Tetrahedron Letters,Vol.26,No.30,pp 3605-3608,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

PROTONATION OF (2-FORMYLNORBORNADIENE)CYCLOPENTADIENYLRHODIUM. FIRST EXAMPLE OF DIRECT TRANSITION METAL PARTICIPATION IN STABILIZING OF α-CARBOCATIONIC CENTRE IN O-PROTONATED ACYL-SUBSTITUTED π-COMPLEXES

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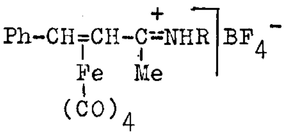
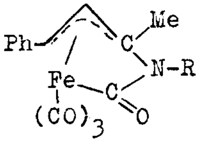
Summary: Cationic hydroxyallylolefin π-complexes 10a,b whose stabilization of the α-carbocationic centre is achieved with simultaneous participation of both rhodium and oxygen atoms were prepared from the reaction of HCl or F_2POOH with aldehyde 8 in ether.

It is known that the heteroatom adjacent to α-C^+ centre in organometallic α-carbocations can stabilize this centre competing in this respect with the metal atom in the rest of the molecular fragment[1]. The metal participation may occur as follows: by electron release from the metal to carbocationic centre via the coordinated ligand (conjugative stabilization), or by direct metal-C_α^+ interection (neighboring metal participation). Which of the mechanism will predominate depends on the resonance-stabilizing effect of the heteroatom-containing substituents at C_α^+. In the π-olefin iron carbonyl complexes two extreme structures 1 and 2 are fixed[1b], each corresponding to one of the above mentioned α-C^+ stabilization mechanisms. In the most of the other cationic π-complexes (for example compounds 3-5) the stabilization of the cationic centre occurs as a rule without the direct participation of a metal by a σ,π-conjugation mechanism.



$$\left[\begin{array}{l}\mathrm{Ph{-}CH{=}CH{-}\overset{+}{C}{=}NHR}\\ \qquad\ \ \mathrm{Fe}\qquad \mathrm{Me}\\ \qquad\mathrm{(CO)_4}\end{array}\right]\mathrm{BF_4^-}$$

1 R=Alk



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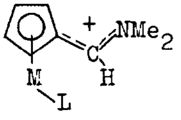
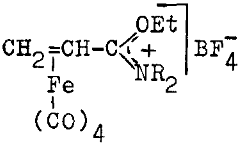


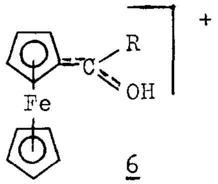
3[2] M=Fe,L=C_5H_5
4[3] M=Cr^-,L=$(CO)_3$



$$\left[\begin{array}{l}\mathrm{CH_2{=}CH{-}\overset{+}{C}\genfrac{}{}{0pt}{}{OEt}{NR_2}}\\ \qquad\mathrm{Fe}\\ \qquad\mathrm{(CO)_4}\end{array}\right]\mathrm{BF_4^-}$$

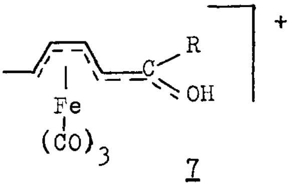
5[4] R=H,Alk

The same α-C^+ stabilization mechanism is also considered for hydroxycarbocations 6[5] and 7[1a], which are formed by protonation of the corresponding acyl-derivatives with strong protonic acids. However, this mechanism is not the only possible one in organometallic cations of the related type; the stabilization of the α-C$^+$ within one complex can be achieved by the direct participation of both the heteroatom and the transition metal atom simultaneously.



6

R=Alk



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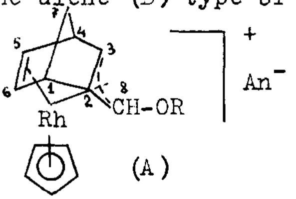
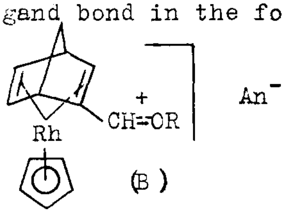
Earlier, we prepared stable O-alkylated products 9a-c from the reaction of (2-formylnorbornadiene)cyclopentadienylrhodium 8 with aliphatic alcohols in the presence of strong acids[6]. The X-ray analysis of one of these (9a, R=Me, An=PF$_6$) has revealed not only the presence of direct Rh-C(8) bond (2.39 Å) but also has shown an appreciable involvement of the oxygen atom of the methoxy group in stabilizing the neighboring cationic centre (C(8)-O bond length is equal to 1.36 Å; C(3)C(2)C(8)O = 170 °). These data were interpreted from the position of the realizing allylolefin (A) but not from the position of the diene (B) type of the metal-ligand bond in the following complexes[6].



(A)



(B)

(9a-c) a,b R=Me,Et, An=PF$_6$
c R=Et, An=BF$_4$
(10a,b) a R=H, An=Cl; b R=H, An=F$_2$POO

In this work we succeded in isolating O-protonated cationic complexes 10a,b as crystalline salts[7] from the direct protonation of aldehyde 8 with HCl or F$_2$POOH in ether. The IR, ^{1}H and ^{13}C NMR spectra of 10a,b confirm that the protonation site is the carbonyl oxygen atom. These data are also in accordance with only the (A)-type structure for these complexes while it is known that the resonance-stabilizing effect of the OH-group is enormously large and significantly higher than that of the AlkO-groups (see discussion in[1a]).

The IR spectra of complexes 10a,b in nujol mull differ markedly from those of initial aldehyde 8 in that they do not show $\nu_{C=O}$ band which was present in the spectrum of 8 at 1658 cm^{-1}. New intensive bands appear instead at 1557 (10a) and 1575 (10b) cm^{-1} along with a broad absorption in the region of 2100-2800 cm^{-1}. The latter bands are assigned to the stretching vibration of H-bonded OH-groups[8]. The presence of analogous intensive IR bands in the region of 1550-1600 cm^{-1} for O-protonated acylferrocenes was related with the decrease in the carbon-oxygen bond order[9]. However, we observe in the IR spectrum of the cation 10a enriched with 75% ^{18}O-isotope no isotopic shift of band at 1557 cm^{-1} while the corresponding shift of $\nu_{C=O}$ for the ^{18}O-8 (see [6] for preparation) was 30 cm^{-1}. With this in mind we assign the observed IR bands of the complexes 10a,b at 1557 and 1575 cm^{-1} respectively to a mixed stretching vibration of the oxoallylic fragment $C_3{\cdots}C_2{\cdots}C_8{\cdots}O$. The absence in the IR spectrum of 10a of bands corresponding to $[HCl_2]^-$ complex anion[10] rules out an alternative dimeric structure of 10a with a bridged hydrogen atom.

^{1}H NMR spectra of complexes 10a,b as compered with those of aldehyde 8[11] exhibit signals which are noticeably shifted downfield (with the exception of the H(8) signal). This is typical when a positive charge appears in the norbornadiene π-complexes[12]. The signal of H(8) is shifted upfield on passing from 8 to 10a,b which is consistent with a decrease in the anisotropic effect of the protonated carbonyl group[13]. The ^{1}H NMR spectra of 10a,b also revealed single broadened signals at 11-12 ppm which are assigned to the OH-group protons of these complexes[14]. The structure of F_2POO-anion in complex 10b is confirmed by the ^{19}F and ^{31}P NMR spectra[15].

Analysis of ^{13}C NMR spectra of complexes 8-10a,b (see Table) show that the chemical shift and the coupling constants $J_{103(Rh)-13(C)}$ of the carbon signals in the spectra of 10a,b are practically identical to those of cation 9a whose structure was discussed above. Also typically, the carbon signal C(8) in the ^{13}C NMR spectra is strongly shielded ($\Delta\delta$~30-50 ppm) on passing from aldehyde 8 to cations 9a or 10a,b. The upfield shift of the α-carbon signal is seen in the ^{13}C NMR spectra on passing from π-olefin complexes $(CO)_4Fe(\eta^2\text{-}RCH{=}CHMe{=}NR^1)$ 11 to cyclic allylic analog 2[16] and at the same time this signal is deshielded[17] in the spectra of cations 1 where there is no direct Fe-C^+_α interection.

Table. ^{13}C NMR spectra of complexes 8-10a,b in CH_2Cl_2

Compounds	Chemical shift, δ (ppm)/$J_{103(Rh)-13(C)}$ in Hz									
	C1(4)	C2	C3	C4(1)	C5(6)	C6(5)	C7	C8	R	C_5H_5
8	42.0	47.9	30.7	47.2	32.7	34.3	55.0	188.2	-	85.2
	2.2	9.8	11.0	2.2	10.6	10.6	5.2	3.0		4.4
9a	39.5	63.1	32.3	47.0	43.8	47.6	54.4	132.0.	14.9	89.4
	s.	4.5	10.5	s.	7.4	7.4	2.2	3.0	s.	4.5
10a	39.3	62.7	32.0	46.6	39.6	43.5	53.4	142.0	-	89.1
	s.	5.6	11.0	s.	8.1	9.3	2.9	s.br.		4.4
10b	39.8	60.1	31.6	46.8	39.4	43.0	53.6	149.0	-	88.8
	s.	5.7	10.7	s.	8.0	8.3	2.6	s.br.		4.6

Thus, IR, ^{1}H and ^{13}C NMR spectra confirm the realization of the allyl-olefin type of the metal-ligand bond in the cations 10a,b which can be regarded as organometallic hydroxycarbocations additionally stabilized by direct interection of the metal-C^+_α.

References and Notes

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7. 10a: (Anal. Calcd.: C, 48.16; H, 4.39; Rh, 31.29%. Found: C, 48.00; H, 4.31; Rh, 31.69), m.p. 103° (without dec.): 10b: (Anal. Calcd.: C, 40.00; H, 3.59; P, 7.95%. Found: C, 39.78; H, 3.44; P, 8.23%)
8. The IR spectra of 10a,b in the region of $\nu_{C=O}$ and ν_{OH} are close to those of 6, where the intramolecular H-bond of OH···Fe-type is considered to be present[9]. In our opinion, in complexes 10a,b the interionic H-bond of the OH···An-type is realized.
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11. (CD_2Cl_2, TMS); 8: δ 8.68(s,1,H_8), 5.23(d,5,J^*=0.8,C_5H_5), 3.80(m,1,H_1), 3.68 (m,1,H_6), 3.53(m,1,H_5), 3.46(m,2,$H_{3,4}$), 1.17(d,1,J_{AB}=10.0,H_{7A}), 1.02 (d,1, J_{AB}=10.0,H_{7B}); 10a: δ 11.0(s.br.,1,OH), 7.88(s,1,H_8), 5.64 (d,5,J^*=0.9,C_5H_5), 4.12(m,2,$H_{5,6}$), 3.82(m,1,H_1), 3.67(m,1,H_3), 3.61(m,1,H_4), 1.53 (d,1,J_{AB}=10, H_{7A}), 1.36(d.t.,1,J_{AB}=10,J_t=1.8,H_{7B}); 10b: δ 12.2(s.br.,1,OH), 7.85(s,1, H_8), 5.56(d,5,J^*=0.8,C_5H_5), 4.14(m,2,$H_{5,6}$), 3.83(m,1,H_1), 3.63(m,2,$H_{3,4}$), 1.55(d,1,J_{AB}=10,H_{7A}), 1.36(d.t.,1,J_{AB}=10,J_t=1.6,H_{7B}). $J^*=J_{^{103}Rh-^{1}H}$ (Hz).
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13. M.Brookhart, G.C.Levy and S.Winstein, J. Am. Chem. Soc., 89, 1735 (1967)
14. The signals observed in ^1H NMR spectra of 10a,b at 11.0 and 12.2 ppm disappear upon D_2O addition.
15. (CD_2Cl_2, CF_3COOH); $\delta_{^{19}F}$=+5.57(d,J_{P-F}=960Hz); (CD_2Cl_2, H_3PO_4): $\delta_{^{31}P}$= =-16.9(t,J_{P-F}=956Hz).
16. A.N.Nesmeyanov, L.V.Rybin, N.A.Stelzer and M.I.Rybinskaya, J. Organometal. Chem., 182, 393 (1979)
17. The C_{α}-signal in the ^{13}C NMR spectra of 11 (R=H, R^1=i-Pr) is observed at 146 ppm whereas in spectra of 1 (R=H,Alk) at 186-188 ppm. The authors are grateful to Prof. M.I.Rybinskaya, Dr. L.V.Rybin and N.A.Stelzer for supplying us with these data.

(Received in UK 3 April 1985)