coordination mode.[26] The IR spectrum contains a $\nu_{NC}$ band at 2206 cm$^{-1}$ for the coordinated isocyanide, which is higher than in the free ligand (2125 cm$^{-1}$). Only a single isomer is observed for **1**; it is likely that the iminoacyl nitrogen occupies the central coordination site, as found for the Ti analogue. Complex **1** is air stable for short periods of time and does not react with alkynes or alkenes, presumably because the isocyanide ligand is not labile.[27] These results suggested that $Cp_2Zr(\eta^2\text{-}COR)(CO)^+$ species might indeed be stable, and we therefore investigated the carbonylation of several base-free $Cp_2Zr(CH_3)^+$ species.



**1**

(2)

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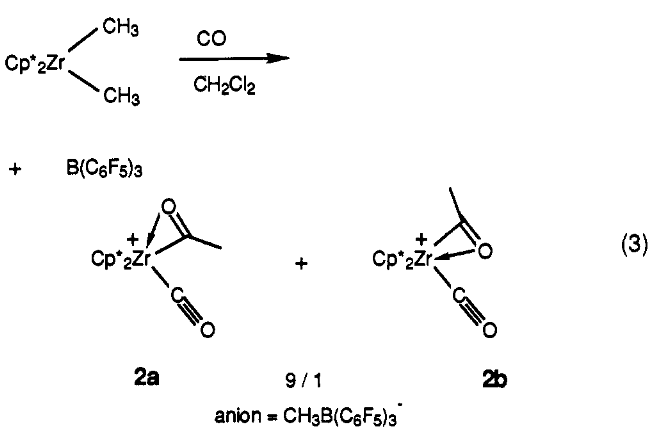
**Carbonylation of $Cp^*_2Zr(CH_3)(\mu\text{-}CH_3)B(C_6F_5)_3$. Synthesis of $[(C_5Me_5)_2Zr(\eta^2\text{-}COCH_3)(CO)][CH_3B(C_6F_5)_3]$ (2).** Marks has shown that $(C_5R_5)_2ZrR_2$ complexes react with $B(C_6F_5)_3$ to yield $(C_5R_5)_2ZrR(\mu\text{-}R)(B(C_6F_5)_3$ adducts which, due to the high lability of the $[(R)B(C_6F_5)_3]^-$ anion, are convenient sources of base-free $(C_5R_5)Zr(R)^+$ species.[28] The reaction of $Cp^*_2Zr(CH_3)_2$ with 1 equiv of $B(C_6F_5)_3$ under ca. 3 atm of CO in $CD_2Cl_2$ at 23 °C results in uptake of 2 equiv of CO and formation of the $\eta^2$-acyl carbonyl complex $[(C_5Me_5)_2Zr(\eta^2\text{-}COCH_3)(CO)][CH_3B(C_6F_5)_3]$ (**2**, eq 3). NMR and IR data establish that in $CD_2Cl_2$ solution **2** exists as a 9/1 mixture of isomers **2a,b**, which differ in the orientation of the $\eta^2$-acyl ligand ("O-outside" vs "O-inside").[10d] Cooling a $CH_2Cl_2$/hexane solution of **2a,b** to −40 °C under 1 atm of CO yields pale yellow crystals which were identified as the major isomer **2a** by IR spectroscopy (KBr). This isomer was determined to be the "O-outside" isomer by X-ray crystallography (*vide infra*).[29]



(3)

The $^{13}C$ NMR spectrum of **2** contains two low field $ZrCOCH_3$ resonances for the major and minor isomers (**2a**, $\delta$ 299.0; **2b**, 309.3) characteristic of $\eta^2$-acyl ligands.[26] The Zr–CO resonances (**2a**, $\delta$ 204.5; **2b**, $\delta$ 197.3) appear somewhat downfield of the free CO resonance ($\delta$ 184) and close to that reported for $[Cp_2Zr\{\eta^2\text{-}CH(Me)(6\text{-ethylpyrid-}2\text{-yl})\text{-}C,N\}(CO)^+$ ($\delta$ 206.1).[12] For **2**-$^{13}C_2$, which is $^{13}C$-labeled in the $ZrCOCH_3$ and Zr–CO positions, coupling is observed between the acyl and Zr–CO carbons, as expected for a C-bonded carbonyl ligand. The $^2J_{CC}$ value of **2a**-$^{13}C_2$ (10.5 Hz) in which the Zr–C(acyl) and Zr–CO bonds are cis, is larger than that for **2b**-$^{13}C_2$ (2.7 Hz).

The IR $\nu_{CO}$ band for **2a** (2105 cm$^{-1}$) appears at lower energy, and that for **2b** (2152 cm$^{-1}$) at slightly higher energy than the band for free CO (2139 cm$^{-1}$, $CH_2Cl_2$). A single $\nu_{acyl}$ band is observed at 1576 cm$^{-1}$, which is consistent with an $\eta^2$-acyl group. It was not possible to establish whether the $\nu_{acyl}$ bands of **2a** and **2b** are coincident, or whether the latter is obscured.

The $CH_3B(C_6F_5)_3^-$ $^1H$ NMR resonance ($\delta$ 0.48) is shifted downfield from the corresponding resonances for the $(C_5R_5)_2Zr(CH_3)(\mu\text{-}CH_3)B(C_6F_5)_3$ species (R = H, $\delta$ 0.04; R = $CH_3$, $\delta$ 0.2 in $CD_2Cl_2$) and is close to the resonances for compounds in which the anion is known to be free (e.g. $Cp_2Zr(\eta^2\text{-pyridyl})(\text{pyridine})^+$ species).[30] Thus in $CD_2Cl_2$ solution, the anion does not interact strongly with the coordinatively saturated $Cp^*_2Zr(\eta^2\text{-}COCH_3)(CO)^+$ cation.

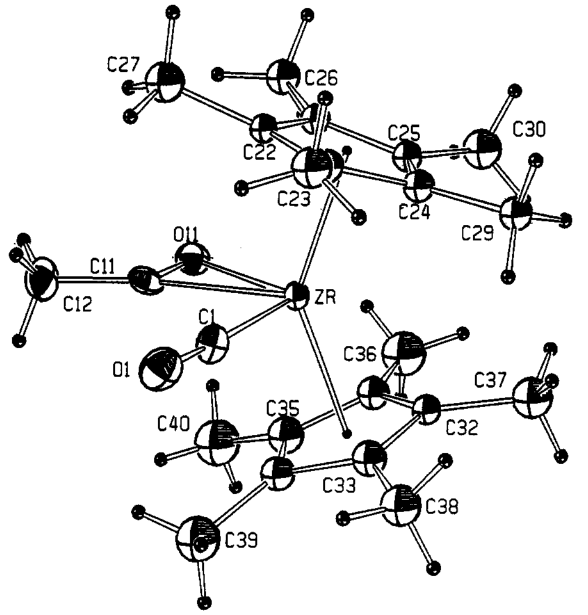


**Figure 1.** ORTEP view of the $(C_5Me_5)_2Zr(\eta^2\text{-}COCH_3)(CO)^+$ cation of **2a**.

When isolated **2a** was dissolved in $CD_2Cl_2$ at ca −20 °C under 3 atm of CO, cooled immediately (min) to −78 °C, and analyzed by NMR spectroscopy at −60 °C, the equilibrium 9/1 mixture of **2a**/**2b** was observed. Thus, exchange of **2a** and **2b** is rapid on the laboratory time scale at −20 °C.[31]

**Solid State Structure of 2a.** The solid state structure of **2a** was determined by single-crystal X-ray diffraction and consists of discrete $Cp^*_2Zr(\eta^2\text{-}COCH_3)(CO)^+$ and $CH_3B(C_6F_5)_3^-$ ions.[29] The structure of the cation is shown in Figure 1. Crystallographic details and key bond distances and angles are listed in Tables 2 and 3.

The $Cp^*_2Zr(\eta^2\text{-}COCH_3)(CO)^+$ cation of **2a** adopts a normal bent metallocene structure with the centroid–Zr–centroid angle and Zr–centroid distances in the range observed for other $Cp^*_2Zr$ complexes.[32] The $\eta^2$-acyl and CO ligands are located in the plane between the two Cp* ligands, as expected, and the Zr, C1, O1, C11, and O11 atoms are all coplanar. The $\eta^2$-acyl ligand bonds to Zr in an O-outside fashion and is highly distorted. The $Zr\text{–}C_{acyl}$ and $Zr\text{–}O_{acyl}$ bond distances are nearly equal (2.22(1), 2.242(7) Å), the value of $\Delta = d_{Zr\text{–}O} - d_{Zr\text{–}C} = 0.02$ Å is at the extreme small end of the range observed for early metal $\eta^2$-acyl complexes,[33] and the Zr–C–O angle is highly acute (74.7(6)°). Collectively, these data indicate that the

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[29] To correlate the IR and X-ray results, the following experiments were performed. Four crystals were examined by X-ray crystallography and determined to have the same unit cell parameters. One crystal was subjected to a full X-ray diffraction study and determined to be the "O-outside isomer". The four crystals were then combined, and an IR spectrum (KBr) was obtained. This spectrum showed only the $\nu_{CO}$ band for the major isomer **2a**, confirming that **2a** is the O-outside isomer.

[30] Rodewald, S. R.; Jordan, R. F. Unpublished results.

[31] Complex **2a** did not dissolve in $CD_2Cl_2$ at an appreciable rate at temperatures below ca. −20 °C.

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**Table 1. Spectroscopic Data for New Compounds**[a]

| compd (NMR solvent) | $^1$H NMR ($\delta$, $J$ values in Hz) | assign | $^{13}$C NMR ($\delta$, $J$ values in Hz) | assign | IR ($CH_2Cl_2$) (cm$^{-1}$) | assign |
|---|---|---|---|---|---|---|
| **1** ($CD_2Cl_2$, 23 °C) | 5.72 (s, 10 H) | $C_5H_5$ | 226.4 | $\mathrm{Zr{-}}\mathit{C}\{=\mathrm{N^tBu}\}$ | 2202[b] | $\nu_{CN}$ |
|  | 2.86 (s, 3H) | $CH_3$ | 106.4 | $\mathit{C}_5\mathrm{H}_5$ | 1662 | $\nu_{C=N}$ |
|  | 1.67 (s, 9H) | $^t$Bu | 61.2 | $\mathit{C}\mathrm{Me}_3$ |  |  |
|  | 1.30 (s, 9H) | $^t$Bu | 60.4 | $\mathit{C}\mathrm{Me}_3$ |  |  |
|  |  |  | 29.8 | $\mathrm{C}\mathit{Me}_3$ |  |  |
|  |  |  | 29.1 | $\mathrm{C}\mathit{Me}_3$ |  |  |
|  |  |  | 24.0 | $\mathit{C}\mathrm{H}_3$ |  |  |
|  |  |  | CN$^t$Bu resonance not observed |  |  |  |
| **21** ($CD_2Cl_2$, 23 °C) | 3.00 (s, 3H) | $\mathrm{COC}\mathit{H}_3$ | 300.2 | $\mathit{C}\mathrm{OCH}_3$ | 2105 | $\nu_{ZrCO}$ |
|  | 1.84 (s, 30H) | $\mathrm{C}_5\mathit{Me}_5$ | 204.5 | $\mathrm{Zr}\mathit{C}\mathrm{O}$ | 1576 | $\nu_{acyl}$ |
|  | 0.48 (br s, 3H) | $\mathrm{C}\mathit{H}_3\mathrm{B}$ | 119.6 | $\mathit{C}_5\mathrm{Me}_5$ |  |  |
|  |  |  | 29.6 | $\mathrm{CO}\mathit{C}\mathrm{H}_3$ |  |  |
|  |  |  | 10.8 | $\mathrm{C}_5\mathit{Me}_5$ |  |  |
|  |  |  | 9.1 br | $\mathit{C}\mathrm{H}_3\mathrm{B}$ |  |  |
| **2a** ($CD_2Cl_2$, –20 °C) | 2.99 (s, 3H) | $\mathrm{COC}\mathit{H}_3$ |  |  |  |  |
|  | 1.80 (s, 30H) | $\mathrm{C}_5\mathit{Me}_5$ |  |  |  |  |
|  | 0.43 (br s, 3H) | $\mathrm{C}\mathit{H}_3\mathrm{B}$ |  |  |  |  |
| **2a**-$^{13}C_2$ ($CD_2Cl_2$, –40 °C) | 2.99 (d, $^2J_{CH}$ = 5.9, 3H) | $\mathrm{COC}\mathit{H}_3$ | 299.0 (d, $^2J_{CC}$ = 10.5) | $\mathit{C}\mathrm{OCH}_3$ | 2058 | $\nu_{ZrCO}$[c] |
|  | 1.78 (s, 30H) | $\mathrm{C}_5\mathit{Me}_5$ | 204.2 (d, $^2J_{CC}$ = 10.5) | $\mathrm{Zr}\mathit{C}\mathrm{O}$ | 1540 | $\nu_{acyl}$ |
|  | 0.39 (br s, 3H) | $\mathrm{C}\mathit{H}_3\mathrm{B}$ | 29.5 (d, $^1J_{CC}$ = 21.0) | $\mathrm{CO}\mathit{C}\mathrm{H}_3$ |  |  |
|  |  |  |  | other resonances same as for unlabeled **2a** |  |  |
| **2b** ($CD_2Cl_2$, –20 °C) | 2.90 (s, 3H) | $\mathrm{COC}\mathit{H}_3$ |  |  | 2152 | $\nu_{ZrCO}$[d] |
|  | 1.81 (s, 30H) | $\mathrm{C}_5\mathit{Me}_5$ |  |  |  |  |
|  | 0.43 (br s, 3H) | $\mathrm{C}\mathit{H}_3\mathrm{B}$ |  |  |  |  |
| **2b**-$^{13}C_2$ ($CD_2Cl_2$, –40 °C) | 2.89 (d, $^2J_{CH}$ = 5.0, 3H) | $\mathrm{COC}\mathit{H}_3$ | 309.3 (d, $^2J_{CC}$ = 2.7) | $\mathit{C}\mathrm{OCH}_3$ | 2104 | $\nu_{ZrCO}$ |
|  | 1.81 (s, 30H) | $\mathrm{C}_5\mathit{Me}_5$ | 197.3 (d, $^2J_{CC}$ = 2.7) | $\mathrm{Zr}\mathit{C}\mathrm{O}$ |  |  |
|  | 0.39 (br s, 3H) | $\mathrm{C}\mathit{H}_3\mathrm{B}$ | other resonances not observed |  |  |  |
| **3a** ($CD_2Cl_2$, 23 °C) | 6.14 (s, 10H) | $\mathrm{C}_5\mathit{H}_5$ | 298.2 | $\mathit{C}\mathrm{OCH}_3$ | 2123 | $\nu_{ZrCO}$[f] |
|  | 3.18 (s, 3H)[e] | $\mathrm{COC}\mathit{H}_3$ | 198.3 | $\mathrm{Zr}\mathit{C}\mathrm{O}$ |  |  |
|  | 0.53 (b s, 3H) | $\mathrm{C}\mathit{H}_3\mathrm{B}$ | 110.0 | $\mathit{C}_5\mathrm{H}_5$ |  |  |
|  |  |  | 33.2 | $\mathrm{CO}\mathit{C}\mathrm{H}_3$ |  |  |
|  |  |  | 10.4 | $\mathit{C}\mathrm{H}_3\mathrm{B}$ |  |  |
| **3a**-$^{13}C_2$ ($CD_2Cl_2$, –40 °C) | 6.10 (s, 10H) | $\mathrm{C}_5\mathit{H}_5$ | 297.6 (d, $^2J_{CC}$ = 9.5) | $\mathit{C}\mathrm{OCH}_3$ | 2076 | $\nu_{ZrCO}$[g] |
|  | 3.16 (d, $^2J_{CH}$ = 5.0, 3H) | $\mathrm{COC}\mathit{H}_3$ | 198.3 (d, $^2J_{CC}$ = 9.5) | $\mathrm{Zr}\mathit{C}\mathrm{O}$ |  |  |
|  | 0.44 (br s, 3H) | $\mathrm{C}\mathit{H}_3\mathrm{B}$ | 109.6 | $\mathit{C}_5\mathrm{H}_5$ |  |  |
|  |  |  | other resonances not observed |  |  |  |
| **3b** ($CD_2Cl_2$, 23 °C) | 6.04 (s, 10H) | $\mathrm{C}_5\mathit{H}_5$ | 306.3 | $\mathit{C}\mathrm{OCH}_3$ | 2176 | $\nu_{ZrCO}$ |
|  | 3.18 (s, 3H) | $\mathrm{COC}\mathit{H}_3$ | 192.0 | $\mathrm{Zr}\mathit{C}\mathrm{O}$ | 1558 | $\nu_{acyl}$ |
|  | 0.53 (br s, 3H) | $\mathrm{C}\mathit{H}_3\mathrm{B}$ | 108.8 | $\mathit{C}_5\mathrm{H}_5$ |  |  |
|  |  |  | 33.9 | $\mathrm{CO}\mathit{C}\mathrm{H}_3$ |  |  |
|  |  |  | 10.4 | $\mathit{C}\mathrm{H}_3\mathrm{B}$ |  |  |
| **3b**-$^{13}C_2$ ($CD_2Cl_2$, –40 °C) | 6.01 (s, 10H) | $\mathrm{C}_5\mathit{H}_5$ | 305.7 (d, $^2J_{CC}$ = 2.7) | $\mathit{C}\mathrm{OCH}_3$ | 2127 | $\nu_{ZrCO}$ |
|  | 3.17 (d, $^2J_{CH}$ = 5.9, 3H)[h] | $\mathrm{COC}\mathit{H}_3$ | 192.0 (d, $^2J_{CC}$ = 2.7) | $\mathrm{Zr}\mathit{C}\mathrm{O}$ | 1523 | $\nu_{acyl}$ |
|  | 0.44 (br s, 3H) | $\mathrm{C}\mathit{H}_3\mathrm{B}$ | 108.3 | $\mathit{C}_5\mathrm{H}_5$ |  |  |
|  |  |  | other resonances not oberved |  |  |  |
| **4** ($CD_2Cl_2$, 23 °C) | 2.93 (s, 3H) | $\mathrm{COC}\mathit{H}_3$ | 320.5 | $\mathit{C}\mathrm{OCH}_3$ |  |  |
|  | 1.84 (s, 30H) | $\mathrm{C}_5\mathit{Me}_5$ | 121.7 | $\mathit{C}_5\mathrm{Me}_5$ |  |  |
|  | 0.48 (br s, 3H) | $\mathrm{C}\mathit{H}_3\mathrm{B}$ | 30.8 | $\mathrm{CO}\mathit{CH}_3$ |  |  |
|  |  |  | 11.3 | $\mathrm{C}_5\mathit{Me}_5$ |  |  |
|  |  |  | 10.3 br | $\mathit{C}\mathrm{H}_3\mathrm{B}$ |  |  |
| **5** (THF-$d_8$, 23 °C)[i] | 6.13 (s, 10H) | $\mathrm{C}_5\mathit{H}_5$ | 318.6 | $\mathit{C}\mathrm{OCH}_3$ | 1600[b] | $\nu_{acyl}$ |
|  | 3.20 (s, 3H)[j] | $\mathrm{COC}\mathit{H}_3$ | 111.4 | $\mathit{C}_5\mathrm{H}_5$ |  |  |
|  | 0.50 (br s, 3H) | $\mathrm{C}\mathit{H}_3\mathrm{B}$ | 33.4 | $\mathrm{CO}\mathit{C}\mathrm{H}_3$ |  |  |
|  |  |  | 10.5 | $\mathit{C}\mathrm{H}_3\mathrm{B}$ |  |  |

[a] $BPh_4^-$ and $B(C_6F_5)_3$ resonances omitted. [b] KBr pellet. [c] $\nu_{CO}$ for the $^{13}C^{18}O$ isotopomer is observed at 2007 cm$^{-1}$. [d] $\nu_{acyl}$ for **2b** not observed; this band may be coincident with $\nu_{acyl}$ for **2a**. [e] This resonances is coincident with the $\mathrm{ZrCOC}\mathit{H}_3$ resonances for **3b**. These resonances are resolved at –30 °C; **3b** $\delta$ 3.18, **3a**, 3.16. [f] $\nu_{acyl}$ for **3a** not observed; this band may be coincident with $\nu_{acyl}$ for **3b**. [g] $\nu_{acyl}$ not observed; this band may be coincident with $\nu_{acyl}$ for **3b**-$^{13}C_2$. [h] $J$ value from ambient temperature spectrum. [i] Dissolution of **5** in THF-$d_8$ yields $[Cp_2Zr(COCH_3)(THF)][CH_3B(C_6F_5)_3]$. [j] $^2J_{CH}$ = 6.0 Hz for **5**-$^{13}C_1$.

Zr–O interaction is quite strong, consistent with the highly electrophilic character of cationic Zr(IV) centers.[22] For comparison, $Cp_2Ti(\eta^2\text{-}COCH_3)Cl$,[34] $Cp_2Zr(\eta^2\text{-}COCH_3)CH_3$,[35] and $Cp_2Zr(\eta^2\text{-}COCH_3)(\mu\text{-}OC)Mo(CO)_2Cp$[36] all adopt O-inside structures in which the metal–O interaction (as assessed by the parameter $\Delta$) is less pronounced than in **2a**.

The most interesting feature of the structure of **2a** is the terminal carbonyl ligand, which is nearly linear (Zr–C–O = 175.1(7)°). The Zr–C distance (2.25(1) Å) is identical to the Zr–C(sp) bond distance in the Zr acetylide complex $Cp_2Zr(CCMe)_2$ (2.249(3) Å), in which Zr–C $\pi$-bonding is believed to be absent,[37,38] and is within the range observed for Zr–C(sp$^3$) distances in related zirconocene systems where Zr–C $\pi$-bonding is not possible,

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**Table 2. Summary of Crystallographic Data for $[(C_5Me_5)_2Zr(COCH_3)(CO)][CH_3B(C_6F_5)_3]$ (2a)**

| | |
|---|---|
| empirical formula | $C_{42}H_{36}BF_{15}O_2Zr$ |
| fw | 959.76 |
| cryst size, mm | 0.11 × 0.34 × 0.42 |
| cryst color | pale yellow |
| space group | $Pca2_1$ |
| $a$, Å | 16.951(5) |
| $b$, Å | 10.642(4) |
| $c$, Å | 22.217(6) |
| $V$, Å$^3$ | 4008(4) |
| $Z$ | 4 |
| $d$(calcd), g/cm$^3$ | 1.59 |
| no. of reflns; $\theta$ range deg | 25; $19 < 2\theta < 25$ |
| λ (Mo K$\alpha$), Å | 0.7107 |
| temp K | 120(2) |
| scan ratio ($\Omega/\theta$) | 1 |
| scan speed, deg/min | 0.83–5.0 |
| scan range, deg Ω | $0.80 + \tan(\theta)$ |
| $2\theta$ range, deg | $4 < 2\theta < 40$ |
| data collcd $h$; $k$; $l$ | −10, 4; −16, 0; −21, 21 |
| no. reflns collcd | 5201 |
| no. unique reflns | 3654 |
| reflns $I > 2\sigma_I$ | 2906 |
| $R_{int}$ | 0.027 |
| max decay corr factor | 1.032 |
| abs coeff, cm$^{-1}$ | 3.72 |
| refinement | Zr, all F, all O, C1, C11, C12 anisotropic, all other non-H isotropic, H calculated positions, $B_H = 1.3B_C$ |
| total no. of params | 349 |
| $R$ | 0.044 |
| $R_w$ | 0.050 |
| weighting coeff $P$, $Q$[a] | 0.02, 0.0 |
| SDOUW[b] | 1.58 |
| max param shift/esd | 0.02 |
| max resid e density, e/Å$^3$ | 0.80 |

[a] $W = (\sigma_F^2 + (PF)^2 + Q)^{-1}$. [b] Standard deviation of unit weight.

**Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[(C_5Me_5)_2Zr(COCH_3)(CO)][CH_3B(C_6F_5)_3]$ (2a)**

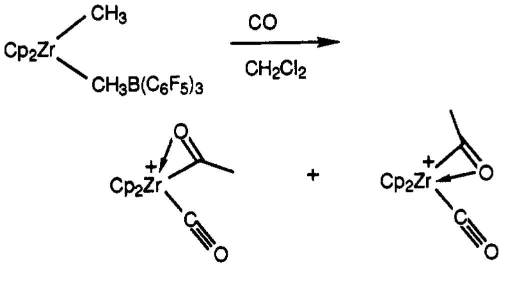
| | | | |
|---|---|---|---|
| Zr–C1 | 2.25(1) | av Zr–$C_{ring1}$ | 2.51(2) |
| Zr–C11 | 2.22(1) | av Zr–$C_{ring2}$ | 2.52(2) |
| Zr–O11 | 2.242(7) | av C–$C_{ring1}$ | 1.41(1) |
| Zr–C100[a] | 2.20 | av C–$C_{ring2}$ | 1.42(2) |
| Zr–C200[a] | 2.21 | av C–$C_{Me\ ring1}$ | 1.50(2) |
| C1–O1 | 1.13(1) | av C–$C_{Me\ ring2}$ | 1.51(2) |
| C11–O11 | 1.24(1) | | |
| C11–C12 | 1.48(1) | | |
| | | | |
| C1–Zr–C11 | 75.3(4) | C1–Zr–O11 | 107.6(3) |
| C1–Zr–C100 | 99.1 | C1–Zr–C200 | 99.9 |
| C11–Zr–C100 | 106.5 | C11–Zr–C200 | 108.8 |
| O11–Zr–C100 | 102.1 | O11–Zr–C200 | 101.9 |
| C100–Zr–C200 | 143.0 | Zr–C1–O1 | 175.1(7) |
| Zr–C11–O11 | 74.7(6) | Zr–C11–C12 | 163.3(9) |
| O11–C11–C12 | 122.0(9) | O11–Zr–C11 | 32.3(3) |

[a] C100 is the centroid of the C21–C25 Cp* ring; C200 is the centroid of the C31–C35 Cp* ring.

e.g. $Cp_2Zr(CH_3)(THF)^+$ (2.256(10) Å)[39] and $(C_5H_4Me)_2Zr(CH_3)(CB_{11}H_{12})$ (2.270(3) Å).[40] These results are consistent with the expectation that there should be no (conventional) Zr–C $\pi$-bonding in this d$^0$ complex. In contrast, shorter Zr–C bond distances are observed in cases where Zr–C $\pi$-bonding is present, e.g. the Zr(II) carbonyl complexes $Cp_2Zr(CO)_2$ (2.187(4) Å) and $Cp^*_2Zr(CO)_2$ (2.145(9) Å)[17,41] and the dimetalloacetylene complex $Cp_2Zr(Cl)CCRu(CO)_2Cp$ (2.141(15) Å).[42] In good agreement with the observed CO stretching frequency, which is only slightly perturbed from that of free CO, the C–O distance of **2a** (1.13(1) Å) is equal within experimental error to that of free CO (1.12822(7) Å)[43] and $H_3B$–CO 1.13(2) Å).[44] For comparison, longer C–O bond distances are observed for systems in which d→$\pi^*$ back-bonding is important (e.g. $Cp^*_2Ti(CO)_2$ 1.149 Å, $Cp^*_2Zr(CO)_2$ 1.16(1) Å, $Cp_2Ti(CO)(PMe_3)$ 1.185(6) Å)[17,45] while shorter C–O bond distances are observed when only C→M $\sigma$-donation is important (e.g. $Ag(CO)B(OTeF_5)_4$ 1.08(2) Å; $[Ag(CO)_2][B(OTeF_5)_4]$ 1.08 Å).[2]

The $MeB(C_6F_5)_3^-$ anion adopts a slightly distorted tetrahedral structure and does not interact strongly with the coordinatively saturated cation. The closest contact is between a fluorine and the carbonyl oxygen (F53–O1 2.89 Å) and is longer than the sum of the relevant van der Waals radii (ca. 2.75 Å).[46]

**Synthesis of $[(C_5H_5)_2Zr(\eta^2\text{-}COCH_3)(CO)][CH_3B(C_6F_5)_3]$ (3). Comparison of Structures of 2 and 3.** Exposure of preformed $Cp_2Zr(CH_3)(\mu\text{-}CH_3)B(C_6F_5)_3$ to CO (3 atm) in $CD_2Cl_2$ at 23 °C results in rapid, quantitative formation of $[Cp_2Zr(\eta^2\text{-}COCH_3)(CO)][CH_3B(C_6F_5)_3]$ (**3**, eq 4). NMR and IR data establish that **3** exists as a 5/1 mixture of isomeric $\eta^2$-acyl complexes in $CH_2Cl_2$ solution. As summarized in Table 1, NMR and IR data for the major isomer **3b** are similar to data for the O-inside $Cp^*_2Zr$ analogue **2b**, and data for the minor isomer **3a** are similar to data for the O-outside $Cp^*_2Zr$ analogue **2a**. Accordingly, we conclude that **3b** is the O-inside isomer and **3a** is the O-outside isomer. The $\nu_{CO}$ value for **3b** (2176 cm$^{-1}$) is greater than the free CO value, while $\nu_{CO}$ for **3a** (2123 cm$^{-1}$) is less than the free CO value.



(4)

**3a** 1/5 **3b**

anion = $CH_3B(C_6F_5)_3^-$

The structural preferences for 2 and 3 are consistent with previous observations that the O-inside isomers of $Cp_2M(\eta^2\text{-acyl})X$ species are preferred for electronic reasons[47] but that this preference may be overridden by steric factors.[48] Presumably, steric interactions between the acyl methyl group and the Cp* ligands disfavor the O-inside

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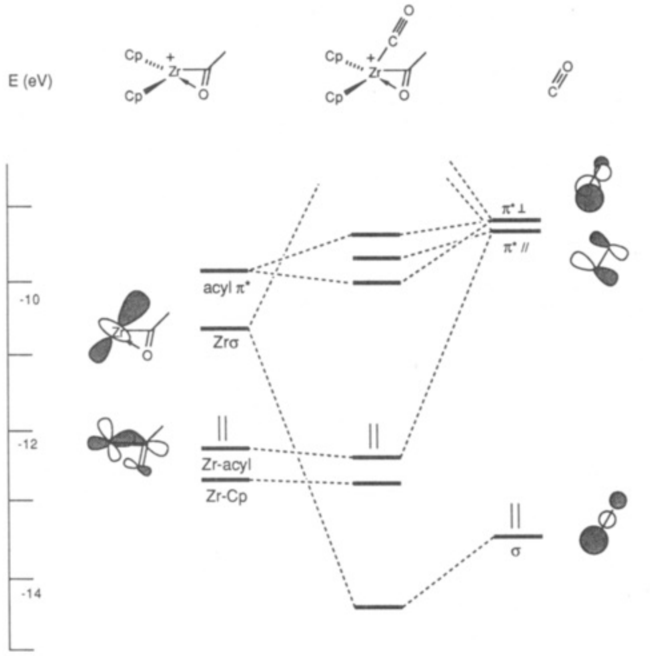

**Figure 2.** Frontier orbitals of the O-inside isomer of $Cp_2Zr(\eta^2\text{-}COCH_3)(CO)^+$ (**3a**) derived by interaction of the frontier orbitals of $Cp_2Zr(\eta^2\text{-}COCH_3)^+$ and CO. Results are based on EHMO calculations.

isomer **2b**. However, as both the O-inside and O-outside isomers of these cationic systems are observed in solution, the energy differences must be small.

**Bonding Considerations.** The $\nu_{CO}$ values for the O-inside isomers **2b** and **3b** are greater than the free CO value, indicating that the Zr–CO bonds are predominantly σ-donor in character. In contrast, $\nu_{CO}$ values for the O-outside isomers **2a** and **3a** are slightly less than the free CO value. As these are $d^0$ species, this reduction in $\nu_{CO}$ likely arises from overlap of a bonding MO of the $(C_5R_5)_2Zr(\eta^2\text{-acyl})^+$ fragment with a CO π* orbital, analogous to the proposed overlap of M–H bonding orbitals with a CO π* orbital in $Cp^*{}_2MH_2(CO)$ (M = Zr, Hf).[14]

To elucidate the nature of the Zr–CO bonding in these systems, extended Hückel calculations were performed on **3a**.[49] The structure of **3a** was based on the X-ray determined structure of **2a**. A qualitative orbital interaction diagram for **3a** which is constructed from the orbitals of $Cp_2Zr(\eta^2\text{-}COCH_3)^+$ and CO is shown in Figure 2. The two most important frontier orbitals of the $Cp_2Zr(\eta^2\text{-}COCH_3)^+$ fragment are the LUMO (Zrσ) which is a σ-acceptor orbital, and the HOMO (Zr–acyl), which is a Zr–acyl bonding orbital. A set of Zr–Cp bonding orbitals lies below the HOMO, and the acyl π* and several Zr–acyl antibonding orbitals lie above the LUMO; these orbitals are not important for our analysis. Zr–CO σ bond formation occurs by interaction of the CO σ-donor orbital with the Zr LUMO. As the CO σ-donor orbital is weakly C–O antibonding, this should raise $\nu_{CO}$. Additionally, however, the CO π*‖ (in-plane) acceptor orbital overlaps with the Zr HOMO, resulting in population of the π* orbital and reduction of $\nu_{CO}$. For **3a**, the net result of this σ → π* back-bonding and the σ-donation and is a decrease in $\nu_{CO}$ by 16 $cm^{-1}$ (from the free CO value). The CO $\pi^*_\|$ orbital also mixes with higher lying Zr–acyl antibonding orbitals, and the CO $\pi^*_\perp$ mixes with the Zr–acyl π* and higher lying orbitals.

The situation is similar for the O-inside isomer **3b**. However, in this case, because the positions of the acyl oxygen and acyl carbon are reversed in the $Cp_2Zr(\eta^2\text{-}COCH_3)^+$ fragment, the smaller lobes of the Zr HOMO are directed toward the vacant coordination site, and overlap with the CO $\pi^*_\|$ acceptor orbital is reduced. For **3b**, the weaker σ→π* back-bonding is insufficient to compensate for the σ-donation, and $\nu_{CO}$ is raised by 37 $cm^{-1}$ (from the free CO value).

The $\nu_{CO}$ values for the Cp* analogues **2a** and **2b** are lowered by 18–25 $cm^{-1}$ from the values for the corresponding isomers of **3**, as a result of the weaker acceptor and stronger back-donor properties of the more electron rich $Cp^*{}_2Zr(\eta^2\text{-}COCH_3)^+$ fragment. Greater reductions in $\nu_{CO}$ values from values for $Cp_2M$ analogues are observed for $Cp^*{}_2M(CO)_2$ compounds ($\Delta\nu_{CO}$ = 30–40 $cm^{-1}$) and $Cp^*{}_2Ti(CO)Cl$ ($\Delta\nu_{CO}$ = 68 $cm^{-1}$).

**CO Exchange and Decarbonylation of 2 and 3.** Exposure of $CD_2Cl_2$ solutions of **2a,b** and **3a,b** to $^{13}CO$ (1 atm) results in immediate incorporation of label into the carbonyl sites but not the acyl sites.[50] Thus in both cases, the carbonyl ligands are labile but acetyl deinsertion is slow.

Exposure of a $CD_2Cl_2$ solution of **2a,b** to vacuum at −78 °C results in rapid but reversible CO loss (ca. 25% after 10 min). In contrast, crystalline **2a** is much more resistant to CO loss; this species shows only minimal CO loss after hours at room temperature and is stable enough for elemental analysis. Evidently, the solid morphology has a large effect on the rate of CO loss. The decarbonylation product, $[Cp^*{}_2Zr(\eta^2\text{-}COCH_3)][CH_3B(C_6F_5)_3]$ (**4**) was generated *in situ* by the reaction of $Cp^*{}_2Zr(CH_3)_2$ and $B(C_6F_5)_3$ with 1 equiv of CO (75% NMR) but could not be isolated cleanly.[51] The low temperature (197 K) $^{13}C$ NMR spectrum of **4**-$^{13}C$ (labeled in the acyl positions) exhibits two $\eta^2$-acyl resonances (δ 319.2, 318.1), consistent with the presence of two (O-inside and O-outside) isomers. Above 223 K, these resonances coalesce, indicating rapid isomer exchange. The existence of two isomers for **4** at low temperature suggests that an additional ligand is coordinated to the $Cp^*{}_2Zr(\eta^2\text{-}COCH_3)^+$ cation. The $CH_3B(C_6F_5)_3^-$ resonances of **4** are not perturbed from those of the free anion, which suggests that the anion is not coordinated. It is possible that **4** exists as a $CD_2Cl_2$ solvent complex, although this could not be confirmed.[52]

At CO pressures below ca. 1 atm, **3** readily loses CO to form $[Cp_2Zr(\eta^2\text{-}COCH_3)][CH_3BC_6F_5)_3]$ (**5**), which precipitates from solution as an isolable pale yellow solid. For example, exposure of a solution of **3** to vacuum at −78 °C results in near quantitative formation of **5** (85%). Sur-

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(49) For pertinent calculations on metallocene systems see ref 47 and: (a) Petersen, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6432. (b) Lauher, J. W.; Hoffman, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. (c) Hofmann, P.; Stauffert, P.; Schore, N. E. *Chem. Ber.* **1982**, *115*, 2153. (d) Zhu, L.; Kostic, N. M. *J. Organomet. Chem.* **1987**, *335*, 395. (e) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788. (f) Sontag, C.; Berke, H.; Sarter, C.; Erker, G. *Helv. Chim. Acta* **1989**, *72*, 1676. (g) Hyla-Kryspin, I.; Gleiter, R.; Krüger, C.; Zwettler, R.; Erker, G. *Organometallics* **1990**, *9*, 517.

(50) The irreversibility of the CO insertion of $Cp_2Zr(R)^+$ species implied by the absence of CO exchange into the acyl site was noted previously[21] and contrasts with the reversible CO insertions observed for neutral analogues. For example see: (a) Fachinetti, G.; Floriani, C.; Marchetti, F.; Merlino, S. *J. Chem. Soc., Chem. Commun.* **1976**, 522. (b) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organomet. Chem.* **1980**, *201*, 389.

(51) The major side product (ca. 20%) is $Cp^*{}_2ZrCl_2$.

(52) (a) Bochmann has proposed that $Cp_2Zr(R)^+$ species exist as solvent complexes in $CD_2Cl_2$ solution. Bochmann, M.; Jaggar, A. J.; Nicholls, J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 780. (b) It is also possible that the anion of **4** is coordinated sufficiently weakly that the anion NMR resonances are not significantly perturbed.

prisingly, this decarbonylation is not reversible, presumably due to the insolubility of **5**. However, **5** does dissolve in THF to yield [Cp$_2$Zr($\eta^2$-COCH$_3$)(THF)][(CH$_3$BC$_6$F$_5$)$_3$], which was characterized previously as the BPh$_4^-$ salt.[21] Complex **5** was characterized by IR spectroscopy and elemental analysis, but NMR characterization was precluded by its poor solubility. The IR spectrum of **5** contains a $\nu_{acyl}$ band at 1600 cm$^{-1}$, but not a $\nu_{CO}$ band.

## Conclusion

Carbonylation of (C$_5$R$_5$)$_2$Zr(CH$_3$)$^+$ species leads to the formation of unusual d$^0$ carbonyl complexes (C$_5$R$_5$)$_2$Zr($\eta^2$-COCH$_3$)(CO)$^+$ (**2**, R = Me; **3**, R = H). The O-outside Cp* species **2a**, which has been characterized crystallographically, is in fact the first terminal carbonyl complex of Zr(IV) to be isolated.[20] The existence of **2** and **3** is due in part to the electrophilicity of the cationic d$^0$ (C$_5$R$_5$)$_2$Zr($\eta^2$-COCH$_3$)$^+$ fragment, which promotes OC$\rightarrow$Zr $\sigma$-bonding.[53] The $\nu_{CO}$ values for the O-inside isomers **2a** and **3a** are higher than the free CO value, indicating that the Zr–CO bonding is dominated by the $\sigma$-donor component is these cases. However, the lability of the coordinated CO of **2** and **3** in solution, and spectroscopic and crystallographic comparisons, indicate that the $\sigma$-interaction is relatively weak, e.g. as compared to that in the Ag$^+$ carbonyl complexes characterized by Strauss.[2] For the O-outside isomers **2b** and **3b**, there is some evidence from $\nu_{CO}$ values and MO calculations that back-donation from a filled Zr–acyl bonding MO to the CO $\pi^*_{\parallel}$ orbital contributes to the Zr–CO bonding. However, the $\nu_{CO}$ values are only slightly reduced from the free CO value, indicating that the Zr–CO bonding is dominated by the $\sigma$-donor interaction in these cases as well. A second factor contributing to the stability of **2** and **3** is the absence of CO insertion reactivity, which is largely due to the unfavorability of formation of a weak ZrC(O)–C(O)CH$_3$ bond.

The bonding in these Zr(IV) carbonyl complexes provides insight to the factors which promote insertion reactions in electrophile early metal systems. Base-free cationic (C$_5$R$_5$)$_2$Zr($\eta^2$-COR)$^+$ acyl species readily insert alkenes and alkynes.[23,27,54] Zr–substrate bonding (substrate = alkene or alkyne) in the presumed (C$_5$R$_5$)$_2$Zr($\eta^2$-COR)(substrate)$^+$ intermediates leading to insertion must be similar to the Zr–CO bonding in the O-outside isomers **2a** and **3a**. Both the $\sigma$-donation, which activates the coordinated substrate for nucleophilic attack by the Zr–acyl carbon,[55] and the Zr–acyl $\sigma\rightarrow\pi^*$ back-donation (i.e. incipient C–C bond formation)[49b,56] promote insertion.

## Experimental Section

All manipulations were performed under N$_2$ atmosphere or vacuum using a Vacuum Atmospheres drybox or a high vacuum line. CH$_2$Cl$_2$ was distilled from CaH$_2$, hexane and THF-$d_8$ were distilled from Na/benzophenone, and CD$_2$Cl$_2$ was distilled from P$_2$O$_5$. Solvents were stored in evacuated bulbs and generally vacuum-transferred to reaction flasks or NMR tubes. $^{13}$CO was purchased from MSD Isotopes and contained ca. 14% $^{13}$C–$^{18}$O. NMR spectra were obtained on Bruker AC-300 or AMX-360 instruments; data are listed in Table 1. $^1$H or $^{13}$C NMR chemical shifts are reported vs Me$_4$Si and were determined by reference to the residual $^1$H or $^{13}$C solvent peaks. $^{13}$C NMR spectra of compounds which contained [CH$_3$B(C$_6$F$_5$)$_3$]$^-$ groups (whether coordinated or free) exhibited characteristic aryl resonances: (CD$_2$Cl$_2$, 23 °C) $\delta$ 149 (dm, $^1J_{CF}$ = 251 Hz), 138 (dm $^1J_{CF}$ = 242 Hz), 137 (dm, $^1J_{CF}$ = 240 Hz), 129 (br m). FTIR spectra were recorded on a Mattson Cygnus 25 spectrometer. Elemental analyses were performed by E&R Microanalytical Laboratory Inc. Cp$_2$Zr(CH$_3$)$_2$,[57] Cp*$_2$Zr(CH$_3$)$_2$,[58] [Cp$_2$Zr(Me)(THF)][BPH$_4$),[59] and B(C$_6$F$_5$)$_3$[60] were prepared by literature methods. Spectrometric data for new compounds are listed in Table 1. Extended Hückel calculations were performed on a Tektronix CAChe Worksystem using standard parameters.[47,61]

**[Cp$_2$Zr($\eta^2$-C{N$^t$Bu}CH$_3$-*C,N*)(CN$^t$Bu)][BPh$_4$] (1).** To a slurry of [Cp$_2$Zr(Me)(THF)[BPh$_4$] (98 mg, 0.16 mmol) in CH$_2$Cl$_2$ (2 mL) was added $^t$BuNC (38 mg, 0.46 mmol) via pipet. The reaction mixture was shaken for 5 min at 23 °C producing a colorless solution. Hexane (3 mL) was added dropwise, and a white solid precipitated. The solid was collected by filtration, washed with hexane (3 × 5 mL), and dried (109 mg, 97%). Anal. Calcd for C$_{45}$H$_{51}$BN$_2$Zr: C, 74.87; H, 7.12; N, 3.88. Found: C, 75.02; H, 7.20; N, 3.84.

**Major Isomer of [Cp*$_2$Zr($\eta^2$-COCH$_3$)(CO)][CH$_3$B(C$_6$H$_5$)$_3$] (2a).** A Teflon-valved vial containing Cp$_2$*Zr(CH$_3$)$_2$ (27 mg, 0.069 mmol), B(C$_6$F$_5$)$_3$ (36 mg, 0.069 mmol), and 2 mL of CH$_2$Cl$_2$ was charged with 1 atm of CO at −196 °C. The vial was warmed to 23 °C to afford a clear yellow solution of **2a,b**. The CO pressure was reduced to 1 atm at 23 °C, and hexane (ca. 3 mL) was added. The solution was cooled to −40 °C for 24 h under 1 atm of CO, resulting in the formation of yellow crystals of **2a**. The crystals were collected by filtration and dried under vacuum for 5 min (35 mg, 54.5%). IR (KBr, cm$^{-1}$): 2103 ($\nu_{CO}$), 1577 ($\nu_{acyl}$). An analogous preparation using $^{13}$CO yielded crystals of **2a**-$^{13}C_2$. IR (KBr, cm$^{-1}$): 2066 ($\nu_{^{13}CO}$), 1541 ($\nu_{^{13}C-acyl}$).[62] Anal. Calcd for C$_{42}$H$_{36}$BF$_{15}$O$_2$Zr: C, 52.56; H, 3.78. Found: C, 52.70; H, 3.82.

**X-ray Diffraction Study of 2a.** A crystal of **2a** was sealed in a capillary under a partial pressure of CO. Diffraction data were obtained with an Enraf-Nonius CAD4 diffractometer and all calculations were performed using the Enraf-Nonius Molen computer program package. Temperature control was achieved with a locally modified Enraf-Nonius low temperature system. H atoms were located in several successive electron density difference maps and were fixed in idealized positions ($d$(C–H) 0.95 Å; ∠H–C–H 109.5°).

***In Situ* Preparation of [Cp*$_2$Zr($\eta^2$-COCH$_3$)(CO)][CH$_3$B(C$_6$H$_5$)$_3$] (2a,b).** A resealable NMR tube containing Cp*$_2$Zr(CH$_3$)$_2$ (21 mg, 0.054 mmol), B(C$_6$F$_5$)$_3$ (28.8 mg, 0.056 mmol), and 0.5 mL of CD$_2$Cl$_2$ was charged with 1 atm of CO at −196 °C. The tube was warmed to 23 °C to afford a clear yellow solution. The $^1$H NMR spectrum of this solution indicated quantitative formation of **2a,b**; major/minor isomer ratio 9/1 at −20 °C. **2**-$^{13}$C$_2$ labeled in the Zr*C*OCH$_3$ and Zr–*C*O positions was prepared by using the same procedure with $^{13}$CO.

***In Situ* Preparation of [Cp$_2$Zr($\eta^2$-COCH$_3$)(CO)][CH$_3$B(C$_6$H$_5$)$_3$] (3a,b).** A resealable NMR tube containing a solution of Cp$_2$ZrCH$_3$($\mu$-CH$_3$)B(C$_6$F$_5$)$_3$ (54 mg, 0.071 mmol, generated *in situ*) in CD$_2$Cl$_2$ (0.30 mL) was charged with 1 atm of CO at −196 °C. The tube was warmed to 23 °C and agitated for 5 min to afford a pale yellow solution. The $^1$H NMR spectrum of this solution indicated quantitative formation of **3a,b** (isomer ratio

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(53) The crowded structures of the formally 8-coordinate (C$_5$R$_5$)$_2$Zr($\eta^2$-COCH$_3$)$^+$ fragment may also promote coordination of the small linear CO ligand at the expense of the CH$_3$B(C$_6$F$_5$)$_3^-$ counterion.

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(55) See discussions in refs 22 and 25c.

(56) However, it should be noted that the extent of C(acyl)–C(carbonyl) bonding in **2a** is very minor at best. The C(acyl)–C(carbonyl) distance is long (2.73 Å), and the C–Zr–C angle (75.3(4)°) is only slightly smaller than the O–Zr–CH$_3$ angle in the ("O-inside") complex Cp$_2$Zr($\eta^2$-COCH$_3$)(CH$_3$) (79.6(2)° [35]).

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(61) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(62) The $\nu_{CO}$ band for the $^{13}$C$^{18}$O isotopomer is observed at 2015 cm$^{-1}$.

1/5, 23 °C). 3-$^{13}C_2$ labeled in the $ZrCOCH_3$ and Zr–CO positions was prepared by an identical procedure using $^{13}CO$.

***In Situ* Preparation of [$Cp^*_2Zr(\eta^2\text{-}COCH_3)$][$CH_3B(C_6H_5)_3$] (4).** A resealable NMR tube containing $Cp^*_2Zr(CH_3)_2$ (21.5 mg, 0.055 mmol), $B(C_6F_5)_3$ (28.1 mg, 0.055 mmol), and 0.5 mL of $CD_2Cl_2$ was charged with 1 equiv of CO at 23 °C. The tube was agitated for 5 min to ensure proper mixing, and a clear yellow solution was obtained. The $^1H$ NMR spectrum of this solution indicated the formation of 4 (75%), $Cp^*_2ZrCl_2$ (25%), and an unknown $Cp^*_2Zr$ species ($\delta$ 2.04, Cp*, ca. 5%). A solid sample of 4 (for IR) was obtained by removal of the solvent under vacuum. The use of $^{13}CO$ in this procedure yielded 4-$^{13}C$, labeled in the $ZrCOCH_3$ position. Detailed comparison of the IR spectra ($CH_2Cl_2$ solution and KBr pellet) of 4 and 4-$^{13}C$, did not allow conclusive assignment of $\nu_{acyl}$.

**[$Cp_2Zr(\eta^2\text{-}COCH_3)$][$CH_3B(C_6H_5)_3$] (5).** A Teflon-valved vial containing a solution of $Cp_2ZrCH_3(\mu\text{-}CH_3)B(C_6F_5)_3$ (81.3 mg, 0.103 mmol, generated *in situ*) in 3 mL of $CH_2Cl_2$ was charged with 1 atm of CO at −196 °C. The tube was warmed to 23 °C to afford a pale yellow solution of 5. The solution was degassed at −78 °C under vacuum (ca. 10 min), and a pale yellow crystalline solid precipitated. The solid was collected by filtration, washed with hexane, and dried under vacuum (35 mg). Evaporation of the filtrate afforded another 30 mg of the pale yellow solid (total yield 85%). 5-$^{13}C$ labeled in the $ZrCOCH_3$ position was prepared in an identical fashion using $^{13}CO$. Anal. Calcd for $C_{31}H_{16}BF_{15}OZr$: C, 47.04; H, 2.04. Found: C, 46.95; H, 2.12.

**Note Added in Proof.** Stryker et al. have recently isolated a closely related Zr(IV) carbonyl complex, [$Cp^*_2Zr(\eta^3\text{-allyl})(CO)$][$BPh_4$].[63]

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**Supplementary Material Available:** Tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, and hydrogen atom bond distances and angles for **2a** (10 pages). Ordering information is given on any current masthead page.

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[63] Antonelli, D. M.; Tjaden, E. B.; Stryker, J. M. *Organometallics*, precedinig paper in this issue.