seven-coordinate metallocycle so that $W(CO)_5$ may be eliminated rather than the much less stable $W(CO)_4$ fragment. The direct reaction of alkenes with **3** is much faster than the direct reaction with **1** owing to the greater electrophilicity of the phenylcarbene complex and to its lesser steric hindrance.[18]

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(15) In contrast, nucleophilic tantalum–carbene complexes react with alkenes to give products derived from initial bonding of the carbene to the least substituted carbon of the alkene.[16] Gassman has explained the reactions of ethylcyclopropane with terminal alkenes in the presence of a metathesis catalyst in terms of a nucleophilic carbene complex.[17]
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(19) M. Brookhart and G. O. Nelson, *J. Am. Chem. Soc.*, following paper in this issue.

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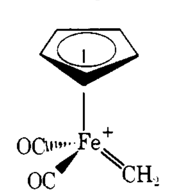
Isolation of Stable Secondary Cationic Iron Carbene Complexes η^5-$C_5H_5(CO)_2FeCHC_6H_5PF_6$ and η^5-$C_5H_5(CO)[P(C_6H_5)_3]FeCHC_6H_5PF_6$

Sir:

The majority of transition metal-carbene complexes prepared to date have contained at least one heteroatom directly bound to the carbene carbon atom.[1] Such groups serve as electron-donating substituents to the electrophilic carbene carbon atom and provide substantial stabilization to these types of complexes. Recently several carbene complexes have been described which lack heteroatom stabilization.[2-6] Such complexes have generated considerable interest due to their potentially higher chemical reactivity and specifically due to their probable intermediacy in the olefin metathesis reaction.[7] Examples of such species include the Cp(benzocyclobutenylidene) iron dicarbonyl cation,[2] $(CO)_5W{=}C(C_6H_5)_2$,[3] $Cp(CO)_2Mn{=}CR_1R_2$ (R_1,R_2 = phenyl or methyl),[4,5a,6] $Cp(CO)_2Mn{=}C(C_6H_5)(COC_6H_5)$,[6] and several complexes of the type $(CO)_5M{=}CR_1R_2$ (M = W or Cr; R_1, R_2 = aryl, thienyl, or furyl) reported by Fischer.[5c]

In a series of recent papers, Schrock has reported a number of remarkably stable neutral alkylidene-tantalum complexes in which the carbene carbon atom appears nucleophilic in nature.[8] These complexes include the first isolated unsubstituted methylene complex $Cp_2(CH_3)Ta{=}CH_2$[8b] and the first reported secondary alkylidene complexes $(Cp)_2(C_6H_5CH_2)Ta{=}CHC_6H_5$ and $[(CH_3)_3CCH_2]_3Ta{=}CH[C(CH_3)_3]$.[8a,d]

We wish to report here some recent observations regarding nonheteroatom-stabilized cationic iron-carbene complexes. Our work in this area was prompted by earlier observations of Pettit and Jolly[9] and Green.[10] Pettit reported that treatment of $Cp(CO)_2FeCH_2OCH_3(FpCH_2OCH_3)$, **1**, with HBF_4 in the presence of cyclohexene led to norcarane.[9,11] The intermediacy of the cationic methylene complex, **2**, was suggested. Both Pettit[9] and Green[10] have reported that treatment of ether complex, **1**, with strong acids at 25 °C in the absence of olefins led to mixtures of iron complexes which were not readily separated and which always included the cationic ethylene complex, $Fp(CH_2CH_2)^+$. Again the cationic methylene complex **2** was judged a reasonable intermediate to account for the observed chemistry and for the formation of the ethylene complex.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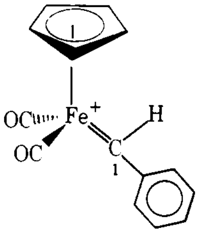
In an effort to observe **2** we have carried out a low temperature protonation of **1**. Treatment of a solution of HSO_3F-SO_2ClF at −100 °C with a cooled (−100 °C) solution of **1** in CD_2Cl_2 resulted in formation of a deep red solution. Immediate examination of the ^1H NMR spectrum of this solution at −80 °C revealed that a clean disproportionation had occurred with formation of equimolar amounts of $FpC_2H_4^+$[12] and $CpFe(CO)_2^+$.[13] If the methylene complex **2** is formed in this reaction, then disproportionation occurs quit rapidly even at −80 °C.

Success in preparing secondary derivatives of this class of nonheteroatom-stabilized carbene complexes was achieved through phenyl substitution at the carbene carbon atom. Treatment of $FpCH(C_6H_5)OCH_3$, **3**, at low temperatures (<−10 °C) with trifluoroacetic, fluorosulfonic, or triflic acid resulted in deep orange solutions of the benzylidene complex **4**. The ^1H NMR of **4** at −25 °C in triflic acid shows resonances at δ 16.86 (1 H, s, C_1 H), 7.70–8.13 (5 H, br m, C_6H_5), and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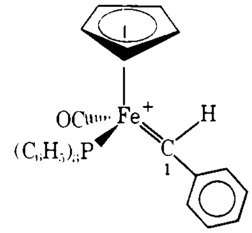
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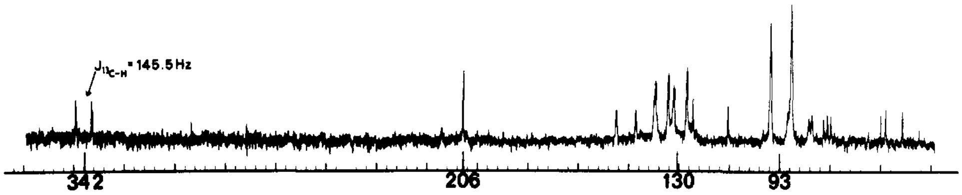

Figure 1. The coupled ^{13}C spectrum of **4** in CF_3SO_3H at −40 °C. Signals due to species other than **4** appear at 76.9 ppm (t, $CDCl_3$); 111.7, 124.4 (half of CF_3SO_3H quartet); 52.6 ppm (q, $CH_3{}^+OH_2$); and 82-83 ppm (impurities). The upfield half of the para ^{13}C doublet overlaps the downfield half of the ortho doublet (138 ppm).

5.87 (5 H, s, Cp). (A signal for protonated methanol (3 H) also appears at δ 4.06.) The coupled ^{13}C spectrum of **4** in triflic acid (see Figure 1) shows signals in parts per million downfield from TMS at 342.4 (C_1, d, $^1J_{CH}$ = 146 Hz), 206.5 (CO, s), 151.8 (C_{ipso}, s), 141.5 (C_{para}, d, $^1J_{CH}$ = 166 Hz), 134.5 (C_{ortho}, dd, $^1J_{CH}$ = 164 Hz, $^2J_{CH} \sim 6$ Hz), 130.0 (C_{meta}, d, $^1J_{CH}$ = 164 Hz), and 93.2 (Cp, dd, $^1J_{CH}$ = 185 Hz, $^2J_{CH}$ = 7 Hz).[14] In a similar manner the triphenylphosphine-substituted complex **5** can be prepared from the corresponding ether, $Cp(CO)(PPh_3)FeCH(C_6H_5)OCH_3$, **6.** The ^1H NMR spectrum of the deep maroon solution of **5** in TFA at 0 °C exhibits resonances at δ 17.43 (1 H, d, J_{P-H} = 1.12 Hz), 7.10-8.00 (20 H, br m, C_6H_5 and $(C_6H_5)_3P$), and 5.39 (5 H, d, Cp, J_{P-H} = 1.25 Hz). From the coupled and decoupled ^{13}C spectrum of **5** in TFA at 0 °C the following data was obtained: 341.2 (C_1, dd, $^1J_{CH}$ = 136 Hz, J_{CP} = 21 Hz), 215.4 (CO, d, J_{CP} = 29 Hz), 154.0 (C_{ipso}, t, $^2J_{CH}$ = 7 Hz), 137.5 (C_{para}, d, $^1J_{CH}$ = 164 Hz), 93.3 ppm (Cp, dt, $^1J_{CH}$ = 181 Hz, $^2J_{CH}$ = 7 Hz) (C_{ortho} and C_{meta} were obscured by resonances from triphenylphosphine in the region from 129 to 133 ppm).[17]

The NMR data clearly indicate that the species generated are indeed carbene complexes **4** and **5.** Most indicative are the ^{13}C resonances at 342 and 341 ppm. Such large downfield shifts are uniquely characteristic of carbene carbon resonances in such complexes, and in fact these values are near the lower extreme of the range of previously observed resonances.[18] Additional data which supports carbene formation are the remarkably low shifts (δ 16.96 and 17.43) of the protons directly bound to the carbene carbon atom. Although relatively few electrophilic secondary carbene complexes have been prepared, these low-field shifts are consistent with the observation of Lappert that the chemical shift of the carbene bound hydrogen in the resonance-stabilized $(CO)_4Fe{=}CH(NMe_2)$ appears at δ 11.[19] The analogous ^1H shifts in **4** and **5** would be expected at substantially lower fields as is observed.

An interesting feature of the ^{13}C NMR spectrum of **4** is that the resonances of the phenyl ring carbons have moved considerably downfield and are spread over a substantial shift range relative to the un-ionized ether, **3.**[20] The value of the para ^{13}C (141.5 ppm) and the meta ^{13}C (130.0 ppm) shifts of **4** and the difference between these shifts are similar to those in the triphenylmethyl cation (para, 144.0 ppm; meta, 131.2 ppm).[21] These data suggest that there is substantial positive charge at C_1 which may be partially delocalized into the aromatic ring. Such charge delocalization into the ring demands that it be perpendicular or nearly perpendicular to the p orbital at C_1. This is in contrast to aryl-substituted heteroatom carbene complexes where the ring plane lies parallel to the p orbital at C_1.[22] Other data supporting high charge at C_1 are the exceedingly low field shifts of H_1 in **4** and **5.**

Remarkably, stable salts of both **4** and **5** can be prepared. Reaction of $FpCH(C_6H_5)OCH_3$, **3,** with trityl hexafluorophosphate in CH_2Cl_2 results in precipitation of an orange hexafluorophosphate salt.[23] Dissolution of the salt in TFA/SO_2 at −25 °C gives an orange solution whose ^1H NMR spectrum is identical with that of **4** generated from the ether, **3,** in TFA. Quenching of the orange salt of **4** in CH_3OH/CH_3O^- results in regeneration of **3.** The maroon hexafluorophosphate salt of **5** can be prepared similarly by precipitation from CH_2Cl_2 with hexane. The ^1H NMR spectrum of this salt in CD_2Cl_2 indicates the presence of species **5** identical with that previously generated from the phosphine substituted ether, **6.**

The stability of **4** and **5** in solution differ considerably. The dicarbonyl complex **4** disappears completely after 1 h at 25 °C in TFA. The decomposition of **4** in TFA appears by ^1H NMR to be relatively clean, and we have isolated *trans*-stilbene in reasonable yield (~50%) from the solution after decomposition. In contrast the triphenylphosphine-substituted complex **5** shows only ~50% decomposition after 60 h at 25 °C.

Complexes **4** and **5** and the $(CO)_5WCHC_6H_5$ species described by Casey in the accompanying communication[24] are the first reported secondary, nonheteroatom-stabilized carbene complexes in which the carbene carbon is *electrophilic* in nature and, in this regard, represent an extreme on the present spectrum of observed, stable carbene complexes. The chemistry of the highly electrophilic species **4** and **5** promises to be rich and varied and the many synthetic modifications possible in this system should allow considerable control of the reactivity of these types of carbene complexes. Preliminary experiments indicate high reactivity toward simple unsaturated species such as olefins and carbonyl-containing compounds and we are currently exploring these reactions in detail.

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(23) In a typical preparation, 1.0 g of ether **3** in 25 mL of methylene chloride at −20 °C was treated with 1.3 g of trityl hexafluorophosphate. The orange hexafluorophosphate salt of **4** precipitated from solution and additional salt was obtained by treatment with 50 mL of pentane. Filtration and vacuum drying yielded 1.1 g of the hexafluorophosphate salt of **4** (~77% yield).

(24) C. P. Casey and S. W. Polichnowski, *J. Am. Chem. Soc.*, preceding paper in this issue.

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Inversion Barriers of AsH_3 and SeH_3^+

Sir:

The inversion barriers of group 5A molecules have been the subject of many studies.[1] The simplest molecules of this type are the hydrides of general formula AH_3, but, owing to the large magnitude of the inversion barriers in these molecules, only the barrier in NH_3 has been measured experimentally.[2] Several theoretical determinations of the barrier in NH_3 at the Hartree–Fock level are in excellent agreement with experiment.[3] In addition, the inversion barriers for a variety of hydrocarbon-substituted phosphines and arsines have been obtained experimentally;[1] for example, the barriers in $C_6H_5CH_3AR$, where R is an alkyl or aryl group and A is P or As, are ~33 kcal/mol for A = P and ~43 kcal/mol for A = As.[4] Accurate calculations of the barrier in PH_3 give ~36 kcal/mol,[5] which is quite similar to the experimental results for the substituted compounds. Similar results are found for hydrocarbon-substituted amines. The values of the inversion barriers for simple AH_3-type molecules are, therefore, of considerable chemical interest. In this paper we present ab initio SCF calculations using large basis sets on the pyramidal and planar forms of AsH_3 and the isoelectronic SeH_3^+ ion. We estimate the inversion barriers to be 46 and 30 kcal/mol, respectively. In addition, we present optimized minimum basis set exponents and geometries for these molecules and show that the minimum basis set inversion barriers for AsH_3 and SeH_3^+ are 44 and 35 kcal/mol, respectively, in reasonable agreement with the more reliable large basis set calculations.

All calculations employed Slater orbital basis sets and computer programs previously described.[3] The large basis sets (Table I) were of the "polarized double zeta" type augmented by one additional 3d function on the central atom to ensure adequate treatment of the 3d orbitals. The inner shell exponents on the central atom were taken from best atom double zeta results,[6] while the 3d and valence orbital exponents were optimized for the ground state of the free atom. The exponent for the 4d polarization function on As and Se was chosen by analogy to an optimized value of the corresponding polarization function in PH_3.[5b,7] The hydrogen basis sets were chosen as that of PH_3 for AsH_3 and that of SH_3^+ for SeH_3^+.[8] Similar quality basis sets are known to yield calculated barriers within 1–2 kcal/mol of the Hartree–Fock limit for PH_3. For instance, polarized double zeta Slater orbital calculations on PH_3 yield a calculated barrier of 37 kcal/mol,[5a] compared with a very large gaussian lobe basis (including f functions) of 38 kcal/mol.[5d]

Table I. Large Basis Set Geometries and Exponents

Molecule	Symmetry	Geometries Bond length, Å	 Bond angle, degree
AsH_3	C_{3v}	1.520	91.6
	D_{3h}	1.480	120
SeH_3^+	C_{3v}	1.450	93.0
	D_{3h}	1.434	120

	Basis sets As	 Se
1s	34.0214	35.0365
1s′	23.6356	24.3614
2s	16.2147	16.5867
2s′	13.2611	13.7371
3s	7.55246	7.95809
3s′	5.31126	5.66700
4s	2.931	3.188
4s′	1.736	1.918
2p	21.7642	22.4336
2p′	13.3553	13.8318
3p	7.0563	7.27814
3p′	4.50827	4.68101
4p	2.493	2.699
4p′	1.403	1.503
3d	11.961	12.018
3d′	6.544	6.611
3d″	3.482	3.658
4d	2.270	2.440
H1s	1.331	1.431
H2s	1.4054	1.7054
H2p	1.500	1.340

For the large basis set calculations, the geometry of AsH_3 was taken from experiment,[9] while the bond length for the planar molecule was shortened 0.04 Å by analogy to accurate geometry optimizations for PH_3.[5] This bond-length shortening is also consistent with optimized minimum basis set results described below. Estimates of the possible errors in the calculated barrier for AsH_3 due to inaccuracies in the transition state bond length can best be made by comparison with PH_3. For PH_3, the P–H stretching force constants in the planar form calculated at the minimum basis set SCF and the polarized double zeta SCF-CI levels of approximation differ by only ~15%. Calculation of the corresponding minimum basis set force constant for planar AsH_3 allows us to estimate a maximum error of 1.0 kcal/mol in our calculated barrier owing to inaccuracies in the bond length in the planar form, assuming the estimated transition state bond length of 1.480 Å is within 0.030 Å of the correct value and the minimum basis set force constant is accurate to within 30%. For pyramidal SeH_3^+, the bond length and angle were assumed to be 1.45 Å and 93°, respectively, and the bond length of the planar molecule was fixed at 1.434 Å. These values were obtained from optimized minimum basis set results (see below) along with estimates of minimum basis set errors associated with several other AH_3 molecules.[3,5b,10] We expect that all geometries are accurate