putational methods[26] which will be described in a full paper.

Examination of the ^{13}C NMR shieldings for **6** and **9** (Table I) reveals the customary trend[27] in which the nonterminal C_2 and C_4 positions carry the greatest positive charge. Accordingly, nucleophilic addition to these cationic complexes cannot operate under charge control since no correlation exists between π- or σ-electron density and regioselectivity.[28] Rather, nucleophilic capture gives indication of being controlled by frontier MO interactions which direct attack to a specific terminal carbon because of silicon's electronic contributions. This point will also be detailed in our full paper.[29]

Registry No. 4a, 63031-70-9; **4b**, 81064-06-4; **4c**, 81044-35-1; **4d**, 81044-36-2; **5a**, 81064-40-6; **5b** isomer 1, 81064-41-7; **5b** isomer 2, 81130-67-8; **5c**, 81064-42-8; **5d**, 81064-43-9; **6a**, 81064-26-8; **6b** isomer 1, 81064-37-1; **6b** isomer 2, 81132-00-5; **6c**, 81064-39-3; **6d**, 81064-35-9; **7**, 81044-37-3; **8**, 81064-33-7; **9**, 81064-31-5; **13a**, 81064-32-6; **13b**, 81095-47-8; **14a**, 81064-28-0; **15**, 81064-29-1; **16**, 81130-66-7.

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[26] Studies carried out in collaboration with R. Gleiter and M. C. Böhm (Universität Heidelberg).

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[29] The National Science Foundation has provided the financial support for this work for which we are grateful.

Spectroscopic Characterization of Electrophilic d^4 Methylene and Benzylidene Complexes of the Type $Cp(CO)_2(L)M{=}CHR^+$ ($L = PPh_3, PEt_3$; $M = Mo, W$; $R = H, Ph$). Experimental Determination of Barriers to Rotation about the Tungsten–Methylene Multiple Bond[1]

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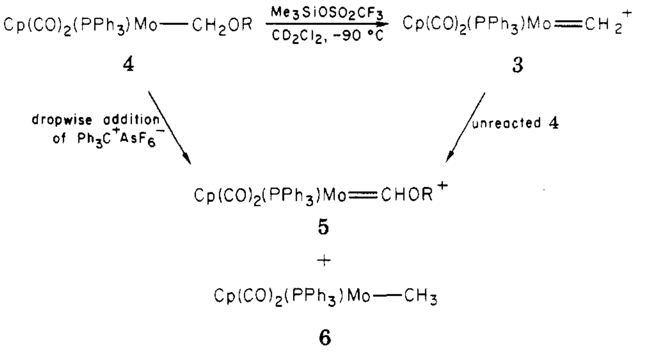
Summary: The first spectrally characterized examples of nonheteratom-stabilized carbene complexes of the type $Cp(CO)_2LM{=}CHR^+$ ($L = PPh_3, PEt_3$; $M = Mo, W$; $R = H, Ph$) are reported. The parent methylene complexes **2a** ($M = W$, $L = PPh_3$) and **2b** ($M = W$, $L = PEt_3$) and the benzylidene complex **2c** ($M = W$, $L = PPh_3$) are synthesized by hydride abstraction from the alkyl complexes $Cp(L)(CO)_2WCH_2R$ ($R = H, Ph$) using $Ph_3C^+AsF_6^-$.

The chemistry of d^6 electrophilic carbene complexes of the general type $CpL_1L_2M{=}CRR'$ is rapidly developing, and a variety of both heteroatom and nonheteroatom-stabilized species is now known. Several structures have been examined crystallographically,[2] while both structure and dynamics have been scrutinized spectroscopically and theoretically.[3-6] The more electrophilic species exhibit high reactivity toward nucleophilic reagents.[3c,4-8] In contrast, relatively few electrophilic carbene complexes in the parallel d^4 series with general structure $CpL_3M{=}CRR'$ have been studied. Isolable or spectroscopically characterized examples include only heteroatom-stabilized complexes: for example, $Cp(CO)_2(Ph_3M)M' = Cr(OR')$ ($M = Sn, Ge$; $M' = Mo, W$; $R = CH_3, C_6H_5$),[9] $Cp(CO)_2(PPh_3)Mo{=}C(CH_3)(OCH_3)^+$,[10] $Cp(CO)_2LMo{=}CFR^+$ ($L = CO, PPh_3$; $R = F, C_2F_5$),[11] $Cp(CO)_2(PPh_3)Mo{=}\overline{CCH_2CH_2CH_2O}^+$,[12] and $Cp(CO)_2\overline{W{=}C(NEt_2)CH(CH_3)}CO$.[13] No nonheteratom-stabilized species have been well characterized.[14]

Scheme I



We describe here the facile synthesis and spectral characterization of the d^4 cationic methylene complexes in the series $Cp(CO)_2LM{=}CH_2^+$ ($L = PEt_3, PPh_3$; $M = Mo, W$) and the benzylidene complex $Cp(CO)_2(PPh_3)$-

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[14] (a) The methylene species $Cp(CO)_3Mo{=}CH_2^+$ has been postulated as an intermediate in the acid-induced ionization of the α-ether $Cp(CO)_3Mo{-}CH_2OCH_3$ (Green, M. L. H.; Ishaq, M.; Whiteley, R. N. *J. Chem. Soc. A* **1967**, 1508. (b) Similarly, $Me_3SiOSO_2CF_3$ reacts with $Cp(CO)_3W{-}CH_2OCH_3$ at low temperatures to precipitate $Cp(CO)_3W{-}CH_2OSO_2CF_3$ which reacts with a variety of nucleophiles (X^-) to yield complexes of the type $Cp(CO)_3W{-}CH_2X$ (Beck, W. A.; Schloter, K.; Ernst, H. Ninth International Conference on Organometallic Chemistry, Sept 1979, Dijon, France; Abstract No. C53). No spectroscopic data related to these methylene complexes have been reported.

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Table I. ^1H NMR Data for $[Cp(CO)_2(L)M{=}CHR]^+$ Complexes in CD_2Cl_2 [a]

complex	*T*, °C	δ(Cp)	δ(H_a, H_b)
$[Cp(CO)_2(PPh_3)MoCH_2]^+OSO_2CF_3^-$ (3)	−90	5.84 (d, $J_{P\text{-}H}$ = 1.2 Hz)	H_a, H_b 15.4 (d, $J_{P\text{-}H}$ = 12.5 Hz)
$[Cp(CO)_2(PPh_3)WCH_2]^+AsF_6^-$ (2a)	−110	5.93 (d, $J_{P\text{-}H}$ ca. 1 Hz)	H_a 14.2 (br) H_b 16.0 (d, $J_{P\text{-}H}$ = 24 Hz)
	−50		H_a, H_b 15.1 (d, $J_{P\text{-}H}$ = 16.2 Hz)
$[Cp(CO)_2(PEt_3)WCH_2]^+AsF_6^-$ [b] (2b)	−110	6.04 (d, $J_{P\text{-}H}$ ca. 1 Hz)	H_a 13.9 (aparent t, *J* = ca. 7 Hz)[c] H_b 15.5 (dd, $J_{H\text{-}H}$ = 5 Hz, $J_{P\text{-}H}$ = 24 Hz)
	−40		H_a, H_b 14.8 (d, $J_{P\text{-}H}$ = 16.2 Hz)
$[Cp(CO)_2(PPh_3)WCHPh]^+AsF_6^-$ [d] (2c)	+20	5.97 (d, $J_{P\text{-}H}$ = 1.6 Hz)	H_a 14.1 (d, $J_{P\text{-}H}$ = 4.9 Hz)

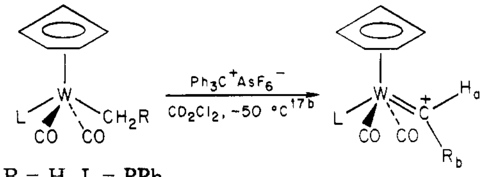
[a] NMR data for the carbene complexes were obtained at 250.13 MHz. Shifts are referenced to $CHDCl_2$ taken as δ 5.32. All aromatic resonances are observed in the δ 7–8 range and, with the exception of 5, are overlapped by Ph_3CH. [b] ^1H NMR (PEt_3) δ 1.8 (m, 6 H, PCH_2CH_3), 1.04 (m, 9 H, PCH_2CH_3). [c] The apparent triplet is a result of the near equivalence of $J_{P\text{-}H}$ and $J_{H\text{-}H}$. Because of viscosity broadening, only approximate values were obtainable. [d] ^{183}W satellites can be observed for H_a, $J_{W\text{-}H}$ = 6.9 Hz.

Table II. ^{13}C NMR of $[Cp(CO)_2(L)W{=}CHR]^+AsF_6^-$ Complexes in CD_2Cl_2 [a]

complex	δ(Cp)	δ(carbene)	δ(CO)
$[Cp(CO)_2(PPh_3)WCH_2]^+AsF_6^-$ (2a)	99.7 (s)	303.6 (br)	207.6 (d, $J_{P\text{-}C}$ = 21.5 Hz)
$[Cp(CO)_2(PEt_3)WCH_2]^+AsF_6^-$ [b] (2b)	98.5 (s)	296.8 (br)	206.4 (d, $J_{P\text{-}C}$ = 21.4 Hz)
$[Cp(CO)_2(PPh_3)WCHPh]^+AsF_6^-$ [c] (2c)	99.7 (d, $J_{C\text{-}H}$ = 183 Hz)	299.8 (br, d, $J_{C\text{-}H}$ = 138 Hz)	214.1 (d, $J_{P\text{-}C}$ = 16.8 Hz)

[a] Proton noise-decoupled spectra were obtained at 62.89 MHz. Shifts referenced to CD_2Cl_2 at 53.8 ppm. All aromatic resonances were observed in the δ 125–150 range and are overlapped by $Ph_3C\text{-}H$. [b] ^{13}C NMR (PEt_3): δ 19.4 (d, $J_{P\text{-}C}$ = 30.5 Hz, PCH_2CH_3), 8.1 (d, $J_{P\text{-}C}$ = 5.4 Hz, PCH_2CH_3). [c] Coupled spectrum obtained.

$W{=}CHPh^+$.[15] Treatment of the readily prepared tungsten alkyl complexes **1a–c**[16] with 1 equiv of trityl hexafluoroarsenate in methylene chloride at −50 °C leads to quantitative generation of the cationic alkylidene species **2a–c**.[17] The ^{13}C and ^1H NMR data for these complexes are summarized in Tables I and II. The characteristic low-field ^1H resonances for the hydrogen(s) attached directly to the carbene carbon, and ^{13}C resonances of the carbene carbon atom are clearly indicative of the carbene structure. These shift values compare closely with those for analogous electrophilic d^6 complexes.[3-4]



1a, R = H, L = PPh_3
b, R = H, L = PEt_3
c, R = C_6H_5, L = PPh_3

2a, R = H, L = PPh_3
b, R = H, L = PEt_3
c, R = C_6H_5, L = PPh_3

The molybdenum methylene complex, $Cp(CO)_2(PPh_3)Mo{=}CH_2^+$, **3**, is generated by the reaction of ether precursors $Cp(CO)_2(PPh_3)Mo{-}CH_2OR$, **4** (R = CH_3, CH_2Ph, $COC(CH_3)_3$,[14b,16b,18] with $(CH_3)_3SiOSO_2CF_3$ at −90 °C in CD_2Cl_2. Quantative generation of **3** is difficult and samples of **3** are normally contaminated with small amounts of the heteroatom carbene, **5**, and the methyl complex, **6**, due to hydride transfer from **4** to **3**[19] (see Scheme I). Indeed, when trityl hexafluoroarsenate is added dropwise to solutions of **4** in CD_2Cl_2 (−90 °C), no methylene complex can be detected. Instead complexes **5** and **6** are generated in equimolar amounts. A similar reaction has been observed between $Cp(NO)(PPh_3)Re{-}CH_2OCH_3$ and $Cp(NO)(PPh_3)Re{=}CH_2^+$.[4a]

Complex **3** decomposes rapidly above −70 °C by disproportionation to $Cp(CO)_2(PPh_3)Mo(C_2H_4)^+$ and $Cp(CO)_2(PPh_3)Mo^+$, the latter presumed to be stabilized by coordination to a solvent molecule or the triflate counterion.[20b] The same mode of decomposition is observed for the tungsten methylene complexes above −20 °C ($t_{1/2}$(−20 °C) ca. 2 h).[20] In contrast, the tungsten benzylidene complex **2c** is stable in CD_2Cl_2 solution at room temperature in a sealed tube for long periods of time. At 50 °C, decomposition occurs with $t_{1/2}$ ca. 15 h, but no decomposition products could be characterized. The benzylidene complex can be isolated as an air-stable green hexafluoroarsenate salt in nearly quantitative yield by precipitation from a CH_2Cl_2 solution with hexane at 0 °C.

The nonequivalence of the methylene hydrogens in the tungsten complexes **2a**,**b** confirms that the methylene

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(15) An X-ray crystallographic study of a neutral d^4 benzylidene complex $Cp_2W{=}CHPh$ has recently been reported (Caulton, K. G.; Marsella, J. A.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 5596.).

(16) (a) ^1H NMR ($CDCl_3$): $Cp(CO)_2(PPh_3)W{-}CH_3$, δ 0.50 (d, $J_{P\text{-}H}$ = 2.4 Hz, 3 H, CH_3), 4.79 (d, $J_{P\text{-}H}$ = 1.8 Hz, 5 H, Cp), 7–8 (m, 15 H, Ph); $Cp(CO)_2(PEt_3)W{-}CH_3$, δ 0.37 (d, $J_{P\text{-}H}$ = 2.6 Hz, 3 H, CH_3), 1.04 (m, 9 H, PCH_2CH_3), 1.8 (m, 6 H, PCH_2CH_3), 4.95 (d, $J_{P\text{-}H}$ = 1.5 Hz, 5 H, Cp); $Cp(CO)_2(PPh_3)W{-}CH_2Ph$, δ 3.06 (d, $J_{P\text{-}H}$ = 2.8 Hz, 2 H, CH_2Ph), 4.76 (d, $J_{P\text{-}H}$ = 1.8 Hz, 5 H, Cp), 7–8 (m, 20 H, Ph). (b) The Mo and W carbene precursors were determined to be the trans isomers by the observation of a single ^{13}C resonance in each case, indicating equivalence of the carbonyls. (c) **1a–c** were prepared by reaction of $Cp(CO)_2LW^-$ with methyl iodide or benzyl chloride.

(17) (a) Complex **2a** can also be generated by dropwise addition of $Ph_3C^+AsF_6^-$ in CD_2Cl_2 to the α-ether $Cp(CO)_2(PPh_3)W{-}CH_2OCH_2Ph$ in CD_2Cl_2 at −78 °C. (b) The generation of **2c** was carried out at 0 °C.

(18) ^1H NMR ($CDCl_3$): $Cp(CO)_2(PPh_3)Mo{-}CH_2OCH_3$, δ 3.37 (s, 3 H, CH_3), 4.75 (d, $J_{P\text{-}H}$ = 3.6 Hz, 2H, CH_2), 4.85 (d, $J_{P\text{-}H}$ = 1.6 Hz, 5 H, Cp), 7–8 (m, 15 H, Ph); $Cp(CO)_2(PPh_3)Mo{-}CH_2OCH_2Ph$, δ 4.54 (d, $J_{P\text{-}H}$ = 3.7 Hz, 2 H, W-CH_2), 4.83 (d, $J_{P\text{-}H}$ = 1.8 Hz, 5 H, Cp), 5.29 (s, 2 H, CH_2Ph), 7–8 (m, 20 H, Ph); $Cp(CO)_2(PPh_3)Mo{-}CH_2OCOC(CH_3)_3$, δ 1.21 (s, 9 H, t-Bu), 4.87 (d, $J_{P\text{-}H}$ = 1.8 Hz, 5 H, Cp), 5.55 (d, $J_{P\text{-}H}$ = 3.8 Hz, 2 H, CH_2), 7–8 (m, 15 H, Ph).

(19) ^1H NMR (CD_2Cl_2): $Cp(CO)_2(PPh_3)Mo{=}CH(OCH_3)^+OSO_2CF_3^-$, δ 4.58 (s, 3 H, OCH_3), 5.56 (d, $J_{P\text{-}H}$ = 1.2 Hz, 5 H, Cp), 7–8 (m, 15 H, Ph), 12.10 (s, 1 H, carbene proton); $Cp(CO)_2(PPh_3)Mo{-}CH_3$, δ 0.34 (d, $J_{P\text{-}H}$ = 3.2 Hz, 3 H, CH_3), 4.70 (d, $J_{P\text{-}H}$ = 1.6 Hz, 5 H, Cp), 7–8 (m, 15 H, Ph).

(20) (a) The identity of the ethylene complexes $Cp(CO)_2(PPh_3)Mo(C_2H_4)^+AsF_6^-$ and $Cp(CO)_2(PPh_3)W(C_2H_4)^+AsF_6^-$ was verified by independent synthesis from the reaction of $Cp(CO)_2(PPh_3)M{-}CH_2CH_3$ with $Ph_3C^+AsF_6^-$. ^1H NMR (CD_2Cl_2) $Cp(CO)_2(PPh_3)Mo(C_2H_4)^+AsF_6^-$, δ 3.53 (d, $J_{P\text{-}H}$ = 1.8 Hz, 4 H, C_2H_4), 5.28 (d, $J_{P\text{-}H}$ = 1.5 Hz, 5 H, Cp), 7–8 (m, 15 H, Ph); $Cp(CO)_2(PPh_3)W(C_2H_4)^+AsF_6^-$, δ 3.28 (d, $J_{P\text{-}H}$ = 2.4 Hz, 4 H, C_2H_4), 5.36 (d, $J_{P\text{-}H}$ = 2.0 Hz, 5 H, Cp), 7–8 (m, 15 H, Ph); $Cp(CO)_2(PEt_3)W(C_2H_4)^+AsF_6^-$, δ 1–2 (m, 15 H, PEt_3), 3.02 (d, $J_{P\text{-}H}$ = 2.8 Hz, 4 H, C_2H_4), 5.36 (d, $J_{P\text{-}H}$ = 1.2 Hz, 5H, Cp). (b) Upon decomposition of **2a** and **2b**, Cp signals at δ 5.79 (**2a**) and δ 5.86 (**2b**) appear simultaneously with the Cp signals for the ethylene complexes $Cp(CO)_2(PPh_3)W(C_2H_4)^+$ or $Cp(CO)_2(PEt_3)W(C_2H_4)^+$. Similarly, in the decomposition of $Cp(CO)_2(PPh_3)Mo{=}CH_2^+$ a Cp signal at δ 5.65 appears together with the Cp signal for the ethylene complex $Cp(CO)_2(PPh_3)Mo(C_2H_4)^+$. In analogy with Beck's observation of $Cp(CO)_3M^+$ (M = Mo, W) coordinated to either BF_4^-, PF_6^-, or CH_2Cl_2 (Beck, W. A.; Schloter, K. *Z. Naturforsch. B. Anorg. Chem. Org. Chem.* **1978**, *33B*, 1214), we assume these signals are due to solvent or counterion coordinated $Cp(CO)_2LM^+$.

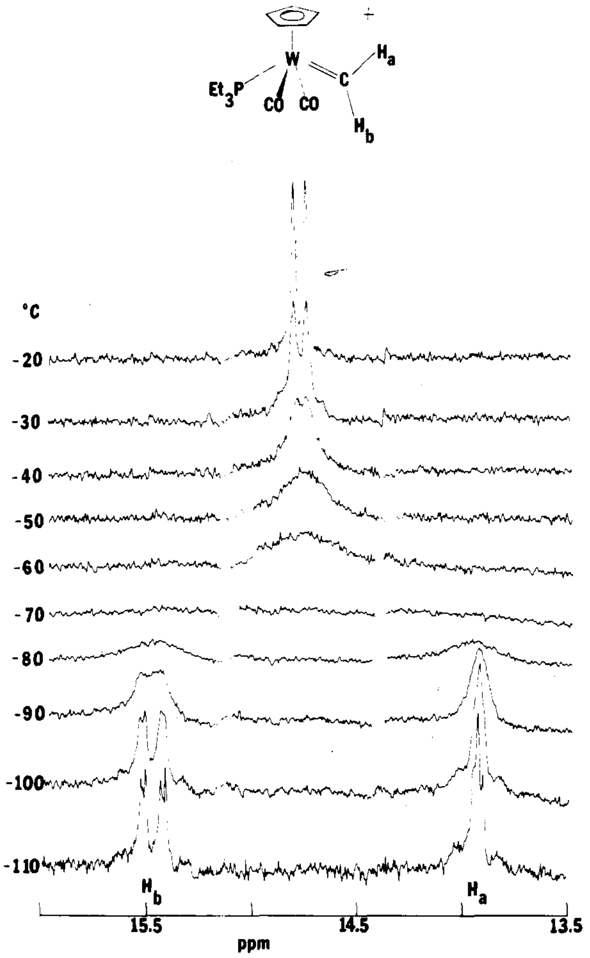

Figure 1. Variable-temperature 250-MHz ^1H NMR of $Cp(CO)_2(PEt_3)W{=}CH_2^+$ in CD_2Cl_2.

moiety adopts the "upright" conformation with the H_a–C–H_b plane aligned with the W–P bond. Using extended Hückel calculations for the similar system $Cp(CO)_2(PH_3)Mo{=}CH_2^+$, Hoffmann[21] has predicted such a ground-state conformation, with a calculated barrier to rotation around the Mo=C bond of 15 kcal/mol. The upright conformation is also that observed by X-ray crystallography for the structurally similar heteroatom carbenes, $Cp(CO)_2(Ph_3M)M'{=}CR(OR')$.[9] The assignment of H_a resonances to the synclinal hydrogen is based on the close comparison of the chemical shifts and ^{31}P–^1H coupling constants to those in the benzylidene complex **2c**. In **2c** the aryl ring is assumed to be in the sterically less crowded anticlinal position. Thus the benzylidene hydrogen occupies the synclinal position.

The ^1H NMR spectra of both tungsten methylene complexes **2a** and **2b** are temperature dependent and allow calculation of the barrier to rotation around the tungsten–carbon multiple bond (see Figure 1). As the temperature is raised above −110 °C, the two resonances for the nonequivalent methylene hydrogens begin to broaden. Coalescence for **2a** occurs at −85 °C (250 MHz) and for **2b** at −70 °C (250 MHz). Each spectrum sharpens to a doublet above −40 °C. Line-shape analysis yields free energies of activation, $\Delta G^{\ddagger}$, for bond rotation of 8.3 ± 0.1 kcal/mol for **2a** and 9.0 ± 0.1 kcal/mol for **2b**. The higher barrier for **2b** is consistent with the better donor properties of Et_3P relative to PPh_3.

For the molybdenum methylene complex, **3**, only a two-proton doublet (δ 15.4 (J_{P-H} = 12.5 Hz)) can be observed even at temperatures as low as −90 °C. The similarity of the chemical shift and J_{P-H} to those observed for the high-temperature averaged spectra of **2a** (δ 15.1 (J_{P-H} = 16.2Hz)) and **2b** (δ 14.8 J_{P-H} = 16.2Hz)) suggests that the molybdenum complex also adopts the upright conformation, but that the rotational barrier is quite low. With the use of the high-temperature approximation formula to obtain a minimum rate constant for the exchange, a conservative upper limit to the rotational barrier can be set at 6.7 kcal/mol.[22] The observed values of $\Delta G^{\ddagger}_{rot}$ for the Mo and W methylene complexes are somewhat lower than those of the $Cp(diphos)Fe{=}CH_2^+$ system ($\Delta G^{\ddagger}_{rot}$ = 10.4 kcal/mol)[3d] and considerably lower than the $Cp(NO)(PPh_3)Re{=}CH_2^+$ system whose nonequivalent methylene signals remain sharp to 10 °C ($\Delta G^{\ddagger}_{rot} \geq$ ca. 15 kcal/mol).[4a]

The high electrophilicity of these complexes is substantiated by their observed reactivity with olefins. Transfer of the methylene moiety of **2a**, **2b** and **3** to styrene in CH_2Cl_2 occurs within 10–15 min at −78 °C to produce phenylcyclopropane in > 50% yields. On the basis of these results, the readily generated and easily modified $Cp(CO)_2LM{=}CHR^+$ systems appear to have potential as carbene-transfer reagents. Synthetic modifications of these complexes as well as reactions with other nucleophilic and unsaturated organic substrates are currently under investigation.

Acknowledgment. We are grateful to the Army Research Office and the University of North Carolina for support of this research. We thank Dr. David L. Harris for help with NMR spectral analysis and Dr. Derrick Tabor for synthetic advice.

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[22] Line broadening of the methylene signal of **3** is ca. 8.8 Hz at half-height (ΔW) at −90 °C (broadening may be viscosity related). Assuming the chemical shift difference, $\nu_A - \nu_X$, in the static spectrum will be similar to that for the tungsten species **2a** (458 Hz) and applying the high-temperature approximation $k = (\nu_A - \nu_X)^2/2(\Delta W)$, we can estimate the minimum rate constant for exchange at −90 °C as 3.64×10^4 s^{-1} ($\Delta G_{rot} \leq 6.7$ kcal/mol).

Controlled Hydroboration of Alkenes by Lithium Borohydride Induced by the Reduction of Carboxylic Esters

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Summary: Alkenes, which are normally inert to lithium borohydride, are rapidly hydroborated in the presence of carboxylic esters in ether at 25 °C to dialkylborinates, valuable intermediates for various conversions. At the same time, catalytic amounts of alkenes markedly enhance the rate of reduction of esters of lithium borohydride.

Lithium borohydride is a valuable reagent for the selective reduction of carboxylic ester groups in the presence of many other reducible substituents.[1-3] In the course of

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