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Articles

Permethyl Yttrocene 2-Furyl Complexes: Synthesis and Ring-Opening Reactions of the Furyl Moiety[†]

Stéphanie N. Ringelberg, Auke Meetsma, Sergei I. Troyanov,[‡] Bart Hessen,* and Jan H. Teuben

Center for Catalytic Olefin Polymerization, Stratingh Institute for Chemistry and Chemical Engineering, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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Permethyl yttrocene 2-furyl ate-complexes $Cp^*_2Y(\mu\text{-}C_4H_3O)(\mu\text{-}Cl)Li(THF)_2$ (**1**, Cp* = C_5Me_5) and $Cp^*_2Y(\mu\text{-}C_4H_3O)_2Li(TMEDA)$ (**2**) were obtained by reaction of $Cp^*_2Y(\mu\text{-}Cl)_2Li(OEt_2)_2$ with 1 and 2 equiv of 2-lithiofuran, respectively. Furan is metalated by $(Cp^*_2YH)_2$ in hydrocarbon solvents to give the 2-furyl complex $Cp^*_2Y(\eta^2\text{-}C_4H_3O)$ (**3**). With Lewis bases, **3** reacts to give the adducts $Cp^*_2Y(\eta^1\text{-}C_4H_3O)(L)$ (L = THF, **4**; pyridine), of which **4** was crystallographically characterized. Compound **3** decomposes through deprotonation and ring-opening of the 2-furyl group to give the (crystallographically characterized) bimetallic ynyl-enolate complex $(Cp^*_2Y)_2(\mu\text{-}OCH{=}CHC{\equiv}C)$ (**5**). With excess H_2, **3** is transformed into the crystallographically characterized oxo-complex $(Cp^*_2Y)_2(\mu\text{-}O)$ (**6**), free furan, and *n*-butane. In the presence of a large excess of furan, this reaction stops at the enolate species $Cp^*_2YOCH{=}CHEt$.

Introduction

There is a substantial interest in group 3 and lanthanide metal metallocene alkyl and hydride complexes for their high reactivity in C−H activation reactions as well as for the wide range of insertion reactions into the metal-hydride/alkyl bond.[1,2] Recently, we have employed the decamethyl yttrocene and lanthanocene systems to combine these two reaction types into a single catalytic conversion, integrating catalytic ethene polymerization with thiophene C−H activation to give 2-thienyl end-functionalized polyethene.[3] Extension of this chemistry to the analogous oxygen heterocyle, furan, is expected to be more challenging due to the harder Lewis basicity of furan, which may obstruct coordination and subsequent insertion of olefin substrates, and the enhanced possibility for C−X activation reactions, which will yield inactive oxo, alkoxide, or enolate species. The latter has been observed on several occasions in the reactions of group 3 and lanthanide metal alkyls and hydrides with ethers.[1b,g,4,5]

To probe this reactivity, we have investigated the synthesis and properties of permethyl yttrocene 2-furyl complexes. The formation of such species through metalation of furan by $(Cp^*_2YH)_2$ (Cp* = $\eta^5\text{-}C_5Me_5$) was briefly mentioned in a previous paper from our group, but the characterization of the yttrium furyl species was less than satisfactory at that time.[5] Here we describe the synthesis and characterization of Cp^*_2Y-furyl complexes prepared through metalation and salt metathesis reactions, as well as some reactivity involving C−O bond activation. The base-free $Cp^*_2Y(\eta^2\text{-}2\text{-furyl})$ complex was found to decompose in solution by ring-opening and deprotonation of the furyl moiety to give an unusual bimetallic ynyl-enolate complex.

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[‡] Permanent address: Moscow State University, Department of Chemistry, Leninskie Gory, 119899 Moscow, Russia.

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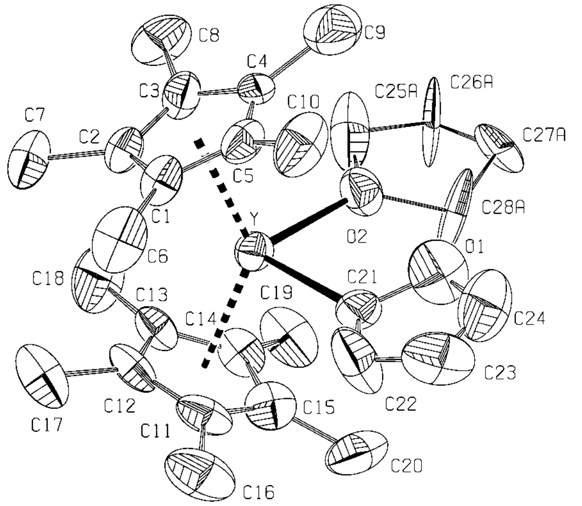
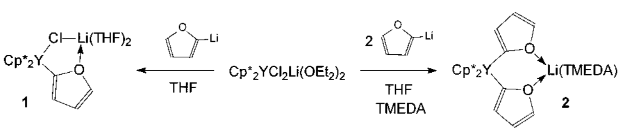


Figure 1. Molecular structure of $Cp^*_2Y(C_4H_3O)(THF)$ (**4**). Thermal ellipsoids are drawn at the 50% probability level.

Scheme 1



Results and Discussion

Synthesis of Permethyl Yttrocene 2-Furyl Complexes. Two different routes were taken for the synthesis of Cp^*_2Y(2-furyl) species: (a) a salt metathesis reaction between $Cp^*_2Y(\mu\text{-}Cl)_2Li(OEt_2)_2$[6] and 2-lithiofuran, and (b) metalation of furan by $(Cp^*_2YH)_2$[7]. Reaction of $Cp^*_2Y(\mu\text{-}Cl)_2Li(OEt_2)_2$ with 1 equiv of 2-lithiofuran in THF, followed by extraction with pentane, yielded a compound that was characterized by NMR spectroscopy and elemental analysis as the ate-complex $Cp^*_2Y(\mu\text{-}C_4H_3O)(\mu\text{-}Cl)Li(THF)_2$ (**1**, Scheme 1). In the ^{13}C NMR spectrum of **1**, the furyl 2-carbon resonance is found at δ 210.08 with a $^1J_{YC}$ of 62 Hz, indicating that the 2-furyl unit is C-η^1-bound to yttrium (see below) and that the furyl unit is likely to bridge Y and Li in a Y[μ-(η^1-C, η^1-O)]Li fashion. Attempts to remove the coordinated LiCl from **1**, e.g., by refluxing in hexane, were not successful. It proved possible to substitute the remaining chloride in **1** by another 2-furyl group. Reacting $Cp^*_2Y(\mu\text{-}Cl)_2Li(OEt_2)_2$ with 2 equiv of 2-lithiofuran in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) yielded the bis(2-furyl) ate-complex $Cp^*_2Y(\mu\text{-}C_4H_3O)_2Li(TMEDA)$ (**2**, Scheme 1). The NMR characteristics of the (equivalent) 2-furyl groups in **2** are very similar to those seen for **1**, suggesting a similar bonding mode.

Reaction of $(Cp^*_2YH)_2$ with furan in pentane at 0 °C leads to rapid gas evolution. Upon concentrating and cooling the reaction mixture, the base-free 2-furyl complex $Cp^*_2Y(\eta^2\text{-}C_4H_3O)$ (**3**, Scheme 2) was obtained in 60% isolated yield. Performing the same reaction and adding THF to the solution of **3** in pentane allowed isolation of the THF adduct $Cp^*_2Y(\eta^1\text{-}C_4H_3O)(THF)$ (**4**, Scheme 2). The latter was characterized by single-crystal X-ray diffraction (Figure 1, pertinent interatomic distances and angles in Table 1). The compound has a typical bent metallocene structure with a Ct(1)−Y−Ct(2) angle of 136.6(2)° (Ct = centroid of the Cp* ligand). The planar 2-furyl group (the mean deviation from the O(1)−C(21/24) least squares plane is 0.012 Å) is essentially η^1-bound to the metal center. The furyl oxygen occupies the *endo* position, and the distance of the furyl O(1) atom to yttrium is 3.278(8) Å. The Y−C(21)−O(1) angle of 116.3(7)° is smaller than the Y−C(21)−C(22) angle of 137.3(8)°, but this appears to be typical of η^1-2-furyl groups, as seen for example in the structure of (η^1-2-furyl)$_2$Hg (Hg−C−O = 117.1(4)°).[8] The Y−C(21) distance of 2.436(9) Å is typical for Y−C(sp^2) distances in permethyl yttrocene derivatives (e.g., 2.452(3) Å in $Cp^*_2Y(o\text{-}C_6H_4PPh_2CH_2)$[9]). The coordinated THF molecule in **4** shows extensive ring-twist disorder, but it can be observed that the Y−O(2) distance of 2.373(7) Å is very similar to the Y−O(THF) distance in other $Cp^*_2YR(THF)$ compounds (2.38−2.41 Å).[10]

Scheme 2

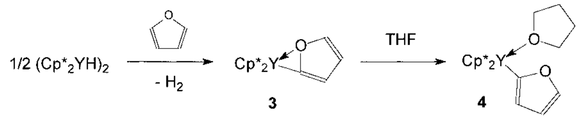


Table 1. Selected Interatomic Distances (Å) and Angles (deg) for Compound 4 (Ct denotes cyclopentadienyl centroid)

Y−C(21)	2.436(9)	O(1)−C(21)	1.365(13)
Y−O(2)	2.373(7)	O(1)−C(24)	1.384(14)
Y···O(1)	3.278(8)	C(21)−C(22)	1.333(15)
Y−Ct(1)	2.388(5)	C(22)−C(23)	1.409(17)
Y−Ct(2)	2.389(5)	C(23)−C(24)	1.27(2)
O(2)−Y−C(21)	94.5(3)	C(22)−C(23)−C(24)	106.8(11)
Y−C(21)−O(1)	116.3(7)	C(23)−C(24)−O(1)	109.7(11)
Y−C(21)−C(22)	137.3(8)	C(24)−O(1)−C(21)	108.4(9)
C(21)−C(22)−C(23)	109.8(11)	Ct(1)−Y−Ct(2)	136.63(18)

The base-free furyl complex **3** could not be obtained as crystals suitable for X-ray diffraction, but it is formulated as a monomeric species with a dihapto-2-furyl moiety, $Cp^*_2Y(\eta^2\text{-}2\text{-}C_4H_3O)$, based on the following arguments. First, compound **3** is much more soluble than the related 2-thienyl complex $[Cp^*_2Y(\mu\text{-}C_4H_3S)]_2$, which was shown to be dimeric by single-crystal X-ray diffraction.[3a] Compound **3** is quite soluble in pentane, whereas the dimeric thienyl derivative is poorly soluble even in aromatic solvents. Second, a comparison of the NMR spectra of **3** and its THF adduct **4** shows several differences that can also be observed in comparing the spectra of the dihapto-2-pyridyl complex $Cp^*_2Y(\eta^2\text{-}C_5H_4N)$ with its pyridine adduct $Cp^*_2Y(\eta^1\text{-}C_5H_4N)(C_5H_5N)$. In the ^{13}C NMR spectrum of **3** it is seen that the Y−C coupling constant on the furyl 2-carbon ($^1J_{YC}$ = 44 Hz) is significantly smaller than in the THF adduct **4** ($^1J_{YC}$ = 65 Hz); a reduced Y−C coupling constant was

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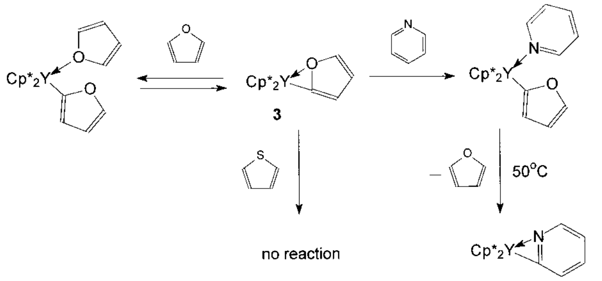
Scheme 3



also observed in the dihapto-2-pyridyl complex Cp$^*_2$Y(η^2-C_5H_4N) ($^1J_{YC}$ = 33 Hz).[11] Furthermore, upon complexation of THF, the resonance of the proton on the 5-position of the 2-furyl group shifts downfield (from δ 7.42 ppm in **3** to δ 7.92 ppm in **4**), a feature that was also observed for the proton on the 6-position of the 2-pyridyl moiety upon complexation of pyridine to Cp$^*_2$Y(η^2-C_5H_4N).[11,11] The monomeric nature of the decamethyl yttrocene 2-furyl species and the dimeric nature of its 2-thienyl analogue contrasts with the cyclopentadienyl-amide yttrium complexes [($C_5Me_4SiMe_2N$*t*-Bu)Y(μ-XC_4H_4)]$_2$, which are dimeric for both X = O and S.[12] This behavior probably reflects the greater steric demand of the (C_5Me_5)$_2$-ligand set.

Reactivity and Thermolysis of Cp$^*_2$Y(2-furyl). The reaction of the base-free 2-furyl complex **3** with several Lewis bases was studied by ^{1}H NMR spectroscopy in C_6D_6 solvent. Addition of 1 equiv of pyridine to **3** leads to formation of the corresponding adduct Cp$^*_2$Y(η^1-C_4H_3O)(C_5H_5N), as seen, for example, from the characteristic downfield shift ($\Delta\delta$ +0.60 ppm) of the furyl proton in the 5-position (the same phenomenon as mentioned above for the THF adduct). This adduct appears to be stable at ambient temperature, but warming the solution at 50 °C shows gradual formation of the base-free pyridyl complex Cp$^*_2$Y(η^2-C_5H_4N)[11] and free furan (Scheme 3). Concurrently, a small amount of a product resulting from another reaction is observed. This reaction is a thermolysis involving ring-opening of the furyl moiety and is described below. Addition of 1 equiv of furan to **3** leads only to small, but distinct, chemical shift differences for the furyl 5-H and the furan α- and β-protons ($\Delta\delta$ +0.05, +0.06, and +0.02 ppm, respectively). This suggests a dynamic equilibrium between an adduct Cp$^*_2$Y(η^1-C_4H_3O)(C_4H_4O) and free furan with unsolvated **3** (Scheme 3). Attempts to isolate the furan adduct on a preparative scale only led to the recovery of the base-free species **3**. Addition of thiophene, a softer Lewis base, to a solution of **3** does not give rise to any changes in the NMR spectrum, suggesting that its interaction with **3** (if any) is extremely weak.

Whereas the dimeric 2-thienyl compound [Cp$^*_2$Y(μ-C_4H_3S)]$_2$ is thermally robust (by NMR no degradation could be observed after warming at 80 °C for 3 days in aromatic solvent),[3a] the monomeric base-free 2-furyl compound **3** is thermally quite labile. By NMR spectroscopy it can be seen that, even at ambient temperature, free furan is formed in C_6D_6 solutions of **3** and that this liberation of furan is accompanied by the clean formation of a new organometallic species. Diffusion of pentane into a toluene solution of this decomposition product led to the separation of red crystals that were analyzed by single-crystal X-ray diffraction. The structure determination (Figure 2, pertinent interatomic distances and angles in Table 2) showed that the product can be formulated as (Cp$^*_2$Y)$_2$(μ-OCH=CHC≡C) (**5**, Scheme 4), a bimetallic complex in which two permethyl yttrocene fragments are bridged by a but-1-ene-3-yn-4-yl-1-olate group. Despite the relatively large standard deviations in the structure determination, the CC distances within the OCHCHCC group (double, single, triple: C(41)−C(42) 1.323(16) Å, C(42)−C(43) 1.435(14) Å, C(43)−C(44) 1.227(13) Å) suggest a dominance of the ynyl-enolate resonance structure over the other possible resonance structure, an allenediyl aldehyde. The Y(2)−O(1) distance of 2.213(6) Å is close to the Y−O(enolate) distance of 2.179(2) Å in the complex {Cp$^*_2$Y[μ-OCMe=CHC(O)OEt]}$_2$ and clearly shorter than the Y−O(ester) distance of 2.292(2) Å in the same complex.[13] The distance of the alkynyl α-carbon C(44) to Y(1), 2.424(10) Å, is substantially shorter than that to Y(2), 2.696(10) Å, and the distance of the alkynyl

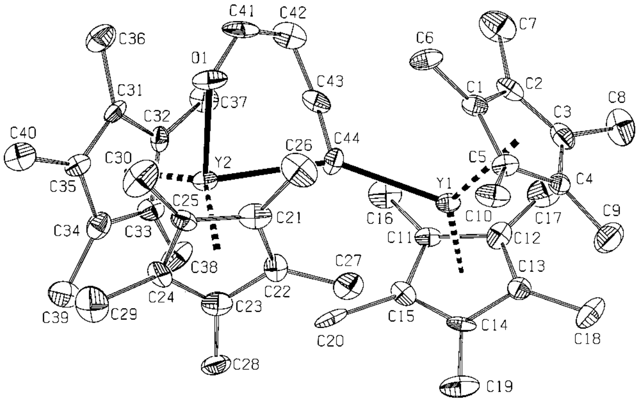
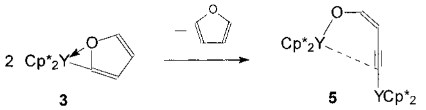


Figure 2. Molecular structure of (Cp$^*_2$Y)$_2$(μ-OCH=CHC=C) (**5**). Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Compound 5 (Ct denotes cyclopentadienyl centroid)

Y(1)−C(44)	2.424(10)	C(42)−C(43)	1.435(14)
Y(2)−C(44)	2.696(10)	C(43)−C(44)	1.227(13)
Y(2)−C(43)	2.809(10)	Y(1)−Ct(1)	2.371(4)
Y(2)−O(1)	2.213(6)	Y(1)−Ct(2)	2.350(4)
O(1)−C(41)	1.332(13)	Y(2)−Ct(3)	2.392(4)
C(41)−C(42)	1.323(16)	Y(2)−Ct(4)	2.409(4)
Y(1)−C(44)−Y(2)	144.9(4)	Ct(1)−Y(1)−Ct(2)	134.37(15)
O(1)−Y(2)−C(44)	88.2(3)	Ct(3)−Y(2)−Ct(4)	132.60(15)
Y(1)−C(44)−C(43)	125.8(8)	Ct(1)−Y(1)−C(44)	114.3(3)
Y(2)−O(1)−C(41)	119.7(6)	Ct(2)−Y(1)−C(44)	106.9(3)
O(1)−C(41)−C(42)	125.7(10)	Ct(3)−Y(2)−C(44)	103.1(2)
C(41)−C(42)−C(43)	117.3(10)	Ct(4)−Y(2)−C(44)	114.7(2)
C(42)−C(43)−C(44)	171.1(10)	Ct(3)−Y(2)−O(1)	103.44(19)
		Ct(4)−Y(2)−O(1)	105.21(20)

Scheme 4



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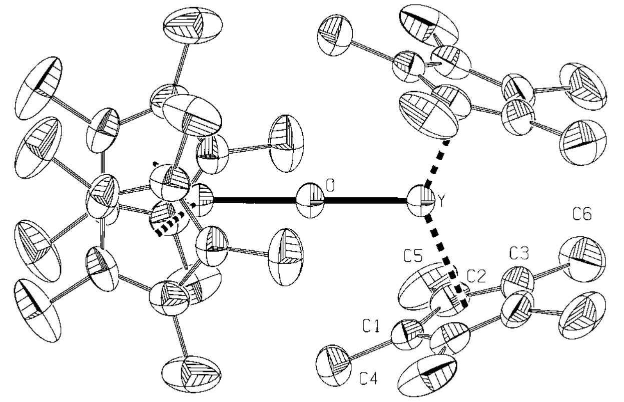


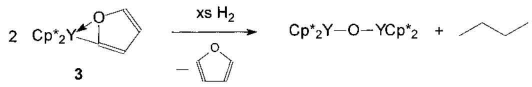
Figure 3. Molecular structure of $(Cp^*_2Y)_2(\mu\text{-}O)$ (**6**). Thermal ellipsoids are drawn at the 50% probability level.

β-carbon C(43) to Y(2), 2.809(10) Å, may suggest some additional interaction, as proposed for some dimeric group 3 and lanthanide metal μ-alkynyl complexes.[14] The ^{13}C NMR spectrum of **5** shows the resonance of the α-acetylenic carbon at δ 144.1 ppm, with two distinct Y−C coupling constants: one large (53 Hz) to Y(1), and one small (12 Hz) to Y(2).

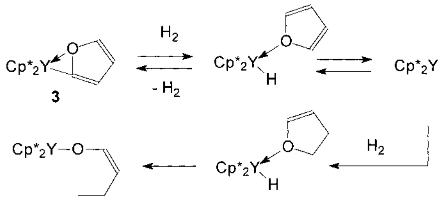
The precise route of formation of the thermolysis product **5** is as yet unclear. Preliminary kinetic experiments to determine, for example, the order of the reaction were inconclusive, possibly associated with the fact that furan is liberated in the course of the reaction. The decomposition of **3** is retarded by Lewis bases and, as mentioned above, furan is able to coordinate to **3**, which may complicate the reaction kinetics. Relevant rearrangements of the 2-furyl group are known from organosilicon chemistry, where the 2-trimethylsilylfuran was found to rearrange photochemically to the allenyl aldehyde $Me_3SiHC{=}C{=}CHC(O)H$[15] and where the related allenyl ketone $Me_3SiHC{=}C{=}CHC(O)SiMe_3$ rearranges thermally to the stable yn-enol $Me_3SiC{\equiv}CCH{=}C(SiMe_3)OH$.[15] Although the structure of the latter is directly related to the fragment found in **5**, it is unclear if their respective routes of formation are related in any way. Clarification of this point awaits further study.

Generating $(Cp^*_2YH)_2$ in the presence of furan (1 equiv per Y) by hydrogenolysis of $Cp^*_2YCH(SiMe_3)_2$ with an excess of H_2 in a C_6D_6 solution resulted initially in clean formation of the base-free 2-furyl complex **3** and $CH_2(SiMe_3)_2$, as seen by NMR spectroscopy. Allowing this solution to stand at ambient temperature under H_2 atmosphere resulted, in the course of several days, in the formation of a colorless crystalline solid, together with free furan and *n*-butane in equimolar amounts. Repeating the reaction on a preparative scale (in pentane solvent) allowed isolation of the organometallic product, which was identified by IR and NMR spectroscopy, as well as an X-ray structure determination, as the μ-oxo dimer $(Cp^*_2Y)_2(\mu\text{-}O)$ (**6**, Scheme 5). This compound was obtained previously from a cleavage reaction of diethyl ether by $(Cp^*_2YH)_2$.[5] Compound **6** crystallizes in a highly symmetric tetragonal space group ($I\bar{4}\,2m$), reflecting the linear arrangement of the Y−O−Y bridge and a 90° rotation of the two Cp^*_2Y moieties relative to each other. The structure is similar to that of the corresponding Sm complex $(Cp^*_2Sm)_2(\mu\text{-}O)$.[16] The Y−O distance in **6** (2.053(1) Å) is significantly shorter than that in the Sm complex (2.094(1) Å). The difference between the two M−O distances (0.041 Å) is somewhat less that the difference in ionic radius between Sm(III) and Y(III) (the latter is 0.060 Å smaller[17]), suggesting that the Y complex is sterically relatively crowded, stretching the Y−O bond.

Scheme 5



Scheme 6



Group 3 metal and lanthanide metallocene hydrides are known to effect C−O activation of a range of ethers and alkoxides.[4,5] In the present reaction, no intermediates could be observed, and it is difficult to assess whether this reaction proceeds either through partial or complete hydrogenation of the furan prior to C−O cleavage or through direct cleavage of the furan C−O bond followed by subsequent hydrogenation of the unsaturation. Interestingly, performing the reaction in the presence of a large excess (20 equiv) of furan led to the selective formation of another product, which was identified by ^1H and $^1H,^1H$ COSY NMR spectroscopy as the enolate species $Cp^*_2YOCH{=}CHEt$. Apparently, the excess furan prevents the further hydrogenation of the unsaturation, as well as the cleavage of the second C−O bond. One possibility (Scheme 6) is that furan is initially hydrogenated to 2,3-dihydrofuran, after which the O−C(sp^3) bond is cleaved through a σ-bond metathesis process, as suggsted for the C−O activation of diethyl ether and THF by various group 3 metal and lanthanide metallocenes.

Concluding Remarks

Metalation of furan by $(Cp^*_2YH)_2$ is the most convenient way to prepare salt- and solvent-free permethyl yttrocene 2-furyl species. Monomeric $Cp^*_2Y(\eta^2\text{-}2\text{-}C_4H_3O)$ (**3**) is a reactive and thermally labile compound that decomposes even at ambient temperature via a combination of C−H and C−O activation steps to give a bimetallic ynyl-enolate complex. In the presence of H_2, **3** is converted into an yttrium oxo complex in what can be described as a stoichiometric hydrodeoxygenation reaction. Furan is a relatively poor Lewis base, relative to THF and pyridine, and forms only a weak adduct with **3**. Nevertheless, its interaction with **3** is probably stronger than that of thiophene, for which, under the same conditions, no evidence could be found for adduct formation. Although preliminary experiments suggest

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(14) See e.g.: Duchateau, R.; Van Wee, C. T.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4931, and references therein.

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that **3** is able to polymerize ethene in the absence of added furan, it is likely that the increased Lewis basicity of furan, combined with the observed ease of C−O activation, will make it difficult (if not impossible) to perform catalytic combined ethene/furan conversions similar to those observed in the $\mathrm{Cp^*_2La}$(2-thienyl)/ethene/thiophene catalytic system.

Experimental Section

General Procedures. All experiments were performed under nitrogen atmosphere using standard glovebox and Schlenk techniques. Deuterated benzene (Aldrich) was dried over Na/K alloy and vacuum transferred before use. Toluene, THF, diethyl ether, and pentane were distilled from Na or Na/K alloy before use. The compounds $\mathrm{Cp^*_2YCl_2Li(OEt_2)_2}$,[6] $\mathrm{(Cp^*_2YH)_2}$,[7] $\mathrm{Cp^*_2Y[CH(SiMe_3)_2]}$,[18] and 2-lithiofuran[19] were prepared according to literature procedures. Furan (Janssen) was degassed and distilled from KOH before use. NMR spectra were run at ambient temperature on a Varian VXR-300 spectrometer. IR spectra were recorded on a Mattson-4020 Galaxy FT-IR spectrophotometer. Elemental analyses were performed by the Microanalytical Department of the University of Groningen. Every value is the average of at least two independent determinations.

Synthesis of $\mathrm{Cp^*_2Y(\mu\text{-}C_4H_3O)(\mu\text{-}Cl)Li(THF)_2}$ (1). At −78 °C, 46.3 mL of a 0.28 M solution (12.9 mmol) of 2-furyllithium in THF was added to a stirred solution of $\mathrm{Cp^*_2Y(\mu\text{-}Cl)_2Li(OEt_2)_2}$ (6.90 g, 11.78 mmol) in 90 mL of THF. The mixture was warmed to room temperature and stirred for 1 h, after which the solvent was removed in vacuo. Residual THF was removed by stirring 3 times with 15 mL of pentane, which was subsequently pumped off. Extraction with pentane (100 mL) and subsequent concentration and cooling (−20 °C) of the extract yielded **1** as pale pink crystals (3.06 g, 5.0 mmol, 42%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.48 (d, $J = 1.5$ Hz, 1H, OCH=), 6.51 (m, 1H, OCH=C*H*), 6.45 (d, $J = 3.1$ Hz, 1H, C=CH), 3.42 (m, 8H, α-THF), 2.15 (s, 30 H, Cp*), 1.29 (m, 8H, β-THF). ^{13}C{^{1}H} NMR (75.4 MHz, C_6D_6, 25 °C): δ 210.08 (d, $J_{CY} = 62$ Hz, YC), 142.36 (O*C*H=), 119.52 and 110.07 (CH=), 116.51 (Cp* C), 68.27 (α-THF), 25.38 (β-THF), 11.94 (Cp* Me). ^{7}Li NMR (116.6 MHz, C_6D_6, 25 °C): δ 2.30. Anal. Calcd for $\mathrm{C_{32}H_{49}O_3YLiCl}$: C, 62.70; H, 8.06; Li, 1.13. Found: C, 62.70; H, 8.07; Li, 1.09.

Synthesis of $\mathrm{Cp^*_2Y(\mu\text{-}C_4H_3O)_2Li(TMEDA)}$ (2). Solid $\mathrm{Cp^*_2Y(\mu\text{-}Cl)_2Li(OEt_2)_2}$ (1.5 g, 2.6 mmol) was added to a solution of 2-furyllithium, prepared in situ from *n*-BuLi (2.4 mL of a 2.5 M solution in hexane), furan (0.56 mL, 7.7 mmol), and TMEDA (0.36 mL, 2.39 mmol) in 50 mL of diethyl ether. The mixture was stirred for 18 h at room temperature, after which the solvent was removed in vacuo. The solid was washed with pentane (50 mL) and extracted with diethyl ether (80 mL). Concentrating and cooling (−20 °C) the extract yielded **2** (0.90 g, 1.5 mmol, 58%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.41 (d, $J = 1.5$ Hz, 2H, OCH=), 6.54 (d, $J = 2.9$ Hz, 2H, C=CH), 6.46 (dd, $J = 2.9$ and 1.5 Hz, 2H, OCH=C*H*), 2.09 (s, 30 H, Cp*), 1.69 (br, 4H, NCH_2), 1.61 (s, 12 H, NMe). ^{13}C NMR (75.4 MHz, C_6D_6, 25 °C): δ 211.7 (d, $J_{CY} = 57$ Hz, YC), 143.5 (d, $J = 192$ Hz, O*C*H=), 120.4 and 110.3 (d, $J = 168$ Hz, CH=), 115.9 (s, Cp* C), 56.9 (t, $J = 136$ Hz, NCH_2), 45.5 (q, $J = 135$ Hz, NCH_3), 12.0 (q, $J = 125$ Hz, Cp* Me). IR (KBr/Nujol, cm^{-1}): 2341 (m), 1352 (w), 1282 (w), 1169 (w), 1158 (w), 1116 (m), 1058 (w), 1029 (w), 829 (w), 794 (w), 648 (s). Anal. Calcd for $\mathrm{C_{34}H_{52}O_2N_2LiY}$: C, 66.22; H, 8.50; N, 4.54; Y, 14.42. Found: C, 66.12; H, 8.62; N, 4.60; Y, 14.97.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for Compound 6 (Ct denotes cyclopentadienyl centroid, prime denotes symmetry-related atom)

Y−O	2.0525(10)	C(1)−C(2)	1.421(7)
Y−C(1)	2.656(5)	C(2)−C(3)	1.390(7)
Y−C(2)	2.661(5)	C(3)−C(3′)	1.432(8)
Y−C(3)	2.710(5)	Y−Ct(1)	2.396(3)
Y−O−Y′	180	C(2)−C(1)−C(2′)	106.8(5)
Ct−Y−Ct′	136.23(9)	C(2)−C(3)−C(3′)	107.8(4)
O−Y−Ct	111.88(6)	C(1)−C(2)−C(3)	108.8(5)

Synthesis of $\mathrm{Cp^*_2Y(\eta^2\text{-}C_4H_3O)}$ (3). Furan (0.107 mL, 1.48 mmol) was added to a suspension of $\mathrm{(Cp^*_2YH)_2}$ (0.53 g, 0.74 mmol) in pentane (15 mL) at 0 °C. Gas evolution was observed immediately, and the reaction mixture was stirred for an additional 30 min. Filtration and concentration of the solution, followed by cooling to −80 °C, yielded **3** (0.38 g, 0.89 mmol, 60%) as a microcrystalline solid. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.42 (d, $J = 1.5$ Hz, 1H, OCH=), 6.60 (d, $J = 2.9$ Hz, 1H, C=CH), 6.39 (m, 1H, OCH=C*H*), 1.84 (s, 30 H, Cp*). ^{13}C NMR (75.4 MHz, C_6D_6, 25 °C): δ 211.3 (d, $J_{CY} = 44$ Hz, YC), 141.1 (ddd, $J = 198$, 12 and 6 Hz, O*C*H=), 118.5 (s, Cp* C), 116.2 (d, $J = 168$ Hz, CH=), 113.3 (ddd, $J = 169$, 14 and 4 Hz, CH=), 10.5 (q, $J = 126$ Hz, Cp* Me). The compound is thermally labile at ambient temperature, gradually losing furan.

Synthesis of $\mathrm{Cp^*_2Y(\eta^1\text{-}C_4H_3O)(THF)}$ (4). Furan (0.17 mL, 2.3 mmol) was added to a suspension of $\mathrm{(Cp^*_2YH)_2}$ (0.83 g, 1.15 mmol) in pentane (50 mL) at 0 °C. Gas evolution was observed immediately. After stirring for 5 min, THF (5 mL) was added, upon which the solution turned yellow. The solvent was removed in vacuo and the remaining solid was dissolved in diethyl ether. Concentration of the solution and subsequent cooling to −20 °C gave **4** (0,71 g, 1.4 mmol, 61%) as a white crystalline solid. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.92 (d, $J = 1.5$ Hz, 1H, OCH=), 6.58 (dd, $J = 2.9$ and 1.5 Hz, 1H, OCH=C*H*), 6.49 (d, $J = 2.9$ Hz, 1H, C=CH), 3.57 (m, 4H, α-THF), 1.94 (s, 30 H, Cp*), 1.23 (m, 4H, β-THF). ^{13}C NMR (75.4 MHz, C_6D_6, 25 °C): δ 205.34 (d, $^1J_{CY} = 65$ Hz, YC), 144.14 (ddd, $J = 193$, 12 and 6 Hz, O*C*H=), 118.39 (dddd, $^3J_{CY} = 5$ Hz, $J_{CH} = 165$, 11 and 6 Hz, CH=), 117.46 (s, Cp* C), 109.21 (ddd, $J = 169$, 15 and 5 Hz, CH=), 70.69 (t, $J = 150$ Hz, α-THF), 25.18 (t, $J = 126$ Hz, β-THF), 11.47 (q, $J = 126$ Hz, Cp* Me). IR (KBr/Nujol, cm^{-1}): 1377 (m), 1342 (w), 1176 (w), 1122 (w), 1035 (w), 1014 (w), 1005 (m), 940 (m), 923 (w), 864 (m), 853 (m), 840 (w), 789 (w), 725 (s), 666 (w), 600 (w), 591 (w). Anal. Calcd for $\mathrm{C_{28}H_{41}O_2Y}$: C, 67.46; H, 8.29; Y, 17.83. Found: C, 67.38; H, 8.27; Y, 17.92.

Reaction of 3 with Pyridine. Pyridine (3.8 μL, 47 μmol) was added to a solution of **3** (20 mg, 47 μmol) in 0.5 mL of C_6D_6, resulting in instantaneous formation of the adduct $\mathrm{Cp^*_2Y(\eta^1\text{-}C_4H_3O)(C_5H_5N)}$. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 8.48 (br, 2H, py *o*-H), 8.02 (br, 1H, OCH=), 6.80 (m, 1H, py *p*-H), 6.65 (m, 2H, C_4H_3O), 6.56 (m, 2H, py *m*-H), 1.86 (s, 30 H, Cp*). After warming at 50 °C for 1 day, 34% was converted to $\mathrm{Cp^*_2Y(\eta^2\text{-}C_5H_4N)}$[11] and free furan.

Reaction of 3 with Furan. Furan (3.4 μL, 47 μmol) was added to a solution of **3** (20 mg, 47 μmol) in 0.5 mL of C_6D_6. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.47 (br, 1H, OCH=), 7.17 (m, 2H, furan α-H), 6.59 (d, $J = 2.9$ Hz, 1H, OCH=C*H*), 6.40 (br, 1H, C=CH), 6.04 (m, 2H, furan β-H), 1.84 (s, 30 H, Cp*).

Synthesis of $\mathrm{(Cp^*_2Y)_2(\mu\text{-}C_4H_2O)}$ (5). A suspension of $\mathrm{(Cp^*_2YH)_2}$ in hexane was prepared in situ by exposing a solution of $\mathrm{Cp^*_2YCH(SiMe_3)_2}$ (0.77 g, 1.48 mmol) in 40 mL of hexane to H_2 atmosphere at ambient temperature for 4 h. Addition of furan (0.5 mL, 6.9 mmol) to this suspension resulted in immediate gas evolution. After stirring for 15 min, the solution was filtered and the solvent was removed in vacuo. The resulting solid was dissolved in toluene (15 mL), and this solution was allowed to stand at 50 °C for several days. The solvent was removed in vacuo, and the residue was rinsed with

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Table 4. Crystallographic Data for 4, 5, and 6

	4	**5**	**6**
formula	$C_{28}H_{41}O_2Y$	$C_{44}H_{62}OY_2$	$C_{40}H_{60}OY_2$
mol wt	498.54	784.79	734.73
cryst syst	monoclinic	orthorhombic	tetragonal
space group	$P2_1/n$ (No. 14)	*Pbca* (No. 61)	$I\bar{4}2m$ (No. 121)
a, Å	11.357(1)	17.233(1)	11.517(4)
b, Å	17.894(3)	18.237(1)	
c, Å	12.903(2)	24.864(1)	14.155(2)
β, deg	90.17(1)		
V, Å^3	2622.2(6)	7814.9(5)	1877.5(10)
Z	4	8	2
D_{calc}, g cm^{-3}	1.263	1.334	1.300
F(000)	1056	3296	722
μ(Mo K$\bar{\alpha}$), cm^{-1}	22.4	29.9	31.0
cryst size, mm	0.2 × 0.3 × 0.6	0.07 × 0.25 × 0.38	0.4 × 0.4 × 0.7
Data Collection			
radiation	Mo K$\bar{\alpha}$	Mo K$\bar{\alpha}$	Mo K$\bar{\alpha}$
λ (Mo Kα), Å	0.71073	0.71073	0.71073
T, K	295	130	295
θ range, deg	1.95, 25.0	1.64, 26.5	2.28, 28.0
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$	$0.90 + 0.34 \tan\theta$	$0.75 + 0.34 \tan\theta$	$0.80 + 0.34 \tan\theta$
data set	0:9, 0:21, −15:15	0:21, 0:22, −25:0	0:15, 0:15, 0:18
horz, vert aperture, mm	3.2 + tg θ; 4.0	3.2 + tg θ; 4.0	3.2 + tg θ; 4.0
total data	3671	8389	1291
unique data	3661	7682	691
data with criterion: ($F_o \geq 4.0\sigma(F_o)$)	1654	3548	553
Refinement			
number of reflns ($F_o^2 \geq 0$)	3661	7682	691
no. of refined params	327 (6 restraints)	452	60
$wR(F^2)^a$	0.1455	0.2012	0.0775
weighting scheme:[b] *a*, *b*	0.044, 0.0	0.0843, 0.0	0.0372, 0.0
R(*F*)	0.0773	0.0821	0.0371
goodness of fit	0.998	0.990	1.062
min, max resid. density, e/Å^3	−0.45, 0.35(7)	−1.44, 1.19(14)	−0.32, 0.72(7)
$(\Delta/\sigma)_{max}$ final cycle	<0.001	<0.001	<0.001

[a] $wR(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ for $F_o^2 > 0$. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R(F) = \sum(||F_o| - |F_c||)/\sum|F_o|$ for $F_o > 4.0\sigma(F_o)$.

hexane (50 mL). The solid was redissolved in toluene, and the solution was then filtered and concentrated to 8 mL volume. Subsequent slow diffusion of pentane into the solution at −20 °C caused **5** to separate as red crystals suitable for X-ray diffraction. The yield (0.17 g, 0.22 mmol, 29%) was not optimized. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.76 (dd, $^3J_{HH}$ = 4.1 Hz, $^3J_{YH}$ = 3.8 Hz, 1H, CH=), 4.36 (dd, $^3J_{HH}$ = 4.1 Hz, $^4J_{YH}$ = 0.8 Hz, 1H, CH=), 2.15 (s, 30H, Cp*), 1.95 (s, 30 H, Cp*). ^{13}C NMR (75.4 MHz, C_6D_6, 25 °C): δ 168.8 (d, *J* = 172 Hz, O*C*=), 144.1 (dd, $^1J_{YC}$ = 53 Hz, $^1J_{YC}$ = 12 Hz, Y*C*≡C), 134.3 (dd, $^2J_{YC}$ = 3 Hz, $^2J_{CH}$ = 14 Hz, YC≡*C*), 121.0 and 117.8 (s, Cp* C), 82.4 (dd, $^1J_{CH}$ = 168 Hz, $^2J_{CH}$ = 20 Hz, OC=*C*), 12.1 (q, *J* = 125 Hz, Cp* Me), 12.0 (q, *J* = 126 Hz, Cp* Me). IR (KBr/Nujol, cm^{-1}): 2972 (s), 2901 (s), 2859 (s), 2724 (w), 1969 (m), 1528 (s), 1437 (s), 1395 (m), 1377 (m), 1271 (s), 1096 (m), 1020 (w), 783 (w), 687 (m). Anal. Calcd for $C_{44}H_{62}OY_2$: C, 67.34; H, 7.96; Y, 22.66. Found: C, 65.99; H, 7.76; Y, 22.36. The found values of the carbon analyses for this compound are consistently too low, whereas the H and Y values are in reasonable agreement. This behavior, which may be associated with metal carbide formation, was observed previously by us for several other yttrium hydrocarbyl species.[20]

Reaction of 3 with Excess H_2: Synthesis of $(Cp^*_2Y)_2(\mu\text{-}O)$ (6). NMR Tube Scale. In an NMR tube, equipped with a Teflon (Young) valve and attached to a vacuum line, a solution of $Cp^*_2YCH(SiMe_3)_2$ (18 mg, 35 μmol) and furan (2.5 μL, 34 μmol) in C_6D_6, frozen in liquid N_2 and degassed, was exposed to 1 bar of H_2, after which the tube was closed and thawed out (Caution: internal pressure in the tube rises to about 4 bar). After 5 min at ambient temperature, quantitative formation of **3** and $CH_2(SiMe_3)_2$ was observed by ^{1}H NMR. After 5 days at ambient temperature, **3** was fully converted. Colorless crystals of **6** had formed, together with furan and *n*-butane.

Preparative Scale. In a thick-walled glass vessel, attached to a vacuum line, a solution of $Cp^*_2YCH(SiMe_3)_2$ (1.39 g, 2.68 mmol) and furan (0.19 mL, 2.61 mmol) in 150 mL of pentane was frozen in liquid N_2, degassed, and exposed to 1 bar of H_2. The vessel was closed and thawed out (Caution: internal pressure in the vessel rises to about 4 bar). The mixture was allowed to stand for 5 days at ambient temperature, during which a white solid was formed. The solution was decanted, and **6** (0.21 g, 0.33 mmol, 24%) was isolated. Its ^{1}H NMR and IR spectra were identical to those reported previously.[5]

Reaction of 3 with Excess H_2 and Excess Furan. In an NMR tube, a solution of $(Cp^*_2YH)_2$ (10.5 mg, 15 μmol) and furan (44 μL, 600 μmol) was exposed to H_2 atmosphere. After 3 days at ambient temperature, full conversion was observed to a species identified by ^{1}H NMR and ^{1}H,^{1}H-COSY NMR as $Cp^*_2YOCH{=}CHEt$ (probably stabilized by reversible coordination of furan that is present in excess). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 6.94 (d, $^3J_{HH}$ = 6.3 Hz, 1H, OCH=), 4.26 (ps.q, $^3J_{HH}$ = 6.6 Hz, 1H, OCH=C*H*), 2.41 (m, 2H, CH_2), 1.83 (s, 30H, Cp*), 1.23 (t, *J* = 7.5 Hz, CH_3).

Crystal Structure Determinations. Suitable crystals of **4** and **6** were mounted in a glass capillary in a drybox, sealed, and transferred to the diffractometer. A suitable crystal of **5** was mounted on a glass needle in a drybox and transferred under inert atmosphere into the cold nitrogen stream of an Enraf-Nonius CAD4-F diffractometer (monochromated Mo

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Kα). For all compounds, accurate cell parameters and an orientation matrix were determined from the setting of 22 reflections in the range of 13° < θ < 20°. Reduced cell calculations did not indicate any higher lattice symmetry.[21] Crystal data and details on data collection and refinement are presented in Table 4. Intensity data were corrected for Lorentz and polarization effects, but not for absorption. The structures were solved using Patterson methods, and the models were extended by direct methods applied to difference structure factors (DIRDIF[22]). All calculations were performed on a HP9000/735 computer with the program packages SHELXL[23] (least squares refinement) and PLATON[24] (calculation of geometric data and the ORTEP illustrations). The Cp* methyl hydrogen atoms were refined riding on their carrier atoms, and the methyl groups were refined as rigid groups that were allowed to rotate freely. In **4**, the coordinated THF molecule shows extensive ring-twist disorder. The fragment was refined using two positions for each of the methylene groups, with refined occupancy factors of 0.62(4) and 0.38(4), and restraints were applied to establish equivalent O−C and C−C distances within the twisted ring. Compound **6** crystallizes in a non-centrosymmetric space group. Enantiomorph twin refinement resulted in a value for Flack's absolute structure parameter x[25] of 0.48(3).

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Supporting Information Available: Tables showing details of crystal structure determinations, atom coordinates, equivalent isotropic displacement parameters, aniosotropic thermal parameters, bond lengths and angles, and hydrogen parameters for **4**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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