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Stabilisation of carbenium ions species by two different adjacent organometallic moieties: synthesis, NMR study and synthetic application

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Abstract

A series of carbenium ions, stabilized by two different organometallic moieties in the α,α' position e.g.: alkynyl-$Co_2(CO)_6$ and ferrocenyl or alkynyl $Mo_2Cp_2(CO)_4$ and ferrocenyl, have been synthesised. NMR and IR studies of these cations show that the stabilising effects of the transition metal units are specific for each system. This situation implies different structures for the carbenium ions adjacent to two different organometallic moieties.

Introduction

The study of the structure and reactivity of carbenium ions adjacent to a transition metal complex has been the subject of much work, particularly in the series of α-ferrocenylcarbenium ions [1]. The main feature of the systems studied so far has been the presence of a single organometallic fragment, whether this is a metallocene as in the benchrotrene [2] and cymantrene series [3], or an acetylenic cluster of the type $C_2M_2L_6$ (where $M_2L_6 = Co_2(CO)_6$, $Mo_2Cp_2(CO)_4$ (4) or $C_2M_3L_{10}$ (with $M_3L_{10} = Os_3(CO)_{10}$ [5]).

In some cases, however, systems have been studied in which the cationic centre is bonded to two identical organometallic groups which can increase the stabilisation of the carbenium ion [6]. Examples of carbenium ion stabilisation by two different organometallic systems are much more rare, and because of this the determination of the balance of their respective stabilisation abilities is less well defined.

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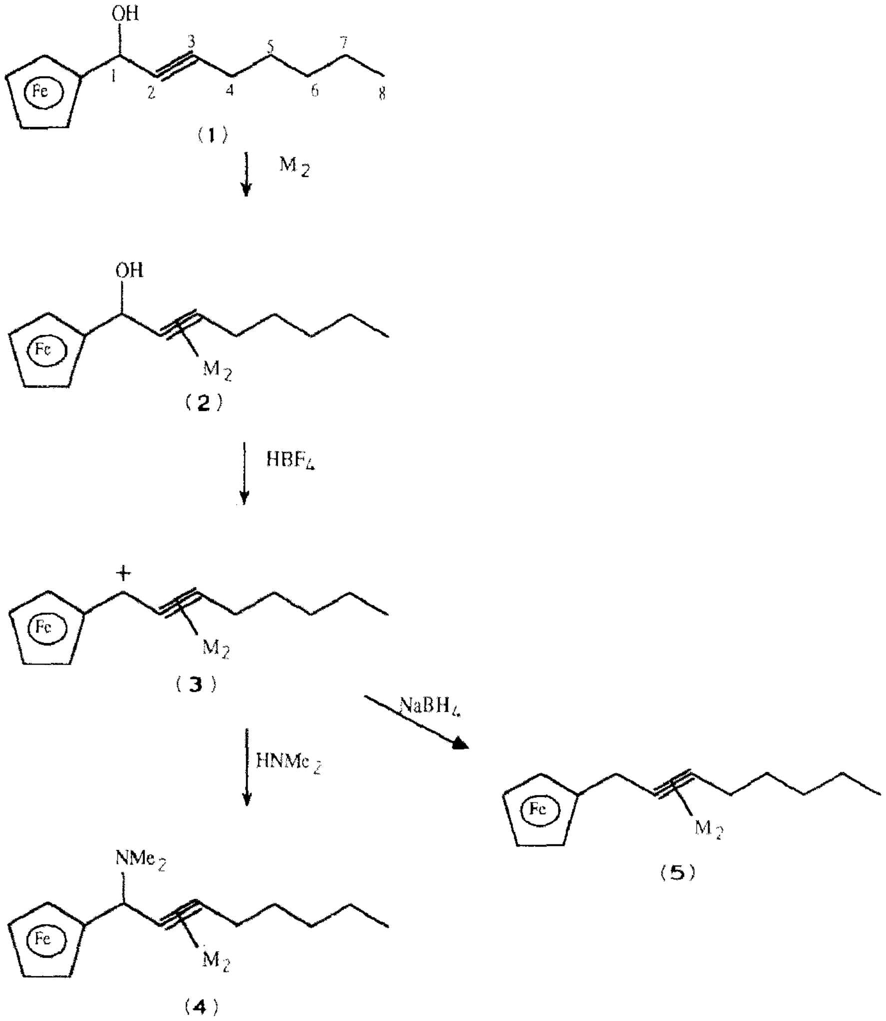
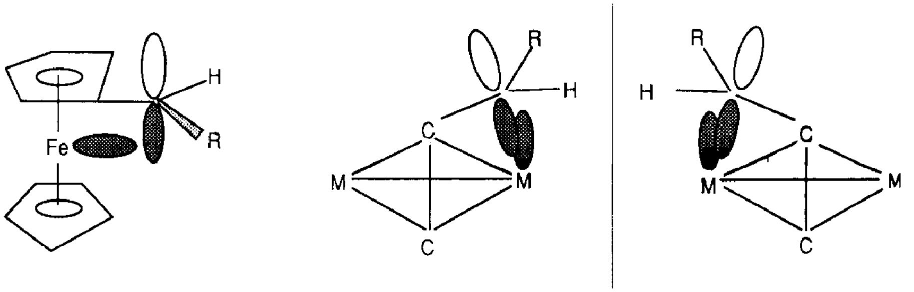


Scheme 1. a: $M_2 = Co_2(CO)_6$; b: $M_2 = Mo_2Cp_2(CO)_4$.

The present work is concerned with the behaviour of cationic centres stabilised by organometallic complexes and evaluation of the stereochemical consequences which result from this mode of stabilisation [7]. It is also related to the synthesis of natural product analogues based on the ferrocene group [8]; a ferrocene-derived molecule **1** which contains a triple bond with a chiral carbon atom α to it has been synthesised, and this enabled us to: (i) introduce a second organometallic group adjacent to the chiral centre in the form of a metallocarbonyl cluster $M_2L_4L'_2$, and (ii) to obtain a carbenium ion **3**, derived from the alcohol intermediate in the synthesis of tertiary amine **4**, necessary for subsequent cyclometallation reaction (Scheme 1).

NMR spectroscopy provides one of the most informative methods for studying carbenium ions [9]. The degree of delocalisation of a positive charge is evaluated from variations of the ^1H and ^{13}C chemical shift relative to the starting materials, and, where possible, from the coupling between the metal atoms and the carbon atom bearing the positive charge [10]. In the system that we have studied there can



Scheme 2.

be stabilisation of the positive charge by the ferrocene group and/or by the C_2M_2 cluster. A priori, the relative participation of these groups can vary according to "M_2". It is known that ferrocenylcarbenium ions of the type Fe^+CHR have a chirality which originates from restricted rotation due to interaction between the iron atom and the positive charge [11]. This chirality also exists, in principle, in carbenium ions adjacent to a cluster, arising from the interaction between the cationic centre and the metal–carbon orbital corresponding to one edge of the M_2C_2 tetrahedron [12] (Scheme 2). However, because of a dynamic exchange process the structure can appear to be virtually achiral in NMR studies.

The study of these stereochemical aspects in the case of the molecules that we have examined is possible because they contain prochiral groups, which makes possible the observation of diastereotopic phenomena by NMR.

Experimental

*Hexacarbonyl-μ-(η-1-ferrocenyloct-2-yn-1-ol)dicobalt(Co–Co) (**2a**)*

To 0.24 g of magnesium (10^{-2} mol), covered with a little dry ether, is added 0.8 ml of bromoethane in 10 ml of ether. The rate of addition is such as to keep the ether refluxing gently. Subsequently 1 ml of heptyne in 8 ml of ether and 4 ml of toluene are added rapidly, the mixture is stirred for 1 h under reflux and 2.1 g of ferrocene aldehyde in 25 ml of ether are then added dropwise still under reflux. A yellow precipitate is formed. The mixture is stirred for 1 h under reflux and then added to crushed ice. After extraction with ether, 3.4 g of hexacarbonyldicobalt is added to the extract under argon, producing vigorous effervescence. When this has subsided the solution is evaporated. The residue is chromatographed on silica plates (ether/pentane 2/8) to give 4 g of a red oil. The yield is 80% based on the ferrocene aldehyde.

^1H NMR (CD_2Cl_2), δ (ppm): 0.98 (3H) t, 1.48 (4H) m, 1.65 (2H) m, 2.57 (1H) d, 2.74 (2H) m, 4.26 to 4.40 (9H), 5.64 (1H) d. ^{13}C NMR $\{^1H\}$ (CD_2Cl_2); δ (ppm): 14.14, 22.90, 31.98, 32.20, 33.94, 64.84, 67.72, 68.50, 68.73, 69.07, 71.28, 94.16, 99.72, 100.00, 200.39. IR KBr disc (cm^{-1}): ν(OH) 3582; ν(CO) 2089, 2050, 2019. Analysis. Found: C, 48.2; H, 3.8. $C_{24}H_{22}Co_2FeO_7$ calcd.: C, 48.3; H, 3.7%.

*Tetracarbonyl(dicyclopentadienyl)-μ-(η-1-ferrocenyloct-2-yn-1-ol)dimolybdenum (Mo–Mo) (**2b**)*

The acetylenic alcohol is prepared in the same way as **2a**. To the ether solution of the alcohol is added 4. g of $Mo_2Cp_2(CO)_4$ [13] in 60 ml of dry THF, and the mixture stirred for 1 h under argon. After evaporation of the solvent the residue is chromatographed on an alumina column, eluted first with an ether/pentane mixture (1/1) and then pure ether. After evaporation of the ether 1.5 g of a reddish-brown solid is obtained.

^1H NMR (acetone-d_6) δ(ppm): 0.9 (3H) t, 1.38 (4H) m, 1.52 (2H) m, 2.85 (2H) m, 3.42 (1H) d, 4.12 (2H) m, 4.16 and 4.30 (2H) m, 4.22 (5H) s, 5.25 (10H) d, 5.49 (1H) d. ^{13}C NMR $\{^1H\}$ (CD_2Cl_2) δ (ppm): 13.74, 22.51, 30.84, 32.06, 37.91, 64.36, 67.27, 67.67, 68.29, 75.33, 91.07, 95.11, 105.89, 229.32, 229.86, 232.20, 232.36. IR KBr disc (cm^{-1}): ν(OH) 3550; ν(CO) 1973.4, 1913.9, 1905.2, 1830.0, 1816.3. Analysis Found: C, 51.8; H, 4.3. $C_{32}H_{32}FeMo_2O_5$ calcd.: C, 51.6; H, 4.3%.

Tetracarbonyl(dicyclopentadienyl)-μ-(η-1-ferrocenylhex-2-yn-1-ol)dimolybdenum (Mo–Mo) (2c)

2c is prepared in the same way as **2b** but from 1-pentyne instead of 1-heptyne.

^1H NMR (acetone) δ(ppm): 1.00 (3H) t, 1.53 (2H) m, 2.82 (2H) m, 3.42 (1H) d, 4.13 (2H) s, 4.16 (1H) s, 4.22 (5H) s, 4.30 (1H) s, 5.23 (10H) d, 5.49 (1H) d.

Hexacarbonyl-μ-(η-1-ferrocenyloct-2-yn-1-ylium)dicobalt (Co–Co) tetrafluoroborate (3a)

To a Schlenk tube containing 1 ml of HBF_4/ether complex under argon is added dropwise a solution of 0.15 g of **2a** in 5 ml of ether. After several minutes the oil initially formed turns to a black precipitate. The supernatant liquid is removed and the precipitate washed six times with dry ether. The solid is then dissolved in the minimum of dichloromethane, and ether is added to the solution just to the onset of precipitation. The solution is set aside in a refrigerator to give 0.12 g of black crystals.

^1H NMR (CD_2Cl_2) δ (ppm): 0.98 (3H) t, 1.6 (4H) m, 1.82 (2H) m, 3.00 (2H) m, 4.92 (5H) s, 5.10 (2H) s, 6.07 (2H) s, 8.78 (1H) s. ^{13}C NMR $\{^1H\}$(CD_2Cl_2) δ(ppm): 13.76, 22.52, 31.63, 32.09, 34.82, 79.41, 87.41, 89.95, 96.77, 107.22, 138.75, 196.41. IR KBr disc (cm^{-1}): ν(CO) 2106, 2066, 2044. $\nu(BF_4^-)$ 1053. Analysis Found: C, 41.8; Fe, 8.2; H, 3.1. $C_{24}H_{21}O_6Co_2FeBF_4$ calcd.: C, 43.3; Fe, 8.4; H, 3.1%.

Complex **3a** is stable in air, and only reacts with water, to give **2a**, if first dissolved in acetone. With methanol the corresponding methyl ether is formed. In solution in a CH_2Cl_2/THF mixture, it is reduced rapidly by $NaBH_4$ at ambient temperature to give the aliphatic derivative **5a**.

Tetracarbonyl(dicyclopentadienyl)-μ-(1-ferrocenyloct-2-yn-1-ylium)dimolybdenum(Mo–Mo) tetrafluoroborate (3b)

A solution of 1 ml of 40% aqueous HBF_4 in 40 ml of ether is added dropwise to an ether solution of complex **2b** (0.3 g in 10 ml of ether). The rapidly formed violet precipitate is filtered off and washed with ether, then recrystallised from a CH_2Cl_2/hexane mixture to give 0.25 g of crystals.

^1H NMR (acetone-d_6) δ(ppm): 0.93 (3 H) t, 1.45 (4H) m, 1.68 (2 H) m, 3.01 (2H) m, 4.29 (5H) s, 4.61 (2H) m, 4.72 (2H) m, 5.76 (10H) s large, 8.16 (1 H) s large. ^{13}C NMR $\{^1H\}$ (CD_2Cl_2) δ(ppm): 13.90, 22.68, 31.81, 33.11, 38.27, 70.61, 72.88, 92.29, 95.61, 111.05, 111.07. IR KBr disc (cm^{-1}): ν(CO) 2025, 1994, 1967, 1938; $\nu(BF_4^-)$ 1054. Analysis Found: C, 47.0; F, 8.9; H, 3.7. $C_{23}H_{31}BF_4FeMo_2O_4$ calcd.: C, 47.2; F, 9.3; H, 3.8%.

Complex **3b** does not react with water, even in aceton solution. Upon treatment with aqueous $NaHCO_3$ **2b** is reformed. It does not react with methanol. With dimethylamine a red product is rapidly formed, but could not be isolated. **3b** is reduced in solution (CH_2Cl_2/THF) by $NaBH_4$ to give the corresponding aliphatic derivative **5b**.

*Hexacarbonyl-μ-(η-1-ferrocenyl-1-dimethylaminooct-2-yn)dicobalt(Co–Co) (**4**)*

To a solution of 0.6 g of **3a** in 20 ml of CH_2Cl_2 is added an excess of dimethylamine. The mixture becomes deep-red. After evaporation of the solvent, the residue is taken up in pentane. Filtration and evaporation of the solution gives 0.5 g of the expected amine as a red oil.

^1H NMR (C_6D_6) δ(ppm): 0.87 (3H) m, 1.25 (4H) m, 1.67 (2H) m, 2.49 (6H) s, 2.78 (2H) m, 3.95 to 4.05 (4H) m, 4.12 (5H) s, 4.63 (1H) s. Analysis Found: C, 50.5; H, 4.6. $C_{26}H_{27}Co_2FeNO_6$ calcd.: C, 50.1; H, 4.3%.

Solvents were purified by the usual methods. ^1H and ^{13}C NMR spectra were recorded with Brucker instruments at 200 and 250 MHz. Proton measurements were carried out with selective irradiation and COSY correlation. ^{13}C measurements were made with total proton decoupling. ^{13}C $\{^1H\}$, accompanied by DEPT and spin modulus echo experiments. Infrared spectra were recorded on a BOMEM instrument (Michelson 100). Elemental analyses were carried out at the analysis centre of the CNRS and that of the Nesmeyanov Institute.

Discussion

The alcohols **2a** and **2b** are chiral, as are the carbenium ions **3a** and **3b** derived from them; if the alcohols possess a chiral carbon centre, the carbenium ions themselves have a pseudo-planar chirality. Thus, in the proton NMR spectra of **2a** and **2b** the protons of the diastereotopic groups of the aliphatic chain give rise to a complex pattern of signals. Parameters were determined in acetone-d_6 for the protons of the CH_2 group closest to the cluster after irradiation of the neighbouring CH_2 group. In the case of an analogue of **2b** with a three carbon aliphatic chain, **2c**, we have evidence for an ABXY system formed by the four protons on carbon atoms 4 and 5. The chiral centre C(1) is at the origin of the diastereotopy of the aliphatic chain protons, as confirmed by study of the spectra of the achiral hydrocarbons **5a** and **5b** formed by reduction of **3a** and **3b** with $NaBH_4$. It is noteworthy that the diastereotopic effects involve protons that are as far as three to four carbon atoms away from the chiral centre. It is possible that this phenomenon results from three-dimensional conformational interactions, of an undetermined nature that influence the environment of C(4) and C(5).

In addition to the diastereotopy of the aliphatic chain protons, that of the protons in the substituted ferrocene ring is also observed for **2a** and **2b**. Moreover, for **2b** the cyclopentadienyl groups bonded to the molybdenum appear in the form of two signals.

The ^{13}C spectra of **2a** and **2b** provide evidence for the diastereotopic nature of the carbon atoms in the substituted ferrocene ring and also in the cyclopentadienyl rings on the molybdenum.

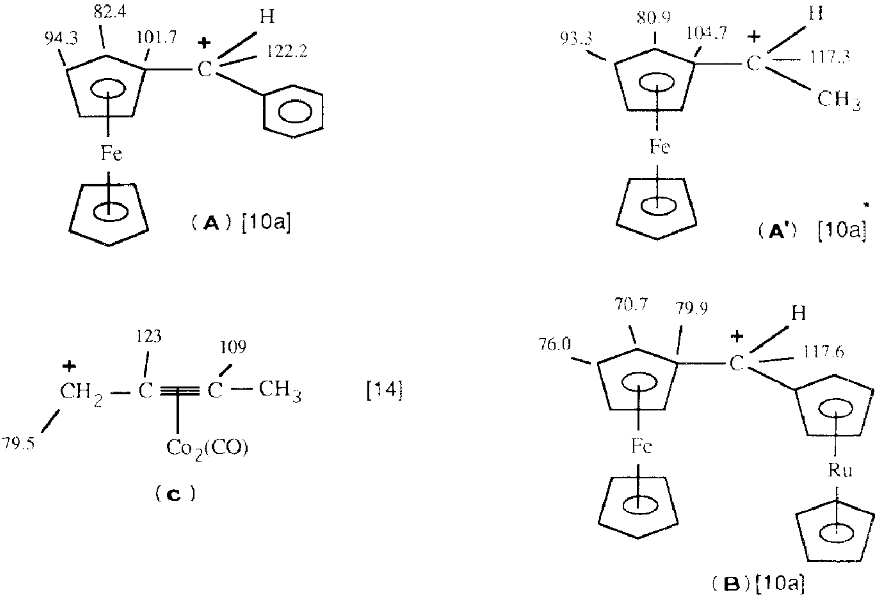
The changes in the ^1H and ^{13}C NMR spectra on going from the alcohols **2a** and **2b** to the corresponding carbénium ions **3a** and **3b** provide interesting information

Table 1

^{1}H NMR chemical shifts for **2a**, **3a**, **2b**, and**3b**, and differences, $\Delta\delta$, between the shifts for the original alcohol and those for the related carbocation

^{1}H NMR	δ(H(1))	δ(H(2′),H(5′))	δ(H(3′),H(4′))	δ(Cp–Mo) (ppm)	δ(Cp–Fe) (ppm)	δ(H(4)) (ppm)
2a acetone-d_6	5.75	4.39 4.32	4.15	–	4.26	2.76
3a acetone-d_6	9.00	5.32	6.25		5.07	3.24
$\Delta\delta$ (δ(**3a**) – δ(**2a**))	3.25	0.93 1.00	2.1	–	0.81	0.48
2b acetone-d_6	5.49	4.16 4.30	4.12	5.25	4.22	2.85
3b acetone-d_6	8.16	4.61	4.72	5.76	4.29	3.01
$\Delta\delta$ (δ(**3b**) – δ(**2b**))	2.67	0.45	0.6	0.51	0.07	0.16

about the interactions between the cationic centre and the neighbouring metal atoms. The observed ^{1}H and ^{13}C chemical shifts indicate that positive charge is present on the molecule as a whole, but for **3a** and **3b** the charge distribution appears to be different. The variations in the ^{1}H and ^{13}C chemical shift on going from the alcohol to the carbenium ion indicate that the ferrocene moiety delocalises the positive charge more for **3a** than for **3b** (Tables 1 and 2). Comparison with literature data (Scheme 3) [10a,14] does not contradict this conclusion. In effect, if



Scheme 3. ^{13}C chemical shift (δ, ppm) non-equivalency of the cations of the C(2,5) and C(3,4) pairs in the carbenium ion $\text{Fc}\underset{+}{\text{C}}\text{HMe}$ resulting from slow $\text{F}\overset{+}{\text{c}}$–C rotation, has been reported [10c]. However, the lack of the resolution of these ^{13}C signals in the present work may be attributable to a solvent effect.

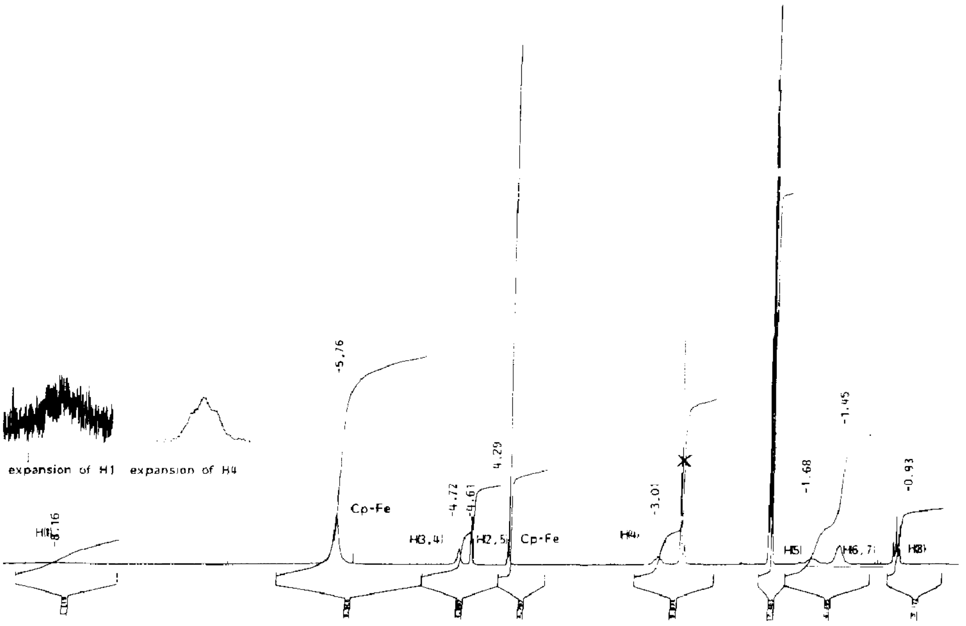


Fig. 1. ^{1}H NMR 250 MHz in CD_3COCD_3 for **3b**.

we compare the chemical shifts of **A** and **A′** on the one hand and those of **B** on the other for the substituted ferrocene system, we find the same situation as for **3a** and **3b**. By analogy, it can be seen that in the first case the ferrocene system plays the principal rôle in the stabilisation of the cation, but not in the second.

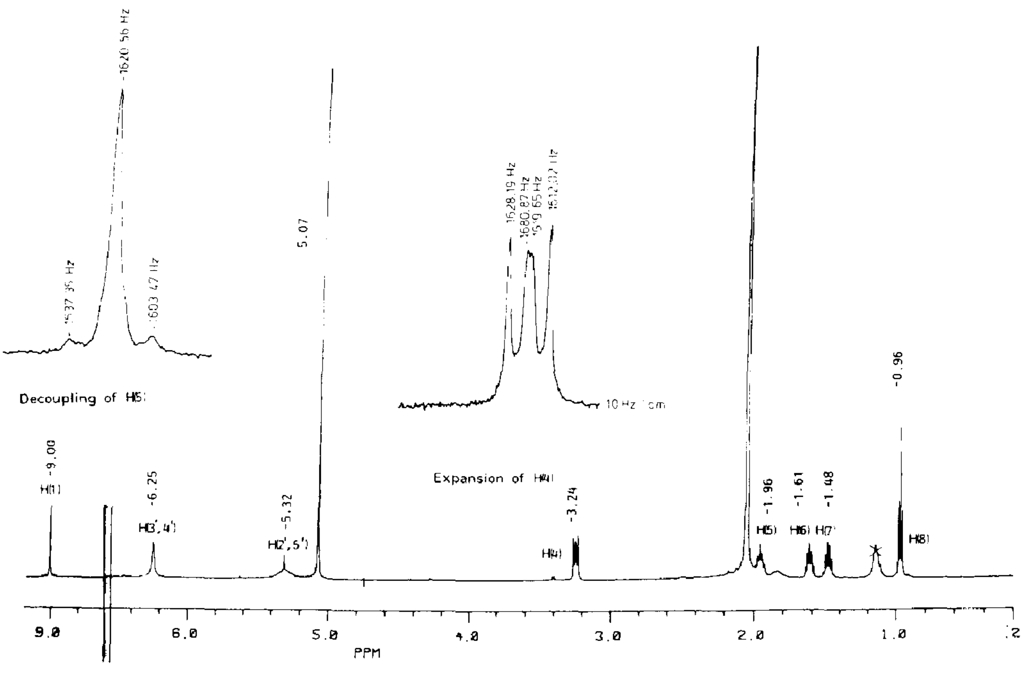


Fig. 2. ^{1}H NMR 250 MHz in CD_3COCD_3 for **3a**.

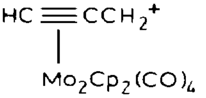
Table 2

^{13}C NMR chemical shifts for **2a**, **3a**, **2b**, and **3b**, and differences, Δδ, between the shifts for the original alcohol and those for the related carbocation

^{13}C NMR	δ(C(1)) (ppm)	δ(C(2)) (ppm)	δ(C(3)) (ppm)	δ(C(4)) (ppm)	δ(C(1′)) (ppm)	δ(C(2′),C(5′)) (ppm)	δ(C(3′),C(4′)) (ppm)	δ(CO) (ppm)	δ(Fe–Cp) (ppm)	δ(Mo–Cp) (ppm)
2a CD$_2$Cl$_2$	71.28	100.00	99.72	33.94	94.16	64.84	68.50 67.72	200.39	69.07	–
3a CD$_2$Cl$_2$	138.75	107.22	87.41	34.82	96.77	79.41	89.95	196.41	79.41	–
Δδ (δ(**3a**) – δ(**2a**))	67.47	7.22	−12.31	0.88	2.61	14.57	21.45 11.69	−3.98	10.34	–
2b CD$_2$Cl$_2$	75.33	95.11	95.11	37.91	105.89	64.36	67.67 67.27	4 sign. ~ 231	68.29	91.07
3b CD$_2$Cl$_2$	111.05	111.05	95.61	38.27	82.56	70.61	72.88	?	70.61	92.29
Δδ (δ(**3b**) δ(**2b**))	35.72	15.94	0.5	0.36	−23.33	6.25	5.21	?	2.32	1.22

To obtain stereochemical information, we can examine the signals from the CH_2 group next to the M_2C_2 cluster, the protons of the ferrocene system, and the protons of the cyclopentadienyl ligands on the molybdenum. The data give significant evidence about the degree of participation of the metal atoms of the ferrocene system and of the cluster. In effect, for the ferrocene system, no diastereotopy is apparent for **3a** or **3b**. For **3b** neither is there any diastereotopy in the cyclopentadienyl bonded to the molybdenum. For **3b** the proton signals of the aliphatic chain are poorly resolved, which is not the case for **3a**. The same applies the proton on carbon C(1). In **3b**, the signal of the CH_2 group next to the cluster is a triplet (Fig. 1), while that of **3a** shows the magnetic inequivalence of the two protons (Fig. 2). We have been able to measure the parameters of this system at 500 MHz after irradiation of the neighbouring CH_2 group ($\Delta\nu_{AB}$ 0.5 Hz J_{AB} -16.8 Hz). The value of $\Delta\nu_{AB}$ in this case is smaller than that for the corresponding alcohol **2a** ($\Delta\nu_{AB}$ 10.5 Hz and J_{AB} -14.5 Hz). The existence of a diastereotopic phenomenon at ambient temperature on the NMR time scale for **3a** and its absence for **3b**, indicates retention of the chirality in the first case and its loss in the second. This retention of chirality for **3a** must be connected with a fairly strong interaction between the organometallic system and the carbenium ion. Taking account of the ^{13}C chemical shifts, we judge that it is the ferrocene group which is involved in this interaction. Moreover, if the cobalt cluster were involved the known fluctuation phenomena between the two metal atoms [12c] would lead to a loss of chirality at ambient temperature.

For molybdenum clusters, it is known that chirality is observed for a primary cation **C**, so that the fluctuation process is slow on the NMR timescale [9d].



$$\underset{Mo_2Cp_2(CO)_4}{HC{\equiv}CCH_2^+}$$

(C)

This is not the case for the secondary cation **3b**, about which one cannot speculate a priori. For the carbenium ion **3b**, the ^1H and ^{13}C NMR chemical shifts show a stronger participation of the molybdenum cluster than of the ferrocene system in stabilising the positive charge. Note that the ferrocene system slightly weakens the interaction of the dimolybdenum cluster with the cationic centre, which leads to a fluxional system at ambient temperature and a loss of chirality; hence the appearance of a single signal from the protons of the cyclopentadienyls attached to the molybdenum (Fig. 1).

Variable temperature ^1H NMR experiments for **3b** (Fig. 3) show clearly the dynamic behaviour of the cluster system under these conditions. Progressive lowering of the temperature leads to a broadening of the signal of the protons of the cyclopentadienyl bound to the molybdenum, then to a splitting into two signals, and finally to resolution of the signal in the form of few sharp bands. The interpretation of this phenomenon has been given previously [12a]; It corresponds to the cessation of the process of interconversion of the two molybdenums with respect to the cationic center and of the pivoting of the cyclopentadienyls on one molybdenum. These two processes have different energy barriers, leading to chirality of the cluster and the formation of few stereoisomers (Scheme 4).

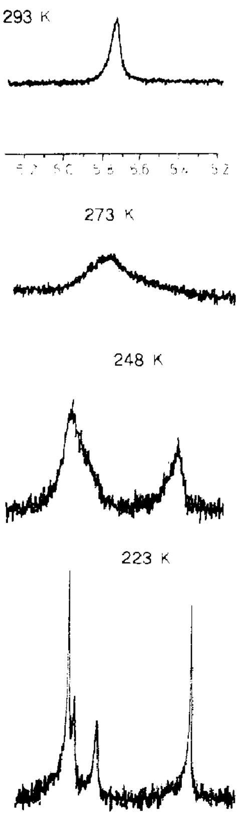
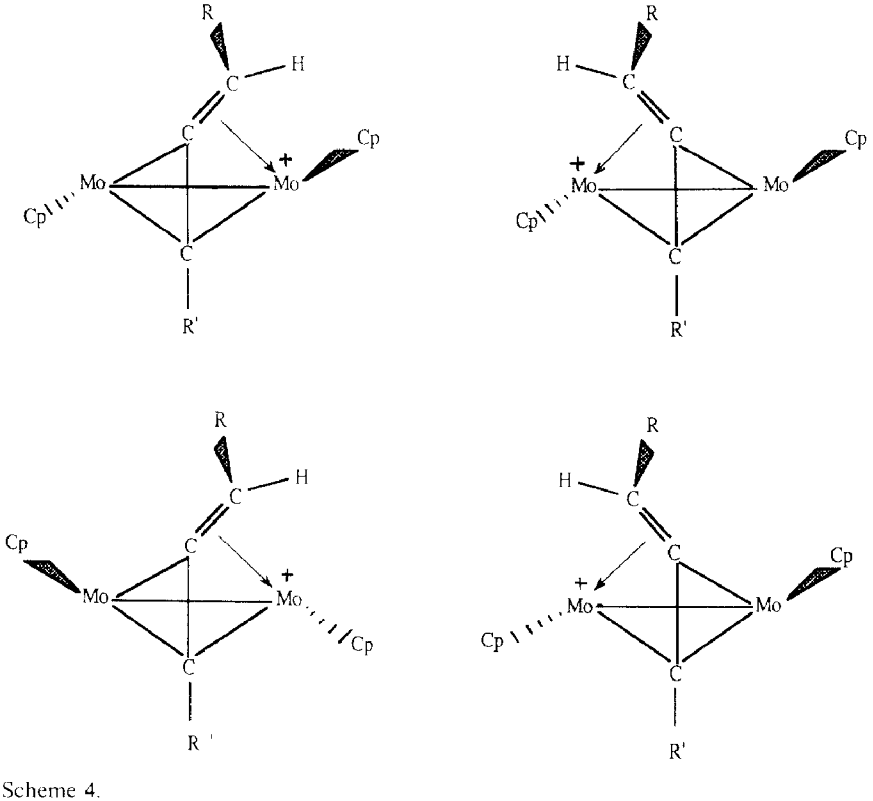


Fig. 3. ^{1}H NMR 250 MHz in CD_3COCD_3 for **3b**. Temperature dependance of Cp–Mo.



Scheme 4.

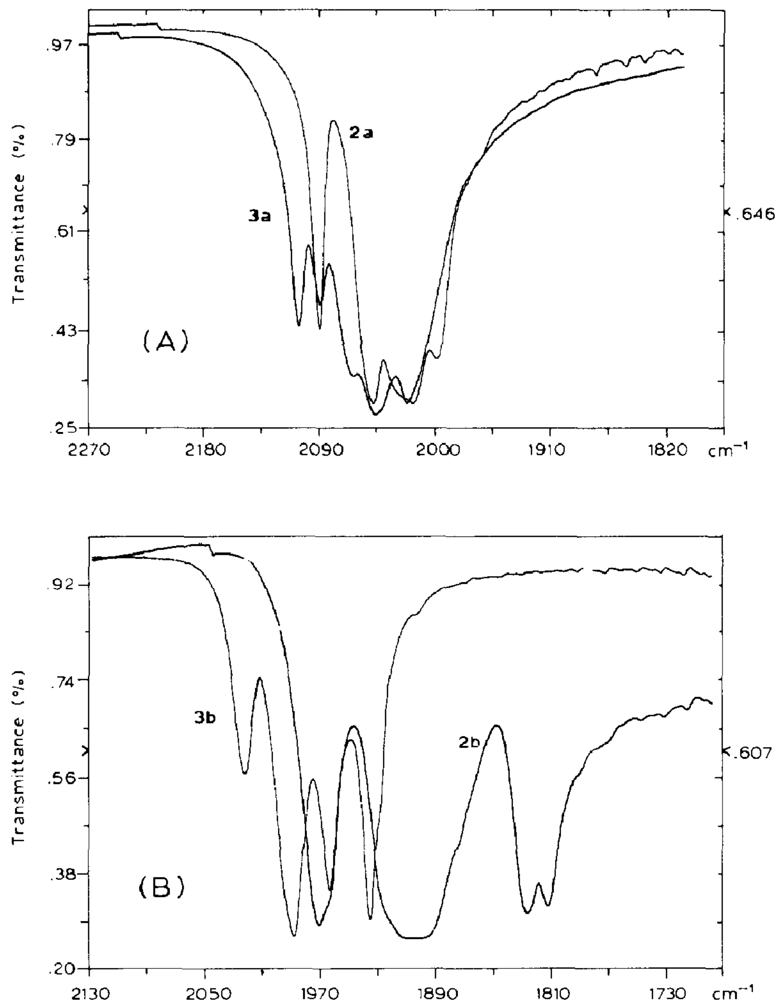


Fig. 4. Comparison of ν(CO), A: **2a**/**3a**; B: **2b**/**3b**.

It is also possible to detect the delocalisation of the positive charge on to the metal by IR spectroscopy by considering the change in frequency of the carbonyl vibrations on going from the alcohol to the carbenium ion [15].

Comparison of the IR spectra in the CO vibration region of the carbenium ions **3a** and **3b** with those of the alcohols **2a** and **2b** (Fig. 4), also reveals a significant electronic perturbation of the cluster in the case of **3b**, and shows that participation of the molybdenum cluster in the distribution of the positive charge is more important than that of the cobalt cluster.

In conclusion, we have noted a great difference between the degree of participation of the ferrocene system and that of an alkyne dimetal cluster in the stabilisation of carbénium ions **3a** and **3b**. In the first case it is the ferrocene system that dominates; in the second, it is the molybdenum cluster which plays the principal rôle in stabilising the cation. It is thus possible to construct a relative scale of cation-stabilising ability for the organometallic groups studied in this work: $[CpMo(CO)_2C]_2 > Fc > [Co(CO)_3C]_2$. However, it should be noted that the ^1H and ^{13}C NMR chemical shifts also show that the cobalt cluster in **3a** and the ferrocene system in **3b** are not entirely inert, and contribute significantly to the stabilisation of the cation. It should be possible to measure the degree of participation of each metal atom by using optically active substrates.

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References

1 (a) K.M. Nicholas, M.O. Nestlé and D. Seyferth, in H. Alper (Ed.), Transition Metal Organometallics in Organic Synthesis H. Alper, Ed, Academic New-York, 2 (1978) 1; (b) W.E. Watts, J. Organometal. Library, Vol. 7, Amsterdam, Elsevier, 1979, p. 399; (c) M. Cais, Organometal. Chem. Rev., 1 (1966) 435; (d) J.H. Richards and E.A. Hill, J. Am. Chem. Soc., 81 (1959) 3484; (e) R. Pettit and W.L. Maynes, in G.A. Olah and P von R. Schleyer, Carbonium Ions, Wiley, New York, 1976, Vol. 5, p. 2263; (f) A.A. Koridze, Uzp. Khim., 2 (1986) 277; (g) G. Jaouen, Pure Appl. Chem., 58 (1986) 597.

2 S. Top, B. Caro and G. Jaouen, Tetrahedron Lett., (1978) 787; D. Seyferth, J.S. Merola and C.E. Eschback, J. Am. Chem. Soc., 100 (1978) 4124.

3 (a) M.C. Ewen, M.E. Manning, J.A. Kleinberg, Tetrahedron Lett., (1964) 2195; (b) N.M. Loim, L.A. Malutschenko, Z.N. Parnes, D.N. Kursanov, J. Organomet. Chem., 108 (1976) 363.

4 (a) K.M. Nicholas, Accounts Chem. Res., 20 (1987) 207; (b) V.I. Sokolov, I.V. Barinov and O.A. Reutov, Izv. Akad. Nauk. SSR, Khim., (1982) 1922.

5 A.J. Deeming, S. Hasso, M. Hunderhill, A. Canty, B.F.G. Johnson, W.G. Jackson, J. Lewis and T.W. Matheson, Chem. Commun., (1974) 807.

6 (a) M. Cais and S. Dan, J. Am. Chem. Soc., 100 (1978) 554; (b) A. Nazzal, U.T. Mueller-Westerhoff and P. Batail, Abstr. IX ICOMC Dijon, 1979, p. 33W.

7 (a) I. Ugi, Rec. Chem. Prog., 80 (1969) 829; (b) V.I. Sokolov, P.V. Petrovskii and O.A. Reutov, J. Organomet. Chem., 59 (1973) C29; (c) M. Gruselle, J.L. Rossignol, A. Vessieres and G. Jaouen, ibid., 328 (1987) C12; (d) S. Greenfield, M. Gruselle, G. Jaouen, V. Varghese and K.M. Nicholas, Appl. Organomet. Chem., 1 (1987) 441.

8 V.I. Sokolov, L.L. Troitskaya and N.S. Krushchova, J. Organomet. Chem., 250 (1983) 439.

9 (a) M. Cais, J.J. Dannenberg, A. Eisenstad, M.I. Levenberg and J.H. Richards, Tetrahedron Lett., (1966) 1695; (b) S. Padmanabhan and K.M. Nicholas, J. Organomet. Chem., 268 (1983) C23; (c) R.T. Edidin, J. Norton and K. Mislow, Organometallics, 1 (1982) 561; (d) I.V. Barinov, O.A. Reutov, V.A. Chertkov and V.I. Sokolov, J. Organomet. Chem., 297 (1985) C25; (e) M.F. D'Agostino, M. Mlekuz and M.J. McGlinchey, J. Organomet. Chem., 345 (1988) 371; (f) M.I. Rybinskaya, A.Z. Kreindlin, S.S. Fadeeva and P.V. Petrovskii, ibid., 345 (1988) 341.

10 (a) A.A. Koridze, N.M. Astakhova and P.V. Petrovskii, J. Organomet. Chem., 254 (1983) 345; (b) A.A. Koridze, O.A. Kizas, N.E. Kolobova, P.V. Petrovskii and E.I. Fedin, ibid., 265 (1984) C33; (c) S. Braun, T.S. Abram and W.E. Watts, ibid., 97 (1975) 429.

11 A.A. Koridze, N.M. Astakhova, P.V. Petrovskii and A.I. Lutsenko, Dokl. Akad. Nauk SSSR, 242 (1978) 117.

12 (a) A. Meyer, D.J. McCabe and D. Curtis, Organometallics, 6 (1987) 1491; (b) S.F.T. Froom, M. Green, K.R. Nagle and D.J. Williams, J. Chem. Soc. Chem. Comm., (1987) 1305; (c) S.L. Schreiber, M.T. Klimas and T. Sammakia, J. Am. Chem. Soc., 109 (1987) 5749.

13 M.D. Curtis, N.A. Fotinos, L. Messerle and A.P. Sattelberger, Inorg. Chem., 22 (1983) 1560.

14 S. Padmanabhan and K.M. Nicholas, J. Organomet. Chem., 268 (1983) C23.

15 R.E. Connor and K.M. Nicholas, J. Organomet. Chem., 125 (1977) C45.