Origin of 1,4-Regiochemistry in the Dicouplings of Ketones with 6,6-Dimethylcyclohexadienyl Complexes of Titanium and Zirconium: A Mechanism Arising from Five-Electron Donation by Alkoxide Ligands

Rehan Basta, Atta M. Arif, and Richard D. Ernst*

Department of Chemistry, University of Utah, 315 S. 1400 E., Salt Lake City, Utah 84112-0850

In an earlier study of the coupling reactions of $Ti(C_5H_5)(6,6\text{-dmch})(PMe_3)$ (dmch = dimethylcyclohexadienyl) with ketones, the initially formed metal complex could not be isolated, but after hydrolysis an unprecedented 1,4-dicoupling product was isolated. To gain further insight into the origin of this regiochemistry, the reaction of a zirconium analogue, $Zr(C_5H_5)(6,6\text{-dmch})(PMe_3)_2$, with acetone was investigated. A solid dimeric product could be isolated and structurally characterized, which revealed that both acetones had coupled, with the unusual 1,4-regiochemistry. This then necessitated the proposal of a new mechanism for these reactions, in which an alkoxide ligand, generated from a coupling of the initially incorporated ketone, serves as a formal five-electron donor, thereby altering the mode of coordination of the diene fragment. This proposal has been supported by the characterization of a mono(benzophenone) coupling product of $Ti(C_5H_5)(6,6\text{-dmch})(PMe_3)$. This coupling product possessed both a large Ti−O−C angle, indicative of at least a partial contribution of a resonance form in which the alkoxide ligand serves as a five-electron donor, and the expected η^2-diene coordination.
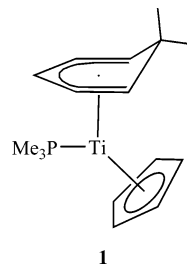
Introduction

Pentadienyl complexes of titanium and zirconium have been found to undergo coupling reactions with a wide variety of unsaturated molecules, including alkynes,[1] ketones, aldehydes, imines, nitriles, and isonitriles. Quite often, multiple couplings can be achieved; in fact, more often than not, these occur in preference to single coupling processes. Until recently, such couplings have inevitably involved the terminal dienyl carbon atoms first. As a result, numerous 1,5-dicoupling processes have been observed for ketones, imines, nitriles, and even combinations of these substrates.[2] However, it was subsequently found that $Ti(C_5H_5)(6,6\text{-dmch})(PMe_3)$, **1**, underwent di(coupling) reactions with ketones with unprecedented 1,4-regiochemistry.[3] Although the resulting metal complex could not readily be isolated and characterized, the organic product could be removed from the metal by either hydrolysis or a combination of oxidation and hydrolysis and subsequently characterized.

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To explain the 1,4-regiochemistry, a mechanism was suggested in which **2** was proposed to be the key intermediate.[4] In this species, only one of the ketones

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had undergone coupling, while the second simply coordinated to the metal center. Such a possibility found support from the fact that reactions with some diones led to one carbonyl group coupling to the dienyl fragment, while the other appeared to simply coordinate,
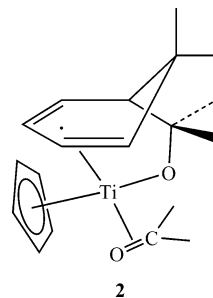
(1) (a) Wilson, A. M.; Waldman, T. E.; Rheingold, A. L.; Ernst, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 6252. (b) Tomaszewski, R.; Hyla-Kryspin, I.; Mayne, C. L.; Arif, A. M.; R. Gleiter, R.; Ernst, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 2959.

(2) (a) Waldman, T. E.; Wilson, A. M.; Rheingold, A. L.; Meléndez, E. M.; Ernst, R. D. *Organometallics* **1992**, *11*, 3201. (b) Kralik, M. S.; Rheingold, A. L.; Hutchinson, J. P.; Freeman, J. W.; Ernst, R. D. *Organometallics* **1996**, *15*, 551. (c) Tomaszewski, R.; Wilson, A. M.; Liable-Sands, L.; Rheingold, A. L.; Ernst, R. D. *J. Organometal. Chem.* **1999**, *583*, 42. (d) Tomaszewski, R.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1999**, *18*, 4174. (e) See also: Paz-Sandoval, M. A.; Coyotzi, R. S.; Villareal, N. Z.; Ernst, R. D.; Arif, A. M. *Organometallics* **1995**, *14*, 1044.

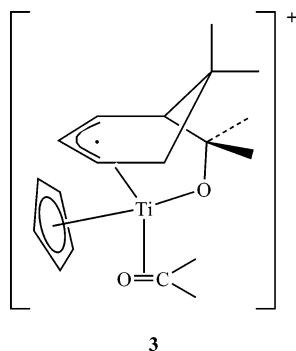(3) Wilson, A. M.; West, F. G.; Arif, A. M.; Ernst, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 8490.

(4) Wilson, A. M.; West, F. G.; Rheingold, A. L.; Ernst, R. D. *Inorg. Chim. Acta* **2000**, *300−302*, 65.

as after hydrolysis the latter had been converted to a secondary alcohol.[5] In any event, it was presumed that after hydrolysis of the other dienyl terminus of **2** an allyl complex (**3**) would result, and coupling of the remaining

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ketone with an allyl terminus would lead to the observed 1,4-regiochemistry and ultimately elimination of an enediol such as **4a**. As stated above, a sequential combination of oxidation and hydrolysis could also be employed, leading to an enetriol (e.g., **5a**). Notably, the stereochemistry of the product revealed that the oxidation of the organic fragment occurred on the side opposite to the metal, i.e., with inversion rather than retention of stereochemistry. Also notable is that the relative configurations of three chiral centers are set selectively by this overall reaction, while five relative configurations may be selectively set for some aldehydes.

4a (R = CH$_3$), **4b** (R = C$_2$H$_5$)

5a (R = CH$_3$), **5b** (R = C$_2$H$_5$)
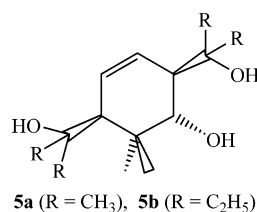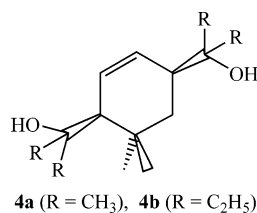
While the occurrence of the 1,4-regiochemistry was much more interesting than simply finding another example of the expected 1,5-regiochemistry, there was reason to seek 1,5-regiochemistry in this case. It can be noted that the 1,5-dicoupling of an appropriate dione to a 6,6-dmch ligand would yield a fragment similar to the AB ring system of Taxol.[6] Hence, it was of interest to coax a dmch metal complex to undergo the more mundane 1,5-dicoupling process with simple ketones as a precursor to a study of reactions involving more complicated diones. As zirconium is more electropositive and oxophilic than titanium, it would have to be expected that in an analogue of **2** the presence of the zirconium center would lead to a rapid coupling of the

coordinated ketone with the 6,6-dmch ligand, leading to the more usual 1,5-regiochemistry. Herein we report the unexpected outcome of such an attempt and additional studies designed to help elucidate the origin of the 1,4-regiochemistry in some of these reactions. As will be shown, it appears that the potential of alkoxide ligands, resulting from the ketone couplings, to serve as five-electron donors[7] can be implicated as the source of the unusual regiochemistry.

Experimental Section

All synthetic procedures and handling of compounds were carried out under a nitrogen atmosphere. Solvents were dried using activated alumina under a nitrogen atmosphere. Spectroscopic data were acquired as described previously.[8] Elemental analyses were obtained from Complete Analysis Laboratories, Inc.

Structural data were obtained with a Nonius Kappa CCD autodiffractometer. Single crystals were protected from the atmosphere with Paratone oil. Initial structural solutions were obtained using direct methods, with further atoms located via difference Fourier maps.[9] For the zirconium compound, all non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were located and successfully refined isotropically. The refinement for the titanium compound was carried out similarly, except that the PMe$_3$ hydrogen atoms were placed in idealized positions, as were three of the C$_5$H$_5$ ligand's hydrogen atoms. Half a molecule of ether was present in the asymmetric unit. Its non-hydrogen atoms were refined anisotropically, while its hydrogen atoms were placed in idealized positions.

{Zr(C$_5$H$_5$)[6,6-dmch-(C$_3$H$_6$O)$_2$]}$_2$. To a solution of CpZr-(dmch)(PMe$_3$)$_2$[10] (0.78 g, 1.9 mmol) in 20 mL of hexane at room temperature was added acetone (0.30 mL, 4.2 mmol). The resulting yellow solution was stirred for 1 h. The solvent was removed in vacuo, and the crude product was extracted using ca. 40 mL of hexane. The solution was filtered through a Celite pad on a coarse frit. The product was then crystallized by concentration of the filtrate to ca. 4−5 mL and placement in a freezer at −20 °C, which afforded yellow crystals (0.62 g, 52% yield). Anal. Calc for C$_{19}$H$_{28}$O$_2$Zr: C, 60.11; H, 7.43. Found: C, 60.10; H, 7.67.

Ti(C$_5$H$_5$)(η^2-dmch-Ph$_2$CO)PMe$_3$. To an orange-brown solution of Ti(C$_5$H$_5$)(6,6-dmch)(PMe$_3$)[3] (0.20 g, 0.68 mmol) in 10 mL of diethyl ether was added benzophenone (0.12 g, 0.68 mmol). The reaction mixture was left overnight without stirring, resulting in a green solution. Placement of the reaction flask in a −30 °C freezer resulted in the formation of dark green crystals (0.13 g, 40% yield). ^{1}H NMR (benzene-d_6, ambient): δ 0.53 (s, 3H, exo CH$_3$), 0.58 (d, 9H, J = 4.8 Hz, PMe$_3$), 1.53 (s, 3H, endo CH$_3$), 1.84 (m, 1H$_4$), 2.06 (d, 1H$_5$, J = 9.6 Hz), 3.76 (d, 1H$_1$, J = 6.3 Hz), 5.48 (m, 1H$_2$), 5.83 (s, 5H, Cp), 6.38 (m, 1H$_3$), 6.90 (m, 2H, Ph), 7.07 (m, 4H, Ph), 7.46 (m, 4H, Ph). ^{13}C NMR (benzene-d_6, ambient): δ 16.5 (broad signal, PMe$_3$), 31.6 (q, overlapping, 1C, J = 126 Hz, exo CH$_3$), 34.9 (q, overlapping, 1C, J = 125 Hz, endo CH$_3$), 35.6 (s, 1C$_6$), 54.2 (d, 1C$_1$, J = 126 Hz), 62.9 (dd, 1C$_4$, J = 160, 10 Hz), 81.3 (d, 1C$_5$, J = 153 Hz), 102.7 (s, 1C$_9$), 108.2 (d of quintets, 5C, J = 171, 7 Hz, Cp), 114.3 (dt, 1C$_2$, J = 160, 7 Hz), 124.0−

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Table 1. Crystallographic Data for {Zr(C₅H₅)(6,6-dmch-(C₃H₆O)₂]}₂ and Ti(C₅H₅)(η²-dmch-Ph₂CO)PMe₃

formula	$C_{19}H_{28}O_2Zr$	$C_{31}H_{40}O_{1.5}PTi$
fw	379.63	515.50
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
color	yellow	green
a (Å)	9.4042(2)	34.3999(10)
b (Å)	9.4956(2)	10.2152(3)
c (Å)	11.7123(3)	18.2981(5)
α (deg)	89.4653(9)	90
β (deg)	70.9506(10)	120.8700(13)
γ (deg)	63.1912(15)	90
temp (K)	200(1)	150(1)
Z	2	8
R (2σ)	0.0243	0.0429
wR_2 (2σ)	0.0553	0.0973
GOF	1.063	1.037

127.6 (10C, Ph), 131.6 (dt, 1C, $J = 149$, 5 Hz, C₃), 151.2 (t, 1C, $J = 7$ Hz, Ph), 152.5 (t, 1C, $J = 7$ Hz, Ph). Anal. Calc for $C_{29}H_{35}OPTi$: C, 72.79; H, 7.26. Found: C, 72.83; H, 7.58.

Results and Discussion

In contrast to the reaction of **1** with ketones, which led to oily products, the reaction of Zr(C₅H₅)(6,6-dmch)-(PMe₃)₂ with acetone led to a crystalline product. Analytical, spectroscopic, and structural characterization revealed that, as expected, both acetones had coupled to each dmch ligand on a given zirconium center, but the unusual 1,4-regiochemistry observed earlier was, unexpectedly, once again present (**6**, Figure 1). It therefore became apparent that the 1,4-regiochemistry for titanium was not the result of a delayed second coupling step, but instead represented an actually preferred regiochemistry for a dicoupling process of ketones with either a titanium or zirconium 6,6-dmch complex.
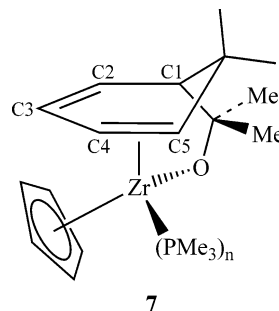

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Before continuing any mechanistic discussion, we can first consider the structural result for **6** and its implications for the regiochemical issues. One of the interesting ramifications of the 1,4-regiochemistry is the formation of a localized Zr—C(5) bond, noticeably shorter than the Zr—C(Cp) bonds (2.353(2) vs ca. 2.59 Å), leading also to a localized C2=C3 bond (1.330(3) Å). More telling, however, are the parameters associated with the Zr—O coordination. As a starting point, it can be observed that the shortest Zr—O distances involve those oxygen atoms that would be expected to be coordinated to Zr in the initial monomeric units (e.g., the labeled O1 and O2 for Zr1). Considering these as forming single bonds to Zr, with lone pair coordination from the other attached O2 center (O2′), would lead to a 14-electron configuration for the complex. It might then be expected that the

Figure 1. Perspective view of {Zr(C₅H₅)[6,6-dmch-(C₃H₆-O)₂]}₂.

zirconium centers would attain an 18-electron configuration through π (three electron) alkoxide coordination from both O1 and O2. The Zr1−O2−C12 angle of 117.64(9)° is in fact fairly close to the ideal value of 120° expected for the formal sp² hybridization on O2.[11] However, the significantly larger Zr1−O1−C9 angle, 144.93(11)°, and the accompanying shorter Zr−O1 distance of 1.923(1) Å suggest a stronger interaction for O1. Given earlier results establishing the ability of alkoxide ligands to serve as five-electron donors,[7] it can be assumed that a second π interaction between O1 and Zr1 is occurring in competition with a (primarily) single π interaction between O2 and Zr1, and likely also with π Zr−Cp interactions.[2c,12]

The large Zr1−O1−C9 angle, associated with the ketone that would have been involved in the first coupling step, appeared to provide some insight into the origin of the 1,4-regiochemistry. Since 1,5-regiochemistry has been observed for couplings of imines with 6,6-dmch ligands,[13] it was clear that it was the initially incorporated, and coupled, ketone that had to be responsible. In examining the potential implications of a large Zr1−O1−C9 angle, brought about by an attempt for a species such as **7** (n probably = 1) to achieve an

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18-electron configuration, it appeared that the large Zr−O−C angle would likely result in the Zr center being

(11) (a) A Ti−O−C value of ca. 133° has been proposed as the ideal for three-electron donation.[11b] (b) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

Table 2. Pertinent Bonding Parameters for {Zr(C₅H₅)[6,6-dmch-(C₃H₆O)₂]}₂

Bond Distances (Å)							
Zr−C15	2.554(2)	C15−C16	1.398(3)	Zr−O1	1.9230(12)	C1−C6	1.548(3)
Zr−C16	2.607(2)	C15−C19	1.402(3)	Zr−O2	2.1421(11)	C2−C3	1.330(3)
Zr−C17	2.638(2)	C16−C17	1.404(3)	Zr−O2′	2.2471(11)	C3−C4	1.501(3)
Zr−C18	2.612(2)	C17−C18	1.403(3)	Zr−C5	2.3534(17)	C4−C5	1.531(2)
Zr−C19	2.550(2)	C18−C19	1.399(3)	C1−C2	1.512(2)	C5−C6	1.556(2)

Bond Angles (deg)					
Zr−O2−Zr′	110.48(5)	Zr−O1−C9	144.93(11)	C9−C1−C6	116.80(15)
O1−Zr−O2	118.21(5)	Zr−O2−C12	117.64(9)	C1−C2−C3	124.85(17)
O1−Zr−O2′	93.38(5)	Zr−O2′−C12′	131.61(9)	C2−C3−C4	124.49(17)
O1−Zr−C5	83.60(6)	Zr−C5−C4	107.74(11)	C3−C4−C5	111.01(15)
O2−Zr−O2′	69.52(5)	Zr−C5−C6	115.24(11)	C4−C5−C6	111.43(14)
O2−Zr−C5	75.98(5)	O1−C9−C1	109.57(14)	C5−C6−C1	109.08(14)
O2′−Zr−C5	138.91(5)	C9−C1−C2	112.54(14)	C6−C1−C2	107.64(14)

Table 3. Pertinent Bonding Parameters for Ti(C₅H₅)[η²-dmch-Ph₂CO]PMe₃

Bond Distances (Å)							
Ti−C22	2.334(3)	Ti−P	2.6150(7)	C1−C6	1.562(3)	C22−C23	1.392(5)
Ti−C23	2.317(2)	Ti−O	1.8219(13)	C2−C3	1.342(3)	C22−C26	1.361(6)
Ti−C24	2.369(2)	Ti−C4	2.235(2)	C3−C4	1.445(3)	C23−C24	1.379(4)
Ti−C25	2.438(2)	Ti−C5	2.158(2)	C4−C5	1.430(3)	C24−C25	1.370(4)
Ti−C26	2.424(3)	C1−C2	1.509(3)	C5−C6	1.530(3)	C25−C26	1.338(5)

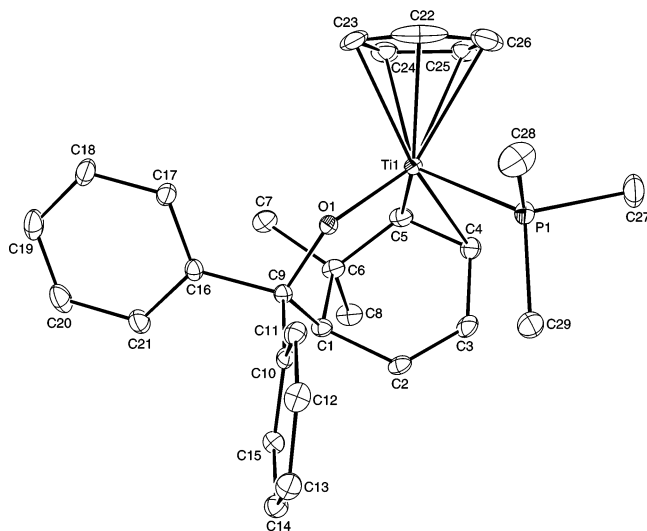| Bond Angles (deg)					
P−Ti−O	96.02(4)	C9−C1−C2	109.52(15)	C2−C3−C4	123.5(2)
Ti−O−C9	140.68(11)	C9−C1−C6	115.61(15)	C3−C4−C5	116.9(2)
O−C9−C1	107.37(14)	C2−C1−C6	108.61(16)	C4−C5−C6	119.0(2)
		C1−C2−C3	122.33(19)	C5−C6−C1	111.2(2)

directed away from a location in which it could interact with the entire diene fragment, particularly C2 and C3, thus leading to attachment of Zr1 to only the C4=C5 bond of the C2−C5 diene fragment. In such a situation, there is no longer an electronic difference between C4 and C5 that would favor coupling of C5, as there would be for a diene. Coupling at C4 could then be favored due to steric hindrance to coupling at C5 that the C(CH₃)₂ bridge may provide, or due to electronic influences (vide infra).

To gain support for the above mechanistic proposals, it became of interest to isolate a mono(ketone) coupling product that should show η²-coordination for the diene fragment, as opposed to the η⁴-coordination observed for mono(imine) products.[14] Unfortunately, in most cases with ketones, it appeared that the second coupling took place more rapidly than the first, making it seem unlikely that such a species could be isolated. Nevertheless, for Ti(C₅H₅)(6,6-dmch)(PMe₃) it was observed that reaction with benzaldehyde yielded a mono(coupling) product,[3,4] and attempts were therefore made to isolate this species. However, that complex was found to be very difficult to handle, being quite susceptible to protonation, perhaps even from hydroxyl groups on the silica surface of the glassware. After a number of attempts with a variety of ketones and aldehydes, it was found that benzophenone yielded a (deep green) product (**8**, Figure 2) that, while also being quite susceptible to oxidation and hydrolysis, could at least be isolated in

(12) It seems likely that many of the complexes previously reported to have M−O−C angles exceeding 120° actually will have partial π donations from both of the oxygen lone pairs, with other bonding interactions suffering as a result.[2c] This should be observable through appropriate theoretical studies. An analogous situation may be considered to exist for C₅H₅ compounds such as Ni(C₅H₅)₂ or Zr(C₅H₅)₃-(η¹-C₅H₅).

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(14) (a) Tomaszewski, R.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1999**, *18*, 4174. (b) Pillet, S.; Wu, G.; Kulsomphob, V.; Harvey, B. G.; Ernst, R. D.; Coppens, P. *J. Am. Chem. Soc.* **2003**, *125*, 1937.

crystalline form and characterized (see Experimental Section). In addition to analytical and spectroscopic
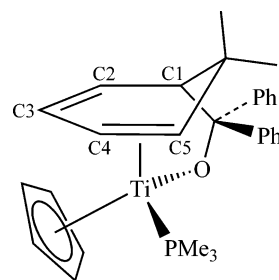
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data, an X-ray structural determination clearly revealed that a single benzophenone had coupled to the 6,6-dmch fragment, leading to alkoxide coordination characterized by a short Ti−O bond (1.822(1) Å) and a wide Ti−O−C

Figure 2. Perspective view of Ti(C₅H₅)(η²-dmch-Ph₂CO)-PMe₃.

angle, 140.7(1)°. Particularly important, however, is that the metal center is coordinated only by the C4=C5 bond of the diene unit, as had been surmised. An additional indication of this can be gained from the comparison of the C2−C3 and C4−C5 distances, 1.342(3) vs 1.430(3) Å, respectively. It is of further note that there is also coordination by phosphine, which impacts on at least two issues. First, relative to an electron count, the presence of the phosphine would allow the titanium center to achieve a 14-electron configuration were the alkoxide to serve just as a one-electron donor. Quite clearly, the large Ti−O−C angle is consistent with π donation by oxygen, and from a comparison with data for other complexes, it can be expected that at least partial donations are occurring from both oxygen lone pairs. In any event, the phosphine ligand may be providing one other important bit of information. Should the second coupling step involve replacement of the coordinated phosphine by the second equivalent of ketone, the ketone would probably coordinate like the phosphine, in a position closer to C4 than to C5, hence favoring the observed 1,4-regiochemistry. It is noteworthy that the Ti−C4 distance of 2.235(2) Å is significantly longer than that for Ti−C5, 2.158(2) Å, which may also reflect a problem for the titanium center interacting not only with C2 and C3 but C4 as well, thereby again making it more favorable for coupling to occur at C4 rather than C5.

With the origin of the unusual 1,4-regiochemistry seeming to be resolved, some attention may be given to the impact of related regiochemical considerations in other situations. First, while the dicoupling reactions of either imines or ketones with titanium or zirconium 6,6-dmch complexes lead to different regiochemistries, it is interesting that mixed imine/ketone couplings should be able to lead to either regiochemistry, depending on which substrate is introduced first. Thus, an imine/ketone sequence should lead to the usual 1,5-regiochemistry, while the opposite sequence should result in 1,4-regiochemistry. Second, given the 1,4-regiochemistry in the dicoupling reactions of acetone with **1** or $Zr(C_5H_5)(6,6\text{-dmch})(PMe_3)_2$, it might be questioned why the dicoupling of ketones to the $Ti(C_5H_5)$-$(2,4\text{-}C_7H_{11})(PEt_3)$ complex (**9**, C_7H_{11} = dimethylpentadienyl) was found to lead to the usual 1,5-regiochemistry. In this case, even though an η^2-diene intermediate may again be proposed, the steric properties of 2,4-C_7H_{11} and 6,6-dmch differ dramatically. As the 2,4-C_7H_{11} ligand does not possess the steric hindrance of the edge-bridge in 6,6-dmch, but instead has a methyl substituent on the C4 position, one could easily expect the C5 position to engage more readily in the second coupling step.
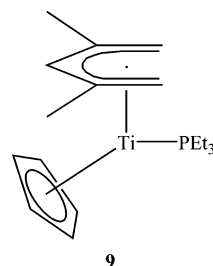
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Conclusions

The unusual 1,4-regiochemistry observed in the dicoupling reactions of ketones or aldehydes with 6,6-dmch complexes of titanium or zirconium demonstrates that the previously established ability of an alkoxide ligand to serve as a five-electron donor can play a determining role in the outcome of a chemical reaction. Concerning the original goal of achieving 1,5-regiochemistry for the dicoupling of a dione with a 6,6-dmch ligand, it seems ironic that this could still be achievable through a straightforward reaction of either a titanium or zirconium 6,6-dmch complex with a dione, as the tether between the two carbonyl groups could prevent the second carbonyl group from approaching the C4 end of the coordinated olefin. However, there is a regiochemical issue that would need to be addressed, in that two orientations could be adopted by the incoming dione, one with the tether directed toward the other dienyl terminus, as desired, but the other having the opposite orientation. Regiochemical results for imine couplings have demonstrated that the less bulky substituent tends to be directed toward the other terminus, so that one could perhaps employ a particularly large substituent such as $SiMe_3$ or $t\text{-}C_4H_9$ on the ends of the dione. As intramolecular dicoupling reactions between 6,6-dmch ligands and diimines tethered at least through the nitrogen atoms have been realized,[15] there is every reason to expect that diones should also be capable of intramolecular dicoupling reactions.

Supporting Information Available: A listing of positional coordinates, anisotropic thermal parameters, and additional bonding parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Basta, R. Ph.D. Thesis, University of Utah, 2004.