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Preliminary communication

REACTIVITY OF LINKED METAL UNITS: THE THERMAL DECOMPOSITION OF DERIVATIVES OF IRON CONTAINING MULTIPLE ALKYLMETAL GROUPS

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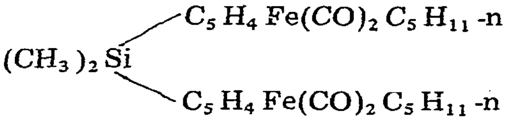
Summary

The results of thermal decomposition studies of derivatives of iron containing multiple alkylmetal groups $(CH_3)_2Si[\eta^5\text{-}C_5H_4Fe(CO)_2C_5H_{11}]_2$ (I), $\{(CH_3)_2Si[\eta^5\text{-}C_5H_4Fe(CO)_2]_2(CH_2)_5\}_2$ (II) and $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2(CH_2)_5$ (III) are presented and compared with the results obtained for $\eta^5\text{-}C_5H_5Fe(CO)_2C_5H_{11}$ (IV). Compounds II and III are found to produce principally 1-pentene and therefore do not decompose by two sequential β-hydrogen elimination steps. Compound I decomposes principally by a β-hydrogen elimination process but produces significantly more pentane in its reactions than does IV.

Postulated mechanisms in heterogeneous catalysis [1] frequently invoke the interaction of two or more metal sites with substrate molecules. In this regard, the novel effect of a second metal on the reactivity of an adjacent metal has recently been demonstrated for a homogeneous linked bimetallic system [2]. Also small multimetal clusters which contain separate hydridometal and/or alkylmetal units in the same molecule have been obtained recently [3,4]. While the thermal decomposition of acyclic [5] and cyclic [6] alkylmetals has been under detailed investigation, the reactivity of multimetallic or even bimetallic acyclic and cyclic alkyl derivatives has not received equivalent attention. An examination of the thermal decomposition of derivatives containing two or more alkylmetal units could yield information on the mutual effect of one metal site on the reactivity of a connected metal site.

We report here the results of thermal decomposition studies of a series of derivatives containing two or more alkylmetal units, I, II and III [7]. Additionally, the monometallic n-pentyl derivative $\eta^5\text{-}C_5H_5Fe(CO)_2C_5H_{11}$ (IV)

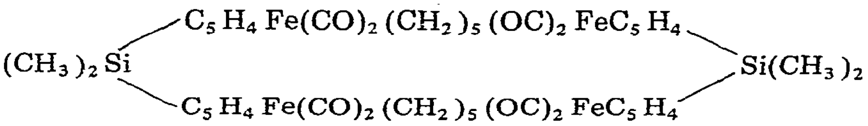


$$(CH_3)_2Si\begin{cases}C_5H_4Fe(CO)_2C_5H_{11}\text{-n}\\C_5H_4Fe(CO)_2C_5H_{11}\text{-n}\end{cases}$$

(I)

$C_5H_5Fe(CO)_2(CH_2)_5(OC)_2FeC_5H_5$

(III)



$$(CH_3)_2Si\begin{cases}C_5H_4Fe(CO)_2(CH_2)_5(OC)_2FeC_5H_4\\C_5H_4Fe(CO)_2(CH_2)_5(OC)_2FeC_5H_4\end{cases}Si(CH_3)_2$$

(II)

was examined. Both I and II* are accessible by reaction of $(CH_3)_2Si[\eta^5\text{-}C_5H_4Fe(CO)_2]_2^{2-}$ (V) with 1-bromopentane and 1,5-dibromopentane, respectively, in tetrahydrofuran.

The data in Table 1 were obtained mainly by the following procedure illustrated with I. A solution of 0.223 g of I in 30 ml of Nujol was heated at 150°C ± 2°C for 4 h under vacuum. The volatile organic products distilled into a liquid nitrogen cooled trap, then were analyzed by GLC. The organometallic product remained in the reaction vessel and was isolated by chromatography on silica gel. It was qualitatively identified by IR and PMR spectroscopy and quantitatively analyzed by visible spectroscopy. The organometallic products formed in the thermal decomposition of I—IV were invariant with reaction conditions. Both I and II yielded $(CH_3)_2Si[\eta^5\text{-}C_5H_4Fe(CO)_2]_2$, while III and IV produced $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$. Molecular weight measurements confirmed that $(CH_3)_2Si[\eta^5\text{-}C_5H_4Fe(CO)_2]_2$ was indeed a monomer and not an oligomer.

The data in Table 1 concerning the organic products require several conclusions. Firstly, compound II, the four-metal cyclic compound, and compound III, the acyclic bimetallic system, react in a similar fashion and substantially differently than do compounds I and IV. Both II and III form predominantly 1-pentene with only small amounts of *trans* and minor amounts of *cis*-2-pentene in good overall yield in dilute Nujol solutions (entries 5, 6 and 8, 9). Equations 1 and 2 best represent these reactions. Only trace amounts

$$\{(CH_3)_2Si[\eta^5\text{-}C_5H_4Fe(CO)_2]_2(CH_2)_5\}_2 \rightarrow 2\ \text{n-}C_3H_7CH{=}CH_2 + 2(CH_3)_2Si[\eta^5\text{-}C_5H_4Fe(CO)_2]_2 \qquad (1)$$

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*I is a viscous dark yellow oil: $\nu(CO)$ in (C_6H_6) 2012 and 1955 cm^{-1}; ^1H NMR (C_6D_6)(TMS δ 0 ppm) 4.33 (s, 8 H, cyclopentadienyl), 1.52 (s, 16 H, methylene chain), 0.96 (t(br), 6 H, terminal methyl), 0.38 ppm (s, 6 H, silyl-methyl); ^{13}C NMR (C_6D_6)(TMS δ 0 ppm) 92.46; 88.80, 85.86 (cyclopentadienyl); 37.53; 36.90, 22.12; 13.73, 3.40 (pentyl); 217 ppm (silyl methyl).

II is a crystalline yellow solid m.p. 143—145°C. Anal: Found: C, 52.9; H, 5.1; Fe, 22.8. mol.wt. ($CHCl_3$, osmomethyl) found 946. $C_{42}H_{48}Fe_4O_8Si_2$ calcd.: C, 52.5; H, 5.0; O, 13.3; Fe, 23.3; Si, 5.8%; mol.wt. 960. Spectral data for II are given in ref. 8a.

$$[\eta^5\text{-}C_5H_5Fe(CO)_2]_2(CH_2)_5 \rightarrow n\text{-}C_3H_7CH{=}CH_2 + [\eta^5\text{-}C_5H_5Fe(CO)_2]_2 \qquad (2)$$

of pentane and cyclopentane were formed. No 1,4-pentadiene was observed nor was *cis*- or *trans*-piperylene. Neither II nor III is decomposing to any substantial amount by two sequential β-hydrogen elimination steps to produce dienes. Apparently reduction of an ω-pentenyl intermediate occurs faster than a second β-hydrogen elimination step.

TABLE 1

PRODUCTS OF THE THERMAL DECOMPOSITION OF I—IV IN NUJOL SOLUTION

Entry	Compound	10^3 *M*	Yield (%) organic products	Relative yield (%)				Yield (%) organometallic product
				1-pentene	*trans*-2-pentene	*cis*-2-pentene	Pentane	
1	I	12.88	57	28	32	19	21	77
2	I	9.69	64	27	32	19	22	67
3	I	7.43	69	30	32	16	22	82
4	I	3.68	78	27	31	19	23	85
5	II	1.14	71	93	6	1	<1	72
6	II	1.12	72	90	9	1	<1	76
7	II[a,b]	55.20	33	85	15	<1	<1	66
8	III	11.04	85	87	9	4	<1	94
9	III	11.48	80	87	9	4	<1	75
10	III[a,b]	167.0	41	68	22	10	<1	94
11	III[a,c]	173.6	42	69	21	10	<1	89
12	III[a]	melt	13	26	32	20	5	99
13	III	melt	13	40	33	18	6	88
14	IV	26.47	52	29	46	13	12	85
15	IV	10.64	59	26	44	15	14	81
16	IV	9.46	69	29	42	16	13	81
17	IV	4.33	71	31	38	14	17	85

[a] Reaction vessel sealed. [b] 2 ml toluene solvent. [c] 2 ml benzene solvent.

A concentration effect was observed in the decomposition of all four compounds. The decompositions proceed quite smoothly in good yield in dilute Nujol solutions. However, as the concentration of the complex increases, the overall yield of volatile organic products decreases. This effect was examined in greatest detail for the decomposition of II and III. For example, entries 10 and 11 are decompositions of III in a sealed system in a solvent of 2 ml of toluene and benzene, respectively. The nature of the organic product does not change from entries 8 and 9 although the distribution changes somewhat. The overall yield, however, decreases substantially from around 80 to about 40%. The absolute amount of *trans*- and *cis*-2-pentene stays about the same. Consequently the major factor causing the decrease in overall yield is the decrease in 1-pentene obtained. Entry 7 shows similar behavior for II. Entries 12 and 13, which are decompositions of III in the melt in a sealed system, and to a vacuum, respectively, further illustrate this phenomenon. In both cases a 13% overall yield was observed. An involatile oil could be isolated by chromatography of the residue from the low yield reactions of

III. The material has a broad PMR resonance around δ 1.0 ppm and presumably is polymerized product.

Lastly, a significant but not pronounced difference exists in the reaction of the bimetallic compound I and the monometallic derivative IV. For both I and IV the major products (the olefins) can be rationalized as resulting from β-hydrogen elimination from n-pentyl or isomeric pentyl derivatives. The distribution of pentenes is, however, different with substantially more *trans*-2-pentene being produced in the case of IV. The alkane product, pentane, comes from some hydrogenation process involving I and IV. It should be noted that in phosphine-substituted derivatives such as η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]C_4H_9$ no alkanes were observed in the organic products [5b,c]. Olefin and alkane products were, however, observed in the decomposition of η^5-$C_5H_5Fe(CO)_2(\eta^1$-acenaphthenyl), as was a significant amount of the coupled organic product, biacenaphthenyl [5a]. In fact, the alkane product was the major organic product. The source of the hydrogen atom for the formation of the alkane product was probed by the decomposition of specifically labeled deuterium derivatives. The hydrogen atom came not only from the β position of the organic group but also from solvent and the cyclopentadienyl ring [5a]. The source of the hydrogen atom for the formation of pentane in the decomposition of I and IV has not yet been ascertained; however, I clearly produces more pentane than does IV. This is consistent with the presence of an intermediate with the reaction of I containing covalently linked metal-hydride and alkylmetal units which could undergo reductive coupling to produce pentane with greater facility than separated units which would be present in reactions of IV. The isolation of monomeric $(CH_3)_2Si[\eta^5$-$C_5H_4Fe(CO)_2]_2$ indicates that in the case of I the reaction could be intramolecular rather than intermolecular.

The effect of varying (a) the alkyl chain linking the metals (b) substituents at the metals and (c) the covalent linkage connecting cyclopentadiene rings are being examined.

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