An *Exo*-Selective Diels–Alder Reaction of a Bimetallic Carbene Complex: A Case of Steric Control?

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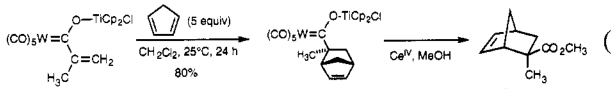
Summary: The α,β-unsaturated bimetallic Fischer carbene complex 1, $(CO)_5WC(OTiCp_2Cl)(C(CH_3){=}CH_2)$, undergoes reaction with cyclopentadiene to give predominantly the exo Diels–Alder adduct in high yield; X-ray crystal structures and molecular mechanics calculations for both reactant and product complexes suggest that the reaction may be controlled by steric factors.

Fischer carbene complexes bearing a vinyl substituent at the carbene carbon are active dienophiles for [4 + 2] cycloaddition reactions with a variety of dienes.[1] Here we report an *exo*-selective Diels–Alder reaction of a Fischer vinylcarbene complex, in which the stereoselectivity may arise as a result of the steric environment of the dienophile, in opposition to stereoelectronic factors usually identified with *endo* selectivity.

The 2-propenyl complex $(CO)_5WC(OTiCp_2Cl)(C(CH_3){=}CH_2)$, **1**, prepared by metalation of the acylate complex $[Me_4N][(CO)_5WC(O)(CCH_3{=}CH_2)]$[2] with Cp_2TiCl_2,[3] underwent condensation with cyclopentadiene in CH_2Cl_2 solution at ambient temperature to afford the Diels–Alder adduct **2**, which was obtained by crystallization from the reaction mixture in 75% isolated yield (eq 1). This material displayed a dominant set of product resonances in the NMR, assigned to the *exo* isomer from the X-ray crystal structure (*vide infra*).



(1)

1 **2** **3**

Treatment of the crude reaction mixture containing **2** with ceric ammonium nitrate in methanol afforded the methyl ester **3** in 40% yield (eq 1). Compound **3** was composed of two isomers by capillary GLC in an 8:1 ratio, which coeluted with the minor (*exo*) and major (*endo*) isomers, respectively, produced in the reaction of methyl methacrylate and cyclopentadiene catalyzed by $AlCl_3$[1c,4] and in the reaction of methacrylic acid with cyclopentadiene catalyzed by $BH_3{\cdot}THF$, followed by methyl esterification.[5] NMR of the crude reaction mixture confirmed the presence of a minor isomer, comprising approximately 10% of the product. The 8:1 diastereoselectivity in favor of the *exo* adduct may be compared with the reaction of the analogous methoxycarbene complex, $(CO)_5W{=}C(OMe)(C(CH_3){=}CH_2)$, which has been found to give a 59:41 *endo*:*exo* ratio with cyclopentadiene.[1c] The *trans*-propenyl *N*-benzoyl carbene complex $(CO)_5W{=}C(NMeCOPh)(CH{=}CHMe)$, which is a highly *exo*-selective dienophile with a derivative of Danishefsky's diene, reacts with cyclopentadiene in a 1:1.1 diastereomeric ratio.[1b] Therefore, substitution of the methoxy substituent with a $OTiCp_2Cl$ moiety leads to enhanced *exo* selectivity.

The vinyl complex $(CO)_5WC(OTiCp_2Cl)(CH{=}CH_2)$, **4**, prepared analogously to **1**, afforded a 7:3 *endo*/*exo* mixture of adducts in 75% yield, as determined by oxidative cleavage to the methyl esters and comparison with authentic samples.[4] The corresponding methoxycarbene complex, $(CO)_5W{=}C(OMe)(CH{=}CH_2)$, gives a 93:7 ratio of *endo* to *exo* isomers.[1c]

These observations can be correlated to the X-ray crystal structures of dienophiles **1** and **4** and *exo* Diels–Alder adduct **2**, which are shown in Figures 1–3 and Tables 1–4. Of note are the nearly linear C(1)–O(1)–Ti bond angles (173.3(5)° for **1**, 170.4(8)° for **2**, and 173.8(5)° for **4**), suggesting sp-hybridization at O1, as has been previously discussed for the chromium congener of **1**.[3a] The Ti and Cl atoms are found in the plane defined by the carbenoxy unit, and the O(1)–Ti–Cl bond angles are near 95°, due to the disposition of π-accepting orbitals on Ti.[3a,6] The $TiCp_2Cl$ unit is found in opposite orientations in **1** and **4**: the Cl atom is *syn* to the propenyl moiety in the former and *anti* to the vinyl group in the latter. In both cases, the titanoxy fragment imposes severe steric constraints on the vinylcarbene moiety.

The most important parameter of the dienophile structures is the orientation of the olefinic group with respect to the carbenoxy plane. In the 2-propenyl complex **1**, the C=C double bond is perpendicular to the carbene plane (W–C(1)–C(2)–C(3) dihedral angle = 84.1°). In contrast, the vinyl complex **4** displays a coplanar conformation (W–C(1)–C(2)–C(3) dihedral angle = 7.9°; C3 lies 0.1 Å out of the plane defined by W, C(1), C(2), and O(1)), with an *s-cis* relationship between C=C and W=C bonds and the vinylcarbene plane bisecting the adjacent OC–W–CO angle (C(14)–W–C(1)–C(2) dihedral angle = 38°).

The maximum electronic activation of the dienophile for cycloaddition would be expected to occur in a coplanar orientation in which the π orbitals of the C=C and W=C bonds can interact. The vinylcarbene complex **4** adopts such a structure in the solid state with an *s-cis* conformation. Molecular mechanics calculations[7] indicate that the *s-trans* rotamer of **4** would be destabilized by at least

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[⊗] Abstract published in *Advance ACS Abstracts*, March 1, 1994.

[1] (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726–6727. (b) Anderson, B. A.; Wulff, W. D.; Powers, T. S.; Tribbitt, S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 10784–10798. (c) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642–3659. (d) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550–4552. (e) Herndon, J. W. *J. Org. Chem.* **1986**, *51*, 2853–2855.

[2] Prepared by a produre similar to that used for the Cr analogue: Dötz, K. H.; Kuhn, W.; Ackermann, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 1351–1356.

[3] For related Cr complexes, see: (a) Sabat, M.; Gross, M. F.; Finn, M. G. *Organometallics* **1992**, *11*, 745–751. (b) Anslyn, E. V.; Santarsiero, B. D.; Grubbs, R. H. *Organometallics* **1988**, *7*, 2137–2145. (c) Raubenheimer, H. G.; Fischer, E. O. *J. Organomet. Chem.* **1975**, *91*, C23–C26.

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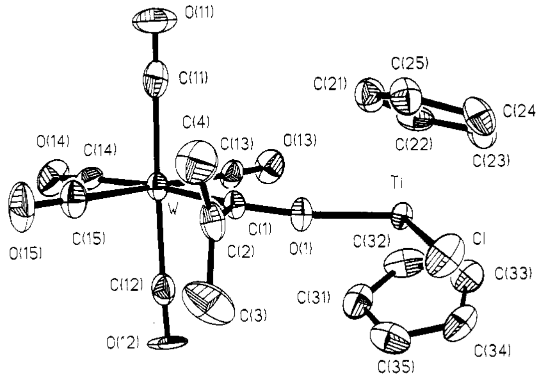

Figure 1. ORTEP diagram of $(CO)_5WC[OTiCp_2Cl][CMeCH_2]$ (**1**) with numbering scheme.

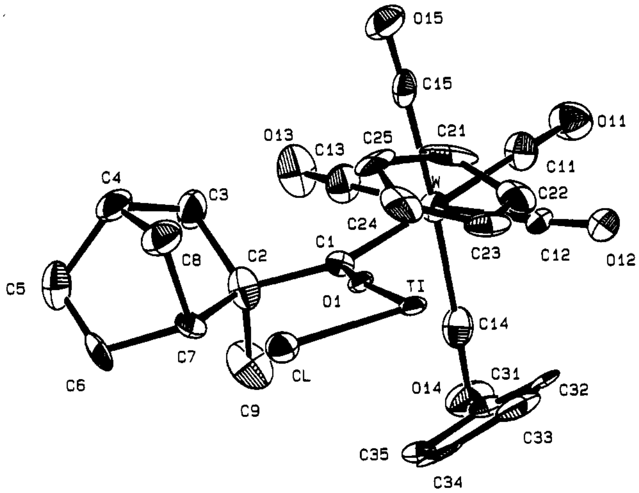

Figure 2. ORTEP diagram of $(CO)_5WC[OTiCp_2Cl][C_8H_{11}]$ (**2**) with numbering scheme.

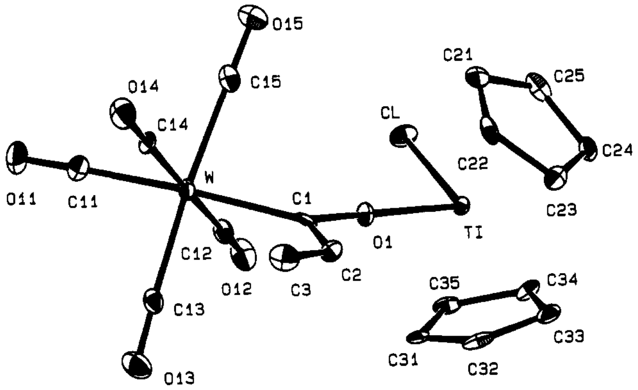

Figure 3. ORTEP diagram of $(CO)_5WC[OTiCp_2Cl][CH{=}CH_2]$ (**4**) with numbering scheme.

Table 1. Positional Parameters for 1 (Å)

atom	*x*	*y*	*z*
W	–0.3347(1)	0.2735(1)	–0.3689(1)
Ti	–0.6526(1)	0.3616(1)	–0.2593(1)
Cl	–0.7389(3)	0.2270(2)	–0.1796(2)
O(1)	–0.5400(4)	0.2789(4)	–0.2873(5)
O(11)	–0.4709(7)	0.2532(8)	–0.6127(7)
O(12)	–0.2054(7)	0.3047(7)	–0.1245(6)
O(13)	–0.4158(6)	0.5025(5)	–0.3778(6)
O(14)	–0.1148(6)	0.3340(7)	–0.4208(6)
O(15)	–0.2520(7)	0.0437(6)	–0.3649(7)
C(1)	–0.4738(6)	0.2222(6)	–0.3163(6)
C(2)	–0.4919(7)	0.1121(6)	–0.2976(8)
C(3)	–0.4470(12)	0.0808(10)	–0.1894(11)
C(4)	–0.5452(10)	0.0536(9)	–0.3784(10)
C(11)	–0.4233(7)	0.2590(8)	–0.5264(8)
C(12)	–0.2505(8)	0.2921(7)	–0.2133(8)
C(13)	–0.3874(8)	0.4207(8)	–0.3741(6)
C(14)	–0.1958(8)	0.3125(8)	–0.4046(8)
C(15)	–0.2828(8)	0.1243(8)	–0.3661(8)
C(21)	–0.6901(8)	0.3788(8)	–0.4477(7)
C(22)	–0.7056(9)	0.4734(8)	–0.4054(8)
C(23)	–0.7660(8)	0.3117(8)	–0.4298(8)
C(24)	–0.8345(8)	0.3649(9)	–0.3826(8)
C(25)	–0.7980(9)	0.4635(10)	–0.3671(8)
C(31)	–0.4880(9)	0.4299(10)	–0.1393(9)
C(32)	–0.5587(11)	0.5097(8)	–0.1819(9)
C(33)	–0.6495(10)	0.5026(9)	–0.1487(8)
C(34)	–0.6367(10)	0.4179(10)	–0.0848(8)
C(35)	–0.5374(10)	0.3712(8)	–0.0814(8)

Table 2. Positional Parameters for 2 (Å)

atom	*x*	*y*	*z*
W	0.24958(7)	0.20766(2)	0.08587(3)
Ti	0.1873(2)	0.40636(9)	0.1703(1)
Cl	0.2213(4)	0.4927(1)	0.0889(2)
O(1)	0.2229(8)	0.3473(3)	0.0847(4)
O(1S)	0.547(3)	0.004(1)	–0.025(2)
O(11)	0.275(1)	0.0772(5)	0.1629(7)
O(12)	0.152(1)	0.2359(5)	0.2659(6)
O(13)	0.347(2)	0.1466(5)	–0.0797(6)
O(14)	–0.168(1)	0.1954(5)	0.0033(7)
O(15)	0.666(1)	0.2302(5)	0.1587(7)
C(1)	0.240(2)	0.3123(5)	0.0377(7)
C(2)	0.245(2)	0.3197(6)	–0.0565(8)
C(2S)	0.650(5)	0.016(2)	0.045(2)
C(3S)	0.759(7)	0.048(2)	0.072(3)
C(3)	0.418(2)	0.2993(7)	–0.080(1)
C(4)	0.502(2)	0.3587(7)	–0.106(1)
C(5)	0.379(2)	0.3800(7)	–0.1906(9)
C(6)	0.234(2)	0.3969(7)	–0.172(1)
C(7)	0.239(2)	0.3870(6)	–0.0751(7)
C(8)	0.441(2)	0.4012(7)	–0.043(1)
C(9)	0.068(3)	0.2920(7)	–0.116(1)
C(11)	0.268(2)	0.1248(6)	0.1355(8)
C(12)	0.186(1)	0.2293(5)	0.1996(7)
C(13)	0.315(2)	0.1703(6)	–0.0217(9)
C(14)	–0.014(2)	0.1988(6)	0.0343(8)
C(15)	0.514(2)	0.2205(5)	0.1329(7)
C(21)	0.446(2)	0.3559(8)	0.250(1)
C(22)	0.340(2)	0.3727(7)	0.307(1)
C(23)	0.338(2)	0.4336(7)	0.3123(9)
C(24)	0.435(2)	0.4585(7)	0.259(1)
C(25)	0.502(2)	0.411(1)	0.2168(8)
C(31)	–0.089(1)	0.3520(7)	0.1429(8)
C(32)	–0.051(1)	0.3685(8)	0.2291(9)
C(33)	–0.052(2)	0.430(1)	0.237(1)
C(34)	–0.099(2)	0.4625(7)	0.151(1)
C(35)	–0.116(1)	0.4039(7)	0.0929(8)

7 kcal/mol due to a steric interaction between the CH_2 group and the $TiCp_2Cl$ fragment. Since conformationally locked *s-cis* enones are known to be *exo* selective in Diels–Alder reactions with cyclopentadiene,[1b,8] it is surprising that **4** is an *endo*-selective dienophile. The orientation of diene and dienophile dipole moments has been suggested as a controlling interaction in these cases,[9] and it is possible that the dipole moment of **4** does not match that of analogous enones (e.g., methyl acrylate) or a methoxycarbene complex in the *s-cis* conformation.

Analysis[7] of the structure of the 2-propenyl complex **1** reveals that both the *s-cis* and *s-trans* conformations are

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(7) Molecular mechanics calculations were done on a CAChe Worksystem[16] with software version 2.7. The mechanics program uses Allinger's MM2 force field[17] with CAChe augmentations.[18]

(8) (a) Roush, W. R.; Essenfeld, A. P.; Warmus, J. S.; Brown, B. B. *Tetrahedron Lett.* **1989**, *30*, 7305. (b) Fotiadu, F.; Michel, F.; Buono, G. *Tetrahedron Lett.* **1990**, *31*, 4863. (c) Adam, W.; Albert, R.; Hasemann, L.; Nava Salgado, V. O.; Nestler, B.; Peters, E.-M.; Peters, K.; Prechtl, F.; von Schnering, H. G. *J. Org. Chem.* **1991**, *56*, 5782.

(9) (a) Rousch, W. R.; Brown, B. B. *J. Org. Chem.* **1992**, *57*, 3380–3387. (b) Berson, J. A.; Hamlet, J.; Mueller, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 297.

Table 3. Positional Parameters for 4 (Å)

atom	*x*	*y*	*z*
W	0.01648(2)	0.25238(3)	0.49935(2)
Ti	0.4187(1)	0.2320(1)	0.59989(9)
Cl	0.3913(2)	0.1630(1)	0.4395(1)
O(1)	0.2469(4)	0.2678(4)	0.6023(3)
O(11)	−0.2318(6)	0.1661(5)	0.3461(4)
O(12)	0.1301(5)	0.0404(4)	0.4819(4)
O(13)	−0.1430(5)	0.1578(4)	0.6752(4)
O(14)	−0.1679(5)	0.4625(5)	0.4975(5)
O(15)	0.1314(5)	0.3549(5)	0.3385(4)
C(1)	0.1371(7)	0.2994(6)	0.6102(5)
C(2)	0.1349(7)	0.3623(6)	0.7008(5)
C(3)	0.0365(8)	0.4106(7)	0.7238(6)
C(11)	0.1540(8)	0.1980(7)	0.4002(6)
C(12)	0.0781(7)	0.1165(6)	0.4883(5)
C(13)	0.0993(7)	0.1920(6)	0.6106(6)
C(14)	0.1121(7)	0.3869(6)	0.5012(5)
C(15)	0.0787(7)	0.3178(6)	0.3950(6)
C(21)	0.4408(7)	0.3912(6)	0.5187(6)
C(22)	0.4227(8)	0.4178(5)	0.6141(6)
C(23)	0.5211(8)	0.3757(6)	0.6778(6)
C(24)	0.6063(7)	0.3298(6)	0.6194(6)
C(25)	0.5550(8)	0.3397(6)	0.5216(6)
C(31)	0.3447(7)	0.0894(6)	0.6865(5)
C(32)	0.4103(8)	0.1568(6)	0.7520(5)
C(33)	0.5358(8)	0.1540(6)	0.7348(6)
C(34)	0.5429(8)	0.0882(6)	0.6547(5)
C(35)	0.4240(8)	0.0480(5)	0.6256(5)

Table 4. Selected Bond Distances (Å) and Angles (deg) and Dihedral Angles (deg) for Complexes 1, 2, and 4

	1	2	4
W–C(1)	2.187(9)	2.25(1)	2.200(8)
C(1)–O(1)	1.264(11)	1.27(1)	1.275(8)
C(1)–C(2)	1.498(12)	1.55(2)	1.50(1)
C(2)–C(3)	1.428(16)	1.52(2)	1.31(1)
Ti–O(1)	1.916(6)	1.951(7)	1.921(5)
W–C(11)	2.049(9)	2.01(1)	2.019(8)
W–C(12)	2.020(9)	2.02(1)	2.046(8)
W–C(13)	2.041(10)	2.05(1)	2.034(8)
W–C(14)	2.020(11)	2.01(1)	2.024(7)
W–C(15)	2.066(11)	2.02(1)	2.061(9)
Ti–Cl	2.353(4)	2.366(4)	2.376(2)
Ti–O(1)–C(1)	173.3(5)	170.4(8)	173.8(5)
O(1)–Ti–Cl	95.3(2)	97.4(2)	95.8(2)
W–C(1)–O(1)	125.9(6)	123.2(8)	118.8(5)
W–C(1)–C(2)	122.0(6)	123.8(8)	130.0(5)
O(1)–C(1)–C(2)	111.8(8)	113(1)	111.1(7)
OC–W–C(1)–C(2)	0.8	10.7	37.9(7)
W–C(1)–O(1)–Ti	104.0	−15.2	162(4)
W–C(1)–C(2)–C(3)	−86.1	−58.1	−8(1)

destabilized by steric interactions of the $TiCp_2Cl$ unit with either the CH_3 or CH_2 groups, respectively, giving rise to the observed perpendicular orientation. A conservative estimate of steric interactions[10] (albeit in the ground state) places the perpendicular conformation at least 10 kcal/mol more stable than either coplanar structure, ignoring solvation effects.

If the Diels–Alder reactions of both 1 and 4 occur in coplanar dienophile conformations the origin of the *exo* selectivity of 1 is not readily apparent. Alternatively, the solid-state structure of 1 could be its reactive form if the transition-state stabilization gained by rotation to a coplanar conformation does not overcome the ground-state barrier to that rotation. If a perpendicular dienophile arrangement is reactive,[11] the *exo* selectivity is consistent with steric control as shown in Figure 4. Approach of cyclopentadiene on the Ti side of the dienophile, where there is more room, can occur in one of two orientations. An *endo* arrangement would be disfavored by a severe interaction between one of the distal CH groups of cyclopentadiene and the nearly linear C(1)–O(1)–Ti axis. The *exo* alignment would suffer no such interaction, as shown in Figure 4. The crystal structure of the Diels–Alder adduct **2** (Figure 2) closely resembles the putatitive *exo* transition state arrangement of reactants shown in Figure 4.

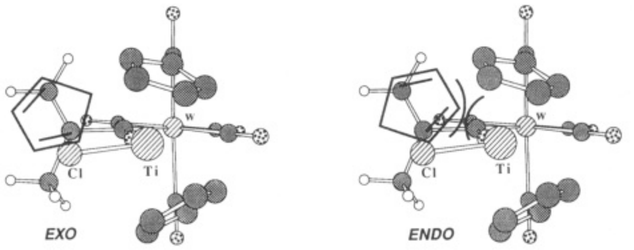

Figure 4. Proposed alignments of diene and dienophile in the Diels–Alder reaction of 1 viewed along the Ti–O–C bond axis, showing steric congestion disfavoring an *endo* configuration.

The Diels–Alder reactions of aminovinylcarbene complexes of tungsten with activated acyclic dienes have been shown to be highly *exo* selective.[1b] The plausible suggestion has been made that the steric bulk of the $(CO)_5W$ fragment is responsible for the observed stereoselectivity.[1b] However, cyclopentadiene undergoes nonselective condensation with such dienophiles.[1b] Thus, the results outlined here demonstrate that additional factors may be brought to bear to influence the reactivity of carbene complex reagents.

Experimental Section

All air-sensitive manipulations were performed in a Vacuum Atmospheres glovebox under dry nitrogen. GLC analyses were performed using a capillary column (30 m × 0.32 mm; DB-Wax; J&W Scientific) and flame ionization detection; the relative response factor for *endo* and *exo* isomers was assumed to be 1.0. Elemental analyses were performed in this department on a Perkin-Elmer 2400 CHN analyzer using (2,4-dinitrophenyl)-hydrazine as standard.

Complex 1 was prepared via the corresponding tetramethylammonium acylate salt[12] in the same manner as the analogous chromium compound[3a] and recrystallized from 1:1 Et_2O/CH_2Cl_2 at −30 °C. Complex 4 was prepared by addition of Cp_2TiCl_2 to the lithium acylate salt generated from vinyllithium[12] and $W(CO)_6$ *in situ*. An X-ray quality crystal was isolated from 2:1 Et_2O/CH_2Cl_2, but the bulk sample was not obtained in analytically pure form, since multiple recrystallizations led to decomposition. For 1: ^1H NMR ($CDCl_3$, δ) 6.51 (s, 10H), 5.10 (br s, 1H), 5.02 (br s, 1H), 1.72 (s, 3H); ^{13}C NMR ($CDCl_3$, δ) 333.07, 204.23, 198.81,

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[10] Accomplished by a correlation of energy with simultaneous rotations about the W–C(1), C(1)–O(1), and O(1)–Ti bonds, and deformation of the C(1)–O(1)–Ti bond angle, using augmented MM2 parameters in the Tektronix CAChe computer system.

[11] Other olefins lacking π-overlap with an electron-withdrawing functionality are known to undergo Diels–Alder reaction. For example, 1,1,1-trifluoro-2-propene reacts slowly with cyclopentadiene to give the [4 + 2] adduct in a 1:4 *exo*:*endo* ratio: Gaede, B.; Balthazor, T. M. *J. Org. Chem.* **1983**, *48*, 276–277.

[12] Lithium acylate salts were generated in the manner of Wulff et al. (Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642–3659) with a modified procedure for preparation of vinyllithium (Smith, G. M.; Suzuki, H.; Sonnenberger, D. C.; Day, V. W.; Marks, T. J. *Organometallics* **1986**, *5*, 549–61). The carbene acylate anions were isolated as NMe_4 salts by treatment with aqueous Me_4NCl as first described by Fischer and Maasbol: Fishcer, E. O.; Maasbol, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580–581.

162.59, 118.46, 114.18, 17.81; IR (ν_{CO}, CH_2Cl_2, cm^{-1}) 2048, 1916 (br). Anal. Calcd for $C_{19}H_{15}ClO_6TiW$: C, 37.63; H, 2.49. Found: C, 37.50; H, 2.75; N, 0.03. For **4**: ^1H NMR ($CDCl_3$, δ) 6.85 (dd, *J* = 10.5, 17.2 Hz, 1H), 6.55 (s, impurity, ≈1H), 6.54 (s, impurity, ≈1H), 6.50 (s, ≈8H), 5.90 (d, *J* = 16.8 Hz, 1H), 5.70 (d, *J* = 10.3 Hz, 1H).

Under a dry nitrogen atmosphere, **1** (250 mg, 0.41 mmol) in 5 mL of CH_2Cl_2 was treated with cyclopentadiene (135 mg, 2.04 mmol). The reaction mixture was allowed to stand at room temperature for 18 h and then was evaporated, taken up in 10 mL of Et_2O, cooled to 0 °C, and filtered to remove a small amount of $W(CO)_6$. Storage of the filtrate at −30 °C for 24 h provided 209 mg (0.31 mmol, 75% yield) of **2** as red-brown crystals, pure by NMR and IR. Single crystals for X-ray and combustion analysis were obtained from Et_2O at −30 °C. For **2**: ^1H NMR ($CDCl_3$, δ) 6.56 (s, 5H), 6.52 (s, 5H), 6.26 (br dd, 1H), 6.04 (br s, 1H), 2.79 (br s, 2H), 1.63–1.43 (m, 4H), 1.05 (s, 3H); IR (ν_{CO}, CH_2Cl_2, cm^{-1}) 2048, 1916 (br). Anal. Calcd for $C_{24}H_{21}ClO_6TiW$: C, 42.86: H, 3.15. Found: C, 42.66; H, 3.18; N, 0.02.

For diastereomeric analysis, an identical crude Diels–Alder reaction mixture was evaporated and then dissolved in 10 mL of CH_3OH treated with 2 mL of a freshly-prepared solution of $(NH_4)_2Ce(NO_3)_6$ in CH_3OH (approximately 1 M). After 30 min at room temperature, the mixture was partitioned between 10 mL of Et_2O and 10 mL of H_2O, and the organic phase was washed with saturated $NaHCO_3$ and water and then dried (anhydrous $MgSO_4$). Due to the potential volatility of the product esters, the resulting ether solution was analyzed directly by capillary GLC, showing the presence of *exo* and *endo* isomers in a ratio of 8.0:1 (4.2 and 4.8 min, respectively). These peaks coeluted with added *exo*- and *endo*-**3** prepared by the reaction of cyclopentadiene and methyl methacrylate catalyzed by $AlCl_3$.[4] Evaporation of the solvent provided 35 mg of a mixture of compounds, approximately 80% of which was composed of the expected ester mixture in an 8:1 diatereomer ration, as judged by NMR in comparison with the authentic compounds.[4] The Diels–Alder reaction of **4** was performed and analyzed in analogous fashion.

X-ray Crystallography

Compound 1. The complex crystallized in the monoclinic space group $P2_1/n$ with a = 12.642(2) Å, b = 13.148(3) Å, c = 13.226(2) Å, β = 107.89(1)°, V = 2092(1) Å^3, Z = 4. The structure was solved by direct methods using SHELXTL PLUS[13] and refined to the R factor of 0.037 (R_w = 0.044) using 2694 absorption-corrected reflections with $I > 2\sigma(I)$ collected up to 2θ = 50° on a Siemens/Nicolet P3m diffractometer (Mo Kα radiation, 25 °C).

Compounds 2 and 4. X-ray measurements were carried out on a Rigaku AFC6s diffractometer using Mo Kα radiation at −120 and −60 °C for **2** and **4**, respectively. All calculations were done using TEXSAN 5.0.[14] The structures were solved by direct methods (SIR88).[15] Crystallographic data for **2**: monoclinic space group $P2_1/n$, a = 7.621(2) Å, b = 22.39(1) Å, c = 15.809(2) Å, β = 102.32(2)°, V = 2635(2) Å^3, Z = 4. R = 0.046 (R_w = 0.063) for 2862 absorption-corrected reflections with $I > 3.5\sigma(I)$ measured up to 2θ = 46°. A disordered diethyl ether solvent molecule was found in the unit cell of the compound. Crystallographic data for **4**: monoclinic space group $P2_1/c$, a = 10.829(2) Å, b = 12.912(2) Å, c = 13.850(4) Å, β = 97.33(4)°, V = 1921(1) Å^3, Z = 4. R = 0.024 (R_w = 0.029) for 2039 absorption-corrected reflections with $I > 3\sigma(I)$ measured up to 2θ = 50°.

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Supplementary Material Available: Crystallographic details for **1**, **2**, and **4** including crystal data, intensity measurements, structure solution and refinement, anisotropic thermal displacement parameters, and bond lengths and angles (17 pages). Ordering information is given on any current masthead page.

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