

PhCH₂CH₂Ph (34% calculated from PhCH₂Br).

Ph₂CHCl. This procedure was the same as for C₁₂H₂₂Br. The mixture was stirred at room temperature for 15 h, filtered, and concentrated to give crystals of Ph₂CHCHPh₂ in 40% yield (calculated from Ph₂CHCl). The filtrate was distilled (bp_{0.4} 70–80 °C) to give 12% Ph₂CH₂.

Ph₃CBr. A solution of Ph₃CBr (2.9 g, 9.0 mmol) was added dropwise to a stirred solution of [HSi(OEt)₄]⁻K⁺ (2.3 g, 9.2 mmol) in THF (60 mL) at room temperature. After it was stirred for 15 h, the reaction mixture was hydrolyzed with a saturated solution of NH₄Cl and extracted with toluene to give a white powder after removal of the solvents. Addition of diethyl ether gave a solution (A) and left a solid (B). Solution A was concentrated to give Ph₃CH as colorless crystals (1.03 g, 4.2 mmol) in 47% yield. Dissolution of the solid B into CCl₄ followed by preparative TLC (eluent CCl₄) gave *p*-Ph₂CHC₆H₄CPh₃²⁴ in 22% yield (0.48 g, 0.99 mmol): mp 215–235 °C (lit.³² mp 226–227 °C); ¹H NMR spectrum identical with that in the literature.³³

4.5. Miscellaneous. Reaction of [HSi(OEt)₄]⁻K⁺ with PhC≡CH. A solution of PhC≡CH (0.55 g, 5.4 mmol) in 10 mL of THF was added to a solution of [HSi(OEt)₄]⁻K⁺ (1.34 g, 5.4 mmol) in the same solvent (10 mL), and the mixture was stirred at room temperature for 4 h. Me₃SiCl (0.65 g, 6 mmol) was added, and the reaction mixture was stirred for 4 h. Hydrolysis with a saturated solution of NH₄Cl, followed by standard workup, gave an oil, which was purified by TLC (silica, eluent hexane) to give PhC≡CSiMe₃ in 87% yield (0.82 g, 4.7 mmol): ¹H NMR (CCl₄) δ 7.0–7.5 (m, 5 H, Ar), 0.1 (s, 9 H, SiMe₃); IR (neat) ν(C≡C) 2159 cm⁻¹.

Reaction of [HSi(OEt)₄]⁻K⁺ with Ph₃CH. A solution of Ph₃CH (0.60 g, 2.5 mmol) in 10 mL of THF was added dropwise to the solution of [HSi(OEt)₄]⁻K⁺ (0.80 g, 3.2 mmol) in 15 mL of THF. The solution turned red. After 48 h of stirring, the ¹H NMR spectrum of the reaction mixture showed the presence of Ph₃C⁻

(about 35%, ¹H NMR spectrum analogous to that in the literature³⁴) and Ph₃CH. After deuteration, a mixture of Ph₃CD and Ph₃CH (35:65) was determined by ¹H NMR spectroscopy.

Reaction of [HSi(OEt)₄]⁻K⁺ with Copper and Silver Salts. With AgBPh₄. A solution of [HSi(OEt)₄]⁻K⁺ (1.6 g, 6.4 mmol) in 20 mL of THF was added to a suspension of AgBPh₄ (2.2 g, 6.4 mmol) in 10 mL of the same solvent. After 4 h of stirring at room temperature, Ag and KBPh₄ were eliminated by filtration. The filtrate was concentrated and distilled, giving Si(OEt)₄ in 83% yield (1.1 g, 5.3 mmol) (bp₁₀ 55–60 °C).

With CuI. This procedure was the same as for AgBPh₄ with [HSi(OEt)₄]⁻K⁺ (1.75 g, 7 mmol) and CuI (1.3 g, 7 mmol) in 30 mL of THF. Distillation gave an 81% yield of Si(OEt)₄ (1.2 g, 5.7 mmol) (bp₁₀ 55–60 °C).

Reaction of [HSi(OEt)₄]⁻K⁺ with Cp(CO)₂FeI. A solution of Cp(CO)₂FeI (0.70 g, 2.3 mmol) in 15 mL of THF was added dropwise to a solution of [HSi(OEt)₄]⁻K⁺ (0.80 g, 3.2 mmol) in 15 mL of THF at 0 °C. After 4 h of stirring at room temperature, the IR spectrum of the reaction mixture showed only the presence of [Cp(CO)₂Fe]₂. Elimination of the solvent under vacuum followed by recrystallization from hexane gave [Cp(CO)₂Fe]₂ in 81% yield (0.33 g, 0.94 mmol).

4.6. EPR Experiments. The following procedure is given as an example. One milliliter of a dilute solution (5–10 mg in 3 mL of THF) of Ph₃CBr was added via a cannula under argon to 1 mL of a dilute solution of [HSi(OEt)₄]⁻K⁺ (5–10 mg in 3 mL of THF) in a 5- or 2-mm-diameter glass tube, which was then put in the field of the instrument: *g* = 1.977; *a* = 1.256 G (spectrum analogous to that in the literature^{22a}). [HSi(OEt)₄]⁻K⁺ with 2,5-di-*tert*-butyl-*p*-quinone: *g* = 1.999; *a* = 1.256 G (spectrum analogous to that in the literature^{20a,29}). [HSi(OEt)₄]⁻K⁺ with *p*-dinitrobenzene gave a nonsymmetrical signal centered at *g* = 2.002 (see refs 20a and 28). A solution of pure [HSi(OEt)₄]⁻K⁺ in THF gave no ESR signal under similar conditions.

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NMR Structural and Dynamic Study of a Carbenium Ion with a Steroidal Substituent, [Mo₂Cp₂(CO)₄(μ-HC≡CC₁₉H₂₄O)]⁺BF₄⁻

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¹³C and ¹H NMR evidence for the fluxional behavior of a carbenium ion with a steroidal substituent, [Mo₂Cp₂(CO)₄(μ-HC≡CC₁₉H₂₄O)]⁺BF₄⁻, is presented. In solution, the NMR spectra are highly temperature dependent. We propose the existence of diastereomers of this ion in solution, one of these being very similar to the solid-state structure previously determined by X-ray diffraction.

Introduction

It is well-known that the organometallic derivatives of ethynylestradiol recognize the estradiol receptor. In the case of a Co₂(CO)₈ derivative, the interaction with the receptor is irreversible, while for a Mo₂Cp₂(CO)₄ derivative

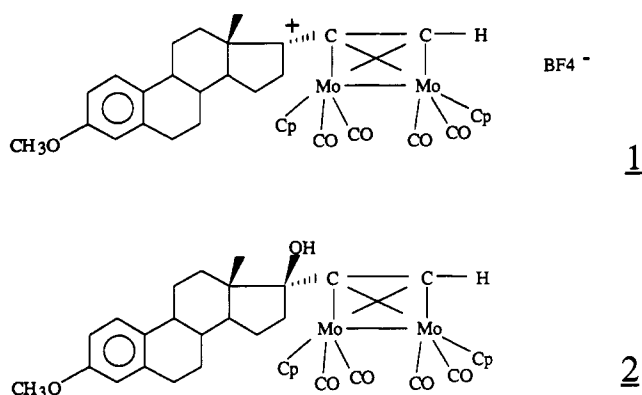
a reversible bond is formed.¹ This result has been attributed to the formation of a carbenium ion, which is stabilized by the presence of a bimetallic cluster coordinated to the position adjacent to the carbenium ion.^{2–5}

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Chart I

**Table I. Proton and Carbon NMR Chemical Shifts of the Alcohol 2^a**

atoms	¹ H (CDCl ₃ , T = 298 K)	¹³ C{ ¹ H} (CDCl ₃ , T = 223 K)	¹³ C CP MAS (T = 298 K)
1	7.18	127.05	125.8
2	6.70	111.6	111.0
3	...	157.19	158.2
4	6.62	113.53	115.6
5	...	138.43	138.7
10	...	132.12	134.2
Cp	5.46	93.60	93.3
	5.41	92.53	
17	...	91.91	^b
22	3.76	55.55	54.0
18	0.96	16.71	17.4
20, 21	6.49	89.44	88.2
		88.03	
CO	...	242.52	243.0
		235.28	236.0
		234.11	
other atoms	1.3-3.0	222.79	223.2
		50.75	51.0
		48.96	48.5
		44.11	43.3
		40.85	41.0
		39.52	
		31.35	
		30.10	30.4
		27.78	
		26.33	25.9
		22.55	24.3

^aThe chemical shifts for the ¹H and ¹³C spectra are reported in ppm relative to TMS with use of the residual solvent signals at 7.27 and 77 ppm as internal references for the experiments in solution. ^bThe C₁₇ signal is hidden in the Cp region.

The extent of stabilization depends upon the cluster fragment and is a result of a difference in the interaction of the p orbital of the positively charged carbon and the orbital system of the molybdenum or cobalt cluster.⁶ We have investigated the stereodynamic properties in solution of the carbenium ion 1, derived from the propargylic alcohol 2 (Chart I). We have also compared the data with those for similar systems reported in the literature. In this paper, we describe the ¹H and ¹³C NMR results for 1 and 2 in both solution and the solid state.

Results and Discussion

Table I shows ¹H, ¹³C, and ¹³C (CP MAS) NMR data for the mestranyl complex 2, which is a precursor to the

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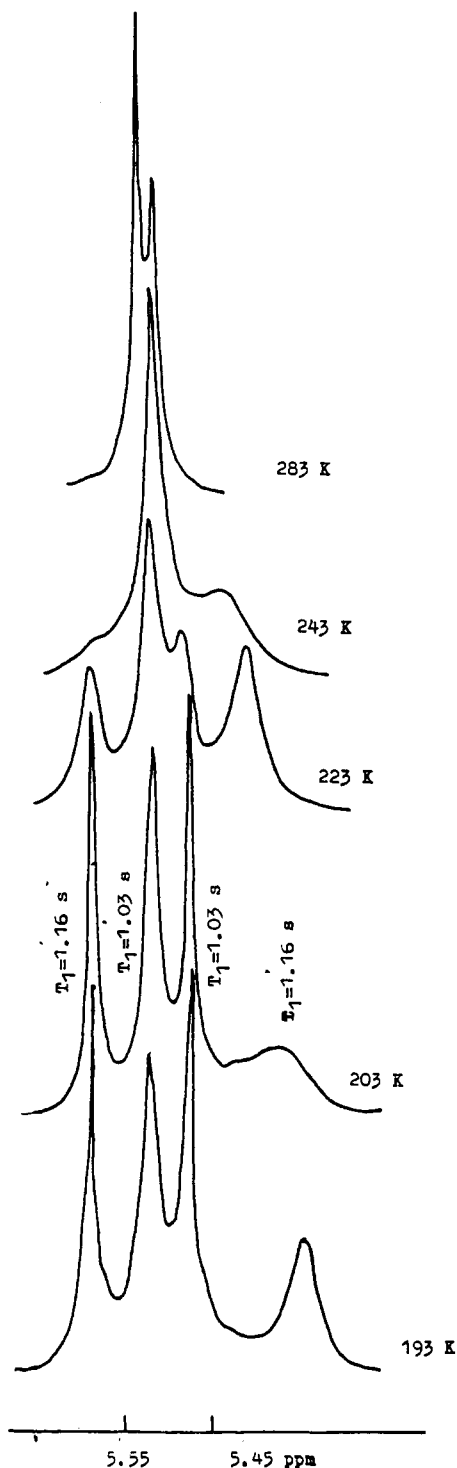
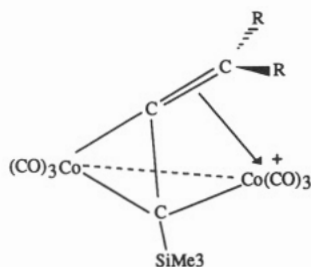
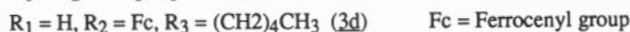
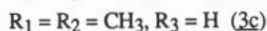
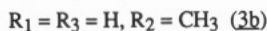
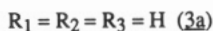
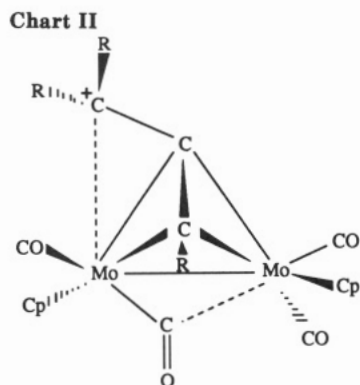


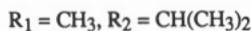
Figure 1. Variable-temperature ¹H NMR spectra of 1 in CD₂Cl₂ in the region of the Cp resonances.

carbenium ion 1. Assignment of the proton signals was made on the basis of the chemical shifts, peak integrations, and peak multiplicities. The ¹³C{¹H} signals were assigned by analogy to previous work.⁷ These results are in agreement with the symmetry of the molecule having free rotation about the C¹⁷-C²⁰ bond. The ¹³C NMR spectrum for 2 in both solution and the solid state are almost identical, the difference in chemical shift values being less than 2 ppm. For the carbenium ion 1, the solution ¹H NMR spectrum is highly temperature dependent, as shown

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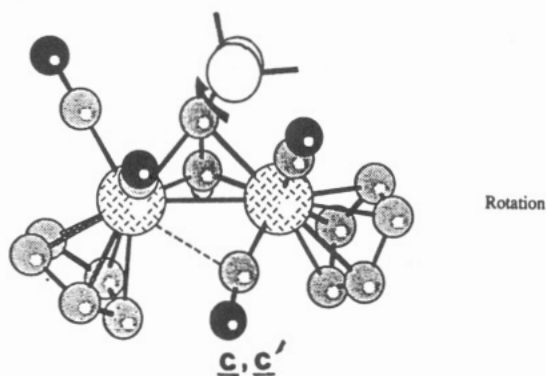
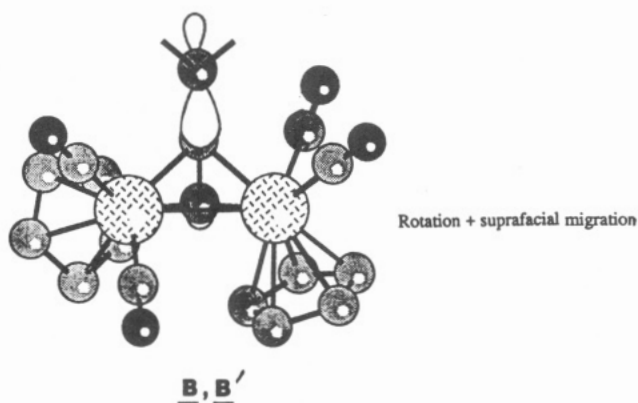
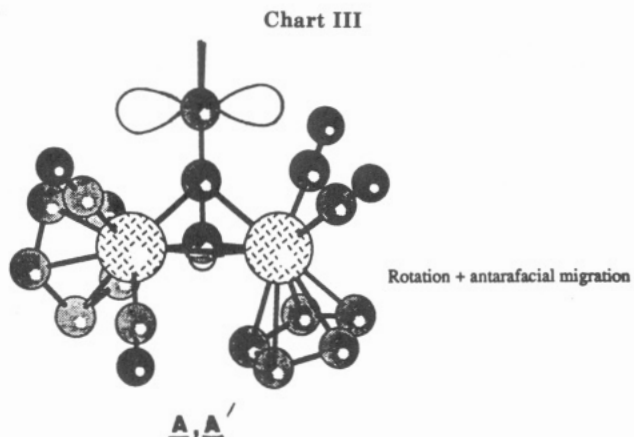
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in Figure 1. This temperature dependence is also observed for the carbenium ions **3a-d** and **4** (Chart II).^{2,8-10}

Theoretically, three mechanisms may be proposed to explain the fluxional behavior of these carbenium ions: (A) simultaneous rotation/antarafacial migration,¹¹ (B) simultaneous rotation/suprafacial migration,¹¹ and (C) simple carbon-carbon bond rotation about the C⁺-cluster bond.

The different transition states for these mechanisms are depicted in Chart III. In order to distinguish between these processes, we use a stereochemical argument.^{2,10} In ions **3a-d** and **4**, an interaction between the p orbital of the positively charged carbon and the d-orbital system of the metal, which stabilizes this positive charge, produces chirality in the cluster itself as the cation is obtained from the alcohol. At low temperature, the carbenium ions **3a,c** and **3b,d** and **4** behave as molecules possessing one and two chiral elements, respectively. Thus, process A acts as an enantiomerization process, while B and C result in diastereomerization of the cation. Curtis² and Schreiber¹⁰ have demonstrated that, for cations **3a** and **4**, simultaneous rotation/antarafacial migration or enantiomerization (A) is the lowest energy process. Schreiber also proposed a higher energy (B or C) process. Barinov⁸ provided ex-



perimental evidence for the diastereomerization of cation **3a** occurring at temperatures higher than those used by Curtis.

An analogous stereochemical model for the carbenium ion **3d**⁹ leads us to conclude that either the simultaneous rotation/suprafacial migration or the simple carbon-carbon bond rotation is the lowest energy process. Indeed, one signal in the ¹H NMR spectra was observed for the cyclopentadienyl groups at ambient temperature for **3d**, implying that the molecule has no chiral elements on the time scale of the NMR measurements. As the temperature is lowered, two signals for the cyclopentadienyls appear and then, on further lowering of temperature, four signals are observed with different intensities. The observation of two signals for Cp is in agreement with the existence of two enantiomers when process A is stopped. Such an

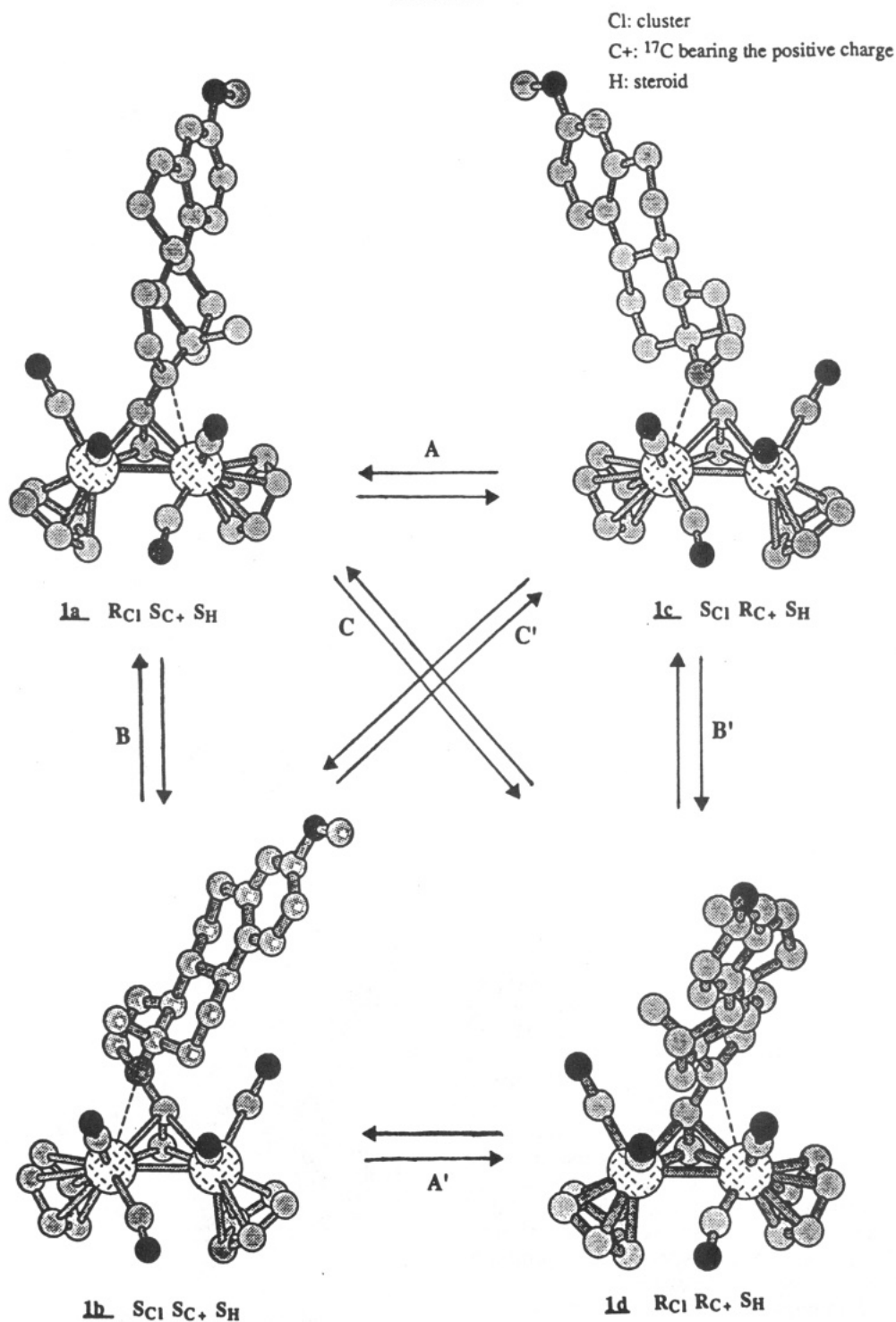
(8) Barinov, I. V. Personal communication.

(9) Troitskaya, L. L.; Sokolov, V. I.; Bakhmutov, V. I.; Reutov, O. A.; Gruselle, M.; Cordier, C.; Jaouen, G. *J. Organomet. Chem.* **1989**, *364*, 195.

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(11) A rotation is necessary in process A and B to obtain a good overlap between the C⁺ p orbital and the metal d orbital.

Scheme I



approach has been applied to ion 1. All the fluxional process A-C, converting one stereoisomer into another, are depicted in Scheme I.

We expect theoretically the four diastereoisomers 1a-d. If we take into account the chirality of the steroid fragment, which possesses a defined stereochemistry, the pure enantiomerization process is not possible. Consequently, four diastereoisomers should be distinguished by NMR spectroscopy with different populations and different activation barriers for the interconversion of one isomer into another. Chart III shows the transition states for the three processes (A/A', B/B', and C/C'). The transition state A/A' can be regarded as a system where the two lobes of the p orbital located on C⁺ interact with hybrid d orbitals

on the two molybdenum atoms. This transition-state structure is capable of maintaining partial delocalization of the carbon p orbital into hybrid d orbitals on the neighboring molybdenum atoms.¹⁰ In transition state B/B', only one lobe of the p orbital on the carbon bearing the positive charge is allowed to interact with the metal d orbitals of the two molybdenums. The behavior is totally different for the transition state C/C', where the d orbital of one molybdenum atom swings from one lobe of the C⁺ p orbital to the other. From Chart III and Scheme I, we notice that the interconversion between the four diastereoisomers proceeds either by the indirect pathway A,B (or A',B'), with the interconversion of the cluster, or via C/C', without cluster fluxionality.

Table II. Proton and Carbon NMR Chemical Shifts of the Carbenium Ion 1^a

atoms	¹ H (T = 223 K)	¹³ C[¹ H] (T = 223 K)	¹³ C CP MAS (T = 298 K)
1	7.21	126.4	127.8
2	6.79	111.25	117.8
3	...	156.84	158.1
4	6.67	113.23	117.8
5	...	137.53	137.7
10	...	131.07	131.6
Cp	5.83	93.87	95.6
	5.76	93.42	94.5
	5.69	92.79	
	5.59	91.26	
17	...	170.2	159.6
		167.0	
22	3.61	55.14	54.9
18	0.84
	1.19
20, 21	7.42	98.05	98.5
	6.79	91-93	96.0
CO	...	230.79	229.7
		226.83	227.3
		222.00	223.4
		220.06	217.5
		220.06	
		218.60	
		215.42	
other atoms	1.3-3.0	53.09	
		51.31	51.1
		42.67	44.6
		39.62	40.1
		34.45	34.0
		33.01	33.6
		29.47	29.7
		26.54	
		24.06	
		22.83	20.9

^a For the ¹H and ¹³C[¹H] spectra in solution, the solvent used is CDCl₃. The chemical shifts are reported in ppm relative to TMS with use of the residual solvent signals at 7.27 and 77 ppm as internal references. ¹³C chemical shifts of the solid-state species are also reported.

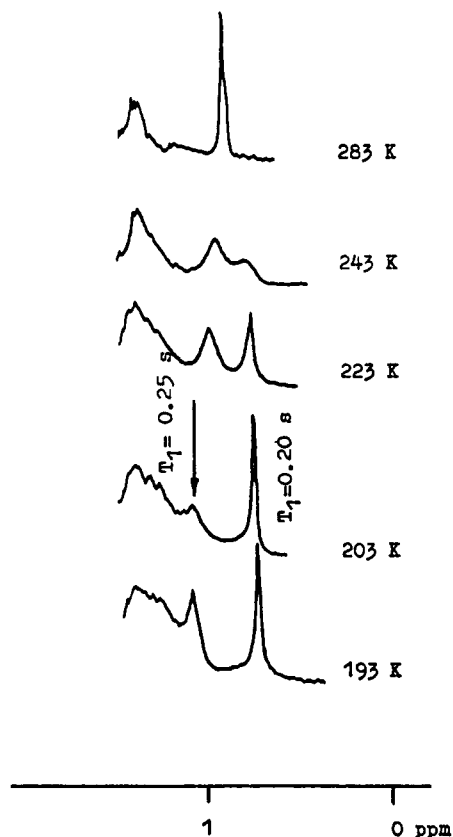
One signal for C¹⁸H₃ and two for cyclopentadienyl protons are observed in the ¹H NMR spectrum of 1 in CD₂Cl₂ solution, but the expected singlet for H²¹ is not visible at ambient temperature. These results correspond to the averaged image of a system with one chiral element due to the steroid substituent. In this case, as in 2, the protons of each Cp ring are diastereotopic. As the temperature is lowered from 283 to 203 K, the number of signals for the Cp protons increases from two to four and the signal for the methyl group C¹⁸H₃ becomes two peaks. Furthermore, the H²¹ signal is observed only as two singlets at $\delta = 7.42$ ppm and $\delta = 6.80$ ppm at low temperature (Table II).

The signal at $\delta = 6.80$ ppm was detected by a saturation transfer experiment. Kinetic data for this process were calculated on the basis of resonances for the C¹⁸H₃ groups as shown in Table III.

Two of the four possible diastereomers are observed with a large difference in the chemical shifts of H²¹ (0.61 ppm) and C¹⁸H₃ (0.35 ppm) resonances (223 K). Examination of molecular models of 1a-d suggests that the large differences can be expected for 1a \rightarrow 1c, 1b \rightarrow 1d, 1a \rightarrow 1d, and 1b \rightarrow 1c transformations. It means that lowering the temperature stops process A/A' and C/C'. According to X-ray data⁶ carbenium ion 1 has the structure 1a in the solid state, where the C¹⁸H₃ group is found adjacent to the Mo²⁺ atom and the stabilization of the carbenium ion results in a direct interaction between C¹⁷, which carries the positive charge, and the metal atom Mo²⁺ ($d(\text{Mo}^{2+}-\text{C}^{17}) = 2.74 \text{ \AA}$) (Scheme II). The isomer with the chemical shifts 7.42 ppm (for H²¹) and 0.84 ppm (for C¹⁸H₃) increases in

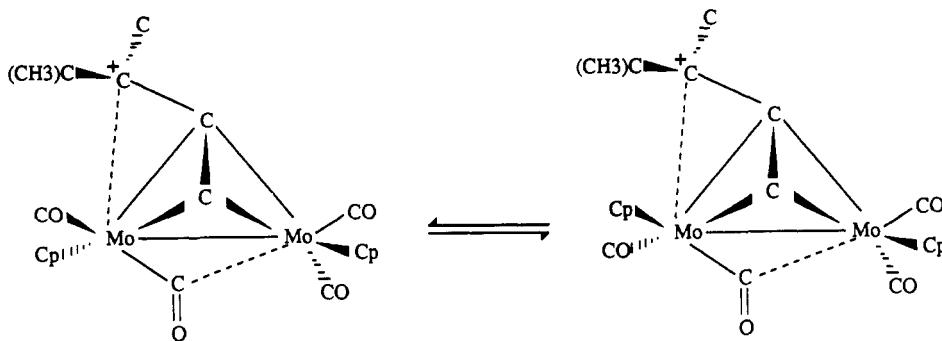
Table III. Kinetic Parameters for the Diastereomerization Processes

exchange	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu	ΔG^\ddagger_{298} , kcal/mol
1a \rightarrow 1c (CDCl ₃)	9.6 \pm 0.4	-13.7 \pm 1.0	13.7 \pm 0.5 12.9 at 233 K 14.3 at 338 K
1c \rightarrow 1a (CDCl ₃)	8.1 \pm 0.4	-18.8 \pm 1.5	13.7 \pm 0.5 12.5 at 233 K 14.4 at 338 K
1a \rightarrow 1c (CD ₂ Cl ₂)	9.5 \pm 0.2	-10.4 \pm 0.8	12.6 \pm 0.2 11.9 at 233 K 13.0 at 338 K
1c \rightarrow 1a (CD ₂ Cl ₂)	8.1 \pm 0.2	-17.6 \pm 0.6	13.3 \pm 0.2 12.2 at 233 K 14.0 at 338 K

Figure 2. Variable-temperature ¹H NMR spectra of 1 in CD₂Cl₂ in the region of the C¹⁸H₃ methyl.

population as the temperature is lowered in CD₂Cl₂ solution. As seen from Figure 2 (203 K), the signal at 0.84 ppm possesses a shorter T₁ value than the C¹⁸H₃ signal for the other isomer. We believe that this observation is predicted for a conformation in which the C¹⁸H₃ group is spatially close to the protons of the Cp ligand, as in 1a. Consequently, the other set of signals belongs to 1c or 1d. As mentioned above, the four Cp signals (5.59, 5.53, 5.49, and 5.41 ppm in Figure 1) are observed at 223 K. The signals at 5.53 and 5.41 ppm with larger intensities belong to 1a. The downfield signal of 1a possesses a shorter T₁ value (1.03 s) than the other Cp signal of the isomer (1.16 s). This suggests that the line at 5.53 ppm belongs to a Cp group that is spatially close to the C¹⁸H₃ protons and is bonded to an atom of Mo interacting with (C¹⁷)⁺. The T₁ values measured at 203 K (Figure 1) allow us to conclude that when the temperature increases the position exchanges 5.41 \leftrightarrow 5.65 ppm and 5.53 \leftrightarrow 5.49 ppm are observed. In other words, the upfield and downfield lines

Scheme II



of Cp groups of **2a** exchange with the downfield and upfield Cp lines of the other isomer, respectively. This remark is also true for the ^{13}C resonance of the four carbonyl groups. At low temperature, whether in solution or in the solid state, we detected four signals; however, at low temperature, seven resonances were observed. Upon examination of the **1a-d** models, it seems that the two carbonyl ligands that are bound to the molybdenum center stabilizing the positive charge are in the β -position relative to the steroidal skeleton in **1a,b**. This situation is clearly reversed for **1c,d**. We believe that this exchange results from transformations **1a** \leftrightarrow **1c** leading to a redistribution of the positive charge in the atom system $\text{C}^+-\text{Mo}^1-\text{Mo}^2$. It should be noted that probably the isomers **1b,d** (processes B/B' and C/C') exist in solution but are not detected, due probably to their small populations. The signal of $(\text{C}^{17})^+$ at 159.6 ppm is shifted to lower field on passing from the solid state to solution, as shown in the ^{13}C NMR spectra (Table II). We observe two signals of relative intensities 1:2 at 170.2 and 167.0 ppm in solution. Considering that, for alcohol **2**, the differences between the chemical shifts in solid state relative to those in solution are not greater than 2 ppm, the above results indicate that the structure of the carbenium ion is markedly different in the two phases. This structural difference is probably due to an elongation of the $\text{Mo}\cdots(\text{C}^{17})^+$ bond, resulting in a modification of the density of the positive charge from the solid to the solution state.

The ΔG^\ddagger value for the diastereomerization process at 338 K is greater than 17 kcal/mol for cation **3a**. This ΔG^\ddagger value diminishes by about 4 kcal/mol on moving to the carbenium ion **1**.¹² Literature precedents^{2,4} show that the chemical shifts of the primary carbenium ion **3a** are observed at 75–76 ppm, for a $\text{C}^+\cdots\text{Mo}$ distance of 2.45 Å. Concomitant with the decrease in ΔG^\ddagger as one goes from **3a** to **1**, the signal for C^+ in the ^{13}C spectra undergoes a downfield shift of more than 90 ppm. This result is directly related to the increase of the positive charge located at $(\text{C}^{17})^+$ in **1** and is paralleled by an elongation of the $(\text{C}^{17})^+\cdots\text{Mo}$ bond to 2.74 Å.⁶ Finally, as the temperature is lowered to 197 K, we notice that two of the four Cp protons signals broaden in the ^1H NMR spectra for **1** when CDCl_3 is the solvent (Figure 3). This can be compared with the broadening and displacement of the C^{18}H_3 signal (Figure 2).

It appears that a new very low energy process begins to operate in the temperature interval investigated. In fact, more detailed ^1H NMR studies of **1** reveal a new state where the Cp groups are nonequivalent. We propose that this is the result of a change in the orientation of the Cp rings, as shown in Scheme II.

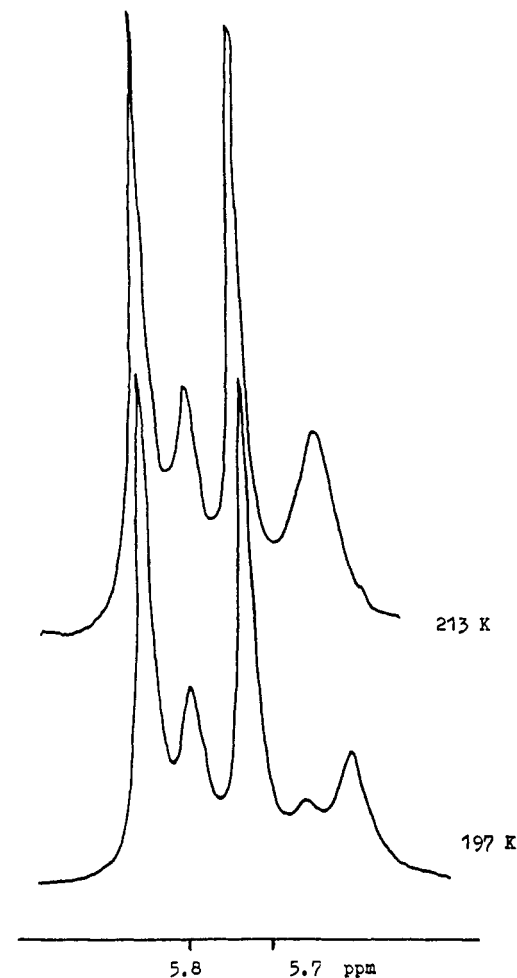


Figure 3. Variable-temperature ^1H NMR spectra of **1** in CDCl_3 in the region of the Cp resonances.

Conclusions

Our NMR results provide information on the solid-state and solution structures of carbenium ion **1**. These structures differ in both the number of stereoisomeric forms and in the $(\text{C}^{17})^+\cdots\text{Mo}$ bond distance. Quantitative stereodynamic studies demonstrate the simplest difference between the fluxional behavior of **3a** and **1**. The rate of dynamic process is faster in the case of **1**. This phenomenon is undoubtedly related to a weakening of the interaction between the p orbital of C^+ and the molecular orbital of the cluster system.

Experimental Section

The syntheses of the cation **1** and its precursor **2** have been described in previous work.² The ^1H NMR spectra were recorded on a Bruker WP-200SY spectrometer, while the carbon-13 spectra

(12) It is important to note that the entropy ΔS^\ddagger is large and negative, which is indicative of a highly organized transition state.

in solution and the solid-state ^{13}C spectra were obtained by using a Bruker CXP 200 spectrometer. For all the variable-temperature experiments, a VT-1000 machine was used. Temperatures mentioned in Figures 1-3 are known with an accuracy of ± 1 K. The solid-state ^{13}C spectra (CP MAS) were recorded with use of the standard PENMR method, including a rotation frequency

of the sample of 3000-4000 Hz. The contact time introduced was 5 ms.

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Square Fe_2Au_2 and Triangular Fe_2Au Clusters: A Reversible Transformation. X-ray Crystal Structure of $[\text{Fe}_2\text{Au}_2(\text{CO})_8(\mu\text{-dppm})]$ (dppm = Bis(diphenylphosphino)methane)

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The salt $(\text{NEt}_4)_2[\text{Fe}_2(\text{CO})_8]$ reacts with $(\text{ClAu})_2(\mu\text{-L})$ (L = bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp)) in tetrahydrofuran to yield $[\text{Fe}_2\text{Au}_2(\text{CO})_8(\mu\text{-L})]$ (L = dppm, **2a**; L = dppe, **2b**; L = dppp, **2c**). The structure of **2a** has been determined by X-ray diffraction methods. Crystals are monoclinic, space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions $a = 16.405$ (5) Å, $b = 17.031$ (8) Å, $c = 12.410$ (4) Å and $\beta = 95.64$ (2)°. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least squares on the basis of 3640 observed reflections to R and R_w values of 0.0291 and 0.0318, respectively. The metal core consists of an unprecedented, nearly square tetrametallic Fe_2Au_2 framework with Au-Au = 2.915 (1) Å, Au-Fe = 2.527 (2) and 2.534 (2) Å, and Fe-Fe = 2.900 (2) Å distances. **2a** does not react with an excess of $(\text{NEt}_4)_2[\text{Fe}_2(\text{CO})_8]$, but **2b,c** add another $[\text{Fe}_2(\text{CO})_8]^{2-}$ fragment to give the hexametallic complexes $(\text{NEt}_4)_2[[\text{Fe}_2\text{Au}(\text{CO})_6(\mu\text{-CO})_2]_2(\mu\text{-L})]$ (L = dppe, **3b**; L = dppp, **3c**), which are postulated to be formed by two Fe_2Au units joined by an L ligand. Furthermore, **3b,c** react reversibly with 1 equiv of $(\text{ClAu})_2(\mu\text{-L})$ to again afford **2b,c**, respectively. An extended Hückel molecular orbital study of the bonding capabilities of two forms of $[\text{Fe}_2(\text{CO})_8]^{2-}$ has been carried out. Formation of terminal Fe-Au bonds is found to be only compatible with the unbridged form of $[\text{Fe}_2(\text{CO})_8]^{2-}$, whereas the formation of a triangular Fe_2Au cluster is most favorable for the bridged form of the iron-carbonyl fragment. Several alternative semibridging interactions between carbonyls and Au atoms in $[\text{Fe}_2\text{Au}_2(\text{CO})_8(\mu\text{-dppm})]$ are analyzed, and the structure with only one cis-equatorial carbonyl bent toward each Au atom is found to be the most stable one.

Introduction

Numerous studies have concentrated on the synthesis of mixed-metal cluster compounds in which the AuPR_3 (R = alkyl, aryl) moiety is incorporated into structures containing other transition metals. At present, derivatives containing two or more AuPPh_3 units are the subject of much current interest.¹ This is due in part to the easy occurrence of direct Au-Au bonds in such species that makes the proposed isolobal relationship between a hydride and a AuPPh_3 unit not always strictly applicable with respect to the structures adopted by hydrides and gold phosphine substituted transition-metal clusters.³

We have recently described the complex $(\text{NEt}_4)[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})_2(\mu\text{-AuPPh}_3)]$, and its X-ray analysis revealed that the iron-iron bond is bridged by a AuPPh_3 fragment, giving a triangular Fe_2Au unit.⁴ Now, we wish to report

the synthesis of several mixed-metal clusters containing Fe_2Au and Fe_2Au_2 skeletons. Moreover, we describe an unprecedented reaction in solution involving both types of derivatives, $\text{Fe}_2\text{Au}_2(\mu\text{-L}) + \text{Fe}_2 \rightarrow (\text{Fe}_2\text{Au})_2(\mu\text{-L})$, and we report the X-ray crystal structure of the compound $[\text{Fe}_2\text{Au}_2(\text{CO})_8(\mu\text{-dppm})]$ (**2a**; dppm = bis(diphenylphosphino)methane).

Results and Discussion

As described earlier,⁴ the reaction of ClAuPPh_3 with $(\text{NEt}_4)_2[\text{Fe}_2(\text{CO})_8]$ in tetrahydrofuran (THF) gives orange-brown microcrystals of the complex $(\text{NEt}_4)[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})_2(\mu\text{-AuPPh}_3)]$ (**1**). Remarkably, the addition of an excess of the gold derivative to $(\text{NEt}_4)_2[\text{Fe}_2(\text{CO})_8]$ solutions did not afford the tetrametallic cluster $[\text{Fe}_2\text{Au}_2(\text{CO})_8(\text{PPh}_3)_2]$, and **1** was recovered unaltered. Steric strains derived from the bulky AuPPh_3 fragment were postulated to be responsible for the inertness of **1** in incorporating an additional gold fragment. This argument is supported by the fact that, according to theoretical molecular orbital calculations (see below), the negative charge of the Fe_2Au complex is localized mostly on the sterically crowded Fe atoms. In order to obtain the Fe_2Au_2

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