Table I. Comparison of U(IV)–C π-Bond Lengths

compound	U–C (mean), Å	ref
$(C_8H_8)_2U$	2.65	7
$[(CH_3)_4C_8H_4]_2U$	2.66	8
$Cp_3U(C{\equiv}CPh)$	2.68	9
$CpU(2\text{-}MeC_3H_4)_3$	2.79 (Cp), 2.66 (term), 2.80 (centr)	10
$U[(Cp)_2CH_2]Cl_2(bpy)$	2.72	11
$(Cp)_4U$	2.81	12
$[U(\eta^3\text{-}C_3H_5)_2(O\text{-}i\text{-}Pr)_2]_2$	2.68	13
$U[(CH_3)_5C_5]_2\{\eta^2\text{-}CO[N(CH_3)_2]\}_2$	2.78	14
$Cp_2U[O_2C_2CHP(Me)_2(C_6H_5)\text{-}Fe_2Cp_2(CO)_2]_2$	2.89	15
$U(\eta^6\text{-}C_6H_6)(AlCl_4)_3$	2.91	1
$\{[U(\eta^6\text{-}C_6Me_6)Cl_2]_2(\mu\text{-}Cl)_3\}AlCl_4$	2.92	this work

complex the distance is longer than most of those observed with the anionic π-ligands. We interpret this as an indication for a rather weak bond, corroborating our experimental observation that it forms only in the absence of any other possible donor.

The important fact, however, is that neutral aromatic systems can bind to a uranium center strongly enough to yield isolable compounds. This implies that conditions can be engineered under which valence shell orbitals, perhaps including f orbitals or hybrids thereof, are forced to participate in some form of bonding, possibly including direct metal–metal interaction.

Acknowledgment. We thank the Robert A. Welch Foundation for support under Grant No. A-494.

Supplementary Material Available: Tables of observed and calculated structure factors, positional parameters, and anisotropic thermal parameters (17 pages). Ordering information is given on any current masthead page.

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Synthesis, Spectral Characterization, and Carbene-Transfer Reactions of $CpFe(CO)_2{=}CH(c\text{-}C_3H_5)^+CF_3SO_3^-$. Stabilization of Cyclopropylmethylidene by an Organometallic Fragment

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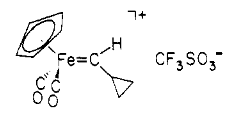
Summary: The synthesis and spectral characterization of $CpFe(CO)_2{=}CH(c\text{-}C_3H_5)^+CF_3SO_3^-$ are described. The cyclopropylmethylidene moiety may be transferred to alkenes to yield dicyclopropyl derivatives.

Iron alkylidene complexes of the type $(CO)(L)CpFe{=}CRR'^+$ (L = CO, PR_3, $P(OR)_3$; R, R′ = C_6H_5, H; CH_3, H; CH_3, CH_3; H, vinyl) are of synthetic interest as reagents for transfer of carbenes to alkenes.[1-7] Such species are readily and inexpensively generated, unusual stereoselectivities and enantioselectivities in their transfer reactions can be observed, and, most significantly, the $Cp(L)(CO)Fe^+$ fragment is capable of stabilizing alkylidene fragments which as free carbenes or traditional carbenoids are too unstable to be synthetically useful. This latter point is illustrated by the transfer of ethylidene, propylidene, and vinyl-substituted carbenes from the corresponding $Cp(CO)(L)Fe^+$ complexes to alkenes.

We report here: (1) the first generation and spectroscopic characterization of a simple cyclopropyl-substituted transition-metal carbene complex, the parent cyclopentadienyliron dicarbonyl cyclopropylmethylidene 1 ($CpFe(CO)_2{=}CH(c\text{-}C_3H_5)^+CF_3SO_3^-$), and (2) the utilization of this complex for the transfer of cyclopropylmethylidene to alkenes. Complex 1 is of particular interest in that cyclopropyl-substituted carbenes and carbenoids normally undergo rapid ring expansions, fragmentations, or rearrangements[8] and are not generally useful for the transfer of cyclopropylmethylidenes.[9] 1 is the only alkyl-substituted derivative of the series $CpFe(CO)_2{=}CHR^+$ to be spectroscopically characterized.



1

Synthesis of the $Fp{=}CH(c\text{-}C_3H_5)^+$ complex is outlined in Scheme I. Treatment of a THF solution of Fp^-M^+ (Fp = $CpFe(CO)_2$; M = Na, K) with 1 equiv of $c\text{-}C_3H_5COCl$ at −78 °C gives the acyl complex $FpC(O)(c\text{-}C_3H_5)$ 2 in 65% yield.[10] Reaction of 2 with $(CH_3)_3O^+BF_4^-$ in CH_2Cl_2 (25 °C, 12 h) gives $Fp{=}C(OCH_3)(c\text{-}C_3H_5)^+$ (3).[11] Quenching

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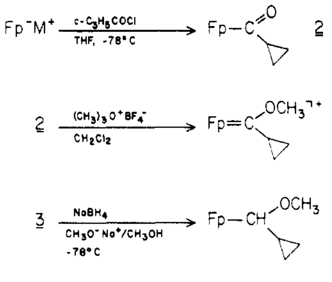
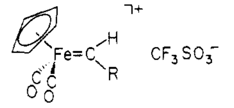
Scheme I



the solution of **3** directly into a cold (-78 °C), stirred solution of $NaBH_4$ in basic methanol gives the alkylidene precursor $FpCH(OCH_3)(c\text{-}C_3H_5)$ (**4**) (50%).[12] Yellow crystals of **4** (hexane, -60 °C) are stable only for short periods at room temperature but may be kept indefinitely under nitrogen below 0 °C.

The cyclopropylmethylidene complex **1** was generated by treatment of **4** in CD_2Cl_2 at -78 °C with a slight excess of trimethylsilyl triflate. The identification of **1** was based on ^1H and ^{13}C NMR data.[13] The ^1H resonance at 16.7 ppm and the ^{13}C resonance at 365 ppm are most indicative of the carbene structure and are consistent with those observed for other $(CO)(L)CpFe{=}CHR^+$ complexes.[2-5] Variable-temperature ^1H NMR indicated that decomposition of **1** began at -30 to -40 °C and was complete on warming to 0 °C, based on the total disappearance of the resonance at 16.7 ppm. The decomposition products are complex and were not characterized.

The thermal stability of **1** clearly surpasses that of other monosubstituted Fp$^+$–alkylidene complexes and rivals the stability of Fp$^+$–arylidene complexes. Fp$^+$–ethylidene (**5a**)

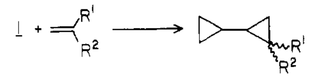


5

a, R = CH_3; b, R = CH_2CH_3; c, R = $CH(CH_3)_2$; d, R = $c\text{-}C_4H_7$; e, R = C_6H_5, $p\text{-}C_6H_4CH_3$, $p\text{-}C_6H_4OCH_3$

and Fp$^+$–propylidene (**5b**) complexes cannot be spectroscopically observed and their transient existence is only implied by the transfer of the alkylidene moiety to an olefinic substrate.[2] The lifetimes of **5c**[2g] and **5d**[14] are even shorter and transfers are unsuccessful. Fp$^+$-arylidene complexes **5e** are spectroscopically observable and, depending on the aryl substituents, may be stable at room temperature.[2b] Fp$^+$–arylidene stability is a consequence of the delocalization of the positive charge into the aryl ring. This property should be shared by the cyclopropyl substituent whose ability to stabilize adjacent carbocation centers is similar to that of the aryl substituent.[15]

Complex **1** transfers $c\text{-}C_3H_7CH$: to alkenes to give dicyclopropyl derivatives (eq 1). In a typical procedure



(1)

trimethylsilyl triflate (1 equiv) is added to a stirred solution of **4** (1 equiv) and alkene (2 equiv) in CH_2Cl_2 at -78 °C and then warmed slowly to room temperature. Neutralizing the burgundy solution with aqueous K_2CO_3 and standard workup[2e] yields clear colorless hexane solutions of the cyclopropanes. Purification and isomer separation is achieved by preparative GLC ($^1/_4$ in. × 19 ft 20% QF-1 on 80/100 Chromosorb W). The reaction of **1** with 2-ethyl-1-butene gives a 64% yield of 2,2-diethyldicyclopropyl[16] while the reaction with styrene gives a 66% yield of *cis*- and *trans*-2-phenyldicyclopropyl (3.4:1 trans:cis ratio).[17] This trans selectivity contrasts with the approximately 4:1 cis selectivity typically observed for the reaction of **5a** with styrenes.

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(10) IR (CH_2Cl_2): $\nu_{C{\equiv}O}$ 2015, 1955 cm^{-1}; $\nu_{C{=}O}$ 1630 cm^{-1}. ^1H NMR (100 MHz, C_6D_6): δ 0.39 (m, 2 H), 1.12 (m, 2 H), 2.33 (m, 1 H), 4.22 (s, 5 H). ^{13}C NMR (62.89 MHz, off-resonance decoupled, C_6D_6): δ 10.5 (t), 39.4 (d), 86.2 (d), 215.1 (s), 250.0 (s). Anal. Found (Calcd): C, 53.35 (53.70); H, 4.10 (4.10).

(11) IR (CH_2Cl_2): $\nu_{C{\equiv}O}$ 2060, 2012 cm^{-1}.

(12) IR (CH_2Cl_2): $\nu_{C{\equiv}O}$ 1998, 1936 cm^{-1}. ^1H NMR (100 MHz, C_6D_6): δ 0.6 (b m, 4 H), 1.3 (b m, 1 H), 3.18 (s, 3 H), 4.18 (d, J = 8 Hz, 1 H), 4.27 (s, 5 H). ^{13}C NMR (62.89 MHz, off-resonance decoupled, C_6D_6): δ 7.0 (t), 10.2 (t), 26.5 (d), 57.6 (q), 86.3 (d), 87.4 (d), 217.7 (s), 218.2 (s).

(13) ^1H NMR (250 MHz, -50 °C, CD_2Cl_2): δ 2.61 (m, 2 H), 2.79 (m, 2 H, $C\mathit{H}_2C\mathit{H}_2$), 4.15 (m, 1 H, $C\mathit{H}CH_2CH_2$), 5.70 (s, 5 H, C_5H_5), 16.73 (d, 1 H, J = 13 Hz, Fe=CH). ^{13}C NMR (62.89 MHz, off-resonance decoupled, -50 °C, CD_2Cl_2): δ 37 (t, $\mathit{C}H_2\mathit{C}H_2$), 62 (d), $\mathit{C}HCH_2CH_2$), 92 (d, C_5H_5), 207 (s, C=O), 365 (d, Fe=CH).

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(16) ^1H NMR (250 MHz, $CDCl_3$): δ -0.05 (m, 1 H), 0.12 (m, 2 H), 0.27 (m, 2 H), 0.42 (m, 2 H), 0.58 (m, 1 H), 0.85 (t, 3 H), 0.96 (t, 3 H), $CH_2C\mathit{H}_3$), 1.16 (q, 2 H), 1.41 (q, 2 H, $C\mathit{H}_2CH_3$).

(17) ^1H NMR (250 MHz, CD_3NO_2): cis isomer, δ 0.1–0.4 (b m, 5 H), 0.8–1.1 (b m, 3 H), 2.14 (dt, J = 6.5, 8.6, 8.6 Hz, 1 H, PhC*H*), 7.17 (m, 1 H), 7.29 (m, 4 H); trans isomer, δ 0.22 (m, 2 H), 0.45 (m, 2 H), 0.81 (m, 2 H) 0.99 (m, 1 H), 1.15 (m, 1 H), 1.72 (dt, J = 7.8, 5.2, 5.2 Hz, 1 H, PhC*H*), 7.10 (b m, 3 H), 7.28 (b m, 2 H). Cis and trans geometries in the products may be assigned on the basis of observed vicinal coupling constants and on the chemical shift of the benzylic cyclopropyl hydrogen, with the resonance for the cis isomer appearing at lower fields.[2g]

Photoinduced Ring Expansion of a Cyclopropyliron σ-Complex to a Metallacyclopentenone: An Example of Alkyl Group Rearrangement from Carbon to Iron To Generate a Carbene Complex

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Summary: Photolysis of acyl complex **1** or σ-complex **2** results in formation of the ring-expanded carbene complex **6**, presumably via the metallacyclobutene complex **4**. The proposed mechanism involves migration of alkyl from carbon to 16-electron coordinately unsaturated iron, thus generating the carbene complex **4** which subsequently ring expands to give **6**.

On the basis of extended Hückel calculations, Hoffmann and co-workers have made the interesting prediction that the interconversion of metal alkyl and metal carbene complexes should be facile (eq 1).[1,2] Indeed, there have

(1)