Journal of Organometallic Chemistry, 213 (1981) C31—C36
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE PREPARATION OF ORGANOIRON η^1-α-ALKOXYETHYL COMPLEXES AND THEIR REACTION WITH ELECTROPHILES: CHARACTERIZATION OF CATIONIC ORGANOIRON ETHYLIDENE COMPOUNDS

THOMAS BODNAR and ALAN R. CUTLER*

Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457 (U.S.A.)

(Received January 27th, 1981)

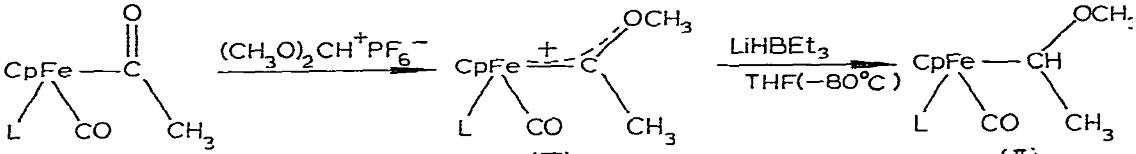
Summary

The η^1-α-alkoxyethyl complexes $CpFe(CO)L[CH(OCH_3)CH_3]$ (IIa, L = CO; IIb, L = PPh_3; IIc, L = $P(OPh)_3$) have been prepared by the $LiHBEt_3$ reduction of the requisite alkoxycarbene compounds $CpFe(CO)L[C(OCH_3)CH_3]^+$ PF_6^-. Treatment of IIb and IIc with acid or Ph_3C^+ selectively affords the ethylidene salts $CpFe(CO)L(=CHCH_3)^+$ (Ib, L = PPh_3; Ic, L = $P(OPh)_3$), which thermally isomerize below 25° C to the η^2-ethylene complexes $CpFe(CO)L(CH_2{=}CH_2)^+$. Ib and Ic, also produced by protonation of the vinyl complexes $CpFe(CO)L(CH{=}CH_2)$, were trapped by PPh_3 adduct formation (L = PPh_3, $P(OPh)_3$), by deprotonation to its vinyl complex (L = $P(OPh)_3$), and by $LiHBEt_3$ reduction (L = $P(OPh)_3$). Treatment of IIa with acid or Ph_3C^+ (or $CpFe(CO)_2CH{=}CH_2$ with acid) gives varying mixtures of $CpFe(CO)_2(CH_2{=}CH_2)^+$ and the β-metallocarbonium ion complex $[CpFe(CO)_2CH_2CHCH(CH_3)Fe(CO)_2Cp]^+$, both necessitating intermediacy of Ia.

Interest in transition organometallic alkylidene complexes lacking α-heteroatom substituents follows from their enhanced reactivity, compared with that exhibited by heteroatom-stablized carbene compounds [1]. Most of the known alkylidene complexes additionally lack β-hydrogens on the alkylidene: recent examples include methylidene [2a—c], neopentylidene [2d, e], and benzylidene [2e—j] systems. Alkylidene ligands bearing β-hydrogens apparently can isomerize to η^2-alkene groups, although only one such example has been reported. The α-phenylethylidene compound $(CO)_5W{=}C(CH_3)Ph$ thus rearranges above ca. —80° C to an unstable η^2-styrene complex [3]. Other alkylidene compounds reported with β-hydrogens, in contrast, are stable at room temperature:

$CpM(CO)_2{=}C(CH_3)R$ ($Cp = \eta\text{-}C_5H_5$; M = Mn, R = CH_3; M = Re, R = Ph) [4a]; $Cp_2TaCH_3({=}CHCH_3)$ [4b]; $CpRe(NO)PPh_3({=}CHR)^+$ (R = CH_3, CH_2CH_3) [2f]. We now report facets of the reaction chemistry and isomerization of the electrophilic ethylidene salts $CpFe(CO)L({=}CHCH_3)^+$ (Ia, L = CO; Ib, L = PPh_3; Ic, L = P $(OPh)_3$).

The α-alkoxyethyl complexes IIa—IIc, which serve as direct precursors to Ia—Ic, were procured from the requisite methoxycarbene compounds IIIa—IIIc. $LiHBEt_3$ reduction of IIIa—IIIc in tetrahydrofuran (—80° C),



(III) (II)

(a, L = CO ;
b, L = PPh_3 ;
c, L = $P(OPh)_3$)

followed by removal of solvent and low temperature crystallization from the pentane extracts, affords the α-alkoxyethyl complexes (70—95% yields) as yellow-brown (IIa), red-orange (IIb), or yellow (IIc) crystals*. The corresponding ethyl complexes were not observed. Others have reported that $NaBH_4$ ethanol reduces $CpFe(CO)PPh_3[C(OEt)CH_3]^+$ to mixtures of the ethyl and α-ethoxyethyl compounds [5], and that Ph_3PMe^+ BH_4^-/CH_2Cl_2 cleanly converts IIIa—IIIc to their ethyl complexes [6]. Transition organometallic hydride complexes also reduce IIIa to IIa [7].

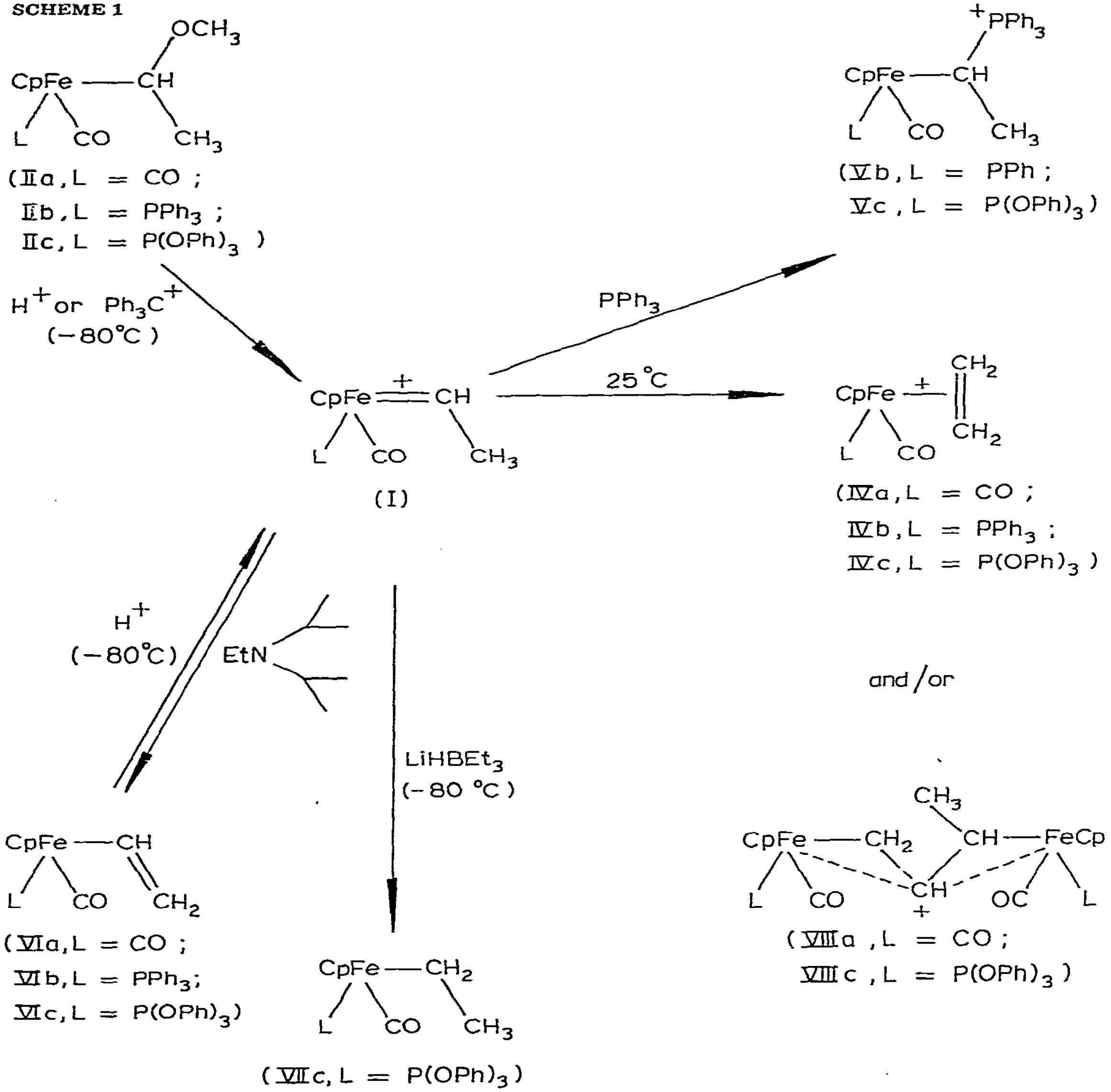
Treatment of IIb or IIc dissolved in CH_2Cl_2 (—80° C) with 1.1 equivalents of $HPF_6 \cdot OEt_2$ produces dark red-orange solutions of the ethylidene compounds Ib or Ic. Addition of cold (—80° C) ether then gives yellow crystals, which turn dark red above ca. —60° C. CH_2Cl_2 solutions of Ib or Ic (either before or after crystallization) likewise decompose slowly at room temperature; the known [5, 8] η^2-ethylene complexes IVb and IVc (Scheme 1) represent the only detectable organometallic complexes. Reaction conditions, however, are critical. Thus CH_2Cl_2 solutions of Ic, either at —80° C or immediately after warming to room temperature, precipitate only trace amounts of IVc from room temperature ether**. Only after the dissolved Ic warms to room temperature for over

---

*Spectroscopic data for IIa: IR (CH_2Cl_2) 1998, 1938 cm^{-1} (C≡O); ^1H NMR ($CDCl_3$) δ (ppm) 4.70 (s, Cp), 4.84 (q, J 6 Hz, FeCH), 3.23 (s, OCH_3), 1.70 (d, J 6 Hz, CH_3). Data for IIb (1/1 mixture diastereomers): IR(CH_2Cl_2) 1897 cm^{-1} (C≡O), ^1H NMR ($CDCl_3$) δ (ppm) 7.32 (br s, PPh_3), 4.33 (S, Cp), 3.90 (m, FeCH), 3.13 (s, OCH_3), 2.74 (s, OCH_3), 1.55 (d, J 6 Hz, CH_3). Data for IIc (1/1 mixture diastereomers): IR (CH_2Cl_2) 1933 cm^{-1} (C≡O); ^1H NMR ($CDCl_3$) δ (ppm) 7.20 (br s, P $(OPh)_3$), 4.27 (s,Cp), 4.18 (s,Cp), 4.60 (m, FeCH), 3.40 (s, OCH_3), 3.24 (s, 3, OCH_3), 1.90 (d, J 6 Hz, CH_3), 1.70 (dd, J 6, 1 Hz, CH_3). All new compounds reported in this communication gave satisfactory C,H-elemental analyses.

**We tentatively assign structure VIIIc to the isolated (55%) organometallic species. Its IR, ν(CO) CH_2Cl_2=1995, 1952 cm^{-1}, and features of its NMR, δ ($CDCl_3$) 4.50, 4.42 (br 3, Cp), are consistent with this assigment, but analytical-quality samples have not been crystallized. Ph_3C^+ PF_6^- also reacts with IIc (1:1 or 1:2) to give VIIIc quantitatively.

SCHEME 1



an hour are moderate yields (50—60% after reprecipitation from CH_2Cl_2 ether) of IVc obtained.

The NMR spectrum of Ib in trifluoroacetic acid (25° C) features a diagnostic downfield quartet (δ 17.85 ppm, J 8.0 Hz) for the ethylidene methine. These reddish solutions, obtained by dissolving IIb in trifluoroacetic acid (—10° C), also contain ca. 10% IVb; the solutions remain unchanged after several hours at room temperature*. IR spectra of Ib and Ic, however, exhibit similar ν(CO) (2005 and 2025 cm^{-1}, respectively, in CH_2Cl_2) as IVb and IVc.

Ethylidene complexes Ib and Ic were trapped with exogenous reagents

---

* ^1H NMR data: Ib (CF_3CO_2H) δ (ppm) 17.85 (q, J 8 Hz, Fe=CH), 7.63 (br s, PPh_3), 5.29 (s, Cp), 2.94 (d, J 8 Hz, CH_3); IVb (CF_3CO_2H) δ (ppm) 7.50 (s, PPh_3), 5.00 (s,Cp), 3.34 (br s, C_2H_4).

(Scheme 1), PPh_3 (1.1 equivalents, —80°C) efficiently intercepts Ib and Ic in situ and forms the α-phosphonium adducts Vb, Vc. Quantitative trapping was established by IR monitoring at room temperature; Vb (78%, salmon-pink solid) and Vc (56%, orange-yellow crystals) were then isolated by ether preciptiation and recrystallization from CH_3NO_2 or CH_2Cl_2 ether*. Ic was further characterized by deprotonation and by reduction. Excess EtN(i-propyl)$_2$ accordingly deprotonates Ic (—80° C) to VIc (52%, yellow-brown crystals after chromatography on activity 3 alumina/CH_2Cl_2) and one equivalent of $LiHBEt_3$ reduces Ic (—80° C) to its known [8b] ethyl complex VIIc (81% after chromatography).

Vinyl complexes VIb and VIc are conveniently accessible from $CHCl_3$ solutions of IIb, IIc containing a trace of acid. Column chromatography of these solutions after 24 h gave 50—60% VIb and VIc as yellow crystalline solids. VIb, VIc serve as alternative precursors to Ib, Ic, via protonation with $HPF_6 \cdot OEt_2$ (—80° C).

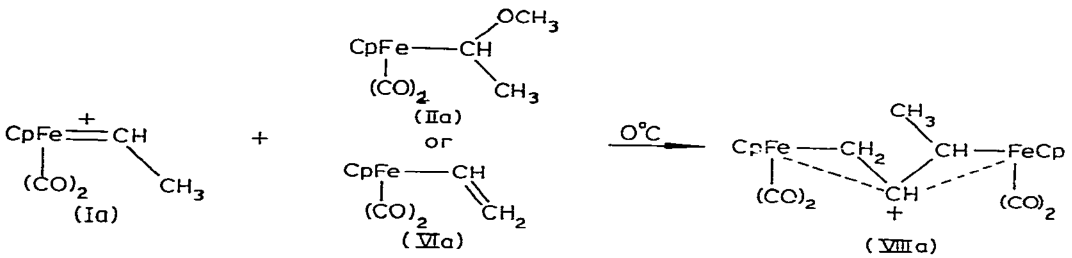
$CpFe(CO)_2{=}CHCH_3^+$ (Ia) appears much more reactive than Ib, Ic. IIa in CH_2Cl_2 (—25° C) thus reacts with one equivalent of $HPF_6 \cdot OEt_2$ or $Ph_3C^+ \ PF_6^-$ and produces the brick-red bimetallic salt VIIIa (68—80% after ether precipitation and recrystallization from CH_3NO_2/ether) as the only detectable organometallic. Similarly, $HPF_6 \cdot OEt_2$ in CH_2Cl_2/(—25° C) converts $CpFe(CO)_2CH{=}CH_2$ (VIa) [9] to VIIIa (78%). Protonation of either IIa and VIa between —25 and 0° C, however, gives mixtures of IVa and VIIIa. Trifluoracetic acid at —10°C, accordingly, dissolves IIa or VIa and gives 5/1 mixtures of VIIIa and IVa. Attempts to trap putative Ia in CH_2Cl_2 (—80 to —25° C) with PPh_3 (1.1 equivalents) afforded quantitative yields of $CpFe(CO)_2PPh_3^+$ instead. The fate of the alkylidene ligand is unknown, although it is reasonable that I could react as carbene-transfer reagents [10].

VIIIa represents another example of a β-metallocarbonium ion complex analogous to $CpFe(CO)_2CH_2^+CHCH_2Fe(CO)_2Cp$ (IX) [11]. The NMR of VIIIa** exhibits four Cp resonances representing a diastereoisomeric mixture of fluxional tautomers [11a]; the α-$CHCH_3$ and complexation of the prochiral β-CH convey the requisite chirality. Chemical shifts for the Cp absorptions of VIIIa, moreover, are symmetrically disposed about that of IX (δ 5.23 ppm), but between those of IVa (δ 5.68 ppm); and VIIa (δ 4.96 ppm) in CD_3NO_2. Further support for structure VIIIa comes from the results of adding one equivalent of IIa or VIa to Ia (0° C). Either two equivalents of IIa plus Ph_3C^+ or one equivalent each of IIa, IVa, and $Ph_3C^+ \ PF_6^-$ (0° C, CH_2Cl_2) affords VIIIa quantitatively. A speculative mechanism for VIIIa entails electrophilic attack of Ia at the β-position [5] on the vinyl ligand of VIa (perhaps

---

*We found no evidence for information of the β-phosphonium adducts in these reactions. One such adduct $CpFe(CO)P(OPh)_3[CH_2CH_2PPh_3]^+$ independently generated from IVc plus PPh_3 in CH_2Cl_2, reverts to starting materials upon attempted precipitation.

**Spectroscopic data for VIIIa: IR(CH_2Cl_2) 2055, 2018, 1967 cm^{-1} (C≡O); NMR (CD_3NO_2) (diastereomer A) δ (ppm) 6.44 (m, CH^+), 5.40 and 5.16 (s,Cp), 4.10 (m, FeCH), 2.61 (m, 1H, $FeCH_2$), 1.56 (d, J 6 Hz, CH_3), 1.90—1.62 (m, 1H, $FeCH_2$); Diastereomer B) δ 5.93 (m, CH^+), 545 and 5.10 (s, Cp), 4.26 (m, FeCH), 2.61 (m, 1H, $FeCH_2$), 1.74 (d, J 6 Hz, CH_3), 1.90—1.62 (m, 1H, $FeCH_2$). Assignments are consistent with the results of spin decoupling experiments.



generated through deprotonation of Ia with IIa and loss of MeOH). The resulting $CpFe(CO)_2CH(CH_3)CH_2CH_2CH{=}Fe(CO)_2Cp^+$ would then rearrange to the observed VIIIa.

Two important conclusions emerge from this preliminary study. First, acid or Ph_3C^+ selectively abstracts the α-methoxide from II and generates the ethylidene complexes I. Similar α-alkoxide abstraction has been documented for synthesizing methylidene [2a,b,j] and benzylidene[2g,i,j] complexes. Either α-hydride abstraction [12], regenerating the starting alkoxycarbene complexes, or β-hydride abstraction, giving η^2-vinyl ether compounds [13], from IIa would have been thermodynamically feasible pathways. Second, the exceedingly reactive ethylidene complexes I isomerize at or below room temperature to their respective η^2-ethylene salts IV. This observation, although contrary to the thermal stability of most ethylidene complexes, is consistent with the postulated intermediacy of $CpFe(CO)_2(=CHCH_2CH_3)^+$ during protonation and conversion of $CpFe(CO)_2\overline{CHCH_2CH_2}$ to $CpFe(CO)_2[CH_2CHCH_3]^+$ [14]. In contrast, isomerization of $CpFe(CO)_2$(benzocyclobutenylidene)$^+$ [15] is precluded by the antiaromaticity of the resulting η^2-benzocyclobutadiene ligand. Work in progress is concerned with the synthesis of the Ru analogues of I. A recent communication by Brookhart, appearing after submission of this article, reports the spectral characterization of Ib and the ethylidene transfer reactions of Ia [16].

We thank Myron Rosenblum for permission to repeat and cite unpublished work on the protonation of VIa and the spectral characterization of VIIIa. Acknowledgment is also made to the Department of Energy, Office of Basic Energy Sciences for support of this research.

References

1 F.J. Brown, Progress Inorg. Chem., 27 (1980) 1; R.J. Goddard, R. Hoffmann, and E.D. Jemmis, J. Amer. Chem. Soc., 102 (1980) 7667; R.R. Schrock, Acc. Chem. Res., 12 (1979) 98; E.O. Fischer, Adv. Organometal. Chem., 14 (1976) 1.

2 (a) M. Brookhart, J.R. Tucker, T.C. Flood, and J. Jensen, J. Amer.Chem. Soc., 102 (1980) 1203, and ref. cited: (b) W. Wong, W. Tam, and J. Gladysz, ibid., 101 (1979) 5440: (c) R.R. Schrock and P.R. Sharp, ibid., 100 (1978) 2389; (d) A. Davison and J.P. Selegue, ibid., 102 (1980) 2455; (e) G.A. Rupprecht, L.W. Messerle, J.D. Fellman, and R.R. Schrock, ibid., 102 (1980) 6236; (f) W.A. Kiel, G. Lin, and J.A. Gladysz, ibid., 102 (1980) 3299; (g) C.P. Casey, S.W. Polichnowski, A.J. Schusterman, and C.R. Jones, ibid., 101 (1979) 7282; (h) L.W. Messerle, P. Jennische, R.R. Schrock, and G. Stucky, ibid., 102 (1980) 6744; (i) M. Brookhart and G.O. Nelson, ibid., 99 (1977) 6099; (j) A.G. Constable and J.A. Gladysz, J. Organometal. Chem., 202 (1980) C21.

3 E.O. Fischer and W. Held, J. Organometal. Chem., 112 (1976) C59; C.P. Casey, L.D. Albin, and T.J. Burkhardt, J. Amer. Chem. Soc., 99 (1977) 2533.

4 (9a) E.O. Fisher, R.L. Clough, and P. Stückler, J. Organometal. Chem., 120 (1976) C6; E.O. Fischer, R.L. Clough, G. Besl, and F.R. Kreissl, Angew. Chem., Int. Ed., 15 (1976) 543. (b) P.R. Sharp and R.R. Schrock, J. Organometal. Chem., 171 (1979) 43.

5 A. Davison and D. Reger, J. Amer. Chem. Soc., 94 (1972) 9237.

6 T. Bodnar, G. Coman, S. LaCroce, C. Lambert, K. Menard, and A. Cutler, J. Amer. Chem. Soc., in press.

7 T. Bodnar, S.J. LaCroce, and A.R. Cutler, J. Amer. Chem. Soc., 102 (1980) 3292.

8 (a) C. Chow, D.L. Miles, R. Bau, and T.C. Flood, J. Amer. Chem. Soc., 100 (1978) 7271; (b) D.L. Reger and C.J. Coleman, Inorg. Chem., 18 (1979) 3155.

9 R.B. King and M. Bisnette, J. Organometal. Chem., 2 (1964) 15.

10 M. Brookhart, M.B. Humphrey, H.J. Kratzer, and G.O. Nelson, J. Amer. Chem. Soc., 102 (1980) 7802.

11 (a) R.C. Kerber, W.P. Geiring, T. Bauch, P. Waterman, and E. Chow, J. Organometal. Chem., 120 (1976) C31; (b) M. Laing, J.R. Moss, and J. Johnson, J. Chem. Soc., Chem. Commun., (1977) 656; A. Davison and J.P. Solar, J. Organometal. Chem., 155 (1978) C8; N.Y. Kolobova, W. Skripkin, G.G. Alexandrov, and Y.T. Struchkov, ibid., 169 (1979) 293.

12 A.R. Cutler, J. Amer. Chem. Soc., 101 (1979) 604.

13 A. Cutler, S. Raghu, and M. Rosenblum, J. Organometal. Chem., 77 (1974) 381.

14 A. Cutler, R.W. Fish, W.P. Giering, and M. Rosenblum, J. Amer. Chem. Soc., 94 (1972) 4354.

15 A. Sander, T. Bauch, C.V. Magatti, C. Lorenc, and W.P. Giering, J. Organometal. Chem., 107 (1976) 359.

16 M. Brookhart, J.R. Tucker, and G.R. Husk, J. Amer. Chem. Soc., 103 (1981) 979.