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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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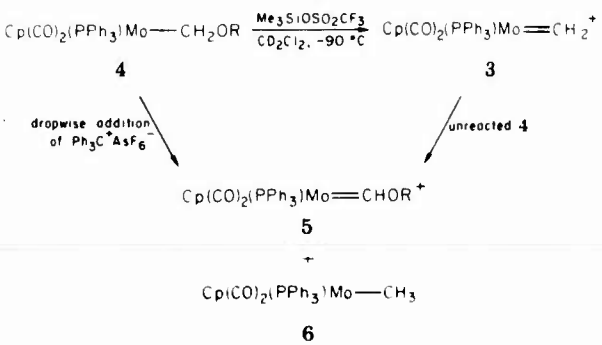
Summary: The first spectrally characterized examples of nonheteratom-stabilized carbene complexes of the type $Cp(CO)_2LM{=}CHR^+$ (L = PPh_3, PEt_3; M = Mo, W; R = H, Ph) are reported. The parent methylene complexes **2a** (M = W, L = PPh_3) and **2b** (M = W, L = PEt_3) and the benzylidene complex **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] $Cp(CO)_2(PPh_3)$-$Mo{=}CCH_2CH_2CH_2O^+$,[12] and $Cp(CO)_2W{=}C(NEt_2)CH(CH_3)CO$.[13] No nonheteratom-stabilized species have been well characterized.[14]

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 $Cp(CO)_2(PPh_3)$-

Scheme I



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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.

Table I. ^{1}H 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)
$[Cp(CO)_2(PPh_3)MoCH_3]^+OSO_2CF_3^-$ (3)	90	5.84 (d, J_{P-H} = 1.2 Hz)	H_a, H_b 15.4 (d, J_{P-H} = 12.5 Hz)
$[Cp(CO)_2(PPh_3)WCH_3]^+AsF_6^-$ (2a)	110	5.93 (d, J_{P-H} ca. 1 Hz)	H_a 14.2 (br)
			H_b 16.0 (d, J_{P-H} = 24 Hz)
	50		H_a, H_b 15.1 (d, J_{P-H} = 16.2 Hz)
$[Cp(CO)_2(PEt_3)WCH_3]^+AsF_6^-$ [b] (2b)	110	6.04 (d, J_{P-H} ca. 1 Hz)	H_a 13.9 (aparent t, J = ca. 7 Hz)[c]
			H_b 15.5 (dd, J_{H-H} = 5 Hz, J_{P-H} = 24 Hz)
	40		H_a, H_b 14.8 (d, J_{P-H} = 16.2 Hz)
$[Cp(CO)_2(PPh_3)WCHPh]^+AsF_6^-$ [d] (2c)	+20	5.97 (d, J_{P-H} = 1.6 Hz)	H_a 14.1 (d, J_{P-H} = 4.9 Hz)

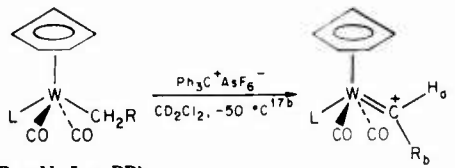
[a] NMR data for the carbene complexes were obtained at 250.13 MHz. Shifts are referenced to $CHDCl_2$ taken as δ 5.32. All aromatic resonances are observed in the δ 7-8 range and, with the exception of **5**, are overlapped by Ph_3CH. [b] ^{1}H NMR (PEt_3) δ 1.8 (m, 6 H, PCH_2CH_3), 1.04 (m, 9 H, PCH_2CH_3). [c] The apparent triplet is a result of th near equivalence of J_{P-H} and J_{H-H}. Because of viscosity broadening, only approximate values were obtainable. [d] ^{183}W satellites can be observed for H_a, J_{W-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)
$[Cp(CO)_2(PPh_3)WCH_3]^+AsF_6^-$ (2a)	99.7 (s)	303.6 (br)	207.6 (d, J_{P-C} = 21.5 Hz)
$[Cp(CO)_2(PEt_3)WCH_3]^+AsF_6^-$ [b] (2b)	98.5 (s)	296.8 (br)	206.4 (d, J_{P-C} = 21.4 Hz)
$[Cp(CO)_2(PPh_3)WCHPh]^+AsF_6^-$ [c] (2c)	99.7 (d, J_{C-H} = 183 Hz)	299.8 (br, d, J_{C-H} = 138 Hz)	214.1 (d, J_{P-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-H. [b] ^{13}C NMR (PEt_3): δ 19.4 (d, J_{P-C} = 30.5 Hz, PCH_2CH_3), 8.1 (d, J_{P-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 hexa-



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

fluoroarsenate in methylene chloride at −50 °C leads to quantitative generation of the cationic alkylidene species **2a–c**.[17] The ^{13}C and ^{1}H NMR data for these complexes are summarized in Tables I and II. The characteristic low-field ^{1}H 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]

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

(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) ^{1}H NMR ($CDCl_3$): $Cp(CO)_2(PPh_3)W{-}CH_3$, δ 0.50 (d, J_{P-H} = 2.4 Hz, 3 H, CH_3), 4.79 (d, J_{P-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-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-H} = 1.5 Hz, 5 H, Cp); $Cp(CO)_2(PPh_3)W{-}CH_2Ph$, δ 3.06 (d, J_{P-H} = 2.8 Hz, 2 H, CH_2Ph), 4.76 (d, J_{P-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) ^{1}H 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-H} = 3.6 Hz, 2H, CH_2), 4.85 (d, J_{P-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-H} = 3.7 Hz, 2 H, W-CH_2), 4.83 (d, J_{P-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-H} = 1.8 Hz, 5 H, Cp), 5.55 (d, J_{P-H} = 3.8 Hz, 2 H, CH_2), 7-8 (m, 15 H, Ph).

(19) ^{1}H 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-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-H} = 3.2 Hz, 3 H, CH_3), 4.70 (d, J_{P-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 $Ph_3C^+AsF_6^-$. ^{1}H NMR (CD_2Cl_2) $Cp(CO)_2(PPh_3)Mo(C_2H_4)^+AsF_6^-$, δ 3.53 (d, J_{P-H} = 1.8 Hz, 4 H, C_2H_4), 5.28 (d, J_{P-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-H} = 2.4 Hz, 4 H, C_2H_4), 5.36 (d, J_{P-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-H} = 2.8 Hz, 4 H, C_2H_4), 5.36 (d, J_{P-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 $Cp(CO)_2LM^+$.

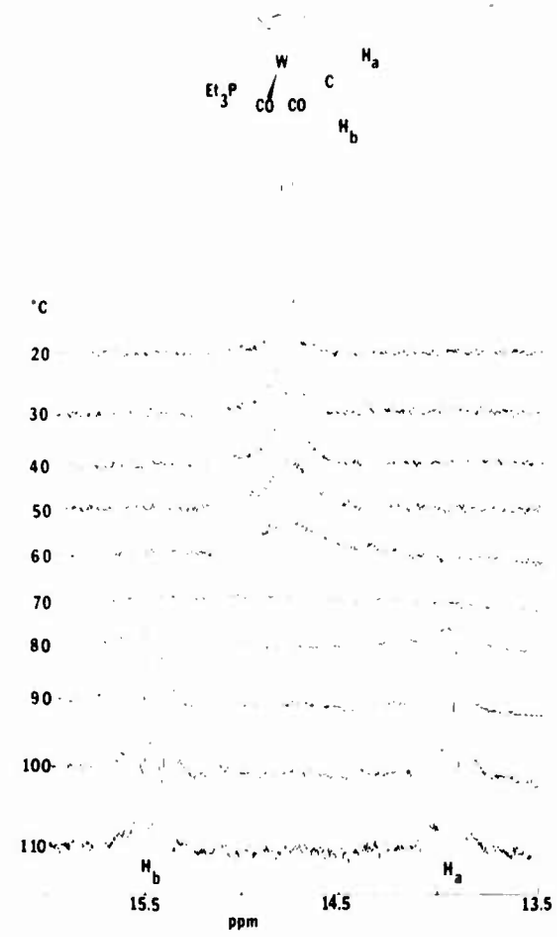


Figure 1. Variable-temperature 250-MHz ^1H NMR of $Cp(CO)_2(PEt_3)W{=}CH_2^+$ in CD_2Cl_2.

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 ($J_{P\text{-}H}$ = 12.5 Hz)) can be observed even at temperatures as low as −90 °C. The similarity of the chemical shift and $J_{P\text{-}H}$ to those observed for the high-temperature averaged spectra of **2a** (δ 15.1 ($J_{P\text{-}H}$ = 16.2Hz)) and **2b** (δ 14.8 $J_{P\text{-}H}$ = 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.

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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).