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Preliminary communication

METALLOCENYL CATIONS

I. STABLE MANGANESE-STABILISED CARBONIUM IONS

A.G. GINZBURG, V.N. SETKINA and D.N. KURSANOV

Institute of Organo-Element Compounds, Academy of Sciences, Moscow V-312, Vavilova 28 (U.S.S.R.)

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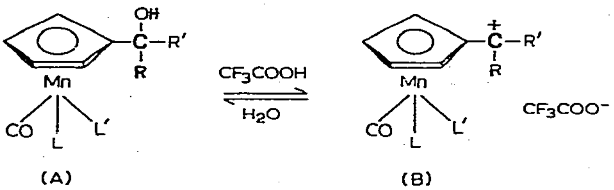
Summary

Stable α-cymantrenylcarbonium ions have been identified by solution IR spectroscopy. The substitution of tert-phosphine for CO markedly stabilises the carbonium ions.

The unusual stability of ferrocenylcarbonium ions is well known [1,2]. Stable carbonium ions whose α-carbonium centre is stabilised with cyclobutadieneiron tricarbonyl [3,4], benzenechromium tricarbonyl [5] or cobalt cluster groups [6,7] have also been reported. Stabilisation involving other transition metals has been studied rather less. α-Cymantrenylcarbonium ions have been briefly mentioned by Cais [2], but the synthesis and identification of these ions have never been reported any further, although kinetic [8] and other evidence predicting their stability may be found in many works [9]. The stability of metallocenylcarbonium ions as a function of substitution of the CO ligand has not been studied at all.

We have found that trifluoroacetic acid added to a solution of the tertiary or secondary carbinols (A) in CH_2Cl_2 at room temperature equilibrates the starting carbinols with the respective stable carbonium ions (B).



(Aa) L = L′ = CO;
(Ab) L = CO, L′ = PPh_3, or $P(iso\text{-}C_3H_7)_3$
(Ac) LL′ = $Ph_2P(CH_2)_nPPh_2$, n = 1,2,3

The reaction written above is reversible; treatment of the mixture by water or removal of the solvents allows one to recover the starting carbinols almost quantitatively.

The A/B equilibrium may be easily observed by measuring the shifts in the IR of the CO stretching frequencies associated with the $Mn(CO)_{3-n}L_n$ ($n = 1,2$) sites. The formation of B increases ν(CO) on the average 50 to 90 cm^{-1}. The spectrum contains bands assignable to one or both the species, depending on the carbonium ion stability and acidity of the medium (the CF_3COOH/CH_2Cl_2 ratio, Fig.1, Table 1).

Transformation of neutral complexes to the cations is known to decrease the $d_\pi(Mn)—p_{\pi^*}(CO)$ back-donation and increase ν(CO). When the formal charge on the metal increases by a unity, e.g. in the substitution of NO^+ for CO [10] or in the protonation at the metal [11], ν(CO) becomes at least 100 cm^{-1} higher. This fits well with our IR data.

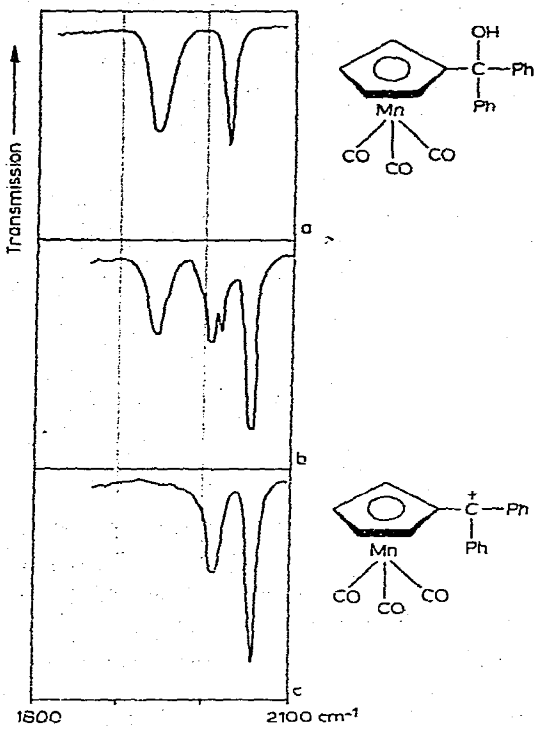


Fig.1. CO stretching frequencies for carbinol V: (a) in CH_2Cl_2; (b) in CF_3COOH/CH_2Cl_2 1/10; (c) in CF_3COOH/CH_2Cl_2 1/4.

The A/B equilibrium is dependent on the ligands L and L', the radicals R and R' attached to the carbonium centre and on acidity of the medium. The effect of R and R' is quite pronounced. The stability of B rises markedly when R equal to H or Me is replaced with phenyl. For compound I, the equilibrium shifted to the carbinol side almost entirely, even when pure CF_3COOH is the solvent. On the other hand, compound V (R = R' = Ph) is ionised completely even when the CF_3COOH/CH_2Cl_2 ratio is 1/4; when it

TABLE 1

IR STRETCHING CARBONYL FREQUENCIES FOR MANGANESE-STABILISED CARBONIUM IONS

No.	Radicals		$Mn(CO)_{3-n}L_n$	(CO) (cm^{-1})			Solvent
	R	R'		Carbinol	Carbonium ions		
I	H	Me	$Mn(CO)_3$	1963	—[a]	—	
				2037	2095	58	CF_3COOH
II	Me	Me	$Mn(CO)_3$	1959	2025	67	CF_3COOH
				2030	2082	52	
III	H	Ph	$Mn(CO)_3$	1948	—[a]	—	[b]
				2031	2080	49	1/2
IV	Me	Ph	$Mn(CO)_3$	1943	2032	91	
				2025	2078	46	1/4
V	Ph	Ph	$Mn(CO)_3$	1950	2005	55	1/10
				2027	2055	28	
VI	Me	Me	$Mn(CO)_2PPh_3$	1867	1960	93	1/50
				1935	2008	75	
VII	Me	Me	$Mn(CO)_2P(iso\text{-}C_3H_7)_3$	1860	1952	98	
				1925	2000	75	1/50
VIII	H	Me	Mn(CO)(P—P) [c]	1832 [d]	1935 [d]	103	1/200 [d]
IX	Me	Me	Mn(CO)(P—P)	1831	1923	92	1/200 [d]
X	H	Ph	Mn(CO)(P—P)	1835	1935	100	1/200 [d]
XI	Me	Ph	Mn(CO)(P—P)	1830	1925	95	1/200 [d]
XII	Ph	Ph	Mn(CO)(P—P)	1825	1910	85	1/200 [d]
				1840 (sh)	1935 (sh)	95	

[a] Degenerate CO band in carbonium ion coincides with symmetrical stretching band in carbinol.

[b] The CF_3COOH/CH_2CI_2 ratios at which both the species are observed in the solution are tabulated.

[c] P—P denotes $Ph_2PCH_2CH_2PPh_2$. [d] Under Nos VIII—XII, the frequencies for carbinols are those obtained in CH_2Cl_2, for carbonium ions in CF_3COOH/CH_2Cl_2 1/200.

is 1/10 concentrations of the carbinol and carbonium species are approximately equal. Increasing the trifluoroacetic acid concentration shifts the equilibrium towards carbonium ion in all cases.

The cations become much more stable when one of the CO groups is substituted with a phosphine ligand. In VI and VII (R = R' = Me), the ionisation is complete at the ratios as small as 1/10 and 1/20. The presence of both the species may be observed only at 1/50 and 1/100 ratios. Consequently, the substitution of CO by a phosphine donor ligand affects the stability much more than does the replacement of radicals attached to the carbonium centre. The effect is especially pronounced when a chelate diphosphine ligand, $Ph_2P(CH_2)_2PPh_2$, or its analogues, is substituted for two CO groups. For the carbinols VIII—XII, the equilibrium lies on the Bc side even when the ratio is 1/200.

The formation of cations B has been confirmed by conductivity measurements. The carbinols A in CH_2Cl_2 are non electrolytes. When CF_3COOH is added the conductivity rises ($C = 1 \times 10^{-3}$ mole/l, $\Lambda_M = 30$—50 ohm^{-1} cm^2 mole^{-1}, consistent with the values for 1/1 electrolytes of the similar structure in CH_2Cl_2). Solutions of the carbinols I and II treated with CF_3COOH do not become electro-conductive since the carbonium ion concentration in these solutions is low.

The carbinol-to-carbonium ion transformation shifts ^{13}C NMR signals of the cyclopentadienyl and carbonium carbons by 10 to 50 ppm downfield. E.g. the α- and β-signals for C_5H_4-carbons in the spectrum of VII are shifted by 17.8 and 10.8 ppm downfield while the equivalence of the α,α′ and β,β′ nuclei is retained. In the ion obtained from IX, all the four cyclopentadienyl carbons become non-equivalent and give four separate signals.

^{31}P NMR spectra of the carbonium ions VIII—XII and containing a $Ph_2PCH_2CH_2PPh_2$ ligand are also of interest. The phosphorus atoms are equivalent in the starting carbinols, and give a broad signal at δ 113 to 114 ppm downfield from an 85% H_3PO_4 external reference. They become non-equivalent in the carbonium ions, the spectrum being a typical AB pattern [$J(^{31}P—^{31}P)$ 26 to 33 Hz, $\Delta\delta(^{31}P)$ 7 to 15 ppm]. Both the signals are shifted to higher fields compared with the starting carbinols. This non-equivalence requires a further study to be undertaken. The ^{13}C NMR spectral analyses and the pK_{R^+} data will be published later.

To sum up, the results obtained here demonstrate that carbonium ions containing a metallocarbonyl site may be identified from ν(CO) infrared data.

IR spectra were recorded on a UR-20 spectrometer in the LiF region in cells with a NaCl window (sample thickness 0.1 mm, carbinol concentration 2×10^{-1} mole/l) and ^{13}C and ^{31}P NMR spectra were obtained on a Brucker HFX-90 instrument at 0 to 30°C. Fourier transform techniques and proton decoupling mode were used.

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