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Preliminary communication

STABILIZATION OF A CARBODICATION BY A TETRAHEDRAL MOLYBDENUM-CARBON CLUSTER

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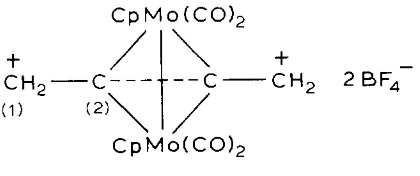
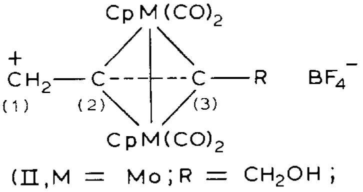
Summary

The reaction of $Cp_2Mo_2(CO)_4$-μ-$(HOCH_2C{\equiv}CCH_2OH)$ with HBF_4 gives the monocation $[Cp_2Mo_2(CO)_4(CH_2CCH_2OH)]^+$ which can be isolated as its fluoroborate salt, which in FSO_3H or CF_3COOH (TFA) solution forms the dication $[Cp_2Mo_2(CO)_4(CH_2C{\equiv}CCH_2)]^{2+}$. Treatment of the monocation solution in TFA by $(CF_3CO)_2O$ followed by addition of aqueous HBF_4 and ether yielded the stable crystalline fluoroborate. ^1H and ^{13}C NMR spectra of the mono- and dications in various solvents were investigated.

Metal-carbon clusters such as Co_3C [1] and Co_2C_2 [2] have been demonstrated to be useful for stabilisation of adjacent carbocationic centres. Recently, we have observed that tetrahedral clusters Mo_2C_2 and W_2C_2 containing both carbonyl and Cp ligands are still more effective in this respect [3]. In the present paper we report some preliminary results on the synthesis of the simplest bis-primary dication of series I in which the Mo_2C_2 cluster takes part in stabilization of two adjacent carbocationic centres [4].



(I)



(II, M = Mo; R = CH_2OH;
III, M = Mo; R = H;
IV, M = Mo; R = CH_3;
V, M = W; R = CH_2OH)

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The adduct of butyn-2-diol-1,4 and $Cp_2Mo_2(CO)_4$ (VI) obtained with 80% yield was chosen as a starting compound for the synthesis of the salt I. ^1H NMR (acetone-d_6): δ 4.30 (t, OH), 4.86 (d, CH_2), 5.40 (s, Cp) ppm. The adduct was

$$Cp_2Mo_2(CO)_4 + HOCH_2C{\equiv}CCH_2OH \rightarrow \underset{(VI)}{Cp_2Mo_2(CO)_4\text{-}\mu\text{-}(HOCH_2C{\equiv}CCH_2OH)}$$

converted to the monocation II by treatment of VI in CH_2Cl_2 with ethereal solution of aqueous HBF_4 in 93% yield.

^1H and ^{13}C NMR spectral data are collected in Tables 1 and 2. As in other related monocations the non-equivalence of protons at C(1) is observed in II, $^2J(HH)$ being close to zero. The assignment of signals in the $^{13}C\{^1H\}$ spectrum was based on the proton-coupled ^{13}C spectrum and on comparison with spectra of related monocations III and IV. Two signals corresponding to Cp ligands occur due to stereochemical non-rigidity of these cations [5].

TABLE 1

^1H CHEMICAL SHIFTS FOR MONO- AND DI-CATIONS[a]

Cation	Solvent	CH_2	Cp	Others
II	CD_3CN	5.63s, 4.56s	5.63bs[b]	4.81, 4.79 (CH_2)
III	CD_3CN	5.34d, 4.68s	5.64, 5.57bs	6.49d (H—C≡)
IV	CD_3CN	5.48s, 4.69s	5.60s	2.78s (Me)
II	FSO_3H	6.50d, 4.98d	6.00s	
II	TFA	6.68d, 5.18d	6.27s	
III	TFA	5.42d, 4.70s	5.63, 5.57bs	6.24d (H—C≡)
IV	TFA	5.50s, 4.70s	5.57s	
V	TFA	7.68d, 5.12d	6.27s	
V	FSO_3H	7.53d, 4.93d	6.02s	
I	FSO_3H	6.50d, 4.98d	6.00s	
I	TFA	6.67d, 5.17d	6.25s	
I	CD_3CN	6.52d, 5.02d	6.10s	

[a] 60 MHz, 27°C; internal standards: TMS in CD_3CN and CF_3COOH, Me_4NBF_4 in FSO_3H (its chemical shift was taken to be 3.10 rel. to TMS). [b] Broad signal.

TABLE 2

^{13}C CHEMICAL SHIFTS FOR MONO- AND DI-CATIONS[a]

Cation	Solvent	C(1)	C(2)	C(3)	Cp	Others and CO
II	CD_3CN	76.16	126.66	94.74	92.14 93.32	67.04 (CH_2OH); 226.65 224.85 221.65 218.40
III	CD_3CN	75.38[b]	118.52[c]	79.99	94.74 94.94[d]	227.71 227.06 220.38 217.65
III	TFA	75.58	120.50	79.60	93.93 95.25	
IV	CD_3CN	73.05	124.30	97.48	93.59 94.48	24.06 (Me); 227.00 224.47 221.59 219.15
II	TFA	79.99[e]	133.32		93.98[f]	215.42 206.11
I	CD_3CN	79.82[g]	131.8		93.16	215.05 206.79

[a] 25.05 MHz, FX-100, 26°C, chemical shifts rel. to TMS. [b] $^1J(CH)$ 164 and 169 Hz. [c] C(2) signal superimposes upon the solvent. [d] $^1J(CH)$ 183 Hz. [e] $^1J(CH)$ 170 and 175 Hz. [f] $^1J(CH)$ 188 Hz. [g] In view of a low stability of I in this solvent $^1J(CH)$ coupling constants are less reliable: 169 and 173 Hz (CH_2), 188 Hz (Cp).

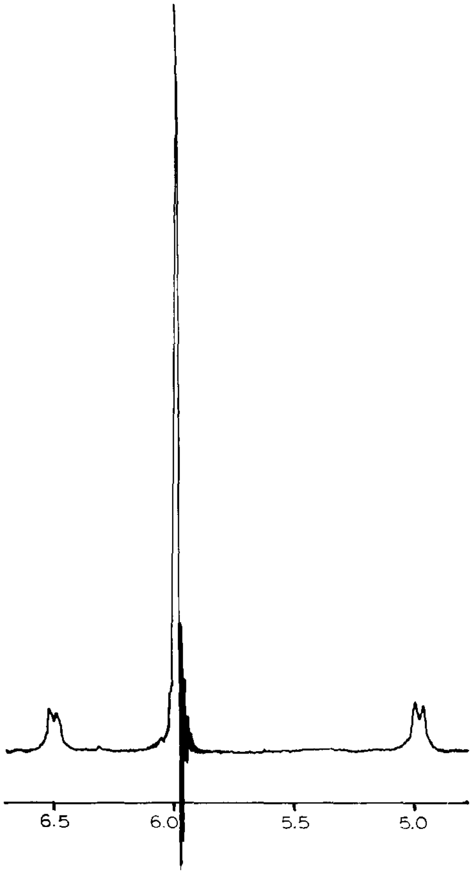

Fig. 1. ${}^1H$ NMR spectra of the monocation II in FSO_3H.

A dramatic change of ${}^1H$ and ${}^{13}C$ NMR spectral patterns was observed when the spectra were recorded in FSO_3H or TFA. In the ${}^1H$ spectrum (Fig. 1, Table 1) protons of the acetylenic ligand are observed as two doublets of equal intensity, $J(HH)$ 1.8 Hz, characteristic for an AX spin system, the singlet being assigned to the Cp protons. Decrease of the number of signals in the spectra provides evidence for increase of overall symmetry of the species that can be reasonably accounted for by transformation of cation II into dication VII.

$$[Cp_2Mo_2(CO)_4(CH_2C{\equiv}CCH_2O)]^+ \xrightarrow[TFA]{FSO_3H\ or} [Cp_2Mo_2(CO)_4(CH_2C{\equiv}CCH_2)]^{2+}$$

(VII)

In general the methylene protons splitting pattern should correspond to an AA'XX'-type spin system. However, in our case all long-range coupling constants are too small (${}^5J(HH) < 0.5$ Hz), therefore only geminal couplings determines the observed splitting. The situation resembles that found for the allene complex $Cp_2Mo_2(CO)_4$-μ-allene [6]. ${}^{13}C$ NMR spectra provide an additional support for the symmetrical structure of the dication VII. The ${}^{13}C\{{}^1H\}$ spectrum of the dication VII (formed in TFA solution of the cation II, see Table 2) exhibits one signal for Cp, two signals for coordinated acetylene and two signals for carbonyls in agreement with C_2 symmetry of the dication VII. The signals for the acetylene ligand were assigned on the basis of the proton-coupled ^{13}C spectrum. Non-equivalence of methylene protons gives rise to two different ^1J(CH) coupling constants 6 Hz higher compared to the parent monocation III. It is noteworthy that ^1J(CH) of Cp ligands increases by 5 Hz on going from II or III to VII. The C(1) signal of the dication VII is slightly shifted downfield with respect to the corresponding signals in monocations II—IV. Greater deshielding was observed in similar monocation—dication pairs of ferrocene systems [7].

The dication VII is formed on solvation of the diol VI in TFA, while the ferrocenyl dication $(Me_2C^+C_5H_4)_2Fe$ (VIII) requires FSO_3H [7]. Moreover, the latter species is only stable at low temperature while dication VII can be prepared as a crystalline fluoroborate. Salt I was obtained by stepwise treatment of cation II in TFA with $(CF_3CO)_2O$, aqueous HBF_4, cooling and addition of dry ether as an extremely moisture sensitive orange crystalline solid. The product is soluble in TFA, but less soluble in acetonitrile.

^{1}H NMR spectra of salt I in TFA and FSO_3H are identical to those of cation II in the same solvents, which unambiguously testifies for the identical nature of the species involved. The spectrum in acetonitrile-d_3 (Fig. 2) resembles that of cation II in FSO_3H (Fig. 1). The signal at 5.63 ppm arises due to the transient nature of salt I in this solvent. In the $^{13}C\{^1H\}$ NMR spectra of salt I (Table

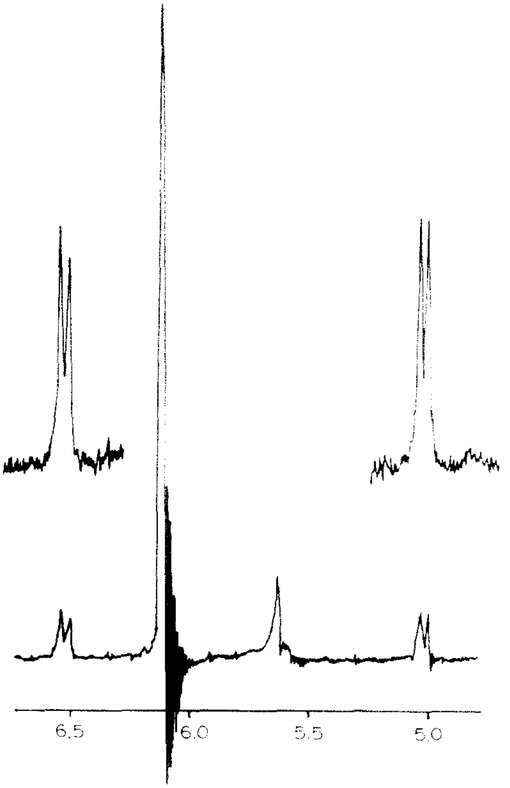

Fig. 2. ^{1}H NMR spectra of the salt I in acetonitrile-d_3.

2) chemical shifts of C(1), C(2) and carbonyl ligands are close to the corresponding values measured for cation II in TFA.

Hydrolysis of salt I yields the initial diol VI, while reduction by means of $NaBH_4$ in acetonitrile results in the dimethylacetylenic adduct $Cp_2Mo_2(CO)_4$-μ-(MeC≡CMe) which is identical to the adduct of dimethylacetylene and $Cp_2Mo_2(CO)_4$ [5]. We are now engaged in studying bis-tertiary and bis-secondary dications as well as dications with different cationic centres.

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