Zirconium-Mediated Reactions of Carbon Monoxide and Alkynes. Insertion Chemistry of Cationic Zr(IV) η^2-Acyl and Alkenyl Complexes

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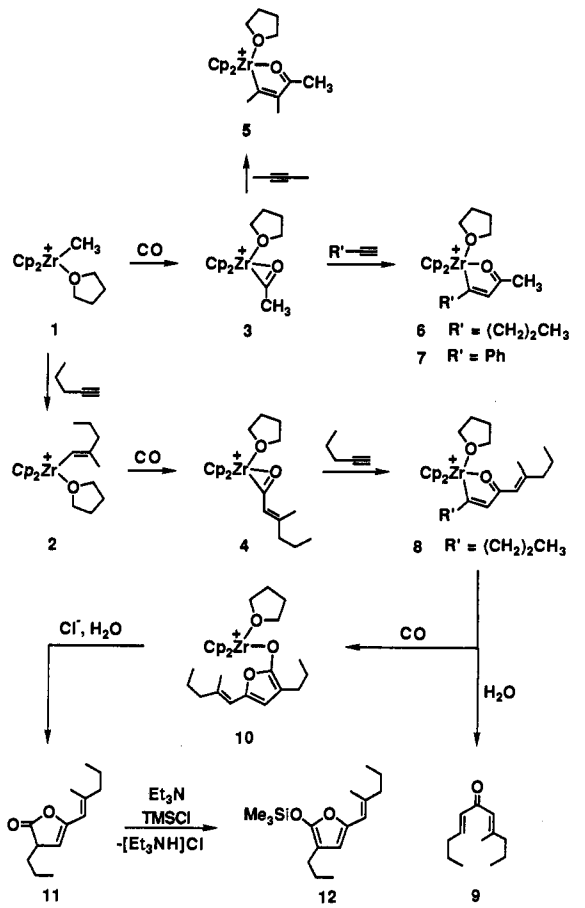
Reactions of carbon monoxide and alkynes mediated by middle- and late-transition-metal complexes provide a general approach to unsaturated carbonyl compounds.[1,2] In contrast, analogous reactions at early-transition-metal centers are unknown. We report here that $Cp_2Zr(R)(THF)^+$ complexes undergo alternating insertion of carbon monoxide and alkyne leading to a variety of useful organic products.

As part of our program to develop synthetic applications of $Cp_2Zr(R)(L)^+$ complexes,[3] we reported that $Cp_2Zr(\eta^2\text{-}N,C\text{-pyridyl})(L)^+$ and related complexes derived via C–H activation[4] regioselectively insert alkenes, alkynes, and other unsaturated substrates.[5] This suggested that isolobal $Cp_2Zr(\eta^2\text{-}O,C\text{-acyl})(L)^+$ complexes, derived from CO insertion of $Cp_2Zr(R)(L)^+$,[6] would exhibit similar insertion chemistry. Our results are summarized in Scheme I.

The cationic complex $Cp_2Zr(CH_3)(THF)^+$ (**1**)[7] reacts rapidly (23 °C, 1–2 h) with 1-pentyne to afford the (*E*)-alkenyl complex **2** (Scheme I).[8,9] No regioisomers, multiple insertion products, or pentyne C–H bond activation products are observed. The configuration of the alkenyl ligand in **2** is established by the lack of coupling between the vinyl-H and the vinyl-CH_3 in the ^1H NMR spectrum, and the downfield Zr—CH= resonance (δ 185, confirmed by a DEPT experiment) in the ^{13}C NMR spectrum. Complexes **1** and **2** react rapidly with carbon monoxide (<23 °C, min, 1 atm) to afford the η^2-acyl complexes **3** and **4** in quantitative yield. The ^{13}C NMR spectra of **3** and **4** exhibit carbonyl resonances at δ 318 and 291, respectively, consistent with the assigned η^2-acyl structures.

Scheme I



Complexes **3** and **4** are inert to carbon monoxide (1 atm) even on prolonged exposure but insert terminal and internal alkynes to afford β-ketoalkenyl complexes which adopt chelated structures. Thus **3** reacts with 2-butyne (23 °C, 3 days), 1-pentyne (23 °C, ~20 h), and phenylacetylene (23 °C, ~8 h) to yield **5–7**, respectively, in high yield.[10] The ^{13}C NMR resonance for the carbonyl carbon (δ 215) of **5** is substantially perturbed from values of organic analogues[11] and establishes that the carbonyl oxygen is coordinated to Zr.[12] Chelated structures for **6** and **7** are similarly evident from the spectroscopic data.[13,14] The regiochemistry (alkyne substituent located on the carbon α to zirconium) of **6** and **7** is unambiguously established from ^1H, ^{13}C, and DEPT NMR experiments.

The chemistry of **1–7** establishes that $Cp_2Zr(\eta^2\text{-acyl})(THF)^+$ complexes insert alkynes cleanly and that the $Cp_2Zr(\text{alkenyl})$-

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(7) The counterion is BPh_4^- in all cases.

(8) Detailed synthetic procedures and complete characterization data are provided in the supplementary material. The presence of 1 equiv of coordinated THF in **2–8** and **10** is established by the observation of ^1H and ^{13}C NMR THF resonances that are shifted from those of free THF. Based on steric grounds and by analogy to previously characterized $Cp_2Zr(\eta^2\text{-}N,C\text{-pyridyl})(L)^+$ complexes, it is likely that the THF ligand is cis to O in **3–8**; however, this was not conclusively established.

(9) For related insertion reactions, see: Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. C. *Organometallics* **1989**, *8*, 2892.

(10) These reactions are nearly quantitative by NMR. Reactions at elevated temperatures (~50 °C) are faster (1–2 h) but are relatively unclean. There is no evidence for the formation of other regioisomers in the case of **6** and **7**.

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(13) Key data for **6**: ^1H NMR (360 MHz, CD_2Cl_2) δ 7.06 (obscured by BPh_4^-, 1H, =C*H*COCH$_3$), 6.01 (s, 10H, Cp), 2.32 (s, 3H, COCH$_3$); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 281.3 (ZrC=), 214.4 (*C*OCH$_3$); FTIR (KBr pellet) 1558.4 (m) cm^{-1}. Anal. Calcd for $C_{45}H_{49}BO_2Zr$: C, 74.66; H, 6.82. Found: C, 74.26; H, 6.54. The regiochemical assignments for **6** and **7** are based on the low-field Zr*C*(R')=C ^{13}C resonances and the low-field ZrC-(R')=C(*H*)C(=O)Me ^1H NMR resonances.

(14) Key data for **7**: ^1H NMR (300 MHz, CD_2Cl_2) δ 7.28 (s, 1H, =C*H*COCH$_3$), 6.13 (s, 10H, Cp), 2.42 (s, 3H, COCH$_3$); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 261.8 (ZrC=), 213.9 (*C*OCH$_3$), 27.5 (CO*C*H$_3$); FTIR (KBr pellet) 1557.9 (m) cm^{-1}. Anal. Calcd for $C_{48}H_{47}BO_2Zr$: C, 76.07; H, 6.25. Found: C, 75.86; H, 6.47.

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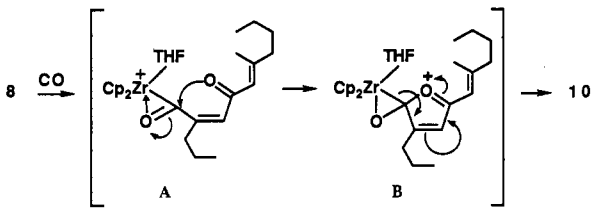
$(THF)^+$ complexes insert CO cleanly. The possibility of achieving multiple CO/alkyne insertions was explored with complex **4**. Complex **4** reacts with 1-pentyne (23 °C, ~8 h) to afford **8**, which like **5–7** adopts a chelated structure. Key data for **8** include quaternary carbon resonances at δ 275 and 201 for Zr—C= and —*C*(O)CH_3 respectively (confirmed by ^{13}CO-labeling) in the ^{13}C NMR spectrum. Hydrolysis of **8** yields 1,4-divinyl ketone **9** as the sole organic product and confirms the regio- and stereoselection of pentyne insertion of **1** and **4**.[8] Treatment of **8** with CO (23 °C, ~2 h, 3–4 atm) affords the thermally unstable zirconoxyfuran **10**. The ^1H NMR spectrum of **10** exhibits a Cp resonance at δ 6.44, two vinyl-H resonances at δ 6.04 and 5.92, and the expected aliphatic resonances. The ^{13}C NMR spectrum of **10** exhibits resonances at δ 164 and 143 for O—C= carbons of the furan ring (confirmed by ^{13}CO-labeling), resonances at δ 111 and 99 for O—C=*C*— carbons of the furan ring, and the anticipated resonances for the Cp, alkenyl, and alkyl carbons. Conspicously absent from the ^{13}C NMR spectrum of **10** are resonances attributable to carbonyl carbons. The NMR data for **10** are nearly identical to those of the analogous siloxyfuran **12** (*vide infra*) and unambiguously establish the assigned structure.

Hydrolysis of **10**, or more preferably treatment with a Cl^- source followed by hydrolysis, affords the β,γ-unsaturated γ-lactone **11**. Key features in the ^1H NMR spectrum of **11** include a multiplet at δ 3.25 for O(CO)CH and multiplets at δ 1.80 and 1.60 for the diastereotopic methylene protons α to the lactone ring (confirmed by ^1H decoupling experiments). The ^{13}C NMR spectrum of **11** exhibits a carbonyl resonance at δ 180. These data and a strong IR ν_{CO} absorbance at 1796 cm^{-1} establish the assigned lactone structure.[11] Treatment of **11** with Et_3N/TMSCl affords the silyloxyfuran **12**, which was unambiguously characterized by ^1H and ^{13}C NMR, IR, and mass spectroscopy.[15]

The formation of complex **10** most likely proceeds via the mechanism depicted in eq 1. Carbonylation of **8** forms intermediate **A**, which undergoes an intramolecular attack at the Zr–acyl carbon by the carbonyl oxygen and subsequent Zr–C bond cleavage.[16]

For Group 4 metal systems, the insertion of alkynes into M–C(acyl) bonds is unprecedented and perhaps surprising given the nucleophilic character of migratory insertion reactions of early-metal alkyls[17] and the electrophilic character of early-metal η^2-acyls.[18] The coupling of coordinated alkynes with η^2-iminoacyl



and η^2-acyl ligands in CpTa(ArCCAr)(η^2-C{N-^{t}Bu}Me) and CpTa(ArCCAr)(η^2–C{O}Me) has been reported.[19] The insertion of carbon monoxide into Group 4 M–C(alkenyl) bonds is also rare.[20] The high reactivity observed in the present study can be ascribed to the high Lewis acidity of the cationic Zr(IV) centers which promote coordination and activation of the inserting substrates.[3] The regioselectivity observed in the insertion of terminal alkynes into Zr–C(acyl) bonds is similar to that observed for analogous reactions of $Cp_2M(pyridyl)(L)^+$, Cp_2M(benzyne), and related complexes (M = Group 4 metal) and has been rationalized on the basis of steric/electronic effects.[5c]

We have demonstrated here that alternating multiple insertions of carbon monoxide and alkynes are feasible at $Cp_2Zr(R)^+$ centers under mild conditions. These reactions exhibit excellent and predictable regio-/stereoselectivities and provide a general approach to α,β-unsaturated ketones, 1,4-divinyl ketones, γ-lactones, and furans. Subsequent reports from our laboratory will describe our efforts to broaden the scope and develop synthetic applications of these reactions, studies with related base-free Cp_2MR^+ systems,[21] and efforts to prepare alternating $\{C(R)=C(R')(CO)\}_n$ oligomers and/or polymers by this approach.[22]

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Supplementary Material Available: Details of experimental procedures and spectroscopic and analytical data for **2–12** (8 pages). Ordering information is given on any current masthead page.

(15) Data for **12**: ^1H NMR (360 MHz, C_6D_6) δ 6.06 (br s, 1H, CH_3C=C*H*), 6.03 (s, 1H, C*H*=C(CH=)O), 2.34 (t, $^3J_{H-H}$ = 7.5 Hz, 2H, C$H_2CH_2CH_3$), 2.00 (t, $^3J_{H\,H}$ = 7.5 Hz, 2H, C$H_2CH_2CH_3$), 1.96 (s, 3H, =CCH_3), 1.57 (sextet, $^3J_{H\,H}$ = 7.5 Hz, 2H, $CH_2CH_2CH_3$), 1.39 (sextet, $^3J_{H\,H}$ = 7.5 Hz, 2H, $CH_2CH_2CH_3$), 0.93 (t, $^3J_{H-H}$ = 7.4 Hz, 2H, $CH_2CH_2CH_3$), 0.84 (t, $^3J_{H\,H}$ = 7.4 Hz, 2H, $CH_2CH_2CH_3$), 0.21 (s, 9H, $OSiMe_3$); ^{13}C NMR (90 MHz, C_6D_6) δ 152.0, 133.9, 115.1, 111.3, 99.5, 43.2, 26.0, 23.7, 21.6, 18.5 (CH_3), 14.1 (CH_3), 13.9 (CH_3), 0.2 ($OSiMe_3$).

(16) Similar mechanisms have been proposed, see refs 1c,e,f.

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