if reaction 2 is carried out under nitrogen purge, pure **7b** is obtained directly and in yields exceeding 90%. Atmospheric carbonylation of **7b** readily gives **7a**, and this two-step sequence is the preferred route to this compound. Similar interconversion in a related dirhodium system has been well-documented by Dixon et al.,[11] who have also chronicled the rich derivatives chemistry of $[(\eta\text{-}C_5H_5)_2Rh_2(CO)](\mu\text{-}\eta^2,\eta^2\text{-HFB})$.[12]

Clearly the $M(CO)_4(\eta^2\text{-HFB})$ complexes show great promise toward the synthesis of a variety of dimetallacyclobutenes. The scope of the reaction, the conversion of the compounds to the corresponding dimetallatetrahedranes and their further derivatization as well as the mechanism[13] of reactions 1 and 2 are being actively pursued in our laboratories.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for financial support.

Registry No. **1a**, 111378-98-4; **1b**, 111378-99-5; **2a**, 16406-48-7; **2b**, 16406-49-8; **3**, 111379-00-1; **4**, 106245-28-7; **5**, 111379-01-2; **6a**, 12129-77-0; **6b**, 32627-01-3; **6c**, 32660-96-1; **7a**, 111379-04-5; **7b**, 111379-03-4; **8**, 111379-02-3; **9**, 111409-11-1; HFB, 692-50-2; $Ru(^{13}CO)_4(\eta^2\text{-HFB})$, 111379-05-6; $RuOs[(^{13}CO)_3(CO)_5](\mu\text{-}\eta^1,\eta^1\text{-HFB})$, 111379-06-7.

Supplementary Material Available: Characteristic data on compounds **1a**, **1b**, **3–5**, and **7–9** (5 pages). Ordering information is given on any current masthead page.

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[11] Dickson, R. S.; Pain, G. N. *J. Chem. Soc., Chem. Commun. 1979*, 277.

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[13] Although reactions 1 and 2 are initiated by two 18-electron species, it is clear that the intimate mechanism of product formation proceeds via the intermediacy of a 16-electron intermediate. The strong π-acceptor nature of HFB favors reversible loss of CO from **1a** and **1b** as the first step of the reaction. This assumption is consistent with the rapid exchange of the carbonyl ligands of **1a** with ^{13}CO and is further strengthened by the preliminary observation that the reaction of $Ru(^{13}CO)_4(\eta^2\text{-HFB})$ with $Os(CO)_5$ gives $RuOs[(^{13}CO)_3(CO)_5](\mu\text{-}\eta^1,\eta^1\text{-HFB})$. The relative ease of reaction 1 is also supportive of this idea. The speed of the reaction is **1a** with **2b** > **1a** with **2a** > **1b** with **2b** and reflects the fact that the putative intermediate, $M(CO)_3(HFB)$, is easier to achieve with Ru than Os. The observation that **1a** reacts more readily with **2b** than **2a** is in accord with the greater basicity of the former and its, now well-recognized, ability to partake in donor–acceptor metal–metal bond formation.[14] It is interesting to note that in addition to helping the dissociation of CO from **1a** and **1b**, the HFB ligand, by virtue of its ability to function as a 4-electron donor, also stabilizes the presumed $M(CO)_3(HFB)$ intermediate. Efforts are underway to isolate and characterize such species.

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Selective Formation of Titanium Enolates from Ketones and Bis(pentamethylcyclopentadienyl)dimethyltitanium(IV)[1a]

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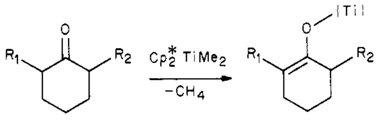
Summary: A variety of ketones react with $(\eta^5\text{-}C_5Me_5)_2Ti{=}CH_2$, formed in situ by thermolysis of the title compound, to yield Ti enolates in a process that is highly regioselective and extraordinarily stereoselective.

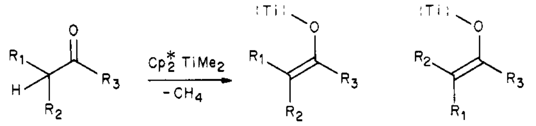
Enolates are among the most important synthetic intermediates due to the variety of C–C bond-forming reactions and other functionalizations they mediate. Following the pioneering studies of Stork and Hudrlik[2] and House et al.,[3] Li enolates have been the most widely used; however, there has been growing interest in the use of other metals[4] in order to obtain improved selectivity. We wish to report the preparation of Ti enolates from ketones and bis(η^5-pentamethylcyclopentadienyl)dimethyltitanium(IV) (**1**)[5] with regioselectivity comparable to hindered amide bases and the best stereoselectivity yet observed.

As summarized in Table I, good to excellent yields of enolates result when the corresponding ketones are heated at 100 °C with a slight excess of **1** in toluene in a sealed tube (or under a static Ar atmosphere). For example 2-methylcyclohexanone (**2b**) yielded 87% of the less substituted enolate **3b** and <0.5% of the more substituted one **3c**. When **2b** was treated with lithium diisopropylamide (LDA) and trimethylsilyl chloride, a 99:1 ratio of less substituted to more substituted trimethylsilyl enol ethers was obtained.[3] With excess **2b**, the mixture of enolates **3b** + **3c** observed initially was converted completely to **3c** by continued heating (48 h at 100 °C). No enolate **3d** was detected when the substrate was 2,6-dimethylcyclohexanone (**2d**). In the acyclic series, methyl isopropyl ketone (**4e**) afforded an 86:3 ratio of yields of less substituted (**5e**) to more substituted (**5f**) enolates. The minor enolate (**5f**) is probably not formed directly from **4e**, as diisopropyl ketone (**4g**) yielded no detectable enolate **5g**.



2 3

a, $R_1 = R_2 = H$
b, $R_1 = H$, $R_2 = Me$
c, $R_1 = Me$, $R_2 = H$
d, $R_1 = R_2 = Me$
$Cp^* = Me_5Cp$, {Ti} = Cp^*_2 TiMe



4 5 6

a, $R_1 = H$, $R_2 = R_3 = Me$
b, $R_1 = R_2 = H$, $R_3 = Et$
c, $R_1 = H$, $R_2 = Me$, $R_3 = Et$
d, $R_1 = H$, $R_2 = Et$, $R_3 = Pr$
e, $R_1 = R_2 = H$, $R_3 = iPr$
f, $R_1 = R_2 = R_3 = Me$
g, $R_1 = R_2 = Me$, $R_3 = iPr$
h, $R_1 = R_2 = H$, $R_3 = tBu$
i, $R_1 = R_2 = H$, $R_3 = Ph$
j, $R_1 = H$, $R_2 = Ph$, $R_3 = Me$
k, $R_1 = R_2 = H$, $R_3 = CH_2Ph$

Although methyl ethyl ketone (**4a**) afforded a mixture of all three possible enolates (**5a**, **6a**, and **5b**), diethyl ketone (**4c**) and dipropyl ketone (**4d**) each yielded only a single enolate (**5c** and **5d**, respectively) within the limit of

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[1] (a) New Titanium Chemistry. 1. For part 2 see: Gibson, C. P.; Dabbagh, G.; Bertz, S. H. *J. Chem. Soc., Chem. Commun.*, in press. (b) Current address: Department of Chemistry, West Virginia University, Morgantown, WV 26505.

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Table I. Enolate Formation from Ketones and $Cp_2{}^*TiMe_2$

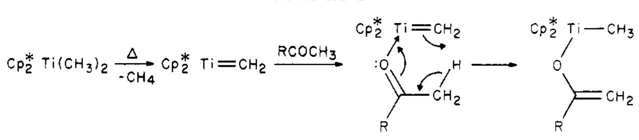
ketone	enolate	% yield[a]	
2a	**3a**	95	
2b	**3b**	87	
	3c	<0.5	
2d	**3d**	<0.5	
4a	**5a**	34	} 79
	6a	11	
	5b	34	
4c	**5c**	91	
	6c	<0.5	
4d	**5d**	81	
	6d	<0.5	
4e	**5e**	86	} 89
	5f	3	
4g	**5g**	<0.5	
4h	**5h**	71 (99)[b]	
4i	**5i**	74 (96)[b]	
4j	**5j**	67	} 75
	6j	7	
	5k	1	
7	**8a**	62	} 66
	8b	4	
9	**10**	63 (80)[b]	
11	**12**	86	
13a	**14a**	94	
13b	**14b**	80	
	15	5	

[a] Determined by ^1H NMR spectroscopy in toluene-d_8 after 21 ± 1 h at 100 ± 2 °C. No enolate detected is signified by <0.5%. [b] After 115 h at 80 °C in toluene-d_8.

detection by ^1H NMR ($\sim$0.5%). The *E* stereochemistry was assigned on the basis of NOE experiments, which showed a 5–10% enhancement of the vinyl H signal for the *E* isomer but a negligible one for the *Z* isomer when the Ti-bound methyl was irradiated.[6] These NOE experiments were performed on samples, prepared by using excess ketone at 80 °C (4 days), which had *E*:*Z* ratios of yields equal to 64:36 and 89:4 starting from **4c** and **4d**, respectively. The chemical shifts of the vinyl H's (Table II, supplementary material) follow the general rule that the (*E*)-enolate H resonance is downfield from the (*Z*)-enolate H resonance.[3] On the basis of these results, we conclude that steric factors play an exceedingly important role in these reactions of **1** (vide infra). Furthermore, they appear in a dramatic fashion as the substrate goes from **4a** to **4c**, a change of but one CH_2 moiety.

For comparison, Clark and Untch[7] reported that treatment of **4d** with LDA and *subsequent* addition of *t*-$BuMe_2SiCl$ gave a 65:35 mixture of (*E*)- and (*Z*)-enolates, respectively. Corey and Gross[8] demonstrated that treatment of **4c** with lithium *tert*-octyl-*tert*-butylamide (LOBA) *in the presence of* Me_3SiCl afforded a 98:2 *E*:*Z* mixture. Ireland et al.[9] had reported that the sequential trapping procedure using LDA and *t*-$BuMe_2SiCl$ on **4c** gave a 77:23 ratio of *E*:*Z* silyl enol ethers, and Corey and Gross[8] reported a 77:23 *E*:*Z* ratio of trimethylsilyl enol ethers from the "internally trapped reaction" of **4c** with LDA/Me_3SiCl. The sequential treatment of **4c** with LOBA and Me_3SiCl was not reported; therefore, it is not clear that the combined reagent is crucial in this particular case, especially in light of the agreement between the (sequential) results of Ireland et al. and the (internally trapped) results of Corey and Gross, when LDA was the base in each case. In any event, our ratio of *E*:*Z* > 180 is the best stereoselectivity yet observed for enolate formation from **4c**.

Scheme I



In some cases, notably methyl *tert*-butyl ketone (**4h**) and acetophenone (**4i**), the yields were substantially improved by running the reactions at 80 °C rather than 100 °C. For comparison with our results for **4j**, the use of LDA followed by Me_3SiCl resulted in an 86:14 ratio of *E*:*Z* trimethylsilyl enol ethers,[3] corresponding to our enolates **5j** and **6j**, respectively. Some other interesting results were obtained from 2-cyclohexenone (**7**), which afforded predominantly the extended enolate (**8a**, see supplementary material) rather than the cross-conjugated isomer (**8b**), and 2,3-epoxycyclohexanone (**9**), which gave chemoselective enolate formation (cf. **10**) rather than epoxide opening. Cyclohexane-1,4-dione (**11**, 0.5 equiv) yielded the 1,3-diene **12** rather than the isomeric 1,4-diene derivative. Steroidal ketones 5α-cholestan-3-one (**13a**) and progesterone (**13b**) yielded the $\Delta^{3,4}$-enolates **14a** and **14b**, respectively.[10] In the latter case, some (5%) of the cross-conjugated enolate (**15**) was formed along with the extended enolate **14b**, as in the case of **7**.

The mechanism of enolate formation was elucidated with the aid of cyclohexanone-*2,2,6,6-d_4*. H-abstraction from the ketone is not rate-limiting, as $k_H/k_D \approx 1.1 \pm 0.1$.[11] Moreover, C^1H_4 was the only methane isotopomer detected by GC–MS in the headspace above the reaction mixture, and the deuterium atom removed from the ketone was located by NMR on the Ti-bound methyl group. Scheme I is consistent with our labeling results and the lack of a significant kinetic isotope effect, assuming that the first step is rate-limiting. The highly ordered transition state helps explain the high levels of selectivity observed, as it prevents the substrate from avoiding the steric constraints imposed by the two pentamethylcyclopentadienyls. Scheme I also incorporates the ideas of McDade, Green, and Bercaw,[5] who studied the thermal decomposition of **1** to the fulvene complex (η^5-C_5Me_5)($C_5Me_4CH_2$)TiMe (**16**) and methane. They interpreted the results of their kinetic and labeling studies in terms of the titanium–methylidene intermediate (η^5-C_5Me_5)$_2TiCH_2$. We also observed **16** in those cases (**2d**, **4g**) where no enolate was produced.

Clawson, Buchwald, and Grubbs[12] reported that the titanocene methylene species Cp_2TiCH_2 (generated in situ) converts enolizable ketones to olefins but that it converts hindered, α,α-disubstituted ketones to the corresponding enolates. They interpreted this change in terms of steric hindrance to the formation of a metallocyclobutane intermediate in the olefination reaction of crowded ketones. Apparently, by making the methylene reagent more crowded, we also effectively suppress the olefination reaction, as we observe at most traces of the corresponding olefins by capillary GLC.

Stille and Grubbs[13] have also prepared Ti enolates from Cp_2TiCH_2 and acid chlorides. Although this reaction is

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(6) The geometry of trimethylsilyl enol ethers has been assigned in an analogous manner: Keller, T. H.; Neeland, E. G.; Weiler, L. *J. Org. Chem.* **1987**, *52*, 1870.

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Organometallics **1988,** *7,* 565–566

limited to the preparation of such enolates as would be obtained by H removal from the methyl group of methyl ketones, it is a useful complement to our approach, which is not regioselective in the case of some methyl ketones (cf. **4a**). The preparation of Ti enolates from $TiCl_4$ and trimethylsilyl enol ethers,[14] from $(i\text{-PrO})_3TiCl$ and Li enolates,[15] or from $Cp_2TiMeCl$ and Li enolates[16] is limited by the selectivity with which the starting materials can be prepared.

Acknowledgment. We thank A. M. Mujsce for GC–MS measurements and L. Clawson for NMR data on Ti enolates.

Supplementary Material Available: Table II, selected NMR data for Ti enolates, and the structures of **8**, **10**, and **12**–**14** (2 pages). Ordering information is given on any current masthead page.

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Bis(arene)vanadium Anions: A New Class of Organovanadium Complexes. X-ray Structural Characterization of Solvated K[(η^6-1,3,5-$C_6H_3Me_3)_2$V]

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Summary: Reduction of bis(η^6-arene)vanadium(0) complexes with potassium gives the corresponding bis(η^6-arene)vanadium(–I) derivatives (arene = C_6H_6, 1,3,5-$C_6H_3Me_3$) as their K^+ salts. A single-crystal diffraction study of solvated K[(η^6-1,3,5-$C_6H_3Me_3)_2$V] shows that the anion presents two different rotameric configurations in the solid, though the sandwich structure is preserved, and that contact ion pairs are established with the K^+ cations, which also interact with THF and dioxane solvent molecules. Crystal data: monoclinic, space group $P2_1$, a = 10.213 (2) Å, b = 18.518 (3) Å, c = 13.402 (3) Å, β = 89.58 (1)°, V = 2534.6 Å^3, and Z = 4.

In 1975 it was reported that the EPR signal of $[V(C_6H_6)_2]$ (**1a**) disappears on contacting the latter with a potassium mirror in chelating solvents.[1] However, in spite of the theoretical and practical implications of this observation, organovanadium(–I) chemistry is still restricted to the hexacarbonylvanadate anion and its substituted derivatives.[2]

We now report that, when **1** is mixed with excess potassium sand in tetrahydrofuran, THF[3] at room temperature, dark exceedingly air-sensitive solutions result.[4]

$$\underset{\mathbf{1a,b}}{[V(\text{arene})_2]} + K \xrightarrow{\text{THF}} \underset{\mathbf{2a,b}}{K[V(\text{arene})_2]} \qquad (1)$$

a, arene = C_6H_6;
b, arene = 1,3,5-$C_6H_3Me_3$ (mesitylene)

After filtration of the unreacted potassium and addition of either diethyl ether or *n*-heptane, **2a** precipitates as a black microcrystalline solid.[5] On the other hand, dilution of a filtered THF solution of **2b** by either of the same solvents causes immediate and quantitative decomposition to **1b** and elemental potassium.[6]

On cooling a concentrated solution (0.22 M) to –40 °C, **2b** was isolated as a black microcrystalline product in low yield (ca. 20%). **2b** is even more air sensitive than **2a** and is decomposed into elemental potassium and **1b** when suspended in *n*-heptane.[7]

When **1b** and potassium sand were mixed in 1,4-dioxane, a burgundy-brown powder separated out. When it was redissolved by adding sufficient THF to the reaction mixture and cooling to –40 °C, black-brown crystals, **2c**, suitable for X-ray data collection, could be grown.[8]

The crystallographic study shows that the asymmetric unit contains two independent $[V(C_6H_3Me_3)_2]^-$ sandwiches and their respective K^+ cations and two THF, and one dioxane solvent molecules.[9] Despite the poor quality of

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[†] Research Associate, Scuola Normale Superiore, Pisa.

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(3) Vanadium concentrations were 0.03–0.1 M.

(4) In the case of benzene as the ligand, by careful filtration and titration of the unreacted potassium, the quantitative formation of a 1:1 K/V adduct was demonstrated.

(5) The composition $KV(C_6H_6)_2\cdot1.25THF$ was established analytically after careful addition of water (alkalimetric titration for K; recovery of **1a**; GC for THF).

(6) On the basis of a titration of the potassium released during such a decomposition, a 70% yield could be evaluated for the formation of **2b** in reaction 1.

(7) From the titration of the released potassium, the approximate composition $KV(C_6H_3Me_3)_2\cdot2THF$ was deduced (K: found, 8.0; calcd, 8.2).

(8) **Crystal data for $K[V(C_6H_3Me_3)_2]\cdot(C_4H_8O)\cdot{}^1/_2(C_4H_8O_2)$ (2c):** monoclinic, space group $P2_1$ from satisfactory refinement (see below); a = 10.213 (2) Å, b = 18.518 (3) Å, c = 13.402 (3) Å, β = 89.58 (1)°, V = 2534.6 Å^3, Z = 4, $F(000)$ = 952, D_{calcd} = 1.17 g/cm^3, Mo Kα radiation, λ = 0.71069 Å, μ(Mo Kα) = 5.56 cm^{-1}, ω –2 θ scan mode, θ range = 2.5–25°, R = 0.057, and R_w = 0.061 for 1181 independent reflections with $F_o > 5\sigma(F_o)$. The space group determination was not straightforward: initial attempts in the orthorhombic $P2_12_12_1$ (from systematic absences) were not successful; the monoclinic choice was adopted after a careful examination of the equivalence conditions.

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