Methyl and Phenyl Rearrangements in Acyclic Fe^{II} Alkylidenes

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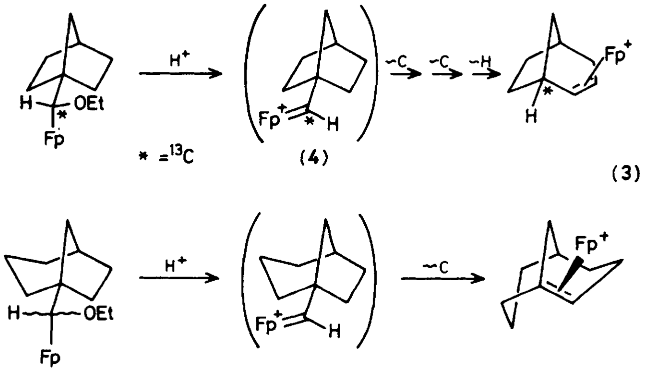
Dicarbonyl(η^5-cyclopentadienyl)-(2,2-dimethylpropylidene)iron(II) and -(2-methyl-2-phenylpropylidene)iron(II) tetrafluoroborates, (**6**) and (**10**), prepared by protonation of the analogous Fe^{II} α-ethoxyalkyls, rearrange to dicarbonyl(η^5-cyclopentadienyl)-(η^2-2-methylbut-2-ene)iron(II) and -(η^2-2-methyl-1-phenylprop-1-ene)iron(II) tetrafluoroborates, (**7**) and (**11**), by shift of a methyl and phenyl group, respectively, from the β to the α carbon atom.

If they possess a β-hydrogen atom cationic Fe^{II} alkylmethylidenes commonly shift this hydrogen atom to the methylidene carbon thereby forming the thermodynamically more stable η^2-alkenes, equation (1).[1] Analogous methyl shifts have not been observed; the single, previously reported, Fe^{II} neopentylidene, *viz.* (**3**), does not rearrange [equation (2)].[2] The only reported examples of a β-to-α carbon atom shift in any transition metal alkylidene is the rearrangement of 1-bicycloalkyl-substituted Fe^{II} methylidenes to η^2-homobicycloalkenes,[3] *viz.*, equations (3).

$$\underset{(\mathbf{1})}{[C_5H_5(CO)(L)Fe{=}\underset{\alpha}{C}H\underset{\beta}{C}H_2Me]^+} \longrightarrow \underset{(\mathbf{2})}{[C_5H_5(CO)(L)Fe(\eta^2\text{-}CH_2{=}CHMe)]^+} \quad (1)$$

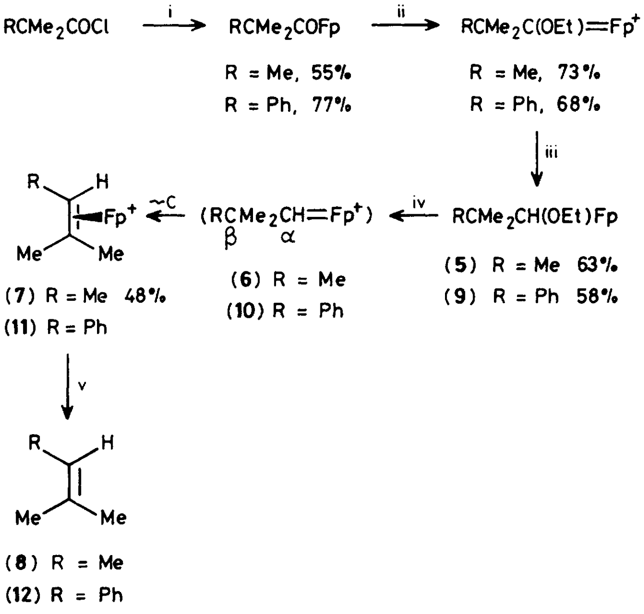
L = CO, PPh$_3$

$$\underset{(\mathbf{3})}{\{C_5H_5[(Ph_2PCH_2)_2]Fe{=}CHCMe_3\}^+} \xrightarrow{\times} \{C_5H_5[(Ph_2PCH_2)_2]Fe(\eta^2\text{-}MeCH{=}CMe_2)\}^+ \quad (2)$$



Fp = (η^5-C$_5$H$_5$)(CO)$_2$Fe, ~C = carbon atom shift.

That the bicyclic methylidenes rearrange whereas the acyclic neopentylidene does not raises the question of whether this difference in reactivity is caused by increased strain relief



Scheme 1. *Reagents and conditions:* i, KFp, tetrahydrofuran, 25 °C, 18—20 h (ref. 9); ii, Et$_3$O$^+$BF$_4^-$, CH$_2$Cl$_2$, 25 °C, 3—4 days; iii, LiBHEt$_3$, CH$_2$Cl$_2$, −78 °C, 1 h; iv, excess of HBF$_4$·Et$_2$O, CD$_2$Cl$_2$, −78 °C, 30 min; v, KI, (CD$_3$)$_2$CO or CD$_2$Cl$_2$, 0—25 °C, *ca.* 5 min.

in the bicyclic cases,[4] or by decreased electrophilicity at the methylidene carbon of the diphosphine ligated[5] acyclic case. To investigate this we have prepared the dicarbonyl(η^5-cyclopentadienyl)alkylmethylideneiron(II) species (**6**) and (**10**) (Scheme 1) and examined their reactivity.

The alkylidenes were generated by the well-precedented method of protonating neutral Fe^{II} α-alkoxyalkyls[2,5,6] which had in turn been prepared from acyl halides (Scheme 1).†‡ Though some cationic mono(alkyl)methylidenes, including (**6**) and (**10**) are too reactive to be observed directly[1b,d] their initial formation is not doubted since others including (**4**),[7] prepared in a similar manner, have been characterized spectroscopically.[1b,d,e,5b,6b]

Protonation of (**5**) in a 5-mm n.m.r. tube in the cooled probe of an n.m.r. spectrometer (Scheme 1) yields (**7**) as the only discernible organometallic species by ^{13}C n.m.r. spectroscopy.‡ When carried out on a larger scale under similar conditions (**7**) can be isolated as the tetrafluoroborate in 48% yield. Decomplexation with KI in $(CD_3)_2CO$ (Scheme 1) provides 2-methylbut-2-ene (**8**) as the only alkene.[8]‡ A similar small-scale protonation of (**9**) yields (**11**) as the only detectable organometallic species. Warming to 25 °C or adding KI to the cold CD_2Cl_2 solution releases (**12**) as the only observable alkene.

Our results provide the first examples of a β-to-α carbon shift in an unstrained, acyclic organotransition metal alkylidene. The shift of a methyl group in (**6**) and a phenyl group in (**10**) demonstrates that when the methylidene carbon of an Fe^{II} alkylidene is sufficiently electrophilic, as it apparently is in these dicarbonyl(η^5-cyclopentadienyl)iron(II) cases, substantial strain relief is not required to induce a carbon shift. The migratory aptitude of β-substituents in cationic Fp alkylidenes is evidently $H > Ph > Me$.

Received, 17th March 1986; Com. 346

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† Dry and oxygen-free atmospheres (N_2) and solvents were used at all times.

‡ Satisfactory analytical data were obtained for the new compounds. (**7**), I.r. (CH_2Cl_2) 2060, 2025 cm^{-1} ($C\equiv O$); ^1H n.m.r. (CD_2Cl_2) δ 5.57, s (C_5H_5); 5.16, q (=C*H*Me); 1.97, d (=CH*Me*); 1.92, s [$CH_3(CH_3)C=$] with the first H_3 italic; 1.74, s [$CH_3(CH_3)C=$]; ^{13}C {^1H} n.m.r. (CD_2Cl_2) δ 111.6 (>C=), 89.0 (C_5H_5), 75.4 (=CH–), 31.1, 23.2, 19.8 (3–CH_3). (**11**), I.r. (CH_2Cl_2) 2069, 2020 cm^{-1} ($C\equiv O$); ^{13}C{^1H} n.m.r, (CD_2Cl_2) δ 213.1, 205.3 (2 × $C\equiv O$), 136.7, 129.4 (2C), 129.0 (3C), Ph, 106.1 (>C=), 89.2 (C_5H_5), 77.3 (=CHPh), 32.9, 26.4 [=CMe_2]. The ^1H and ^{13}C{^1H} n.m.r. spectra of (**8**) and (**12**) are identical to those of authentic samples.