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STRUCTURE AND LIGAND EXCHANGE REACTIONS OF THE COMPLEXES $CpUCl_3L_2$ IN SOLUTION (L = HEXAMETHYLPHOSPHORAMIDE, TETRAHYDROFURAN, TRIPHENYLPHOSPHINE OXIDE)

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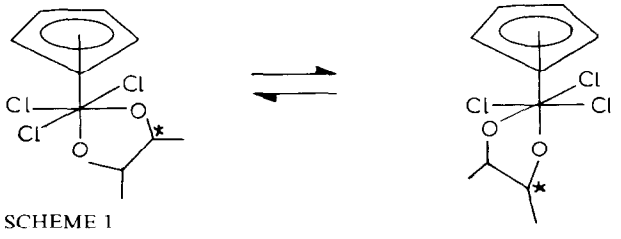
Summary

The dynamic behaviour in solution of the compounds $CpUCl_3L_2$ (L = HMPA, I; THF, II; $OPPh_3$, III) was studied by ^1H and ^{31}P NMR (variable temperature and spin saturation transfer experiments). Two isomers of I in equilibrium (IA and IB) were detected in $CDCl_3$ ($E_a = 92$ kJ mol^{-1}). The two HMPA ligands of the major (70%) isomer IA are relatively *cis* in a *mer* pseudo-octahedral configuration whereas in IB (30%), the two ligands are in *trans* equatorial positions. For all the complexes $CpUCl_3L_2$, the equatorial ligand of isomer A was found to exchange with free added L molecules. In the case of I ($k = 7.0 \pm 0.2$ mol^{-1} l s^{-1} at 260 K), this reaction proceeded by an associative mechanism; at 240 K, the intermediate $CpUCl_3L_3$ was observed. Addition of chloride ions to a solution of I led to the formation of $CpUCl_4(HMPA)^-$.

Introduction

Monocyclopentadienyl complexes of uranium are rare, and are essentially limited to the $CpUX_3L_2$ compounds [1–5] (Cp = η^5-C_5H_5; X = Br, Cl; L = oxygen or nitrogen ligands). The structure in solution of such a complex has been studied only in the case of the derivative $CpUCl_3DME$ [6] (DME = dimethoxyethane); ^1H NMR experiments revealed an intramolecular dynamic exchange of the two ends of the



SCHEME 1

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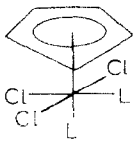


IA :L = HMPA
IIA :L = THF
IIIA :L = $OPPh_3$

chelating DME ligand which occupies one axial and one equatorial position of an octahedron (Scheme 1).

The crystal structure of $CpUCl_3(HMPA)_2$ [3,5] (HMPA = hexamethylphosphoramide), $(\eta^5\text{-}CH_3C_5H_4)UCl_3(THF)_2$ [6] (THF = tetrahydrofuran) and $CpUCl_3(OPPh_3)_2$ [2,5] indicated that in the solid state these complexes all adopt the *mer* pseudo-octahedral configuration, A, with the two L ligands in *cis* positions. However, the ^1H NMR spectra of these compounds were rather complex [1,6].

It seemed to us of interest to study the dynamic behaviour of these complexes in solution and investigate the influence of the ligands L on their fluxionality. We describe and discuss below the results of the NMR experiments undertaken on the complexes $CpUX_3L_2$ (L = HMPA; I, L = THF; II, L = $OPPh_3$; III), which revealed the new intra- and inter-molecular rearrangements of these compounds.

Results and discussion

The structure of the complex $CpUCl_3(HMPA)_2$ (I) in solution

The ^1H NMR spectra of I in $CDCl_3$, CD_2Cl_2 and THF-d_8 at various temperatures are presented in Table 1; they all exhibit two singlets and three doublets assignable to cyclopentadienyl and HMPA ligands respectively (Fig. 1). The resonances obey the Curie's law [6] between 230 and 330 K. Relative integration of these signals indicated that the $CDCl_3$ solutions of I contain two cyclopentadienyl complexes in the ratio 0.45; the most abundant, IA, bears two magnetically different HMPA ligands whereas two equivalent HMPA molecules are coordinated to the minor complex IB. These results were confirmed by the $^{31}P\{^1H\}$ NMR spectrum of I in $CDCl_3$, which exhibited three signals. The NMR spectra of IA are consistent with the *mer* pseudo-octahedral configuration of I (Scheme 2), with *cis* HMPA ligands; this structure was also found in the crystalline form of I [5]. The good agreement between the experimental value (-1.9 ± 0.1) of the ratio $\Delta[\delta(H)_{\text{axial HMPA}}]/\Delta[\delta(H)_{\text{equatorial HMPA}}]$ and the predicted value (-1.7) calculated from the theoretical expression of the pseudocontact shifts in axial symmetry [7] enabled us to assign the high field doublet signal of IA to the equatorial HMPA ligand (*cis* to the Cp ligand). We generalized this assignment to all the complexes described in this work: the Cp and the axial ligands give rise to low field signals whereas the signals of the equatorial ligands appear at high field. Heteronuclear decoupling experiments indicated that the ^{31}P and ^1H NMR chemical shifts of the HMPA signals of IA and IB are in the same order, namely δ(axial HMPA of IA) > δ(HMPA of IB) > δ(equatorial HMPA of IA).

The complementary species IB observable in solution must be the isomer of IA in which the two HMPA ligands are in *trans* positions (Scheme 2). The other isomer with *cis* HMPA ligands in the equatorial plane is less likely because of steric interaction.

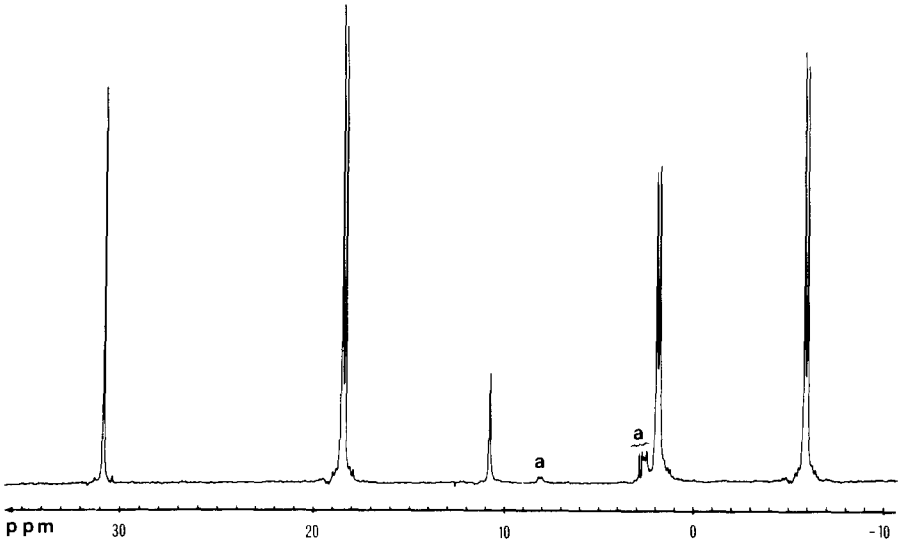


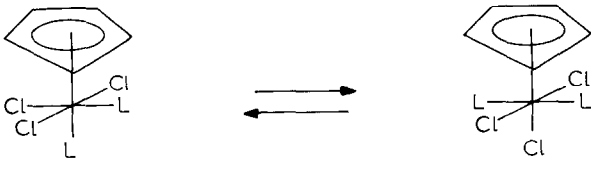
Fig. 1. ^{1}H NMR spectrum of $CpUCl_3(HMPA)_2$ in $CDCl_3$ at 300 K; δ(H)(TMS) = 0. (a) impurities, see text.

TABLE 1

^{1}H NMR DATA[a] FOR $CpUCl_3(HMPA)_2$ (I)

Solvent	T(K)	(IA)			(IB)		ratio
		Cp	axial HMPA	equat. HMPA	Cp	2 HMPA	(IB)/(IA)
$CDCl_3$	333[b]	29	17.5	−5	11.5	1.3	
	300[b]	31	18.6	−5.8	10.9	1.9	0.45
	283	33.5	20	−6.3	10.7	2.3	
	253	37.5	22.4	−7.7	9.3	3.8	
CD_2Cl_2	333	29	18	−5	10.5	2	0.5
THF-d_8	333	28	17	−5			≈ 0.1

[a] Cp signals are singlets, HMPA signals are doublets (J 10 Hz). Assignment of axial and equatorial positions were made according to ref.7. [b] At these temperatures, SST experiments showed the equilibrium between IA and IB.



(IA) (IB)

SCHEME 2

TABLE 2

^{1}H NMR SPECTRA[a] OF A $CDCl_3$ SOLUTION OF I IN THE PRESENCE OF HMPA (10 eq.)

Temperature (K)	Free HMPA	(IA) Cp	(IA) axial HMPA	(IA) equat. HMPA	(IB)[b] Cp	(IV) Cp	(IV) axial HMPA	(IV) 2 equat HMPA
240	2.7	41.2	24	−8.3	7 (2)	25	16	−3
	*					(+)		
		*		(+)				(+)
			*				(+)	
260	2.7	36.5	21.5	7.2	10 (2.6)	22.5	11.5	−3
	*					(+)		
		*		(+)				(+)
			*				(+)	
290	2.7	32.5	19.5	6	10.8 (3.2)	not visible		
	*			(+)				
330	2.7	28	17	5	11.5	not visible		
	*		(+)	(+)				
		*			(+)			

[a] The sign (+) indicates the partial or total disappearance of the signal when the spins marked by * are irradiated. The numbers in parentheses are the ratio (IA)/(IB). [b] The signal of HMPA of IB is hidden by the signal of free HMPA.

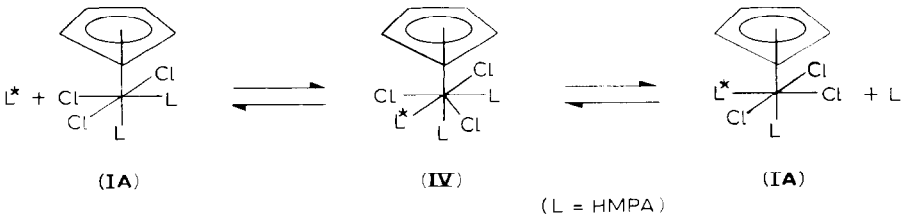
Spin saturation transfer (SST) experiments showed that the two isomers IA and IB are in equilibrium. Above 290 K, irradiation of the cyclopentadienyl signal of IA caused a decrease in the intensity of the Cp signal of IB. Similarly, SST was observed between the HMPA ligands of the two complexes IA and IB. These experiments (see Experimental section) enabled us to evaluate the activation energy for the isomerisation IA ⇌ IB : $E_a = 92$ kJ mol^{-1}. To our knowledge, this equilibrium represents the first example of isomerization of a pseudo-octahedral organometallic complex of the *f*-elements.

Exchange of ligands in the solutions of I

The temperature and the SST effects on the ^{1}H NMR spectra of a $CDCl_3$ solution of I in the presence of 10 equivalents of HMPA are presented in Table 2. Broadening of the resonances were caused by addition of free ligand, and above 300 K, SST experiments indicated exchange between free HMPA and each HMPA ligand of the isomers IA and IB, which are in equilibrium.

Some new interesting facts emerged from the spectra recorded at lower temperature. Between 270 and 300 K, SST was only observed between the free HMPA and the equatorial HMPA ligand of IA, and indicated the stereoselective exchange represented in Scheme 3.

The rate of this exchange was found to increase with the free HMPA concentration, suggesting an associative mechanism. In the hope of observing a species with three coordinated HMPA molecules the temperature was lowered, and below 260 K,



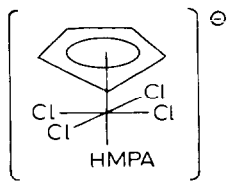
SCHEME 3

new resonances appeared in the NMR spectra of the solutions of I + HMPA: a singlet, a low field doublet and a high field doublet (relative intensities 5, 18, 36). These signals are attributed to the heptacoordinated species IV, which would have a pentagonal bipyramidal configuration with two HMPA and three chlorine ligands in the equatorial plane. This complex IV is the probable intermediate in the exchange of the equatorial HMPA ligand of IA with the free ligand (Scheme 3). The equilibrium between IA and IV was confirmed by SST observed within the three sets of ligands (Table 3), (a) The Cp ligands of IA and IV; (b) the equatorial HMPA ligands of IA, IV (high field resonances) and free HMPA; and (c) the axial HMPA ligands (low field resonances) of IA and IV.

The isomer IB was not involved in any of these exchanges. As expected, the equilibrium IA + HMPA $\rightleftharpoons$ IV was displaced to the right by increased concentrations of free HMPA and lower temperatures.

The formation of complex IV from IA shows the ability of the uranium metal to increase its coordination number and to accept a more negative charge; it also suggests the possible replacement of the equatorial HMPA of IA by another ligand. When chloride ions were added to a solution of I, the intensities of the signals due to IA and IB were lowered, and new resonances, a singlet (5H) and a (low field) doublet (18H), appeared. These resonances are attributed to the new anionic complex $CpUCl_4(HMPA)^-$ (V), which would have a pseudo-octahedral configuration with the four chlorine atoms in the equatorial plane. No exchange was observed between V and IA or IB by SST. It was necessary to add a large excess of chloride ions to the solution of I to observe a nearly quantitative formation of V, however, this could not be isolated.

The information obtained on the dynamic behaviour of the complex I in solution, in particular the existence of two isomers IA and IB and the stereoselective exchange between the equatorial HMPA ligand of IA and free HMPA, prompted us to turn our attention to the NMR spectra of other $CpUCl_3L_2$ complexes in order to be able to make a comparison and eventually to generalize about these phenomena.



(V)

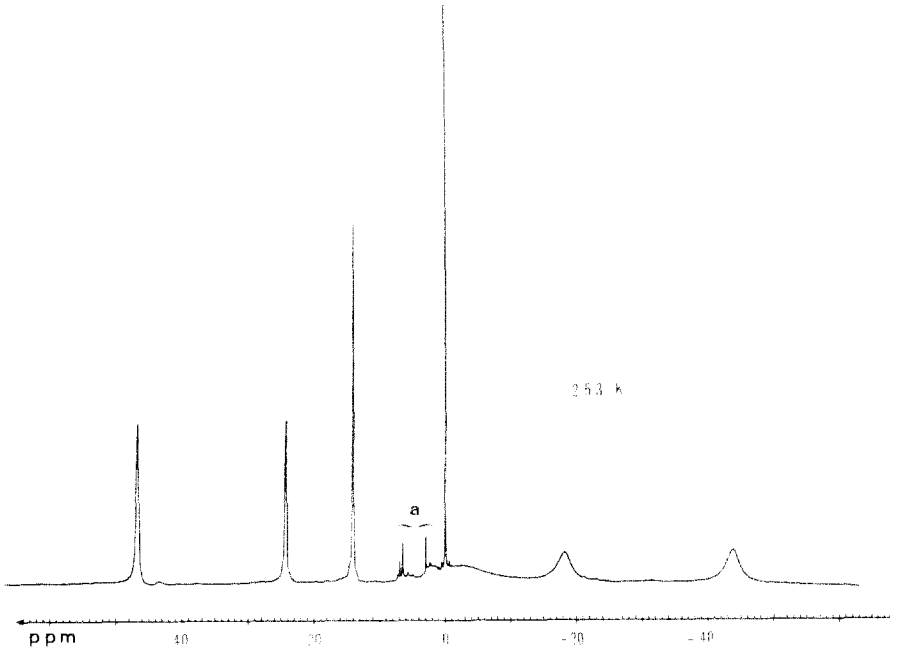


Fig. 2. ^{1}H NMR spectrum of $CpUCl_3(THF)_2$ in $CDCl_3$ at 253 K; δ(H)(TMS) = 0. (a) organic impurities; the broad signal at ≈ 0 ppm is due to free THF molecule in equilibrium with the equatorial (high field) THF ligand.

The dynamic behaviour in solution of the complexes $CpUCl_3L_2$ (L = THF(II) and L = $OPPh_3$ (III)) and general remarks

As reported in the literature [4,6], the ^{1}H NMR spectra of II showed only broad and complex signals at room temperature. However, at 253 K, the spectrum clearly showed the five expected resonances for the isomer IIA (isomer IIB could not be detected) (Fig. 2). A supplementary broad signal near −2 ppm was due to one molecule of free THF, which was presumably a solvation molecule of II. The two high field signals corresponding to the α- and β-CH_2 protons of the equatorial THF ligand were much broader than those of the axial ligand, and a significant diminution of their intensity was observed when the signal of the free THF was irradiated. These results reveal that there is rapid exchange (at 253 K) between the equatorial THF ligand of IIA and the free THF in solution.

The ^{1}H NMR spectrum of III at room temperature (Fig. 3) demonstrated without ambiguity the presence of the isomer IIIA, with its two different triphenylphosphine oxide ligands. Paramagnetic induced shifts and decoupling experiments allowed us to determine the signal position of each set of protons in the phenyl rings as well as their coupling constants. Exchange was found to occur between the two $OPPh_3$ ligands of IIIA. Here again, the rapid exchange between the equatorial triphenylphosphine oxide ligand of IIIA and free added $OPPh_3$ was demonstrated by the broadening of the respective signals and SST experiments. Noteworthy was the presence of some weak additional signals in the spectrum of III, in particular a low field singlet which disappeared completely when the Cp signal of IIIA was irradiated. In the ^{31}P NMR spectrum of III, a third signal appeared, in addition to the two

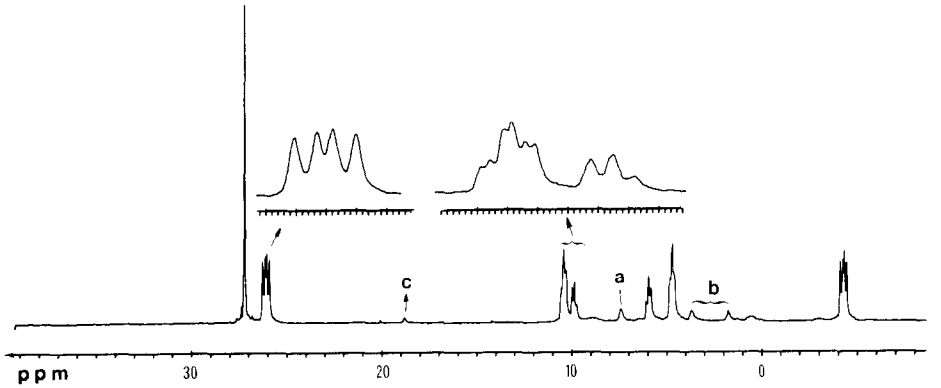


Fig. 3. ^{1}H NMR spectrum of $CpUCl_3(OPPh_3)_2$ in $CDCl_3$ at 300 K: δ(H)(TMS) = 0. Expansion (×10) shows the fine structure of the axial phenyl hydrogens signals. (a) free $OPPh_3$ impurity. (b) free THF, see text and [5]. (c) signal attributed to the Cp ligand of the suspected IIIB isomer.

resonances of the $OPPh_3$ ligands of IIIA. These results suggest that the solution of III contained a small amount (about 5%) of the isomer IIIB.

Some general conclusions may be drawn from these results. The stable structure in solution of the complexes $CpUCl_3L_2$ I–III is the *mer* pseudo-octahedral configuration A, which is also that adopted in the solid state [5]. Interconversion of the axial and equatorial ligands occurs in these complexes; as also observed for the derivative $CpUCl_3$(DME) [6].

The NMR spectra of I and III indicate that IA and presumably IIIA are in equilibrium with their isomers IB and IIIB, which have the two ligands L in equivalent *trans* positions. The existence of isomers IB and IIIB could possibly be easily explained in terms of the steric interaction between the bulkier ligands HMPA and $OPPh_3$, but it is not clear why the relative proportion of IB is greater than that of IIIB. This feature can be considered in the light of the structure of the complexes $UCl_4(HMPA)_2$ [8] and $UCl_4(OPPh_3)_2$ [9], in which the HMPA and $OPPh_3$ ligands are respectively *trans* and *cis* in pseudo-octahedral configuration, and for which π interactions between the phenyl rings were invoked [9] to account for the *cis* geometry of the triphenylphosphine oxide derivative. Intermolecular exchange of ligands takes place when free L molecules are added to solutions of the complexes $CpUCl_3L_2$. We found that at lower temperatures only the equatorial L ligands (the signal from which is always at high field) of the *mer* pseudo-octahedral isomers A are exchanging, and that, at least in the case of the HMPA derivative, an associative intermediate is involved in this reaction. We have demonstrated that the equatorial HMPA ligand of IA can also be replaced by a chloride ion.

These properties lead us to regard the complexes $CpUCl_3L_2$ as potentially useful precursors for the synthesis of new organouranium compounds.

Experimental

All experiments were carried out under argon by Schlenk methods or in a glove box. THF was distilled from sodium-benzophenone before use. HMPA (Merck), CpTI (Ventron) and $OPPh_3$ (Schuchart) were used without purification. UCl_4 [10],

$CpUCl_3(THF)_2$ (II) [4], and $CpUCl_3(OPPh_3)_2$ (III) [1] were prepared and characterized by published methods.

The ^1H and ^{31}P NMR spectra were recorded on a Bruker WH 60 (FT) instrument with its dedicated temperature control unit. The deuteriated solvents were dried over molecular sieves (3 Å) or Na. The chemical shifts were calculated from TMS ($\delta(H) = 0$, internal reference) and $OPPh_3$ ($\delta(P) = 0$, external reference). Positive values denote shifts to low field.

Trichloro(cyclopentadienyl)bis(hexamethylphosphoramide)uranium(I): synthesis

HMPA (0.81 ml, 4.5 mmol) was added to 20 ml of a solution of $CpUCl_3(THF)_2$ (prepared [4] from a mixture of UCl_4 (3 g, 7.9 mmol) and CpTl (2.2 g, 8.17 mmol) in THF (70 ml)) at $-50°C$. The solution was allowed to warm to room temperature and slow crystallization took place during 2 h. The green crystals were filtered off, washed, and dried under vacuum (830 mg, 54%). An X-ray crystal structural determination on this complex [11] showed it to be identical with that of the compound $CpUCl_3(HMPA)_2$ prepared by Bagnall from the reaction of $UCl_4(HMPA)_2$ and CpTl [3].

Trichloro(cyclopentadienyl)bis(hexamethylphosphoramide)uranium: NMR spectra

The ^1H NMR spectra of the complex I in $CDCl_3$, CD_2Cl_2 and THF-d_8 at variable temperatures are listed in Table 1. Additional resonances arising from small and variable amounts of $UCl_4(HMPA)_2$ [12] (δ 8.3 ppm at 30°C, d J 10 Hz) and $UO_2Cl_2(HMPA)_2$ [11,13], (δ 2.92 ppm, d J 10 Hz) were sometimes observed in the spectra of solutions of I. The relative proportions of these impurities increased when the NMR tubes were not sealed; but in sealed tubes chloroform solutions of I were stable for several months at 5°C.

The equilibrium between the species IA and IB (see Scheme 2) was studied by spin saturation transfer experiments [8]. The determination of T_{1A} and T_{1B} (tranversal relaxation time of the hydrogen atoms of the Cp ligand of IA and IB) was effected by the inversion recovery method [12] and measurement of the ratio of the magnetizations M^z/M^0 (calculated as the ratio of the intensities for each of these

TABLE 3

DETERMINATION OF THE RATE CONSTANTS FOR THE EQUILIBRIUM IA ⇌ IB AT DIFFERENT TEMPERATURES

Temperature (K)	304	293	283	280	260
M^0/M^z Cp(IA)[a]	3.24	1.6	1.14	≈ 1	
M^0/M^z Cp(IB)[a]	13	3.2	1.74	1.47	1.06
with SST T_1Cp(IA)[b]	0.22	0.47	0.70	0.78	0.75
with SST T_1Cp(IB)[c]	≈ 0.07	0.27	0.76	0.69	0.97
$1/k_1$ [(IA) → (IB)][d]	0.32	1.24	5.60	very high	very high
$1/k_{-1}$ [(IB) → (IA)][d]	≈ 0.08	0.39	1.73	2.15	very high

[a] Ratio M^0/M^z for the Cp protons of the two isomers IA and IB at different temperatures. [b] Relaxation time (T_1) of the Cp protons of IA during SST experiments when the protons of IB are irradiated. [c] Idem for the Cp protons of IB. [d] Rate constants for the equilibrium: (IA) $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ (IB).

resonances with and without saturation of the other) provided the rate constants: $k = 1/T_1\ (1 - M^{\infty}/M^{0})$. The results are summarised in Table 3.

The activation energy corresponding for the conversion IA $\rightleftharpoons$ IB is 92 ± 6 kJ mol^{-1}.

The ^{31}P NMR spectrum of a solution of I in $CDCl_3$ at 300 K showed three signals (relative intensities ca. 1, 1.1, 1.1) at +267 ppm (axial HMPA of IA), +85 ppm (HMPA of IB) and −26 ppm (equatorial HMPA of IA). The assignment was deduced from heteronuclear decoupling experiments.

Addition of free HMPA to a solution of I in $CDCl_3$

Variable temperature and the spin saturation transfer data for the ^1H NMR spectra of a 0.060 *M* solution of I in $CDCl_3$ in the presence of 10 equivalents of HMPA are presented in Table 2. The ^1H NMR spectra of 0.060 *M* solutions of I with variable quantities of free HMPA (n = (HMPA)/(I) = 10, 8, 5, 2) [15] indicate that, at a given temperature, the ratio (IV)/(IA) increases with n. The results between 230 and 250 K are summarised in Table 4. The rates of the exchange between the equatorial HMPA ligand of IA and free HMPA were calculated as above from SST experiments, and a linear relationship was found between these rates and the concentration of free HMPA. At 260 K, the rates of the reaction are $v_2 = 0.021$, 0.071, 0.10, 0.15 mol l^{-1} s^{-1} for $n = 2$, 5, 8, 10, respectively; the rate constant, k_2, is therefore 7.0 ± 0.2 mol^{-1} l s^{-1}.

Addition of chloride ions to a solution of I in $CDCl_3$: formation of the tetrachloro(cyclopentadienyl)hexamethylphosphoramideuranium anion (V)

A solution of n-Bu_4NCl (42 mg, 0.15 mmol) in $CDCl_3$ (0.5 ml) was added to a solution of I (23 mg, 0.03 mmol) in $CDCl_3$. The ^1H NMR spectrum at 300 K of the resulting green solution showed, in addition to the n-Bu_4NCl resonances, some new signals, a singlet at 36 ppm and a doublet (J 10 Hz) at 22 ppm, with intensities in the ratio 5/18. The intensities of the new singlet signal at 36 ppm and that of the singlet signal at 31 ppm (Cp of IA) were in the ratio 2/1. This ratio increased when more chloride ion was added to the solution. The nearly quantitative ($\approx 90\%$) formation of the species V was observed when a large excess (25 eq.) of n-Bu_4NCl was added. (In all these experiments, the ratio IB/IA retained the same value (≈ 0.45)); however, total disappearance of the signal of IA was never observed. Similar results were obtained when (KCl/18-crown-6) or Ph_3PHCl were used instead of n-Bu_4Cl. Attempts to isolate a pure complex from these mixtures failed.

TABLE 4

RATIOS (IV)/(IA) FOR VARIOUS AMOUNTS OF FREE HMPA (n = (HMPA)/$(I)_{introduced}$ [15]) AT VARIOUS TEMPERATURES

T (K)	n			
	10	8	5	2
230	0.9	0.63	0.4	0.15
240	0.45	0.33	0.2	0.08
250	0.24	0.18	0.09	≈ 0.01

Trichloro(cyclopentadienyl)bis(tetrahydrofuran)uranium (II)

A sample of II was prepared as previously described [4] by mixing 3 g (7.9 mmol) of UCl_4 and 2.2 g (8.17 mmol) of CpTl. 70 ml of THF was added at −50°C and the suspension was stirred overnight at 45°C then filtered to remove TlCl. 1 ml of this solution was transferred to an NMR tube; The solvent was evacuated at room temperature, and the solid residue was dried under vacuum (10^{-2} mmHg) for 2 h, and $CDCl_3$ was introduced into the tube. The ^1H NMR spectrum of II in $CDCl_3$ at room temperature showed only broad resonances [6]. At 253 K, a resolved spectrum corresponding to only one isomer (IIA) was observed (Fig. 2). The low field and high field resonances were assigned to the axial and equatorial THF ligands, respectively, by analogy with the spectra of IA [7]. IIA, 253 K, $\delta(CDCl_3)$: 46.8 (4H, s, $w_{1/2}$ 24 Hz, axial THF), 24.3 (4H, s, $w_{1/2}$ 20 Hz, axial THF), 14.2 (5H, s, $w_{1/2}$ 12 Hz, Cp), −2 (≈ 8H, v br, $w_{1/2}$ 400 Hz, free THF), −18.9 (4H, v br, $w_{1/2}$ 100 Hz, equatorial THF) and −44.8 (4H, v br $w_{1/2}$ 110 Hz, equatorial THF).

At 253 K, irradiation of the signal at −2 ppm brought about a decrease in intensity of the signal at −18.9 and −44.5 ppm to 90% of their original value. At 273 K, the signals were broader; irradiation of the free THF signal lower the intensities of the axial and the equatorial THF signals of IIA to 50 and 10%, respectively, of their original values.

Trichloro(cyclopentadienyl)bis(triphenylphosphine oxide)uranium (III)

At 300 K, the ^1H NMR spectrum of III in $CDCl_3$ showed separated signals for each set of protons of IIIA (Fig. 3). The low field and high field resonances were attributed to the axial and equatorial $OPPh_3$ ligand, respectively, by analogy with the spectra of IA [7]. The assignment of these signals was effected by successive homonuclear decoupling experiments. The free THF resonances were always observed in these spectra, in agreement with the X-ray crystal structure of III [5], which revealed the presence of uncoordinated solvation molecules of THF. IIIA, 300 K, $\delta(CDCl_3)$: 27.2 (5H, s, Cp), 26.1 (6H, d of d, H *ortho* axial, $^3J_{m-p}$ 8 Hz, $^3J(^{31}P\text{-}o)$ 13 Hz), 10.5 (6H, d of t, H *meta* axial, $^3J_{o-m} = {}^3J_{p-m}$ 8 Hz, $^4J(^{31}P\text{-}m)$ 3Hz), 10 (3H, t, H *para* axial, $^3J_{m-p} \approx 8$ Hz), 6 (3H, t, H *para* equatorial), 4.8 (6H, d of t, H *meta* equatorial), 3.5 and 1.8 (≈ 4 H, free THF) and −4.2 (6H, d of d, H *ortho* equatorial). The coupling constants for the corresponding protons in the equatorial and axial ligands were identical. Irradiation of the signals at −4.2, 4.8 and 6 ppm (protons of the equatorial ligand of IIIA) lowered the intensity (to ca. 75% of their original value) of the signals at 26.1, 10.5 and 10 ppm, respectively (protons of the axial ligand).

Additional weak signals were present in the spectrum of III, in particular a singlet at δ 19 ppm. Irradiation of this singlet caused a decrease in the intensity of the signal at 27.2 ppm (Cp ligand of IIIA) to 70% of its original value. The singlet at 19 ppm disappeared completely when the signal at 27.2 ppm was irradiated.

The $^{31}P\{^1H\}$ NMR spectrum of III in $CDCl_3$ at 300 K showed three signals: $\delta(P) = +268$; +30; −44 ppm (relative intensities 10, 1, 12).

Addition of free $OPPh_3$ to a solution of III

The ^1H NMR spectrum of a 1/4 mixture of III and $OPPh_3$ showed a broadening of all the signals of the equatorial ligand, the resonances of the Cp and the axial ligand appeared to be unaffected.

Irradiation of the *ortho* protons of free $OPPh_3$ (7.7 ppm) caused a decrease in intensity (approximately zero) of the signal of the *ortho* protons of the equatorial $OPPh_3$ (−4.2 ppm) and a decrease to ca. 80% of the original value of the signal of the *ortho* protons of the axial $OPPh_3$ (26.1 ppm).

The $^{31}P\{^1H\}$ NMR at 250 K showed resonances at +266, +87, 0 (free $OPPh_3$) and −23 ppm. At 300 K, the smallest signal and that of the free ligand broadened and merged into one another.

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$$\Delta H_{pc}/H_o = (\chi_o - \chi_z)/3N \cdot (3\cos^2\theta - 1)/r^3$$

Assuming the contact contribution to be negligible and the symmetry to be pseudoaxial ($(\chi_0 - \chi_z) \gg (\chi_z - \chi_x)$), then we can predict the ratio $[\Delta\delta(H)_{equatorial}]/[\Delta\delta(H)_{axial}]$ as far as we known the structural data of the molecule.
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