A Transition-Metal−η^4-Diene Cation Can Undergo Nucleophilic Addition at the Internal Carbon

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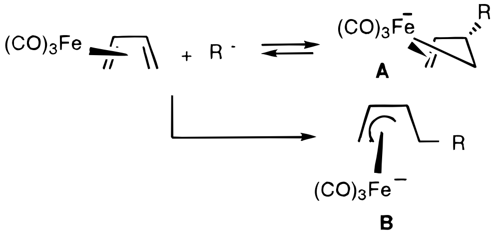
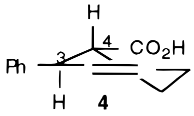
Summary: Treatment of $CpW(CO)_2(\eta^4$-cyclohexadiene)-BF_4 with RMgBr (R = methylvinyl, phenyl, naphthyl) in cold THF (−78 °C) afforded the $CpW(CO)_2[(1,2,4\text{-}\eta)$-1-CO-2-R-cyclohexene] complex as the major product; this result provides an example of a nucleophile attacking the internal carbon of a cationic η^4-diene fragment.

Scheme 1



Nucleophilic attack on a transition-metal η^4-diene complex is a well-studied organometallic reaction,[1,2] and nucleophilic regiochemistry occurs exclusively at the terminal carbon. The (η^4-diene)$Fe(CO)_3$[3−5] complex is the only exception reported in the literature. As shown in Scheme 1, addition of stabilized carbanions at the internal carbon of this iron complex is kinetically favorable and reversible;[3−5] the resulting (1,2,4-η)-σ,π-intermediate **A** can be trapped with electrophiles at −78 °C. Ultimately, species **A** underwent transformation to the more thermodynamically stable species **B** at elevated temperatures.[5] For transition-metal−η^4-diene cations, nucleophilic regiochemistry at the terminal carbon is shown to be both kinetically and thermodynamically favorable according to the Davies, Green, and Mingos rule.[6] There is no exception to this rule for metal−η^4-diene cations. In this communication, we report an atypical case of the Grignard reagent RMgBr effecting alkylation at the central carbon of $CpW(CO)_2$-(η^4-cyclohexadiene)$^+$ (**1**) in an irreversible process; the resulting $CpW(CO)_2[(1,2,4\text{-}\eta)$-1-CO-2-R-cyclohexene] can be isolated and fully characterized. Similar to the case for (η^4-diene)$Fe(CO)_3$,[5,6] the regioselectivity of this cation is temperature-dependent and will be described in detail.

The key compound $CpW(CO)_2(\eta^4$-cyclohexadiene)BF_4 (**1**(BF_4)) was easily prepared according to the published methods.[6−9] ^1H and ^{13}C NMR data for **1** clearly show that the cation is best represented by a typical η^4-diene structure rather than the σ,π-butene structure as known for (η^4-diene)$Fe(CO)_3$.[5,6] As shown in Scheme 2, the reaction of this cation **1** with MeMgBr (5.0 equiv) or PhMgBr (5.0 equiv) in THF at 0 °C (2 h), followed by quenching with H_2O, afforded the expected tungsten π-allyl compounds **2** and **3** in 72% and 58% yields, respectively. In the case of PhMgBr, we were aware that small amount of an organic acid **4** (4%) was also formed, indicating the possibility for regioselectivity at the central diene carbon. The trans configuration of **4** is indicated by the magnitude of the proton coupling constant J_{34} = 10.4 Hz, characteristic of the axial−axial proton coupling.



In an attempt to isolate the corresponding (1,2,4-η)-σ,π-intermediate **A**, we performed the reaction at − 78 °C (2 h), followed by quenching with water at −78 °C, resulting in a significant change of product distributions as shown in Scheme 2. The temperature influence is not significant for MeMgBr but is very pronounced for PhMgBr;[10] in the latter case the acyl σ,π−cyclohexene species **5** was obtained in 54% yield in addition to the π-allyl compound **3** (12%). NMR spectra of **3** and **5** were highly distinguishable. We have also performed the reaction under flowing CO, but the yield of **5** (58%) was not significantly increased. X-ray diffraction studies of **5** and its analogues **6**, **8**, and **9** (Scheme 2) are hampered by their poor fiberlike crystallinities. Assignment of the structure of **5** is made on the basis of NMR and mass spectral data and elemental analyses. ^1H and ^{13}C NMR signals of **5** were assigned on the basis of a sequential proton decoupling experiment as well as $^1H-^{13}C$ cor-

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[1] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry;* University Science Books: Mill Valley, CA, 1987; Chapter 7, p 420.

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[7] (a) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400. (b) Pearson, A. J.; Khan, M. N. I. *J. Am. Chem. Soc.* **1984**, *106*, 1872.

[8] Pearson, A. J.; Khan, M. N. I.; Clardy, J. C.; He, C.-H. *J. Am. Chem. Soc.* **1985**, *107*, 2748.

[9] Wang, S.-H.; Cheng, Y.-C.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1993**, *12*, 3282.

[10] Previously, Pearson et al. reported[8] that PhMgBr reacted with $CpMo(CO)_2(\eta^4$-cyclohexadiene)BF_4 in THF at 0 °C to yield a Mo−η^3-allyl compound in high yield; it is unclear whether reaction at −78 °C would yield (1,3,4-η)-σ,π-cyclohexenyl species.

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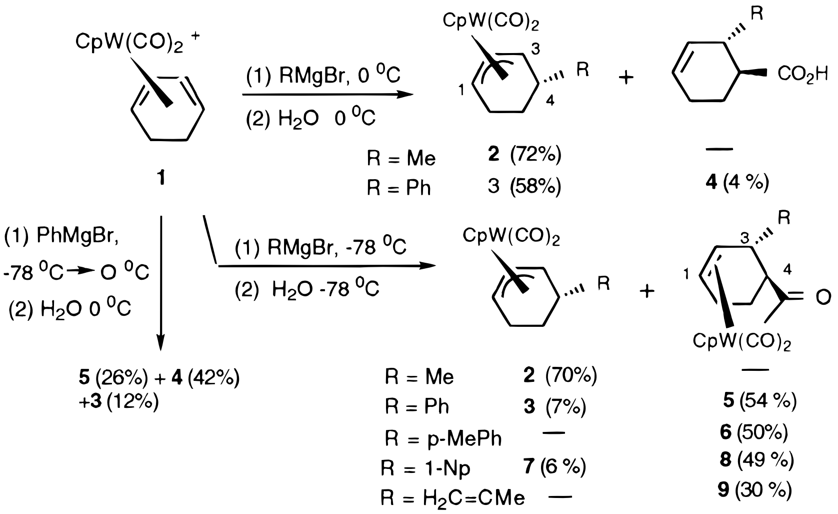
Scheme 2



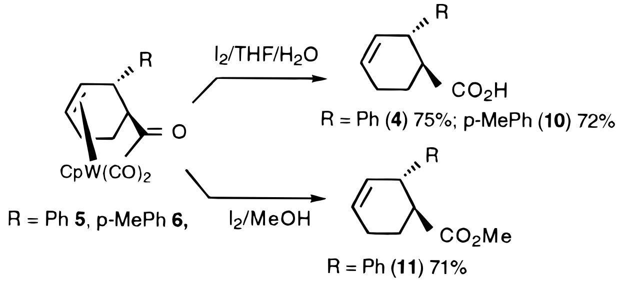
relation spectra. The two η^2-olefin protons have NMR signals at δ 4.78 and 4.45 ppm, and the corresponding carbons have signals at δ 77.8 and 60.4 ppm, respectively. The H^3 and H^4 protons resonate at δ 3.85 and 2.20 ppm, respectively. One of the C^6H_2 methylene protons has a large δ value (3.15 ppm), which may be due to deshielding of the cyclopentadienyl group. Diagnostic for the structure of **5** is the presence of an acyl group that is clearly indicated by the ^{13}C NMR signal at δ 273.4 ppm as well as an IR absorption band at 1620 cm^{-1}. The two remaining W−CO carbonyls have ^{13}C NMR signals at δ 224.5 and 218.4 ppm, respectively.

Scheme 2 also shows the products for several Grignard reagents; the reaction was performed at −78 °C, including the quenching with water, to achieve maximum yields of the desired (1,2,4-η)-σ,π-species such as **5**. Treatment of the cation **1** with p-MePhMgBr and 1-NapMgBr (Nap = naphthyl) at −78 °C also effected arylation at the central carbon, so that the (1,3,4-η)-σ,π-cyclohexene complexes **6** and **8** were obtained in 50% and 49% yields, respectively; the yields of π-allyl complexes **6** and **8** were low, i.e., 0% and 13%, respectively. (CH_2=CMe)MgBr is less effective for the central carbon alkylation; the desired (1,2,4-η)-σ,π-species **10** was obtained in 30% yield, and the unreacted η^4-diene was recovered in 35% yield. PhC≡CMgBr, $LiCMe_2CN$, $LiCH(CN)_2$, and 1,3-dithianyllithium were unreactive toward **1**, although these three lithium carbanions[3−5] are known to effect alkylation at the central carbon of (η^4-diene)$Fe(CO)_3$.

To examine whether the (1,2,4-η)-σ,π-species **5** is formed reversibly and whether the kinetics are favorable, the reaction of PhMgBr with **1** was performed in cold THF (−78 °C, 1 h), which was then warmed to 0 °C over a period of 8 h; finally the reaction was quenched with water at 0 °C, and the products shown in Scheme 2 indicated that the species **4** (42%) and **5** (26%) were formed predominantly. This information suggests that alkylation at the diene central carbon is an irreversibe process at −78 °C. This phemonenon is very distinct from the (η^4-diene)$Fe(CO)_3$ system.[3−5]

To show the synthetic applications, we performed the demetalation reactions on (1,2,4-η)-σ,π-species **5** and **6** to obtain difunctionalized cyclohexenes. As shown in Scheme 3 treatment of **5** and **6** with I_2 (1.0 equiv) in THF/H_2O (0 °C) afforded the acids **4** and **10** in 75% and 72% yields, respectively. The ester **12** can also be produced from I_2 oxidation of **5** in MeOH.

Scheme 3



In summary, we report here that a metal−diene cation such as **1** can be alkylated at the central carbon by PhMgBr at −78 °C;[10] the resulting $CpW(CO)_2$[(1,2,4-η)-1-CO-2-R-cyclohexene] complex can be isolated and fully characterized. It is unclear whether this reaction violates the Davies, Green, and Mingos rule.[11] This new system is complementary to (η^4-diene)$Fe(CO)_3$[3−5] because different types of nucleophiles are utilized here. We are now studying this reaction with changes of both tungsten−η^4-diene cations and Grignard reagents to rationalize the controlling factors of this atypical regiochemistry.

Acknowledgment. We gratefully acknowledge financial support from the National Science Council of the ROC for financial support of this work.

Supporting Information Available: Text giving spectral data for compounds **1**−**11** (7 pages). Ordering information is given on any current masthead page.

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(11) The mechanism for alkylation at internal carbons of **1** presumably follows the rule that PhMgBr preassociates with the tungsten−diene cation **1** before addition of the second PhMgBr. In the future, we will carry out a detailed kinetic study to elucidate the mechanism.