Journal of Organometallic Chemistry, 190 (1980) C39—C42

Preliminary communication

SYNTHESIS, CRYSTAL STRUCTURE AND REACTIVITIES OF THE FIRST η^4-VINYLKETENIMINE METAL COMPLEXES

TAKE-AKI MITSUDO*, HIROYOSHI WATANABE, YUKIATSU KOMIYA, YOSHIHISA WATANABE, YOSHINOBU TAKAEGAMI,
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku Kyoto 606 (Japan)
KAZUMI NAKATSU*, KENJI KINOSHITA and YOSHIKI MIYAGAWA
Faculty of Science, Kwansei Gakuin University, Uegahara, Nishinomiya, Hyogo 662 (Japan)

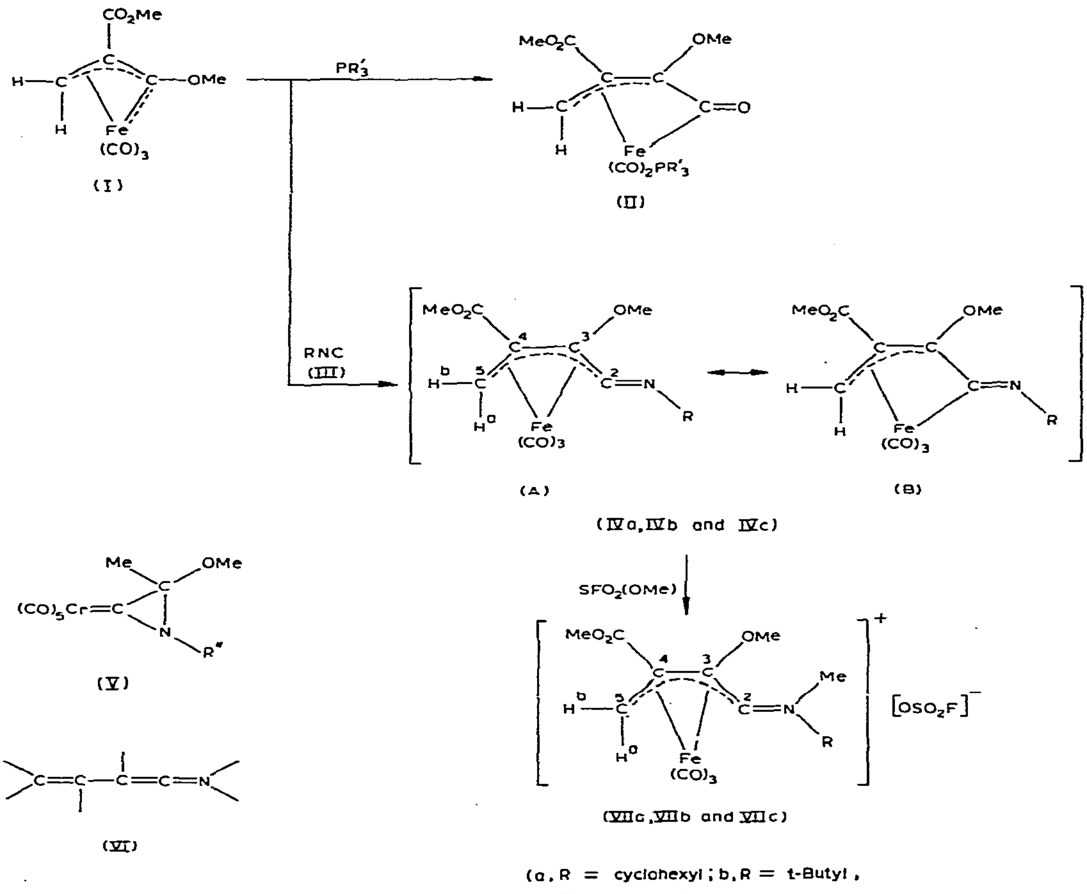
(Received January 4th, 1980)

Summary

The first examples of η^4-vinylketenimine metal complex (IV) were prepared by the reaction of (η^3-vinylcarbene)tricarbonyliron with isonitriles. The molecular structure of IV was determined by an X-ray diffraction study. Methylation of IV gave novel η^4-vinylketeniminium metal complexes.

Much attention has been devoted to the stabilization of unstable organic intermediates such as carbenes, cyclobutadiene, trimethylenemethane or benzyne on transition metal complexes and the chemistry of these complexes has shown great development for the last decade [1]. Recently, the first η^3-vinylcarbene metal complex (I), in which the adjacent olefin and the carbene are coordinated to one iron atom, has been prepared [2]. A novel mode of linkage between the three-carbon ligand and the iron atom was revealed by an X-ray analysis [3]. The reaction of I with tertiary phosphines led to the formation of (η^4-vinylketen)iron complexes (II) by the coordination of the phosphine to the iron atom, thus inducing the insertion of a carbonyl group into the carbene carbon—iron bond (Scheme 1) [4]. In this communication we report the synthesis, molecular structure and alkylation reaction of the first (η^4-vinylketenimine)iron complexes.

η^3-{(1-Methoxycarbonylvinyl)methoxycarbene}tricarbonyliron (I) reacted with 1 molar equiv. of an isonitrile (IIIa, IIIb and IIIc) in methylene dichloride at room temperature under an argon atmosphere to afford orange-yellow crystals of 1/1 adducts (IVa, IVb and IVc) in 61, 44 and 38% yields, respectively. The following spectral data represented by those of IVa showed that IVa—IVc are (η^4-vinylketenimine)tricarbonyliron complexes (Scheme 1). The infrared spectrum of IVa (KBr) showed three bands of terminal ν(C≡O) at 2070, 1995



SCHEME 1

and 1969 cm^{-1} and ν(C=N) at 1690 cm^{-1}, as well as ν(C=O) of the ester at 1714 cm^{-1}. The ^1H NMR spectrum (100 MHz in $CDCl_3$) exhibited resonances at δ 0.48 (d, *J* 2.4 Hz, H^a), 1.25—1.97 (m (br), 10H, methylene of cyclohexyl), 2.50 (d, *J* 2.4 Hz, H^b), 3.19 (m, 1H, methine of cyclohexyl), 3.75 (s, 3H, OMe) and 3.89 (s, 3H, CO_2Me) ppm. The ^{13}C NMR spectrum (25.05 MHz, in $CDCl_3$, Me_4Si as int. standard, at −34°C) showed four peaks at δ 30.2 (dd, *J* 168.0, 162.1 Hz, C^5), 85.1 (s, C^4), 112.1 (s, C^3) and 185.3 (s, C^2) ppm. Anal. Found C, 50.9; H, 5.1; N, 3.7. $C_{16}H_{19}O_6NFe$ calcd.: C, 50.95; H, 5.08; N, 3.71%. Mol. wt: Found 350 (cryoscopic in benzene), calcd. 377.2.

To elucidate the molecular structure of the vinylketenimine complex a full single-crystal X-ray diffraction study of IVa was performed. Crystal data: $FeC_{16}H_{19}O_6N$ (IVa: triclinic, space group $P\bar{1}$; *a* 10.090(2), *b* 10.596(1), *c* 8.621(1) Å, α 92.63(2), β 99.06(1), γ 89.91(2)°; $Z = 2$, D_x 1.378 g cm^{-3}; 2253 Non-zero independent reflections (Mo-K_α radiation) were measured and the structure was solved and refined by the standard heavy atom procedures to a final *R* value of 6.6%. The results of the X-ray study, shown in Fig. 1 demonstrate that the structure of IV is intermediate between A and B (Scheme 1).

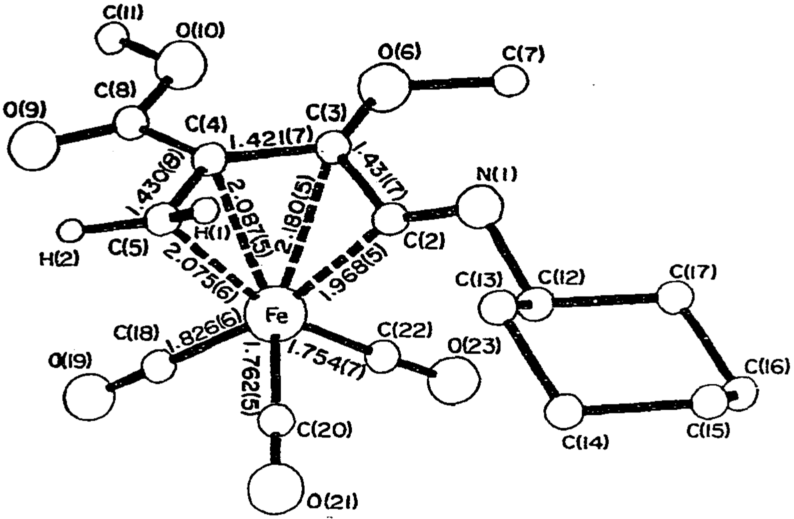


Fig. 1. Molecular structure of $Fe(C_{13}H_{19}O_3N)(CO)_3$ (IVa).

The almost equal bond lengths of C(2)—C(3), C(3)—C(4), and C(4)—C(5) imply the delocalization of the $p\pi$-electrons over the four carbon atoms (structure A) as found in (butadiene)$(CO)_3Fe^0$ *. However, the short Fe—C(2) bond [1.968(5) Å] and the nonplanarity of the C(2)—C(3)—C(4)—C(5) moiety suggest the contribution of the structure B (η^3-allyl + η^1-C=N) as found in the complex (II) [4]. The N(1)=C(2) length of 1.264(6) Å and the N(1)—C(2)—C(3) angle of 133.4(4)° show the characteristic structure of the (η^4-vinylketenimine)iron complex. The cyclohexyl group and the C(3) atom are in the *trans* position about the N(1)=C(2) bond, probably because of the steric repulsion by the cyclohexyl group.

The present reaction is considerably different from that of I with tertiary phosphines [4]. In the former reaction insertion of the isonitriles into the carbene carbon—iron bond (or coupling of the isonitriles with the carbene carbon) occurs (Scheme 1). However, the formation of (η^4-vinylketene)$(CO)_2$-(RNC)Fe derived by the insertion of a carbonyl group could not be detected. The present results are also different from that in the reaction of (methoxymethylcarbene)pentacarbonylchromium with isonitriles affording an unusual complex (V) [5]. Although several ketenimine [6] and vinylketene [4,7] complexes are known, no η^4-vinylketenimine complexes have been reported so far. The complexes IVa—IVc are the first examples in which a probably unstable vinylketenimine (VI) is stabilized by complex formation.

The reaction of IVa, IVb and IVc with $SFO_2(OMe)$ in methylene dichloride at 25°C afforded yellow crystals of the *N*-methylated complexes, VIIa, VIIb

---

*The corresponding lengths in (butadiene)$(CO)_3Fe^0$ complex (1.45—1.46 Å) are somewhat longer than those in (IVa) [8].

and VIIc, respectively in good yields. On the basis of spectroscopic data*, (VIIa-VIIc) were tentatively assigned to be novel (η^4-vinylketeniminium)tricarbonyliron(1+) fluorosulfonates (Scheme).

Further studies on reactivities of these novel complexes are in progress.

Acknowledgement

This work is supported in part by The Kawakami Foundation and the Ministry of Education (No. 465273).

References

1 For example, R.F. Heck, Organotransition Metal Chemistry, Academic Press, New York, 1974, and ref. cited therein.

2 T. Mitsudo, Y. Watanabe, H. Nakanishi, I. Morishima, T. Inubushi and Y. Takegami, J. Chem. Soc. Chem. Commun., (1976) 146; J. Chem. Soc. Dalton, (1978) 1298.

3 K. Nakatsu, T. Mitsudo, H. Nakanishi, Y. Watanabe and Y. Takegami, Chem. Lett., (1977) 1447.

4 T. Mitsudo, T. Sasaki, Y. Watanabe, T. Takegami, S. Nishigaki and K. Nakatsu, J. Chem. Soc. Chem. Commun., (1978) 252.

5 R. Aumann and E.O. Fischer, Chem. Ber., 101 (1968) 954.

6 J.K.P. Ariyaratne and M.L.H. Green, J. Chem. Soc., (1963) 2676; S. Otsuka, A. Nakamura and T. Yoshida, J. Organometal. Chem., 7 (1967) 339; D.J. Yarrow, J.A. Ibers, Y. Tatsuno and S. Otsuka, J. Amer. Chem. Soc., 95 (1973) 8590.

7 R.B. King, Inorg. Chem., 3 (1963) 642; A.E. Hill and H.M.R. Hoffmann, J. Chem. Soc. Chem. Commun., (1972) 574; P. Binger, B. Çetinkaya and C. Krueger, J. Organometal. Chem., 159 (1978) 63; G. Dettlaf, U. Behrens and E. Weiss, Chem. Ber., 111 (1978) 3019; M.G. Newton, N.S. Pantaleo, R.B. King and C.K. Chu, J. Chem. Soc. Chem. Commun., (1979) 10.

8 O.S. Mills and G. Robinson, Proc. Chem. Soc., (1960) 421.

---

*VIIa: Yield 58%, m.p. 122°C. Anal. Found: C, 41.30; H, 4.50; N, 2.92. $C_{17}H_{22}O_9NSFFe$ calcd.: C, 41.56; H, 4.51; N, 2.85%. The characteristic spectral data for VIIa are: IR (KBr) 2107, 2078, 2050, 2045 ν(C≡O), 1720 ν(C=O), 1647 ν(C=N) cm^{-1}. ^1H NMR (100 MHz, CD_2Cl_2) δ 1.74(d, J 3.0 Hz, H^a), 3.35(d, J 3.0 Hz, H^b), 3.53(s, 3H, NMe), 3.69(s, 3H, OMe), 3.96(s, 3H, CO_2Me) ppm. ^{13}C NMR (25.05 MHz, Me_4Si, CD_2Cl_2) δ 38.1(dd, J 173.8, 164.1, C^5), 45.0(qd, J 144.5, J(CNCH) 3.9 Hz, NMe), 101.7(s, C^4), 119.8(s, C^3), 203.7(s, br, FeC≡O), 218.2(s, C^2) ppm. Satisfactory analytical and spectral data are also obtained for VIIb and VIIc.