ORGANOMETALLICS

Volume 10, Number 4, April 1991

Communications

General and Convenient Procedure for the Preparation of Zirconocene Complexes of Alkenes and Conjugated Dienes

Douglas R. Swanson and Ei-ichi Negishi*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received July 19, 1990

Summary: In situ generation of *i*-$BuZrCp_2Cl$ by treatment of Cp_2ZrCl_2 with 1 equiv of *t*-BuLi followed by addition of 1 equiv more of *t*-BuLi can serve as a satisfactory "$ZrCp_2$" source, permitting direct conversion of various alkenes and dienes into the corresponding $ZrCp_2$ complexes in high yields.

We have reported that treatment of Cp_2ZrCl_2, where Cp = η^5-C_5H_5, with 2 equiv of *n*-BuLi[1] provides a convenient procedure for in situ generation of "$ZrCp_2$", which reacts not only with enynes,[1,2] diynes,[1,2] and isolated dienes[3] to produce the corresponding zirconabicycles but also with certain alkynes[4] and alkenes[1,4,5] in the presence of a phosphine to give the corresponding $ZrCp_2$–phosphine complexes of alkynes and alkenes. In our initial study[1] we also used *t*-BuLi, *t*-BuMgCl, and EtMgBr in the bicyclization of 7-(trimethylsilyl)-1-hepten-6-yne, but less favorable results were obtained. More recently, we have encountered major difficulties in directly converting alkenes[6] and conjugated dienes[7] into the corresponding $ZrCp_2$ complexes using *n*-BuLi–Cp_2ZrCl_2. In these reactions 1-butene generated in situ participated in the formation of zirconacycles.[6,7] We therefore sought alternate reagents that would produce alkene ligands weaker than 1-butene. We now report that treatment of Cp_2ZrCl_2 with 1 equiv of *t*-BuLi at −78 °C followed by warming to 25 °C quantitatively produces *i*-$BuZrCp_2Cl$,[8] which, on treatment with an additional 1 equiv of *t*-BuLi at −78 °C, generates a $ZrCp_2$ derivative that is satisfactory for direct conversion of monosubstituted alkenes and conjugated dienes into the corresponding $ZrCp_2$ complexes *without incorporation of*

Table I. Direct Conversion of Monosubstituted Alkenes and Conjugated Dienes into Their Zirconocene Complexes

	product	
alkene or diene	compd	yield,[a] %
ethylene	**1a**[5b]	80 (55)
1-butene	**1b**[5b]	85 (75)
1-octene	**1c**	85 (65)
cyclohexylethylene	**1d**	70 (60)
tert-butylethylene	**1e**	*b*
styrene	**1f**[5b]	85 (70)
isoprene	**2a**[10c]	70 (60)
2,3-dimethylbutadiene	**2b**[10c]	75 (65)
1-vinylcyclopentene	**2c**	75 (65)
1-vinylcyclohexene	**2d**	70 (60)

[a] By NMR spectroscopy. The numbers in parentheses are isolated yields. [b] This complex decomposes at 25 °C to the known dimeric Zr(III) complex $\{(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)(Cp)Zr(PMe_3)\}_2$.[14]

---

(1) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.

(2) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. See also: RajanBabu, T. V.; Nugent, W. A.; Taber, D. F.; Fagan, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7128.

(3) Rousset, C. J.; Swanson, D. R.; Lamaty, F.; Negishi, E. *Tetrahedron Lett.* **1989**, *30*, 5105. See also: Nugent, W. A.; Taber, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 6435.

(4) Takahashi, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1987**, 623.

(5) (a) Takahashi, T.; Murakami, M.; Kunishige, M.; Saburi, M.; Uchida, Y.; Kozawa, K.; Uchida, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1989**, 761. (b) Binger, P.; Muller, P.; Benn, R.; Rufinske, A.; Gabor, B.; Kruger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 1035.

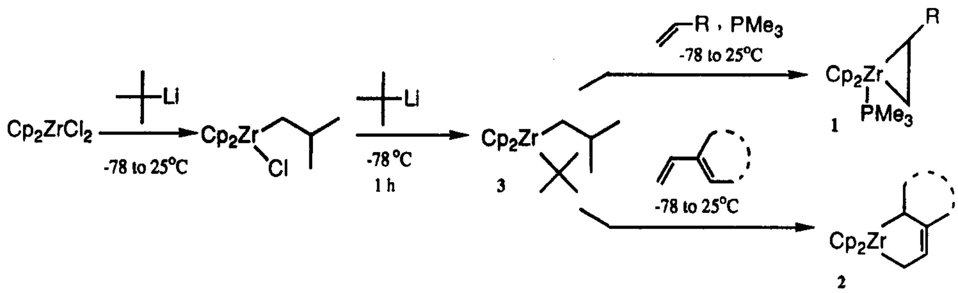
(6) Swanson, D. R.; Rousset, C. J.; Negishi, E.; Takahashi, T.; Seki, T.; Saburi, M.; Uchida, Y. *J. Org. Chem.* **1989**, *54*, 3521.

(7) Negishi, E.; Miller, S. R. *J. Org. Chem.* **1989**, *54*, 6014.

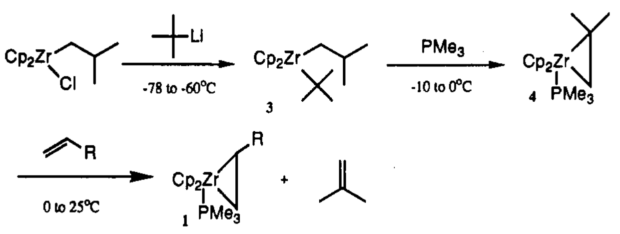
(8) *i*-$BuZrCp_2Cl$: ^1H NMR (*n*-hexane-d_{14}, Et_2O-d_{10}, toluene) δ 0.86 (d, J = 8 Hz, 2 H), 0.90 (d, J = 8 Hz, 6 H), 2.30 (m, 1 H), 6.42 (s, 10 H); ^{13}C NMR (C_6D_6, Me_4Si) δ 27.92, 33.48, 65.57, 112.44.

0276-7333/91/2310-0825$02.50/0

Scheme I



Scheme II



an unwanted alkene, e.g., 1-butene (Scheme I).

The experimental results are summarized in Table I. Of the five monosubstituted alkenes we tested, all except *tert*-butylethylene give the desired alkene–ZrCp$_2$–PMe$_3$ complexes (1)[2,5,9] and their minor stereoisomers in 70–90% yields by ^{1}H NMR spectroscopy. Similarly, all conjugated dienes tested so far provide their 1:1 complexes with ZrCp$_2$ (2)[10] in 60–80% yields. In each case, isobutylene is formed in 90–100% yield. The following procedure is representative. To a mixture of Cp$_2$ZrCl$_2$ (498 mg, 1.70 mmol) suspended in 3 mL of Et$_2$O was added at −78 °C 1.70 M *t*-BuLi in pentane (1.00 mL). After 30 min at −78 °C the mixture was warmed to 25 °C (1 h). This mixture was cooled to −78 °C and successively treated with 1.00 mL of 1.70 M *t*-BuLi for 1 h at and a mixture of 1-octene (191 mg, 1.70 mmol) and PMe$_3$ (162 mg, 2.10 mmol) in 2 mL of Et$_2$O.[11] The reaction mixture was warmed to 25 °C over 1 h and analyzed by ^{1}H NMR spectroscopy which indicated an 80% yield of 1c. After evaporation (0 °C and ≤1 mm), the residue was extracted with benzene, and the extract was filtered through Celite. Evaporating (0 °C, ≤0.1 mm), diluting with Et$_2$O, and cooling to −78 °C induced separation of a yellow solid, which was filtered at −78 °C to give 1c[12] in 65% isolated yield.

Treatment of *i*-BuZrCp$_2$Cl, generated by the reaction of Cp$_2$ZrCl$_2$ with *t*-BuLi, with an additional 1 equiv of *t*-BuLi in *n*-hexane-d_{14} and Et$_2$O-d_{10} at −78 °C for 1 h cleanly produced a dialkylated zirconocene derivative in >95% yield. The compound was stable for at least 1 h at −60 °C. Its ^{1}H and ^{13}C NMR spectra taken at −60 °C identified it as 3: ^{1}H NMR (Et$_2$O-d_{10}, *n*-hexane-d_{14}, toluene) δ 0.41 (d, J = 8 Hz, 2 H), 0.92 (d, J = 8 Hz, 6 H), 1.09 (s, 9 H), 6.31 (s, 10 H); ^{13}C NMR (Et$_2$O-d_{10}, Me$_4$Si) δ 28.68, 35.09, 36.35, 49.94, 78.79, 111.21. The signal for the methine proton was masked by other signals. Little or no isobutylene was seen at this point. Treating 3 with 1 equiv of PMe$_3$ at −78 °C and warming the mixture to −10 °C induced smooth transformation of 3 within 1 h into a new ZrCp$_2$ derivative identified as 4:[13] 92% yield; ^{1}H NMR (Et$_2$O-d_{10}, *n*-hexane-d_{14}, toluene) δ −0.02 (d, J = 8 Hz, 2 H), 1.03 (d, J = 6 Hz, 9 H), 1.50 (s, 6 H), 5.35 (s, 10 H); ^{13}C NMR (Et$_2$O-d_{10}, Me$_4$Si) δ 16.71 (d, J = 13 Hz), 32.48 (d, J = 13 Hz), 35.15 (d, J = 16 Hz), 36.79, 100.59. Little or no free isobutylene was present in the mixture. Formation of isobutane, however, was clearly detected by ^{1}H NMR (δ 0.90, d, J = 7 Hz, coinjection of an authentic sample) and ^{13}C NMR spectroscopy (δ 24.11 and 24.97). Warming the mixture containing 4 to 30 °C led, within 2 h, to the formation of the known PMe$_3$-stabilized dimer[14] of zirconocene in 85% yield with the concomitant release of free isobutylene (85%). In the presence of a 1-alkene, however, 1 and isobutylene were obtained in high yields. These results are in good agreement with Scheme II.[15] The corresponding reaction of *i*-Bu$_2$ZrCp$_2$ was much slower. For example, its reaction with 1-octene and PMe$_3$ to give 1c required 20 h at 25 °C, while the corresponding reaction of 3 was complete in 80–90 min even at 0 °C.

In summary, the present procedure provides, for the first time, a general and convenient method of directly converting monosubstituted alkenes and conjugated dienes into their Cp$_2$Zr complexes.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-8921899) for support of this research.

Supplementary Material Available: Spectroscopic and analytical data for 1a–d,f, 2a–d, *t*-BuHfCp$_2$Cl, *i*-BuHfCp$_2$Cl, *i*-Bu(*t*-Bu)HfCp$_2$, and Cp$_2$Hf(isobutylene)(PMe$_3$) (2 pages). Ordering information is given on any current masthead page.

---

[9] For alternative methods for the preparation of 1, see: (a) Alt, H. G.; Denner, C. E.; Thewalt, U.; Rausch, M. D. *J. Organomet. Chem.* **1988**, *356*, C85. (b) Takahashi, T.; Tamura, M.; Saburi, M.; Uchida, Y.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1989**, 852. (c) Takahashi, T.; Nitto, Y.; Seki, T.; Saburi, M.; Negishi, E. *Chem. Lett.* **1990**, 2259.

[10] For alternative methods for the preparation of 2, see: (a) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Kruger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344. (b) Yasuda, H.; Kajihara, Y.; Mashima, K.; Lee, K.; Nakamura, A. *Chem. Lett.* **1981**, 519. (c) Yasuda, H.; Kajihara, Y.; Mashima, K.; Nagasuna, K.; Lee, K.; Nakamura, A. *Organometallics* **1982**, *1*, 388.

[11] Direct treatment of Cp$_2$ZrCl$_2$ with 2 equiv of *t*-BuLi at −78 °C for 1 h followed by addition of 1-octene and PMe$_3$ led to a low yield of (1-octene)ZrCp$_2$(PMe$_3$). When the reaction of Cp$_2$ZrCl$_2$ with 2 equiv of *t*-BuLi was run at −60 °C for 1 h, the desired (1-octene)ZrCp$_2$(PMe$_3$) was obtained in 80% yield. This can substitute the two-step procedure.

[12] Satisfactory spectral data have been obtained for all isolated products. New compounds either have yielded correct elemental analytical data or have been converted to known compounds.

[13] During this project, we noticed a recent paper reporting an unsuccessful attempt at the preparation of isobutylene–ZrCp$_2$–PMe$_3$ along with a successful preparation of isobutylene–HfCp$_2$–PMe$_3$ (Buchwald, S. L.; Kreutzer, K. A.; Fisher, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 4600).

[14] Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Honold, B. *J. Organomet. Chem.* **1986**, *310*, 27.

[15] The corresponding reaction of Cp$_2$HfCl$_2$ with *t*-BuLi has displayed interesting and somewhat contrasting results. In a 1:1 ratio, the reaction predominantly (ca. 90%) produced *t*-BuHfCp$_2$Cl, which was thermally unstable but isolable and characterizable at ambient temperature.[13] When this compound was heated to 60 °C for 8 h, it was converted mostly (ca. 90%) to *i*-BuHfCp$_2$Cl. Its treatment with 1 equiv of *t*-BuLi led to the formation of a mixture that consisted of more than a few unidentified species in addition to the desired Cp$_2$Hf(Bu-*i*)(Bu-*t*). On the other hand, *t*-BuHfCp$_2$Cl obtained initially reacted with 1 equiv of *i*-BuLi to give a mixture of Cp$_2$Hf(Bu-*i*)(Bu-*t*) and Cp$_2$Hf(Bu-*i*)$_2$ in 45 and 35% yields, respectively. Its treatment with a 3-fold excess of PMe$_3$ at 50 °C gave isobutylene–HfCp$_2$–PMe$_3$.