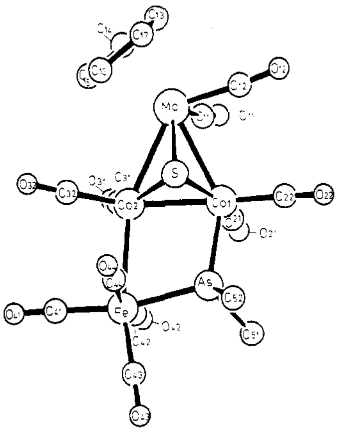

Figure 2. Molecular structure of $FeCo_2MoSAsMe_2Cp(CO)_{10}$ (**6a**).

metal–metal bonds and their additional stabilization by the ligand bridges. One of the simplest such reactions, that with CO, is also depicted in Scheme II. In benzene solution at room temperature under 1 atm of CO, **5a** and **5b** add 2 mol of CO within 1 h. The unfolded clusters **6a**[10] (78%) and **6b**[11] (82%) are obtained as black crystals by recrystallization from hexane. The reconversion of **6a** and **6b** to **5a** and **5b** is equally simple: in benzene solution, in an evacuated flask, after 15 h at 80 °C a small amount ($\sim$ 10%) of a precipitate is formed, and from the solution the closed clusters **5** are crystallized in about 70% yield. The ease of these interconversions contrasts sharply with the major changes in the metal and the ligand atom arrangements in the two types of clusters. The reversible opening and closing of the metal tetrahedra model basic steps of substrate activation by cluster catalysts.

The identities of the molybdenum-containing clusters **5a** and **6a** were established by crystal structure analyses[12] Figures 1 and 2 and Table I show the molecular geometries and some bond lengths and angles. Cluster **5a** contains a distorted tetrahedral $FeCo_2Mo$ core with internal angles between 54 and 67°, and the metal framework of **6a** is a $MoCo_2$ triangle with an external iron atom. In both clusters, especially **5a**, ligand bridging is extensive. The metal–metal bond lengths span a considerable range but are within the limits of their variability.[13] The assignment of the iron and cobalt atoms in both structures is somewhat ambiguous because they could not be distinguished crystallographically. But in both cases the positions chosen for iron are plausible: in the ruthenium analogue[14] of **5a** the Ru atom is in the place assigned to the Fe atom here; an external Co–As unit in **6a** is unlikely due to the extreme instability of the known organometallic Lewis base $(CO)_4Co–AsMe_2$ in the free state.[15,16]

By prolonged warming to 50 °C under 1 atm of CO or under 10 atm of CO at room temperature, in benzene solution, the clusters **6** are fragmented to the known FeCoMo and FeCoW clusters **4**,[5] respectively, in 80–90% yield. Thus a full sequence of cluster transformations **1** → **3** → **5** → **6** → **4** is established, which strongly indicates that the originally reported direct conversion of **3** to **4** also proceeds in this way. Whereas the **3** → **4** conversion involves no net change in CO content, the removal of CO on going from **3** to **5** and the addition of CO on going from **5** to **6** to **4** allow us to understand the reaction conditions necessary for these transformations.

The reversible interconversions between **5** and **6**, although being of simple stoichiometry and high yield, must be mechanistically complex. In each of these clusters the sulfur atom bridges a different metal triangle.[17] Thus more than two bonds have to be broken before 2 mol of CO are added to **5** or removed from **6**. This raises the possibility of further intermediates in the cluster reorganization processes which we are currently trying to find.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and by the Rechenzentrum der Universität Freiburg.

Registry No. 1, 22364-22-3; **2a**, 52456-34-5; **2b**, 52456-36-7; **3a**, 68185-54-6; **3b**, 68212-39-5; **4a**, 68185-55-7; **4b**, 68185-56-8; **5a**, 80926-04-1; **5b**, 80939-28-2; **6a**, 70576-10-2; **6b**, 80939-29-3.

Supplementary Material Available: Listings of the complete crystallographic details, all positional and anisotropic thermal parameters, all bond lengths and angles, and observed and calculated structure factors for both structures (51 pages). Ordering information is given on any current masthead page.

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(10) $FeCo_2MoSAsMe_2Cp(CO)_{10}$ (**6a**): mp 106 °C; IR (cyclohexane) 2068 (m), 2031 (vs), 2008 (s), 2000 (m), 1984 (w), 1970 (w) cm^{-1}; ^1H NMR (benzene) 1.40 (3 H), 1.56 (3 H), 4.53 (5 H) ppm. Anal. Calcd for $[C_{17}H_{11}AsCo_2FeMoO_{10}S]$: C, 27.16; H, 1.47; S, 4.26. Found: C, 27.35; H, 1.47; S, 4.56.

(11) $FeCo_2WSAsMe_2Cp(CO)_{10}$ (**6b**): mp 120 °C; IR (cyclohexane) 2065 (m), 2035 (vs), 2008 (s), 1997 (m), 1983 (w), 1967 (w); ^1H NMR (benzene) 1.47 (3 H), 1.63 (3 H), 4.50 (5 H) ppm. Anal. Calcd for $[C_{17}H_{11}AsCo_2FeO_{10}SW]$: C, 24.31; H, 1.32; S. 3.82. Found: C, 24.31; H, 1.14; S, 3.46.

(12) Crystals of **5a** and **6a** were obtained from hexane. The crystal quality was checked by Weissenberg photographs, all other measurements were done on a Nonius CAD4 diffractometer. **5a**: triclinic, space group $P\bar{1}$, $Z = 2$, $a = 908.5$ (3) pm, $b = 1464.2$ (5) pm, $c = 862.0$ (4) pm, $\alpha = 90.47$ (3)°, $\beta = 101.45$ (3)°, $\gamma = 72.70$ (3)°. **6a**: monoclinic, space group $P2_1/c$, $Z = 4$, $a = 1576.1$ (7) pm, $b = 1136.9$ (2) pm, $c = 1346.0$ (4) pm, $\beta = 93.91$ (3)°. The structures were solved by Patterson and Fourier methods. Anisotropic full matrix refinement for all nonhydrogen atoms using unit weights resulted in R values of 0.069 for **5a** and 0.041 for **6a**. All details of the crystallographic work are documented in the supplementary material: Table A contains all crystallographic data; Tables B and C list all atomic parameters for **5a** and **6a**; Tables D and E list all bond lengths and angles for **5a** and **6a**; Tables F and G give the F_o/F_c listings.

(13) Bruce, M. I. *J. Organomet. Chem.* **1980**, *196*, 295 and previous papers in that series.

(14) Richter, F.; Roland, E.; Beurich, H.; Müller, M.; Vahrenkamp, H., unpublished results.

(15) Müller, R.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 3517.

(16) A structure determination of the ruthenium analogue of **6a** could provide support for the given assignment. This compound, however, could not be obtained as yet.[14]

(17) After each step in the **3** → **5** → **6** → **4** sequence the three metal atoms bridged by the sulfur atom have changed.

Silanes in Organic Synthesis. 15. Silicon-Directed Hydride Abstraction from (2-(Trimethylsilyl)-1,3-cyclohexadiene)iron Tricarbonyl Complexes and Nucleophilic Addition to the Derived Cations[1]

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Evans Chemical Laboratories, The Ohio State University
Columbus, Ohio 43210

Received December 22, 1981

Summary: Several (2-(trimethylsilyl)-1,3-cyclohexadiene)iron tricarbonyl complexes were prepared and treated with triphenylcarbenium cation. In all cases, hydride abstraction proved to be completely regiospecific to

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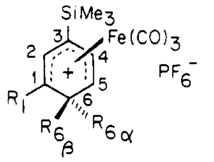
(1) For part 14, see: Paquette, L. A.; Wells, G. J.; Horn, K. A.; Yan, T.-H. *Tetrahedron Lett.* **1982**, 263.

(2) Presidential Fellow, 1981.

Table I. ^{13}C NMR Chemical Shifts for 6 and 9 (ppm, CD_2CN)

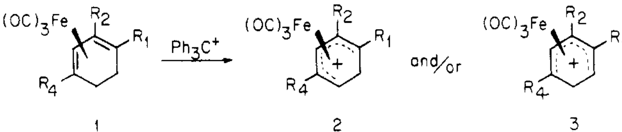


complex	R_1	$R_{6\alpha}$	$R_{6\beta}$	C_1	C_2	C_3	C_4	C_5	C_6
6a	H	H	H	68.4	104.7	99.9	104.7	68.4	23.9
6b	H	CH_3	H	75.3	102.4	99.1	102.4	75.3	27.8
	H	H	CH_3	71.8	103.3	99.1	103.3	71.8	27.8
6c	CH_3	H	H	95.4	102.6	*a*	100.5	65.1	23.9
6d	H	CH_3	CH_3	79.5	101.7	99.5	101.7	79.5	*a*
9	CH_2		H	102.8	109.6	*a*	96.0	78.1	*a*

[a] Inadequate number of scans recorded to obtain shift of quaternary centers.

deliver only silyl-symmetric η^5 cations irrespective of the position and level of additional alkyl substitution. The directive properties of the silicon atom also carry over to nucleophilic additions to these cationic complexes. Isomerically pure products are obtained, bonding occurring at the original site of hydride extraction.

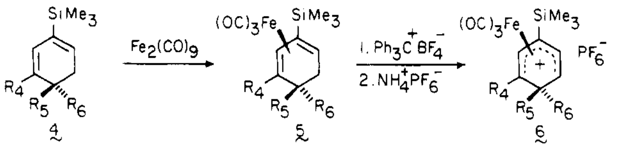
As a direct consequence of pioneering work by Birch[3] and more recently by Pearson,[4] substituted tricarbonylcyclohexa-1,3-dienylium cations (e.g., **2** and **3**)[5] have been developed into reagents holding exceptional promise for organic synthesis. However, the tactical role these substances might play would be heightened if problems associated with the regiochemistry of hydride abstraction from precursors 1 and subsequent nucleophilic capture were better understood. Both processes are recognized to be governed by the nature of the pendant R group as exemplified by the representative data cited below the formulas. However, a detailed understanding of these effects is still lacking, chiefly (in our view) because there has been minimal variation in the types of substituents examined. In an effort to probe these electronic influences to an added extent, we have scrutinized the directive role of the trimethylsilyl group in these reactions and are pleased to describe herein the unparalleled regiospecificity exerted by silicon on the two title reactions.



	2	3
$R_1 = R_4 = H$, $R_2 = CH_3$	60	40 [5a]
$R_1 = H$, $R_2 = R_4 = CH_3$	0	100 [5a]
R_1, $R_2 = (CH_2)_4$, $R_4 = H$	100	0 [6]
$R_1 = R_4 = H$, $R_2 = OCH_3$	94	6 [4b]
$R_1 = H$, $R_2 = OCH_3$, $R_4 = CH_3$	0	100 [5a]
$R_1 = R_4 = H$, $R_2 = COOCH_3$	20	80 [5c]

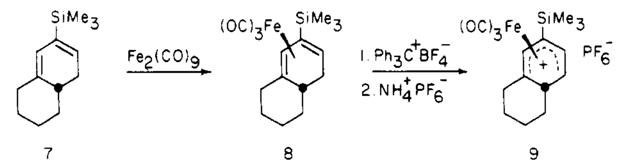
1

The 2-(trimethylsilyl)-1,3-cyclohexadienes 4 and 7 were prepared from 2-cycloalkenone benzenesulfonylhydrazones via the modified Shapiro procedure previously introduced.[7] In those cases where direct synthesis of the arenesulfonylhydrazone was frustrated because of concomitant 1,4 addition (e.g., **4a** and **4b**), recourse was made to the protocol of Dondoni[8] as modified by Lightner[9] which begins with the 2-bromo ketone. 4- and 5-alkyl, as well as 4,5- and 5,5-dialkyl, derivatives were thereby made available[10] and converted to their tricarbonyliron complexes in 54–87% yield by heating with diiron enneacarbonyl in light petroleum ether. As concerns **4d**, geminal dimethyl substitution at C_5 blocks potential isomerization of the 2-trimethylsilyl group to the 1-position during the complexation process. With **4a–c**, such isomerizations are possible but do not occur.[11] Monomethyl derivative **4b**



4 5 6

a, $R_4 = R_5 = R_6 = H$
b, $R_4 = R_5 = H$, $R_6 = CH_3$
c, $R_4 = CH_3$, $R_5 = R_6 = H$
d, $R_4 = H$, $R_5 = R_6 = CH_3$



7 8 9

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(3) Birch, A. J.; Ratnayake Bandara, B. M.; Chamberlin, K.; Chauncy, B.; Dahler, P.; Day, A. I.; Jenkins, I. D.; Kelly, L. F.; Khor, T.-C.; Kretschmer, G.; Liepa, A. J.; Narula, A. S.; Ravety, W. D.; Rizzardo, E.; Sell, C.; Stephenson, G. R.; Thompson, D. J.; Williamson, D. H. *Tetrahedron, Suppl.* **1981**, *No. 9*, 289 and references contained therein.

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(5) Only data for 2-substituted derivatives are considered here. Comparable information concerning isomeric 1-substituted complexes may be found in the following references: (a) Birch, A. J.; Chamberlin, K. B.; Haas, M. A.; Thompson, D. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1882. (b) Pearson, A. J. *Ibid.* **1977**, 2069. (c) Birch, A. J.; Williamson, D. H. *Ibid.* **1973**, 1892.

(6) Birch, A. J.; Cross, P. E.; Lewis, J.; White, D. A.; Wild, S. B. *J. Chem. Soc. A* **1968**, 332.

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(8) Dondoni, A.; Rossini, G.; Mossa, G.; Caglioti, L. *J. Chem. Soc. B* **1968**, 1404.

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(10) Satisfactory elemental and/or accurate mass spectral analyses were obtained on all new compounds described herein.

(11) The ^1H NMR spectra data (δ, $CDCl_3$) for these complexes are as follows. **5a**: 4.89 (d, J = 7.5 Hz, 1 H), 3.31–3.11 (m, 1 H), 3.04 (br s, 1 H), 1.83–1.18 (m, 4 H), 0.06 (s, 9 H). **5b** (exo/endo mixture): 4.90 (t, J = 6 Hz, 1 H), 3.23–2.80 (m, 2 H), 2.20–1.15 (m, 3 H), 0.78 (t, J = 6 Hz, 3 H), 0.07 (s, 9 H). **5c**: 4.78 (s, 1 H), 3.01–2.88 (m, 1 H), 1.99–1.77 (m, 1 H), 1.72–1.58 (m, 1 H), 1.43 (s, 3 H), 1.27–1.22 (m, 2 H), 0.06 (s, 9 H). **5d**: 4.90 (d, J = 7 Hz, 1 H) 2.94 (overlapping m and d, J = 7 Hz, 2 H), 1.51 (dd, J = 8 and 4.5 Hz, 2 H), 1.91 (s, 3 H), 1.75 (s, 3 H), 0.08 (s, 9 H). **8**: 4.77 (br s, 1 H), 2.92–2.72 (m, 1 H), 2.30–0.60 (series of m, 11 H), 0.11 (s, 9 H).

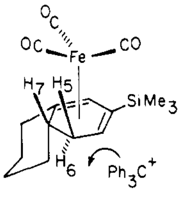
Table II. Compilation of Substituent Constants[24,25]

substituent	σ_m	σ_p	σ_p^+	σ_R^0	σ_R^+	σ_R^-
OMe	−0.12	−0.27	−0.78	−0.45	−1.02	−0.45
Me	−0.07	−0.17	−0.31	−0.11	−0.25	−0.11
$SiMe_3$	−0.04	−0.07	0.02	0.06	0.06	0.14

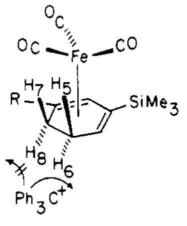
gave a 2:8 mixture of endo/exo complexes, bonding to $Fe(CO)_3$ occurring preferentially from the less hindered face as anticipated. With dienylsilane **7**, greater stereoselectivity was encountered and the single product **8** was obtained.

Treatment of the five complexes with 1.2 equiv of triphenylcarbenium tetrafluoroborate (refluxing CH_2Cl_2, 18–24 h), followed by treatment of the unpurified tetrafluoroborate salts with aqueous ammonium hexafluorophosphate,[5b] afforded the tricarbonyl (1–5-η-3-(trimethylsilyl)-2,4-cyclohexadienylium)iron hexafluorophosphates **6** and **9**. Hydride abstraction proved invariably to be completely regiospecific (^1H NMR analysis), with attack at C_6 occurring to deliver only silyl-symmetric η^5 cations in 45–80% isolated yield, irrespective of the position and level of additional alkyl substitution. This behavior contrasts with the moderate regioselectivity frequently exhibited by alkyl, methoxy, and carbomethoxy analogues.[3,4] The structural assignments to **6** and **9** were easily deduced from ^1H and ^{13}C NMR data (Table I).[13]

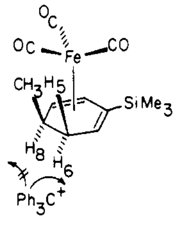
On the basis of stereodrawing **10**, it can be seen that H_5 and H_7 in complex **8** are sterically inaccessible to the bulky triphenylcarbenium cation, thus mandating kinetically controlled H_6 abstraction. However, two avenues of Ph_3C^+ attack are possible from the anti surface in **5a** and **5c** (see **11**, R = H or CH_3), and molecular models suggest that no steric or stereoelectronic barriers exist at either site, especially when R = H. Nonetheless, only the bond to H_6 is cleaved (compare the behavior of **1**). In **12**, a presumably more stable cation would result if H_8 were abstracted, but it is not. Clearly, the Me_3Si substituent exerts a major degree of regioelectronic control in these processes.



10

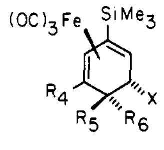


11



12

The directive properties of the silicon atom also carry over to the nucleophilic addition reactions of these cationic complexes. Thus, exposure to tetrahydrofuran solutions of diethyl sodiomalonate leads in excellent yield to isomerically pure products (**13a** and **14a**) which can be degraded to the corresponding 1,3-cyclohexadienes by reaction with trimethylamine *N*-oxide dihydrate in refluxing benzene.[14] With **6d** and ethyl (phenylsulfonyl)sodioacetate,[15] an inseparable mixture of diastereomers **13b** (R_1 = R_2 = CH_3) was formed (70% yield). Comparable regiospecificity was observed with trimethyl[(4,5-dihydro-2-furanyl)oxy]silane[16] in acetonitrile solution at room temperature. In the specific case of **6d**, it proved possible to separate diastereomers **15** and **16** by column chromatography and to subject them independently to decomplexation.



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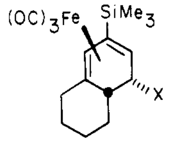
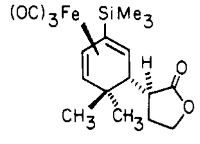


14

a, X = CH(COOC$_2$H$_5$)$_2$; b, X = CH(COOC$_2$H$_5$)(SO$_2$Ph)



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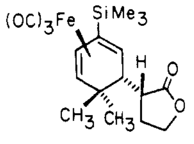

16

Bonding within **5** and **8** is best represented by assigning pseudooctahedral symmetry to the d^8 C_{3v} tricarbonyliron fragment[17] with overlap involving electron donation from the diene HOMO and synergistic back donation from a filled metal orbital combination.[18] The ability of silicon to interact via its vacant 3d orbitals with neighboring π (e.g., vinylsilanes and silylarenes) and pseudo π systems (e.g., silylcyclopropanes) has been demonstrated through physical and chemical means.[19] Chemical studies[20] and ab initio SCF molecular orbital calculations[21] have shown that silicon stabilizes β carbocations and destabilizes α carbocations relative to carbon analogues. This effect has been attributed to both neighboring group participation (the β effect)[20] and σ–π conjugation (hyperconjugation),[22] while the ability of silicon to stabilize α-carbanions has been attributed to (p–d)π back-bonding between silicon and carbon.[23] A more quantitative grasp of the ability of silicon to interact with π systems may be obtained from a selection of substituent constants (Table II).[24,25] The manner and degree to which these properties of silicon affect irreversible, kinetically controlled hydride abstraction in **5** and **8** have been extensively analyzed by com-

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(12) The decomposition points and ^1H NMR data (δ, CD_3CN) for these cationic complexes follow. **6a**: mp 194–195 °C; 5.45 (d, J = 7 Hz, 2 H), 4.17 (t, J = 7 Hz, 2 H), 2.84 (t, J = 7 Hz, 1 H), 2.67 (t, J = 7 Hz, 1 H), 0.37 (s, 9 H). **6b** (19:81 isomer mixture): mp 190–191 °C; 5.39 (d, J = 7.5 Hz, 3 H), 1.78 (overlapping q, J = 7 Hz, 1 H), 1.33 and 0.44 (d, J = 7 Hz and d, J = 7 Hz, 3 H), 0.33 (s, 9 H). **6c**: mp 185–187 °C; 5.48 (d, J = 7 Hz, 1 H), 5.18 (s, 1 H), 4.15 (t, J = 7 Hz, 1 H), 2.95 (br d, J = 7 Hz, 1 H), 2.68 (br d, J = 7 Hz, 1 H), 1.61 (s, 3 H), 0.34 (s, 9 H). **6d**: mp 208–210 °C; 5.32 (d, J = 7 Hz, 2 H), 4.15 (d, J = 7 Hz, 2 H), 1.32 (s, 3 H), 0.52 (s, 3 H), 0.35 (s, 9 H). **9**: mp 174–176 °C; 5.47 (d, J = 8 Hz, 1 H), 5.12 (s, 1 H), 4.55 (d, J = 7 Hz, 1 H), 2.19–1.87 (m, 3 H), 1.67–1.38 (m, 6 H), 0.38 (s, 9 H).

(13) Complex **6d** has been earlier prepared by M. Lotze, Diplom-Arbeit, Marburg (Lahn), West Germany. We are grateful to Professor R. W. Hoffmann for apprising us of this work.

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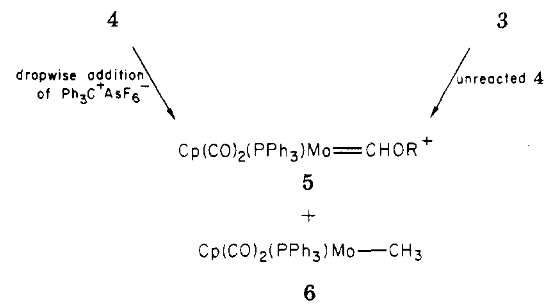
Summary: The first spectrally characterized examples of nonheteratom-stabilized carbene complexes of the type $Cp(CO)_2LM{=}CHR^+$ ($L = PPh_3, PEt_3$; M = Mo, W; R = H, Ph) are reported. The parent methylene complexes **2a** (M = W, $L = PPh_3$) and **2b** (M = W, $L = PEt_3$) and the benzylidene complex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

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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[1] This work was presented in part at the 181st National Meeting of the American Chemical Society, Atlanta, GA, April 1981, "Abstracts of Papers", American Chemical Society: Washington, DC, 1981; INORG 170.

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