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A Thermally Stable Carbonyl Complex of Zirconium(IV). Structure and Reactivity Ramifications of Strong $\sigma \rightarrow \pi^*$ Electron Donation

David M. Antonelli, Erik B. Tjaden, and Jeffrey M. Stryker*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

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Summary: The first isolable d^0 CO complex of Zr(IV), $[Cp^*_2Zr(\eta^3-C_3H_5)CO]^+BPh_4^-$ (2), has been prepared by treatment of $[Cp^*_2Zr(\eta^3-C_3H_5)]^+BPh_4^-$ (1) with CO. The remarkable stability of this complex is attributed to strong $\sigma \rightarrow \pi^*$ donation from the neighboring allyl ligand, completely inhibiting fluxionality in the allyl fragment. The structure of complex 2 is compared to that of $[Cp^*Zr(\eta^3-C_3H_5)(NC_3H_3NCH_3)]^+BPh_4^-$ (3), in which the allyl ligand is fluxional and η^3-bound to the metal center, and $[Cp^*_2Zr(\eta^1-CH_2CH{=}CH_2)(PMe_3)]^+BPh_4^-$ (4), which has a terminally coordinated allyl group. The reactivity of these complexes toward ligand substitution is also explored.

Metal carbonyl complexes in which $d \rightarrow \pi^*$ back-bonding is either highly unfavorable or not possible are extremely rare.[1] This is because CO is only weakly σ-donating and the $d \rightarrow \pi^*$ back-bonding interaction constitutes the major component of the metal–CO bond.[2] In spite of this, a number of CO complexes in which $d \rightarrow \pi^*$ back-bonding is either very weak or completely absent have been characterized. In these complexes, the CO stretch in the IR spectrum is typically higher than that for free CO (2143 cm^{-1}, gas phase) and σ-donation from the CO carbon to the metal center is believed to be the major component of the metal–CO bond. These complexes can be classified into two groups: those involving main-group and higher oxidation state late transition metals such as Au,[3] Ag,[4] Pd,[5] Pt,[6] and Sn,[7] where the d electrons are not disposed for effective back-donation, and those involving d^0 metals such as Zr(IV),[8,9] Hf(IV),[10] and Ti(IV).[11] In these group 4 complexes, an unusual lowering of the CO stretch from that of free CO is often observed. Bercaw *et al.* have proposed that this is due to a favorable overlap of filled M–L bonding orbitals with a CO π^* orbital.[8] The ν_{CO} values in these species can approach those observed for related d^1 complexes.[12]

In spite of the growing number of examples of d^0 CO complexes, thermal instability has precluded their isolation.[13] Herein, we report the first example of a stable and *isolable* d^0 CO species and compare its structure and reactivity to those of related trimethylphosphine and 1-methylimidazole complexes.

Treatment of $[Cp^*_2Zr(\eta^3-C_3H_5)]^+BPh_4^-$ (1;[14] Cp* = C_5Me_5) in dichloromethane with CO (75 psi) leads to a rapid color change from red to bright yellow. Concentrating this solution followed by layering with toluene leads to formation of bright yellow crystals of a new complex (2) that analyzes as $[Cp^*_2Zr(\eta^3-C_3H_5)(CO)]^+BPh_4^-$ [15,16] (Scheme 1). Complex 2 is stable at room temperature under argon both as a solid and in solution. This robust behavior is in contrast to that observed for all other examples of such complexes, which readily lose CO at ambient temperature and/or upon release of the CO atmosphere.[8–11,13] Heating of complex 2, however, at 60 °C in dichloromethane over 30 min results in its complete decomposition, even under CO, as determined by ^1H NMR spectroscopy.[17]

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[1] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organometallic Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 3.

[2] Mingos, D. M. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 3, Section 19.2.

[3] (a) Willner, H.; Schaebs, J.; Hwang, G.; Mistry, F.; Jones, R.; Trotter, J.; Aubke, F. *J. Am. Chem. Soc.* **1992,** *114,* 8972 and references therein. (b) Willner, H.; Aubke, F. *Inorg. Chem.* **1990,** *29,* 2195.

[4] (a) Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1991,** *113,* 6277. (b) Hurlburt, P. K.; Rack, J. R.; Dec, F.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1993,** *32,* 373.

[5] (a) Calderazzo, F. *J. Organomet. Chem.* **1990,** *400,* 303 and references therein. (b) Calderazzo, F.; Belli Dell'Amico, D. *Pure Appl. Chem.* **1986,** *58,* 561.

[6] Usón, R.; Forniés, J.; Milagros, T.; Menjón, B. *Organometallics* **1985,** *4,* 1912.

[7] Tevault, D.; Nakamoto, K. *Inorg. Chem.* **1976,** *15,* 1282.

[8] (a) Manriquez, J. M.; McAlister, D. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978,** *100,* 2716. (b) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976,** *98,* 6733.

[9] Guram, A. S.; Swenson, D. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1992,** *114,* 8991.

[10] Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985,** *4,* 97.

[11] Demersman, B.; Pankowski, M.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1976,** *117,* C10.

[12] (a) Van Raaiji, E. I.; Schmulbach, C. D.; Brintzinger, H. H. *J. Organomet. Chem.* **1987,** *328,* 275. (b) De Boer, E. J. M.; Ten Cate, L. C.; Staring, A. G. J.; Teuben, J. H. *J. Organomet. Chem.* **1979,** *181,* 61.

[13] A related d^0 carbon monoxide complex of zirconium has recently been isolated: Guo, Z.; Swenson, D. C.; Guram, A. S.; Jordan, R. F. *Organometallics,* following paper in this issue. We thank Professor Jordan for communicating his results prior to publication and providing a preprint of his manuscript.

[14] Tjaden, E. B.; Casty, G. L.; Stryker, J. M. *J. Am. Chem. Soc.* **1993,** *115,* 9814.

[15] Complete spectroscopic data for all new compounds is provided as supplementary material.

[16] Preparation and selected spectroscopic data for complex **2**: In the drybox, $[Cp^*Zr(C_3H_5)]^+BPh_4^-$ (1; 0.520 g, 0.720 mmol) was dissolved in 12 mL of CH_2Cl_2, transferred to a pressure bottle, removed from the drybox, and placed under CO (75 psi) at room temperature. The bright red reaction mixture was stirred vigorously for 1.5 h, producing a yellow solution. In the drybox, the solution was concentrated, diluted with toluene, and cooled to −35 °C to precipitate a creamy, pinkish white powder. The mother liquor was removed via pipet and the remaining solid washed with toluene (3 × 5 mL) and dried *in vacuo* (0.501 g, 0.667 mmol, 93%). Analytically pure, colorless, blocklike crystals of complex **3** were obtained by layering toluene onto a CH_2Cl_2 solution at room temperature. Selected spectroscopic and analytical data for complex **2**: IR (CH_2Cl_2) 2079 (s, CO); ^1H NMR (400 MHz, CD_2Cl_2) δ 7.36 (br m, 8H, BPh_4), 7.06 (t, $J = 7.2$ Hz, 8H, BPh_4), 6.91 (t, $J = 7.2$ Hz, 4H, BPh_4), 4.40 (tt, $J = 15.6$, 9.2 Hz, 1H, H_c), 3.51 (d, $J = 9.2$ Hz, 1H, H_s), 3.11 (d, $J = 9.2$ Hz, 1H, H_s), 2.63 (d, $J = 15.6$ Hz, 1H, H_a), 1.88 (s, 15H, C_5Me_5), 1.83 (s, 15H, C_5Me_5), 1.75 (d, $J = 15.6$ Hz, 1H, H_a); ^{13}C NMR (gated decoupled, 100 MHz, CD_2Cl_2; cation only) δ 218.7 (s, CO), 128.7 (d, $J = 152$ Hz, H_c), 117.1 (s, C_5Me_5), 116.1 (s, C_5Me_5), 69.6 (td, $J = 158.0$, 11.0 Hz, C_t), 69.3 (td, $J = 158.0$, 12.0 Hz, $C_{t'}$), 11.7 (q, $J = 127.5$ Hz, $C_5\mathit{Me}_5$), 11.4 (q, $J = 126.9$ Hz, $C_5\mathit{Me}_5$). Anal. Calcd for $C_{48}H_{55}BOZr$: C, 76.87; H, 7.39. Found: C, 76.95; H, 7.56.

[17] The decomposition products obtained upon the thermolysis of complex **2** are the same as those observed for the parent complex **1** by ^1H NMR spectroscopy, suggesting that decomposition of complex **2** occurs via initial loss of CO.

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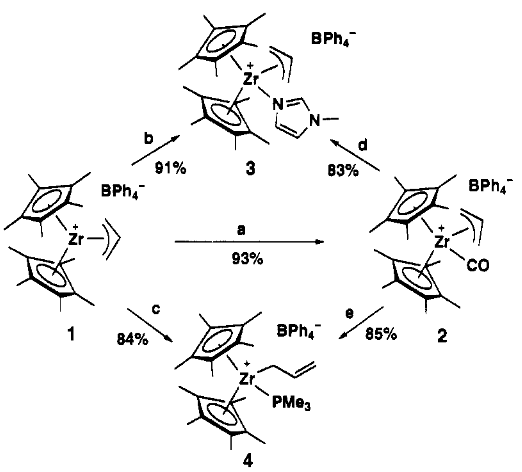
Scheme 1[a]



[a] Reaction conditions: (a) CO (75 psi), CH_2Cl_2, room temperature, 1.5 h; (b) 1-methylimidazole, CH_2Cl_2, room temperature, 10 min; (c) PMe_3, CH_2Cl_2, room temperature, 3 h; (d) 1-methylimidazole, CH_2Cl_2, room temperature, 5 min; (e) PMe_3, CH_2Cl_2, room temperature, 3 h.

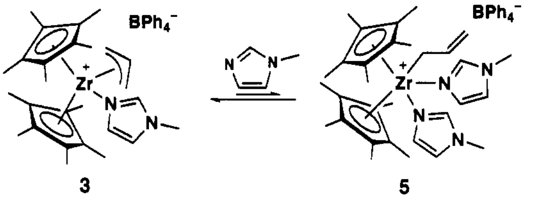
The IR spectrum of complex **2** displays a salient stretch at 2079 cm^{-1}, strongly suggestive of a CO complex. This ν_{CO} value is higher than that observed in the neutral Zr(IV) hydrido carbonyl complex (2044 cm^{-1})[8] but lower than those values recorded for Zr(IV) alkyl (2095 cm^{-1})[9] and acyl (2152, 2105 cm^{-1})[13] carbonyl species. It also compares in magnitude to those observed in many d^1 complexes (2000–2068 cm^{-1}).[12] The ^1H NMR spectrum of this species displays two unique signals for the Cp* methyl groups and five independent multiplets for the allyl proton resonances.[16] This is characteristic of an unusual d^0 *rigid* η^3-allyl ligand, in contrast to the highly fluxional allyl ligand observed in the parent complex **1**.[18] The proposed structure is further supported by the ^{13}C NMR spectrum, which displays a singlet at δ 218.7 for the CO carbon and three distinct allyl carbon signals at δ 128.7, 69.6, and 69.3, as well as two inequivalent sets of Cp* ring carbons and methyl groups.

The rigidity of the allyl ligand in complex **2** and its unusually low CO stretch as compared to other d^0 carbonyl complexes are indicative of significant donation of the M–allyl σ-bonding electrons into the CO π^* orbital. Such σ-electron donation was first proffered by Bercaw to rationalize the low CO stretch observed in $Cp^*_2ZrH_2(CO)$.[8] To correlate the strength of this interaction with the magnitude of ^{13}C–^{13}C coupling between the CO carbon and the allyl carbons, selective decoupling experiments were carried out on a sample of ^{13}CO-enriched complex **2**. In this complex, the allyl terminal carbon signal at δ 69.3, which appears as a singlet in the nonenriched sample, instead resonates as a doublet (J_{CC} = 4.8 Hz) in the enriched sample. Irradiation of the ^{13}CO singlet at δ 218.7 leads to collapse of this coupling. This observation supports the hypothesis that there is an interaction uniquely between these two centers. The complete nature of this interaction, however, has not yet been elucidated.[19]

Complex **2** exchanges CO readily at ambient temperature but does not react further under CO (2 atm) at this temperature to form an acyl carbonyl complex, despite the stability reported for $[Cp^*_2Zr(\eta^2\text{-}CH_3CO)(CO)]^+$.[13]

Treatment of complex **1** with 1-methylimidazole (1 equiv) in dichloromethane results in the immediate formation of an orange complex, identified by ^1H NMR, ^{13}C NMR, and IR spectroscopy to be $[Cp^*_2Zr(\eta^3\text{-}C_3H_5)(NC_3H_3NCH_3)]^+BPh_4^-$ (**3**).[15] The ^1H NMR of this complex displays a doublet at δ 2.91 and a quintet at δ 5.75 for the central and terminal allyl protons, respectively, establishing the allyl ligand as fluxional and η^3-coordinated to the metal center. This is in contrast to the rigid η^3-allyl coordination observed in complex **2** and further corroborates the hypothesis of a bonding interaction between the allyl and CO ligands sufficiently strong to inhibit any fluxionality.

Treatment of complex **3** with an excess of 1-methylimidazole results in the formation of equilibrium amounts of a tentatively assigned bis(1-methylimidazole) complex (**5**) in which the allyl ligand is bound to the metal center in an η^1 fashion (eq 1).[15,20] Stirring complex **3** under a CO atmosphere results in formation of a new complex (**6**) which has not yet been characterized.[21] The same complex is also formed as a minor product along with complex **3** when the CO complex **2** is treated with 1-methylimidazole (1 equiv). This suggests that the CO ligand in complex **2** is bound strongly enough to the metal center to prevent simple ligand substitution reactions and allow its involvement in subsequent chemistry.

 (1)

Treatment of either complex **1** or **2** with PMe_3 (1 equiv) results in the formation of colorless $[Cp^*_2Zr(\eta^1\text{-}CH_2\text{-}CH{=}CH_2)PMe_3]^+BPh_4^-$ (**4**),[15,22] as confirmed by ^1H NMR, ^{13}C NMR, and IR spectroscopy. Surprisingly, the allyl ligand in this complex is terminal, rather than η^3-coordinated as in complex **3**. Furthermore, complex **4** is unreactive toward CO, in contrast with expectations based on the coordinative unsaturation of the metal center and the facile reaction of imidazole complex **3** with CO. Moreover, treatment of complex **4** with excess PMe_3 leads only to exchange, as evidenced by line broadening in the ^1H NMR spectrum, with no formation of a bis(PMe_3) adduct comparable to that formed using 1-methylimidazole. Complex **4** is unreactive toward 1-methylimidazole, but imidazole complex **3** reacts completely with excess

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(18) The allyl ligand in complex **1** is rapidly fluxional at room temperature, approaching but not attaining static η^3 coordination at −78 °C.

(19) (a) The magnitude of this ^{13}C–^{13}C coupling falls between the values of 10.5 and 2.7 Hz reported by Jordan for the *cis* and *trans* isomers of $[Cp^*_2Zr(^{13}CO)(\eta^2\text{-}CH_3{}^{13}CO)]^+$.[13] (b) Efforts to further elucidate the structure of complex **2** by X-ray crystallography have been thwarted by problems with disorder; however, attempts are currently underway to obtain crystallographic data for a more suitable derivative.

(20) Selected ^1H NMR (400 MHz, CD_2Cl_2) spectroscopic data for complex **5**: δ 5.78 (ddt, J = 17.4, 10.0, 6.9 Hz, 1H, $H_{internal\ vinyl}$), 5.21 (ddt, J = 17.4, 2.3, 1.0 Hz, 1H, $H_{terminal\ vinyl}$), 5.02 (ddt, J = 10.0, 2.3, 1.0, 1H, $H_{terminal\ vinyl}$), 1.83 (s, 30 H, C_5Me_5), 1.71 (tm, J = 6.9 Hz, 2H, CH_2). Resonances for the 1-methylimidazole ligands are partially obscured by those of starting complex **3** and excess free ligand.

(21) IR and ^{13}C spectroscopic data for complex **6** clearly establish that it is *not* a CO complex.

(22) Selected ^1H NMR (400 MHz, CD_2Cl_2) spectroscopic data for complex **4**: δ 5.66 (ddt, J = 17.6, 10.3, 6.8 Hz, 1H, $H_{internal\ vinyl}$), 5.32 (ddt, J = 17.6, 2.3, 1.0 Hz, 1H, $H_{terminal\ vinyl}$), 5.08 (ddt, J = 10.3, 2.3, 1.0, 1H, $H_{terminal\ vinyl}$), 1.95 (s, 30 H, C_5Me_5), 1.89 (tm, J = 6.8 Hz, 2H, CH_2), 1.02 (d, J_{PH} = 14.2 Hz, 9H, PMe_3). Homonuclear decoupling experiments: irradiation at δ 5.66, coupled to δ 5.32, 5.08, 1.89; irradiation at δ 1.89, coupled to δ 5.66.

PMe_3 over several days at room temperature to give complex 4 and free 1-methylimidazole. This establishes that PMe_3 is the thermodynamically preferred ligand in this system, followed by 1-methylimidazole and finally CO. Although a consistent rationale for these structural observations is not fully apparent, the steric bulk or greater basicity of PMe_3 relative to 1-methylimidazole may determine the reduced hapticity of the allyl ligand observed in complex 4.

In summary, the first isolable d^0 carbonyl complex has been characterized. The stability of this complex is attributed to a strong $\sigma \rightarrow \pi^*$ interaction with an adjacent allyl ligand and a lack of kinetically accessible reaction pathways. The structural influence of CO, 1-methylimidazole, and PMe_3 on the bonding of the allyl ligand in complexes of the type $[Cp^*_2Zr(C_3H_5)L]^+BPh_4^-$ reveals that in each case the allyl ligand assumes a different coordination mode, depending on the steric and electronic character of the neighboring ligand and its interaction with the metal center. Efforts are currently underway to characterize the reaction product of imidazole complex **3** with CO and to obtain suitable crystals of complex **2** or a related derivative for elucidation of its structure in the solid state. Furthermore, replacement of the counterion with a more inert analog such as $[B(C_6F_5)_4]^-$ [23] may inhibit the thermal decomposition of $[Cp^*_2Zr(\eta^3\text{-}C_3H_5)CO]^+$ and facilitate the exploration of its chemistry.

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Supplementary Material Available: Text giving complete experimental, spectroscopic, and analytical data for complexes 2–4 (4 pages). Ordering information is given on any current masthead page.

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(23) See, for example: Chien, J. C. W.; Trai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570 and references therein.