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FACILE INSERTION OF CARBON MONOXIDE INTO THE U–C AND U–N BONDS OF SOME TRIS(CYCLOPENTADIENYL)URANIUM(IV)-ALKYL AND -DIALKYLAMIDE DERIVATIVES

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Summary

In contrast to some earlier indications, various organo-uranium(IV) complexes of the general type Cp_3UX ($Cp = \eta^5\text{-}C_5H_5$; $X = CH_3$, C_2H_5, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $t\text{-}C_4H_9$, $N(C_2H_5)_2$, and even $P(C_6H_5)_2$ and $NCBH_3$, but not BH_4 or NCS) react in solution with CO under mild conditions, (viz. room temperature and atmospheric pressure of CO). The (IR, ^1H NMR and NIR/VIS) spectroscopic properties of the (1 : 1) insertion products in case of X = alkyl or dialkylamide are in full accord with their formulation as dihapto-acyl and dihapto-carbamoyl complexes, respectively. While the carbenoid η^2-OCX ligands are reluctant to undergo consecutive reactions typical of other oxy-carbene systems, reversible equilibria between monomers and dimers in solution (for $R = CH_3$ and C_2H_5) cannot be ruled out. On the other hand, the dihapto-acyl complexes show a clean reversibility of the CO-uptake at temperatures above 60 °C.

Introduction

While numerous examples of successful insertion of carbon monoxide into the ^fM–X bonds of bis-cyclopentadienyl complexes of actinoid or lanthanoid elements, $Cp'_2{}^fMXY$ (Cp' = either $\eta^5\text{-}C_5Me_5$ or $\eta^5\text{-}C_5H_5$; $^fM = Th^{IV}$ and U^{IV} [1] or Lu^{III} [2]; X = alkyl or dialkylamide ligands) are known [3], reports on comparably facile CO insertion into ^fM–X bonds of tris-cyclopentadienyl actinoid(IV) complexes, $Cp_3{}^fMX$ ($Cp = \eta^5\text{-}C_5H_5$), are remarkably scarce. For X = alkyl, positive results were obtained only very recently for ${}^{f}\mathrm{M} = \mathrm{Th}$ [4], but not for $\mathrm{M} = \mathrm{U}$ [5], though possible CO insertion into the $\mathrm{U{-}C_6H_5}$ bond was briefly mentioned in some early patents on the general chemistry of $\mathrm{Cp_3UR}$ complexes [6]. Quite recently, apparently irreversible CO insertion into the notably unsaturated $\mathrm{U}\stackrel{\cdots}{=}\mathrm{C}$ bond of the complex $\mathrm{Cp_3U}\stackrel{\cdots}{=}\mathrm{CHPMe_2C_6H_5}$ has been demonstrated [7]. $\mathrm{Cp_3UR}$ ($\mathrm{R} = \mathrm{CH_3}$, n-$\mathrm{C_4H_9}$) reportedly [8] also undergoes insertion of $\mathrm{SO_2}$ at very low temperatures, but the incompletely known primary products are likely to undergo facile decomposition.

The crystallographically well-established existence of sterically rather congested complexes such as $(\eta^5\text{-Cp})_4\mathrm{U}$ [9], $(\eta^5\text{-Cp})_3\mathrm{U}(\eta^2\text{-N}_2\mathrm{C}_3\mathrm{H}_3)$ [10] and $(\eta^5\text{-Cp})_3\mathrm{U}(\eta^2\text{-OC-CHPMePh}_2)$ [7] as well as of the novel trigonal bipyramidal species $[(\eta^5\text{-Cp})_3\mathrm{UXY}]^q$ ($q = 0$, $+1$ and -1, respectively [11–13]) clearly indicate that an additional small ligand such as CO could be well accommodated sterically by most pseudo-tetrahedral $\mathrm{Cp_3U}(\eta^1\text{-X})$ systems. This expectation is underscored by comparison of the effective coordination numbers (*ECN*) and so-called solid angle sum (*SAS*) values [14–16], respectively, for a number of representative $\mathrm{Cp_3UX}$ and $\mathrm{Cp_2^{\star}(U,Th)X_2}$ derivatives (Table 1; $\mathrm{Cp^{\star}} = \eta^5\text{-C}_5(\mathrm{CH_3})_5$). While most $\mathrm{Cp_2^{\star}U}(\eta^1\text{-X})_2$ systems (with $FCN = 8$) are likely to give rise to *SAS* values only slightly larger than the statistic average of 0.80, but can, nevertheless, be converted into isolable insertion products $\mathrm{Cp_2^{\star}UX}(\eta^2\text{-COX})$ and $\mathrm{Cp_2^{\star}U}(\eta^2\text{-COX})_2$ with $0.82 < SAS < 0.93$, all crystallographically studied $\mathrm{Cp_3U}$ derivatives display, within a *FCN* range of 10–12, notably lower *SAS* values between 0.77 and 0.82. Hence, on the basis of the "*SAS*-rule", the particularly small bite of the ligands η^2-OCX provides acceptable steric conditions even for many $\mathrm{Cp_3{}^{f}M}$ derivatives (${}^{f}\mathrm{M}$ = actinoid(IV)). Sterically very unsatisfactory situations are, on the other hand, expected for $\mathrm{Cp_3U}(\eta^2\text{-X})$ systems in which a considerably larger bite of the chelate X is provided by cyclic $\mathrm{U}(\eta^2\text{-X})$ arrangements involving four- to six-membered rings [17]. This statement is illustrated, e.g., by the

TABLE 1

COMPARISON OF THE FORMAL COORDINATION NUMBER (*FCN*) AND SOLID ANGLE SUM (*SAS*) VALUES OF SOME REPRESENTATIVE ORGANOURANIUM(IV) COMPLEXES INVOLVING Cp or Cp* LIGANDS

Compound	*FCN*	*SAS* [a]	Ref.
"$\mathrm{Cp_2UCl_2}$"	8	ca. 0.70 [b]	14, 15
$\mathrm{Cp_3U}(\eta^1\text{-CH}_2\mathrm{CMeCH}_2)$	10	0.775	14
$\mathrm{Cp_3U}(\eta^1\text{-n-C}_4\mathrm{H}_9)$	10	0.781	14
$\mathrm{Cp_3U}(\eta^2\text{-N}_2\mathrm{C}_3\mathrm{H}_3)$	11	0.796	14
$\mathrm{Cp_3U}(\eta^2\text{-OCCHPMePh}_2)$	11	0.815	17
$\mathrm{Cp_4U}$	12	0.816	14, 15
$\mathrm{Cp_3U}(\eta^1\text{-C}{\equiv}\mathrm{CPh})$	10	0.818	14
$\mathrm{Cp_3U(NCS)(NCMe)}$	11	0.819	14, 15
$\mathrm{Cp_2^{\star}UCl_2}$	8	ca. 0.82 [b]	
$\mathrm{Cp_2^{\star}ThCl}(\eta^2\text{-COCH}_2\mathrm{CMe}_3)$	9	0.845 [c]	14
$\mathrm{Cp_3}(\eta^2\text{-COCHPMePh}_2)$	11	0.874 [d]	7a, 7b, 17
$\mathrm{Cp_2^{\star}UCl}(\eta^2\text{-N}_2\mathrm{C}_3\mathrm{H}_3)$	9	0.910 [d]	43, 17
$\mathrm{Cp_2^{\star}U}(\eta^2\text{-CONMe}_2)_2$	10	0.923	14
$\mathrm{Cp_2^{\star}U}(\eta^2\text{-N}_2\mathrm{C}_3\mathrm{H}_3)$	10	0.983 [d]	43, 17

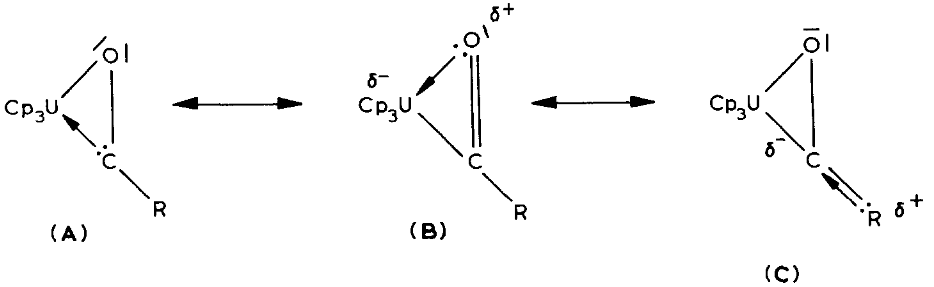
[a] Statistical average of *SAS*: 0.80. [b] Estimated from representative ligand cone angle data [14,15]. [c] A slightly smaller *SAS* value is expected for the corresponding uranium complex. [d] Uncorrected.

fact that the isomers $Cp_3U(\eta^3\text{-}CH_2CMeCH_2)$ and $[Cp_3U(\mu\text{-}N_2C_3H_3)]_2$ of two of the complexes listed in Table 1 are not observed.

General results [18]

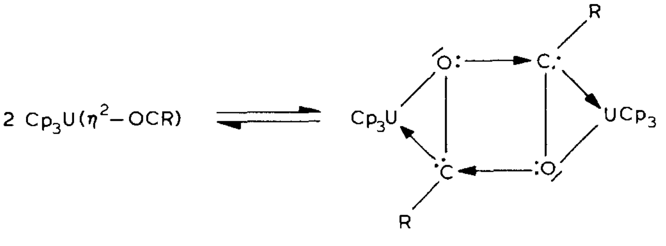
Concentrated solutions of the complexes Cp_3UR in toluene (with $R = CH_3$, C_2H_5, i-C_3H_7, n-C_4H_9, t-C_4H_9 and $N(C_2H_5)_2$) readily undergo insertion of CO when rapidly stirred at room temperature under an atmosphere consisting of CO-enriched N_2 or Ar (N_2 or $Ar/CO \approx 0.5/1.0$). Although this reaction is not accompanied by a characteristic colour change, various spectroscopic features (vide infra) of the solid products obtained after careful solvent evaporation unequivocally confirm that quantitative conversion into products of the general type Cp_3UCOR is achieved within 12–24 h (see Experimental section). At room temperature there is no indication of a reversal of the CO-uptake when either the solid or the dissolved products are exposed to low pressure. On the other hand, except for $R = N(C_2H_5)_2$, prolonged heating of the solutions at ca. 60 °C under N_2 gives solutions (otherwise virtually unchanged) containing both the starting complex Cp_3UR and its carbonylated derivative. CO-uptake at room temperature and partial CO-extrusion at ca. 60 °C can be successively repeated. In full accord with spectroscopic results, there was no evidence for an irreversible conversion of the potentially carbenoid primary adducts into any of the typical stabilized products of carbene species (cf. steps II, III in Scheme 1). Likewise, reaction of the insertion products with excess CO (at room temperature over at least two days) did not give any different products.

Although single crystals suitable for an X-ray diffraction study have not yet been obtained, it is reasonable to assume the formation of rather stable, monomeric η^2-acyl and η^2-carbamoyl complexes, respectively [1e].



The somewhat exceptional superiority of the reversibility of the CO insertion at elevated temperatures over the usually irreversible reactions typical of carbenoid species suggests (in case of R = alkyl) notable participation of valence structure B along with the oxycarbenoid form A. Non-negligible contributions of form C may be envisaged only for $R = N(C_2H_5)_2$ (as well as for $R = CHPMePh_2$ [7]) and are likely to account for the resistance of the carbamoyl complex to CO extrusion above room temperature.

Rather unexpectedly, cryoscopic molecular weight studies in benzene solution indicated for $R = CH_3$ and C_2H_5 notably larger effective molecular weights than expected for the monomeric complexes, suggesting that in solution the η^2-acyl complexes with sterically less expanded groups R may reversibly form dimers such as **D**, or even larger associates:



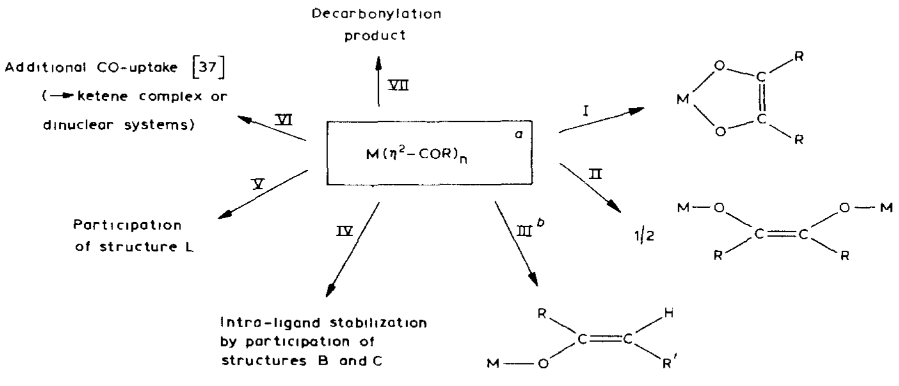
(D)

This unprecedented type of association is, however, not reflected by the ^{1}H NMR spectroscopic data recorded between 200 and 300 K. Likewise, after the protolysis of all η^2-acyl complexes, only formation of the corresponding aldehydes, and not e.g. of 1,2-hydroxyketones, was observed:

$$\mathrm{Cp_3U(\eta^2\text{-}OCR)} \xrightarrow[\text{HX or DX}]{\mathrm{C_6H_6}} \mathrm{RCHO\ \ (or\ RCDO) + Cp_3UX\ \ (X = OH, OCH_3, Cl)}$$

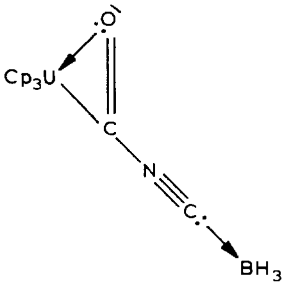
Any formation of dimeric enediolate complexes, $\mathrm{Cp_3UOC(R)}$=$\mathrm{C(R)OCp_3}$, can therefore be ruled out. Addition of methanol to NMR samples of the acyl complexes results in the appearance of clean spectra of $\mathrm{Cp_3UOCH_3}$ [28] as the only paramagnetic component. The carbonylation product $\mathrm{Cp_3UCONEt_2}$ reacts with various protic acids to give exclusively *N*,*N*-diethylformamide, and not *N*-ethylpropionamide, which rules out any rearrangement of the primary complex $\mathrm{Cp_3U(\eta^2\text{-}CONEt_2)}$ into $\mathrm{Cp_3UOC(Et)}$=NEt.

While the complexes $\mathrm{Cp_3UNCS}$ and $\mathrm{Cp_3UBH_4}$ show no evidence of reaction with CO during 2–7 d at temperatures up to 70 °C, at least some spectroscopic changes occur when the complex $\mathrm{Cp_3U(NCBH_3)}$ [19] is stirred in toluene/dichloromethane solution under a pure CO atmosphere. Although the ^{1}H NMR, IR and NIR/VIS, spectroscopic features of the isolated product do not allow the assignment of a single structure, form **F** would match the ^{1}H NMR spectroscopic results (vide infra)

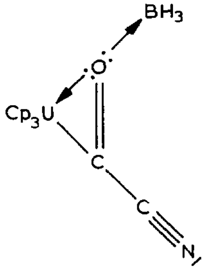


SCHEME 1. Possible stabilization modes of the "oxycarbenoid" ligand η^2-COR. [a] "M" = $\mathrm{Cp_2^*MX}$ or $\mathrm{Cp_3'M}$; $n = 1$ or 2. [b] R = H or $\mathrm{SiMe_3}$. [c] Only if $n = 2$.

somewhat better than form **E**:



(E)



(F)

Interestingly, the ambidentate ligand $NCBH_3^-$ is considerably less tightly bonded to the Cp_3U moiety than NCS^- [19b], and a BH_3 adduct related to form **F** is also expected to be involved during the recently reported reduction of $[CpFe(CO)_3]^+$ with $NCBH_3^-$ to the intermediate $CpFe(CO)_2HC_2OH$ [20]. Probably for steric reasons, the ring-methylated complex $(CH_3C_5H_4)_3U(NCBH_3)$ [19b] shows no reaction with CO. The inertness of the complex $Cp_3U(\eta^3\text{-}BH_4)$ towards CO is similar to that of the bisborohydride system $Cp_2U(\eta^3\text{-}BH_4)_2$ [3d], but contrasts with the chemistry of the formally related zirconium(IV) compounds $Cp_2Zr(\eta^2\text{-}BH_4)_2$ which undergoes reduction to $Cp_2Zr(CO)_2$ [29]. One plausible explanation may be the relatively weak tendency of the two uranium complexes to release BH_3 from their η^3-coordinated BH_4 ligands.

On the other hand, the novel complex $Cp_3UP(C_6H_5)_2$, which involves an extremely labile U–P two-electron bond [21], undergoes rapid reaction under a CO atmosphere at room temperature; however, in this case it appears that the primary addition of CO promotes the well-known potential of the $P(C_6H_5)_2$ ligand as a reductant, since ultimately an organouranium(III) derivative (so far only partially identified) is observed. Unlike Cp_3UBH_4 [19b] and, more unexpectedly, Cp_3UR (R = alkyl, vide infra), $Cp_3UP(C_6H_5)_2$ also adds acetonitrile in C_6H_6 solution. The temperature dependence of the ^1H NMR spectrum between 200 and 300 K is, however, not indicative of trigonal bipyramidal configuration [21].

TABLE 2

OUTLINE OF THE MOST SIGNIFICANT FRAGMENTS IN THE MASS SPECTRA OF SOME COMPLEXES $Cp_3U(\eta^2\text{-}COR)$ (*EI* 70 eV, probe temp. 100 °C)

Fragment	R = CH_3		R = C_2H_5		R = $CH(CH_3)_2$		R = $N(C_2H_5)_2$	
	m/e	I_{rel}	m/e	$I_{rel.}$	m/e	I_{rel}	m/e	I_{rel}
M^+	–	–	490	8	504	19	533	7
$[M-CO]^+$	448	2	–	–	–	–	–	–
$[M-Cp]^+$	–	–	–	–	439	25	468	2
$[M-CO-R]^+$	433	≅100	433	94	433	≡100	433	87
$[M-CO-Cp]^+$	–	–	–	–	411	5	–	–
$[M-2Cp]^+$	–	–	–	–	–	–	403	5
Cp_2U^+	368	80	368	≡100	368	79	368	≅100
CpU^+	303	8	303	2	303	2	303	12

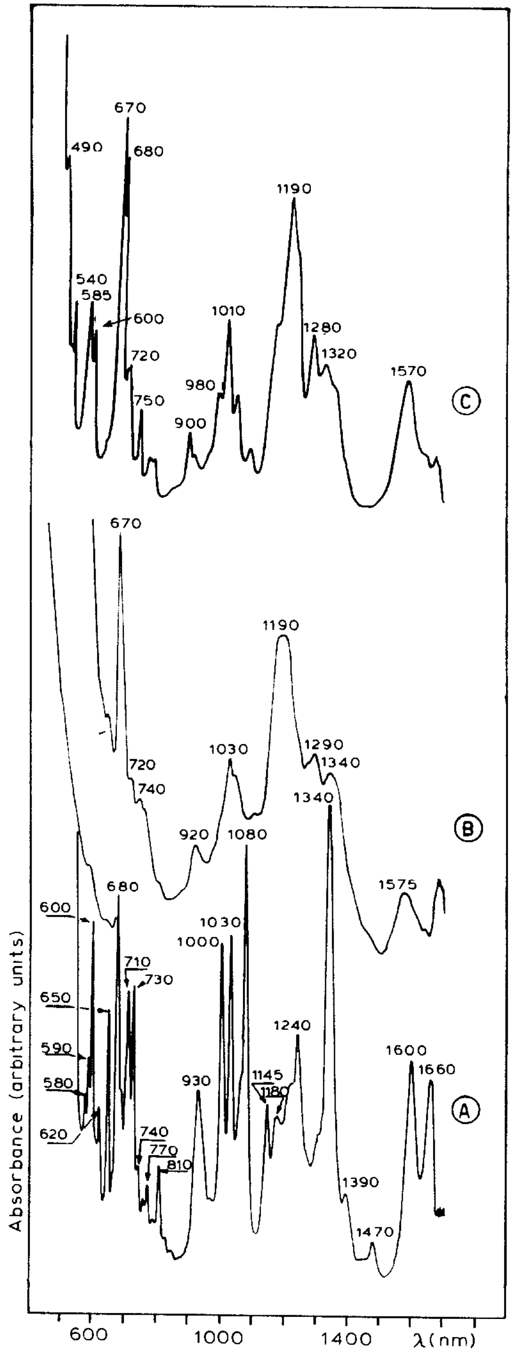


Fig. 1. NIR/VIS absorption spectra of the complexes Cp_3UCH_3 (A) $Cp_3U(\eta^2\text{-}COCH_3)$ (B) and $Cp_3UOC_6H_5$ (C). Solvent: toluene; all absorption maxima are indicated by their wavelengths (nm).

MS, NIR/VIS and IR-spectroscopic properties of the insertion products

The appearance of the mass spectra of the insertion products Cp_3UOCR (Table 2) varies somewhat with the nature of the group R. Thus, the complex $Cp_3UOC(i\text{-}C_3H_7)$ gives quite strong molecular and $[M-Cp]^+$ ions, but not the decarbonylated fragment $Cp_3U(i\text{-}C_3H_7)^+$, while the mass spectrum of the product Cp_3UOCCH_3 is almost identical with that of the parent complex Cp_3UCH_3. The reported mass spectrum of the complex $Cp_3U(\eta^2\text{-}N_2C_3H_3)$ [10], on the other hand, does not clearly differentiate between the appearance of Cp_3U^+ and Cp_2U^+ ions or the fragments $[M-Cp]^+$ and $[M-2Cp]^+$. No further fragments involving U and O were noted.

The near IR and visible absorption spectra of the CO insertion products all differ markedly from the spectra of the corresponding starting complexes (see Fig. 1) and those of trigonal bipyramidal $[Cp_3UXY]^q$ systems [11]. While the starting complexes with R = alkyl give unusually narrow absorption bands, the carbonylated products usually display broader absorptions, probably due to several closely overlapping bands. The spectra are notably similar, however, to the spectrum of the complex $Cp_3UOC_6H_5$, in which the alkoxide ligand is likewise assumed to be bonded by about two electron pairs [21]:

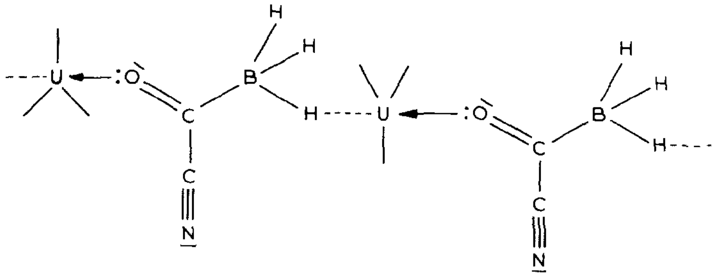
In CH_2Cl_2 or $C_6H_5CH_3$, the adduct "$Cp_3UCONCBH_3$" also gives an absorption spectrum typical of a pseudotetrahedral complex [19b]. The colour of the solvent-free species, however, is green, suggesting the formation of oligomers reminescent of the

TABLE 3

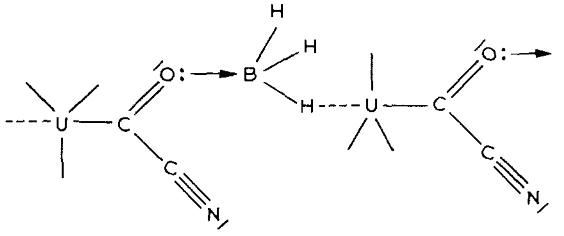
COMPARISON OF THE ν(CO) FREQUENCY (cm^{-1}) FOR VARIOUS DIHAPTO-ACYL (upper part) AND DIHAPTO-CARBAMOYL COMPLEXES (lower part) OF *f*- AND EARLY *d*-ELEMENTS

$Cp^*_2U(\eta^2\text{-}COC_6H_5)Cl$	1429	1f
$Cp^*_2Th(\eta^2\text{-}COCH_2C_6H_5)Cl$	1439	1f
$Cp^*_2Th(\eta^2\text{-}COCH_2CMe_3)Cl$	1469	1c
$Cp^*_2Th(\eta^2\text{-}COCH_3)NMe_2$	1483	1e,1f
$Cp_2Lu(\eta^2\text{-}COCMe_3)$	1490	2
$Cp_3U(\eta^2\text{-}COCMe_3)$	1490	this work
$Cp_3U(\eta^2\text{-}COCHMe_2)$	1493	
$Cp_3U(\eta^2\text{-}CO\text{-}n\text{-}C_4H_9)$	1495	
"$Cp_3U(CONCBH_3)$"	1495	
$Cp_3U(\eta^2\text{-}COC_2H_5)$	1504	
$Cp_3U(\eta^2\text{-}COCH_3)$	1504	
$Cp^*_2Zr(\eta^2\text{-}COCH_3)CH_3$	1537	22
$Cp_2Zr(\eta^2\text{-}COCH_3)CH_3$	1545	23
$Cp_2Zr(\eta^2\text{-}COCH_2CMe_3)Cl$	1550	24
"$Cp_3U(COC_6H_5)$"	1600	6
$^dM(\eta^2\text{-}COR)$ systems	1530–1620	24,26
$Cp^*_2(U,Th)(\eta^2\text{-}CONR_2)NR_2$	1491–1521	1e
$Cp^*_2(U,Th)(\eta^2\text{-}CONR_2)_2$	1499–1523	1e
$Cp_3U(\eta^2\text{-}CON(C_2H_5)_2)$	1521	this work
$Cp^*_2(U,Th)(\eta^2\text{-}CONR_2)Cl$	1515–1559	1e

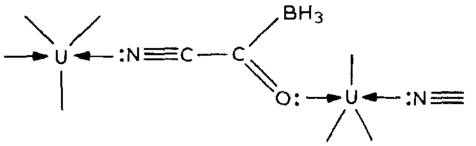
recently postulated oligomeric chain structure of solid $Cp_3U(NCBH_3)$ [19b], e.g.: G, H or K (3 Cp rings are attached to the U atoms).



(G)



(H)



(K)

The vibrational (IR) spectra of all the insertion products show, in addition to the usual absorptions of the η^5-Cp and alkyl ligands, one additional band of medium intensity between 1490 and 1505 cm^{-1} (Table 3) which is assigned to the $\nu(CO)$ absorption of the dihapto-inserted CO molecule. The absence of pronounced absorptions between 1630 and 1680 cm^{-1} clearly rules out the presence of monohaptoacyl ligands [25]. As shown in Table 3, the $\nu(CO)$ absorptions of all the $Cp_3U(\eta^2\text{-}COR)$ systems except for that with $R = C_6H_5$ [6] lie at wave numbers intermediate between those of most complexes of the types $Cp_2^*(U,Th)(\eta^2\text{-}COR)X$ (ca. 1430–1490 cm^{-1}) and $Cp'_2Zr(\eta^2\text{-}COR)X$ (ca. 1530–1550 cm^{-1}). In view of the extremely low $\nu(CO)$ frequency of the well-documented complex $Cp_2^*U(\eta^2\text{-}COC_6H_5)Cl$, the reported insertion of CO into $Cp_3UC_6H_5$ [6] merits re-examination.

While non-conjugated η^2-acyl complexes of the early *d*-transition elements are known to give significantly shorter ^{d}M–C than the corresponding ^{d}M–O distances, the reverse is usually the case for related complexes of the *f*-elements [3a,b]. The

TABLE 4

COMPARISON OF THE INFRARED SPECTRA OF "$Cp_3U(CONCBH_3)$" AND THE STARTING COMPLEX $Cp_3U(NCBH_3)$ (absorptions in cm^{-1}, KBr-pellets)

$Cp_3U(CONCBH_3)$	$Cp_3U(NCBH_3)$	Assignment
3090w	3095	$\nu(CH)$
–	2340	$\nu(BH)$
2320s	–	
2280m	2235	
2175vs	2171	$\nu(CN)$
1495w	–	$\nu(CO)$
1113m	1105	$\delta(BH)$
1011m	1012	$\delta(CH)$
800vs	792	$\gamma(CH)$

intermediate location of the $\nu(CO)$ frequencies of all Cp_3U derivatives in Table 3 might thus suggest for the $Cp_3U(\eta^2\text{-}COR)$ systems a situation of approximately equal U–O and U–C bond lengths.

The location of the η^2-carbamoyl complex $Cp_3U(\eta^2\text{-}CON(C_2H_5)_2)$ in Table 3 agrees well with the frequency range of other η^2-carbamoyl complexes; again no pronounced absorption is found within the range typical of $^dM\text{-}(\eta^1\text{-}CONR_2)$ systems (1665–1615 cm^{-1} [1e]). The complex $Cp_3U(\eta^2\text{-}COCHPMePh_2)$ would also be expected to absorb within this particular range; but no $\nu(CO)$ frequency is mentioned in Ref. 7a. As observed for carbamoyl complexes of the type $Cp_2^*(U,Th)(\eta^2\text{-}CONR_2)X$ [1e], the compound $Cp_3U(\eta^2\text{-}CON(C_2H_5)_2)$ also shows a weak extra absorption at 1334 cm^{-1} which can be attributed to its $\nu(CN)$ vibration.

The vibrational spectrum of the adduct "$Cp_3U(CONCBH_3)$" differs from that of its parent complex $Cp_3U(NCBH_3)$ mainly in the regions of the $\nu(BH)$ and $\nu(CO)$ modes (Table 4). In the $\nu(BH)$ range, the spectrum of the adduct bears more resemblance to those of trigonal BH_3X moieties, whereas the spectrum of the parent compound is more complex [19b].

^1H NMR spectroscopy

Owing to their paramagnetic nature, pronounced and highly informative differences are evident in the ^1H NMR spectra of the individual starting compounds, Cp_3UX, and of their corresponding carbonylation products, Cp_3UCOX. As an example the appearance of the Cp proton resonance of pure $Cp_3U(\eta^2\text{-}CO\text{-}n\text{-}C_4H_9)$ is compared in Fig. 2 with the corresponding resonances of the same solution recorded after being kept at 70 °C for 35 to 105 h (Table 5). The latter spectra must unequivocally be ascribed to mixtures of the insertion product and of the initial starting complex $Cp_3U(n\text{-}C_4H_9)$ in various ratios (see capture of Fig. 2). The appearance of the individual spectra of the two components and not of a single spectrum of intermediate nature, indicates that CO exchange takes place very slowly on the NMR time scale, and underlines the fact that exhaustive carbonylation of the starting complexes takes several hours rather than minutes. Interestingly, slow re-carbonylation occurs even at -5 °C. Similar behaviour is observed in the case of $R = CH_3$, C_2H_5, $t\text{-}C_4H_9$ and $i\text{-}C_3H_7$, but not of $R = N(C_2H_5)_2$. The appearance of only one methyl proton resonances ($I_{rel.} = 6$), along with the observation of a low-lying $\nu(CO)$ vibration (1493 cm^{-1}), but of no $\nu(C{=}C)$ vibration between ca.

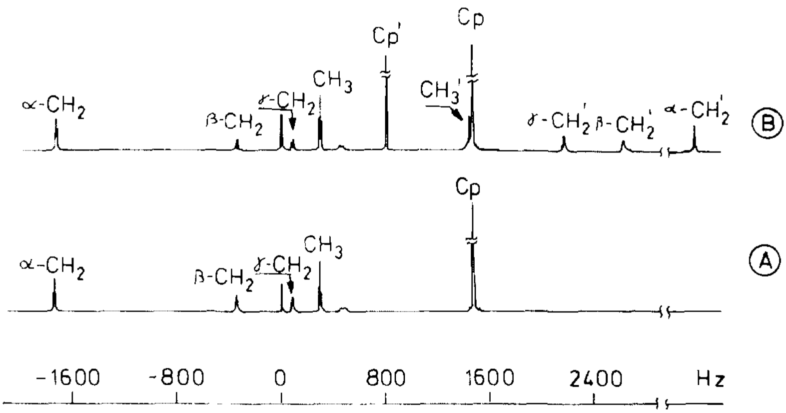


Fig. 2. ^1H NMR spectra at room temperature (solvent: C_6D_6) of pure $Cp_3U(\eta^2\text{-CO-n-}C_4H_9)$ (A), and of the same sample after partial re-decarbonylation (B). All resonances were measured relative to internal C_6D_5H.

1560 and 1660 cm^{-1}, eliminates in the case of $R = i\text{-}C_3H_7$ a possible rearrangement into the enolate complex $Cp_3UOCHC{=}CMe_2$.

Figure 3 shows for the carbonylated complex with $R = n\text{-}C_4H_9$ that the individual isotropic NMR shifts Δ (internal standard: C_6H_6), are essentially proportional to the reciprocal of the absolute temperature. While such behaviour has been observed in case of the other carbonylation products as well as for the species $Cp_3U(\eta^2\text{-}N_2C_3H_3)$ [10], it is worth noting that the majority of $[Cp_3UXY]^q$ systems of trigonal bipyramidal configuration usually display a rather different temperature dependence of the Cp proton resonance [19b,29]. Non-linear Δ vs. T^{-1} plots are observed also in case of the species "$Cp_3UCONCBH_3$", both for the BH_3 and C_5H_5 resonances (Fig. 4). While there is still some qualitative similarity to the NMR behaviour of the parent complex $Cp_3U(NCBH_3)$, the rather significant differences between the actual Δ values at each temperature clearly indicate significant spectroscopic, and thus chemical, changes. In view of the considerable high-field shift of the BH_3 signal, equilibrium mixtures of very rapidly interconverting species involving at least one

TABLE 5

PARTIAL DECARBONYLATION AND RE-CARBONYLATION, RESPECTIVELY, OF AN INITIALLY PURE SAMPLE OF $Cp_3U(\eta^2\text{-COR})$ ($R = n\text{-}C_4H_9$, sealed NMR-tube, solvent C_6D_6) AS A FUNCTION OF TEMPERATURE AND TIME

No.	Percentage [a]		Remarks	
	$Cp_3U(\eta^2\text{-COR})$	Cp_3UR		
1	100	0	Starting material,	$t = 0$
2	53	47	70 °C	t 35 h
3	44	56	70 °C	t 70 h
4	38	62	70 °C	t 105 h
5	46	54	−5 °C	105 h + 1 d
6	57	43	−5 °C	105 h + 7 d
7	81	19	−5 °C	105 h + 30 d

[a] Determined from integrated ^1H NMR signals. [b] All ^1H NMR measurements at room temperature.

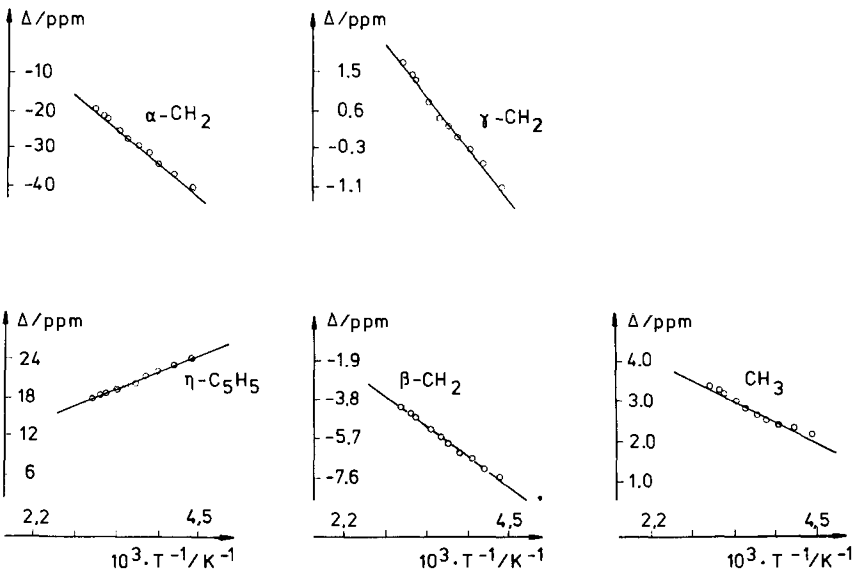


Fig. 3. Δ vs. T^{-1} plots of all ^1H NMR shifts of $Cp_3U(\eta^2\text{-CO-n-}C_4H_9)$. Solvent: toluene-$d_8$, ref. to C_6D_5H. (Δ > 0 = high-field shift.)

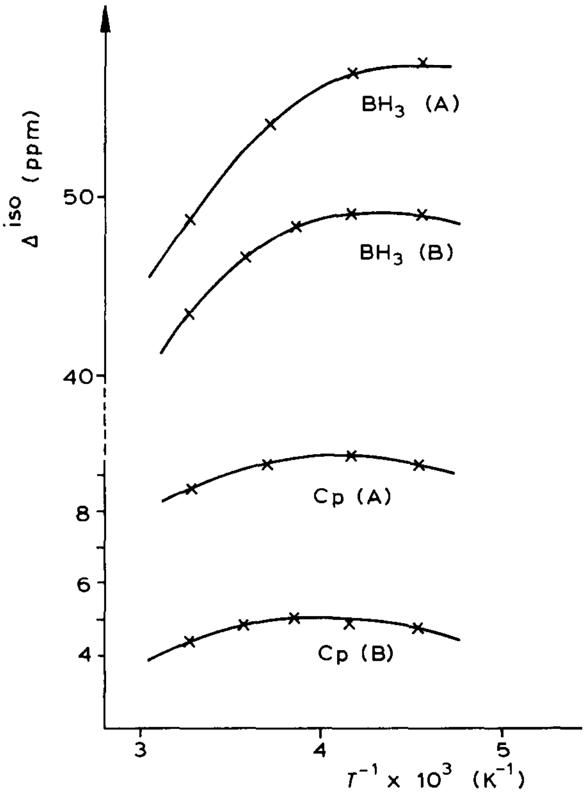
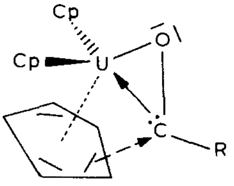


Fig. 4. Δ vs. T^{-1} plots of the two ^1H NMR shifts (C_5H_5 and BH_3) of $Cp_3U(NCBH_3)$ (A) and $Cp_3U(CONCBH_3)$ (B). Room temperature, solvent: CD_2Cl_2; ref. to Cp_3ThCl. (Δ > 0 = high-field shift.)

isomer with rather short U · · H distances cannot be discounted.

Interestingly, only one relatively sharp ($\Delta\nu_{1/2}$ 7.5 Hz) Cp-proton singlet is shown throughout by the carbonylated complexes Cp$_3$U(η^2-COX) even at low temperatures (ca. 200 K), an observation in contrast with the reported splitting into two singlets (intensity ratio: 10/5) in case of the complex Cp$_3$U(i-C$_3$H$_7$) around 180 K [30]. This suggests that, for example, by a second order effect [14,17] the SAS value of Cp$_3$U(i-C$_3$H$_7$) would slightly exceed that of Cp$_3$U(μ^2-CO-i-C$_3$H$_7$), but also indicates that practically all the new η^2-coordinated ligands (including also η^2-N$_2$C$_3$H$_3$ [10]) must be free to rotate almost without restriction about the pseudo-trigonal molecular axis (connecting the metal atom with the centre of gravity of the inserted CO molecule). The apparently rather low barrier of activation of this intramolecular degree of freedom precludes any substantial stabilization of the carbenoid COR ligand by interaction of its electron deficient C atom with part of the (π-)electron cloud(s) of one (or two symmetrically arranged) Cp ligands(s) (cf. structure **L**).



(L)

Cyclopentadienyl ligands bridging two non-interacting metal atoms in the expected μ-(η^5 : η^1)-fashion are fairly well known [31].

A conclusive answer in view of any serious role of structure **L** for systems involving potentially electron-donating ligands X different from Cp (e.g. X = Cl or NR$_2$) is, nevertheless, still lacking. Interestingly, the complex Cp$_2^\star$UCl(η^2-COMe$_2$) seems to form the two expected isomers both in solution and in the crystalline state [1e]. The alternative sequence of atoms within the "equatorial ligand girdle" (i.e. either O,C,Cl or C,O,Cl) is not only reflected by some characteristic differences of corresponding interatomic distances and bond angles, but also by a clear splitting of the methyl proton resonance of the Cp* ligands below ca. 230 K.

Exhaustively carbonylated Cp$_3$UNEt$_2$ gives two pairs of widely separated proton resonances for each C$_2$H$_5$ group (as proved by spin decoupling experiments, see Table 6), the isotropic shifts of which differ even in their signs. As the formation of the hypothetical rearrangement product Cp$_3$UOCEt$^{(1)}$=NEt$^{(2)}$ can be safely ruled out (vide supra), the primary insertion product Cp$_3$U(η^2-OC=NEt^{cis}Et^{trans}) must contain a significant NC π-bond that prevents facile exchange of the two sterically non-equivalent ethyl groups (Et^{cis} being defined as *cis* to the U atom in structure C with R = NEt$_2$) up to at least 40 °C. The positive methyl ^{1}H NMR shift Δ of complex V (X = η^2-CONEt$_2$, see Table 6) compares well with the Δ value of the only CH$_3$ group of complex X (Δ(CH$_3$) 8.63 and 6.88 ppm, respectively) the C(HP)-to-C(UO) bond of which displays considerable π-character [7]. As all the methyl protons of the complexes V and X occupy γ-positions relative to the C atom of the inserted CO molecule, their isotropic shifts, Δ^{iso}, should involve only negligibly small contact contributions, Δ^{con}. Assuming for molecules of X the same (rigid) structure in solution as found by a recent single crystal X-ray analysis [7a], the P(CH$_3$)R$_2$

TABLE 6

LIST OF ROOM TEMPERATURE ^{1}H NMR SHIFTS Δ (ppm) FOR VARIOUS $Cp_3U(\eta^n\text{-}X)$ SYSTEMS ($n > 1$)

(All values are referred to internal C_6H_6, and high-field shifts are taken positive)

Complex Nr.	Ligand X	Δ(Cp)	ΔΔ(Cp)[a]	Δ(α-CH_n)		Δ(β-CH_m), Δ(γ-CH_p), etc.	Ref.
I	"$CONCBH_3$"	5.53 s	−4.3[b]		50.3[c]		this work
II	"SO_2CH_3" (−60 °C)	11.5 s	1.15		6.35		8
III	η^3-$H_3BC_2H_5$	13.81 s	3.4[d]	24.60		18.00	19a
IV	η^2-$N_2C_3H_3$ (35 °C)	15.5 s	4.4[e]		−3.38; −1.45[f]		10
V	η^2-$CON(C_2H_5)_2$	18.32 s	−0.98[g]	–		−44.57 q (β) −11.00 t (γ) 8.84 q (β′) 8.63 t (γ′)	this work
VI	η^2-$COCH(CH_3)_2$	18.40 s	7.5[h]	−8.96 m		−8.06 d	this work
VII	η^2-$CO(t\text{-}C_4H_9)$	18.51 s	7.1[h]	–		−3.50 s	this work
VIII	η^2-COC_2H_5	18.58 s	8.4[h]	−21.45 q		−5.66 t	this work
IX	η^2-$CO(n\text{-}C_4H_9)$	18.61 s	8.3[h]	−22.11 t		−4.55 m (β) 1.00 m (γ) 3.72 t (δ)	this work
X	η^2-$COCHPCH_3(C_6H_5)_2$	18.61 s	−0.7[h]	−53.64 d		6.88 d (γ)	7a,7b
XI	η^2-$COCH_3$	18.62 s	9.0[h]	−26.34 s		–	this work
XII	η^5-C_5H_5	20.00 s	10.7[i]	–		–	32

[a] ΔΔ(Cp) = Δ(Cp; $n > 1$) − Δ(Cp; $n = 1$). [b] Relative to Cp_3UNCBH_3 [19b]. [c] H atoms of BH_3 group. [d] Relative to $Cp_3UC_2H_5$ or corresponding Cp_3UR [32]. [e] Relative to Δ(Cp; $n = 1$) of $Cp_3U(\eta^1\text{-}NC_4H_4)$ [33]. [f] Assignment hindered by lack of relative intensities [10]. [g] Δ(Cp; $n = 1$) for Cp_3UNEt_2 from Ref. 33. [h] Reference data from [7b] and [34]. [i] Relative to Δ(Cp; $n = 1$) for $Cp_3U(\eta^1\text{-}C_6H_5)$ [32].

TABLE 7

ISOTROPIC SHIFTS Δ^{iso} OF α-, β- AND γ-PROTONS (and α-^{31}P) OF VARIOUS $Cp_3U(\eta^2\text{-COX})$ SYSTEMS

Position [a]	$\Delta^{iso} = (\Delta^{dip} + \Delta^{con})$ values (ppm) [b]		
α	ca. −55 (X)	−28.4 (IX)	ca +110 (X, ^{31}P)
β	−48.7 (V)	−8.7 (IX)	+4.7 (V)
γ [c]	−17.4 (V)	−4.5 (IX)	+2.2 (V) +0.8 (X)

[a] Relative to C atom of inserted CO. [b] $\Delta^{iso} = \Delta^{para} - \Delta^{dia}$; Δ^{para} values from Table 6, Δ^{dia} values from Refs. 1e, 7 and 4. [c] $\Delta^{iso} \approx \Delta^{dip}$ (see text).

group will exclusively occupy the position *trans* to the Cp_3U group, for which arrangement the average geometry factor $G(\theta,R)$ [36] of the three methyl protons is unequivocally positive. Since a corresponding situation is also expected for the methyl protons of the Et^{trans} group of V, the experimental Δ value of 8.63 ppm is most satisfactorily assigned to its *trans*-CH_3 group. By the foregoing argumentation, the magnetic anisotropy when term $\chi_{\parallel} - \chi_{\perp}$ [36] of the pseudo-axially symmetric complex X would adopt a negative sign and, consequently, the same situation would hold for complex V.

An alternative reasoning is, however, possible in favour of $(\chi_{\parallel} - \chi_{\perp}) > 0$, since the average over the angular term $(3\cos^2\theta - 1)$ of the geometry factor $G(\theta,R)$ should be largest for γ-protons of *trans*-alkyl groups and smallest (although probably still positive) for γ-protons of *cis* groups. The γ-protons of a η^2-COR (R = alkyl) ligand should adopt intermediate values. From the expected sequence of $(3\cos^2\theta - 1)_{av.}$ not only a corresponding sequence of the $G(\theta,R)_{av}$ values themselves but, moreover of the absolute values of the dipolar shifts Δ^{dip} may be deduced:

$$|\Delta^{dip}(trans\text{-}H_{\gamma})| > |\Delta^{dip}(H_{\gamma})_{av}| \geqslant |\Delta^{dip}(cis\text{-}H_{\gamma})|$$

In view of the $\Delta^{dip}(H_{\gamma})$ values of the complexes V and IX (Table 7) it appears more appropriate to assign Δ^{dip} −16.8 ppm (of V) to *trans*-H_{γ} rather than to *cis*-H_{γ} arriving at $(\chi_{\parallel} - \chi_{\perp}) > 0$. Yet, this latter result conflicts with the *trans*-arrangement of the $P(CH_3)R_2$ group of X as confirmed by X-ray crystallography, and would require complete *cis*/*trans*-isomerization of X in solution.

Similar arguments as the foregoing in favour of $(\chi_{\parallel} - \chi_{\perp}) > 0$ (at least in view of complex V) are also feasible based on the corresponding Δ^{iso} values (Table 7) of protons in the β-positions of V and e.g. VI to IX. However, it appears to us less justified to ignore completely all contact contributions $\Delta^{con}(H_{\beta})$. That appreciable Δ^{con} values have to be taken in account at least for the nuclei in α-positions is demonstrated by rather large approximate $|\Delta^{iso}|$ values for complex X (Table 7).

It is further evident from Table 6 (column 3) that, with the exception of complexes, I, II, V and X, the $\Delta(Cp)$ value, positive throughout, always exceeds that of the corresponding "parent" Cp_3U derivative involving a strictly η^1-bonded extra ligand X. This appears to reflect the transition from systems in which X is exclusively bonded via one electron pair to derivatives with U-to-X′ linkages formally involving two or even more electron pairs. The weakly negative $\Delta\Delta(Cp)$ values in case of V and X simply indicate that the "parent" complexes of V and X contain η^1-coordinated ligands X that are, nevertheless, bonded via more electrons than just one pair [1e,37]. The "regular" increase of $\Delta\Delta$(Cp), which within the sequence: III, IV, VI–IX, XI, XII almost always follows the observed increase of Δ(Cp), probably reflects a continuous decrease of the initially strongly negative quantity $(\chi_{\parallel} - \chi_{\perp})$ (e.g. for X = alkyl [31,35]) and/or an increase of the always positive contact contribution $\Delta(\mathrm{Cp})^{\mathrm{con}}$. In case of the pseudotetrahedral complex XII, $(\chi_{\parallel} - \chi_{\perp})$ is expected to lie close to zero. Somewhat unexpectedly, the Δ(Cp) value of product I appears downfield ($\Delta\Delta(\mathrm{Cp}) \approx -4.3$ ppm) from the resonance of its "parent" complex. While this may preclude any structure involving a η^2-CONCBH$_3$ ligand (e.g. structures **E** and **F**), the rather large $\Delta(\mathrm{B}H_3)$ value favours at least partial U··H–B bonding. The non-linearity of the Δ vs. T^{-1} plots of both the Δ(Cp) and Δ(BH) shift are likely to suggest concerted intramolecular rearrangements which are rapid on the ^{1}H NMR time scale (Fig. 4).

The most spectacular changes usually accompanying the insertion of CO are displayed by the α-H NMR shifts, in that the shift differences $\Delta\Delta(\alpha\text{-C}H_n)$ are of the order of -200 ppm. This feature must mainly be due to the drastic change of the geometry factor by the CO-uptake, which also results in an increase of the number of bonds between the H atom and the paramagnetic centre.

Discussion

The results described above demonstrate conclusively for the first time that migratory CO insertion is easily achieved not only with Cp$_3$UX derivatives which involve a partial U$\overset{..}{=}$X double bond (e.g. X = CHPR$_3$ [34] or NR$_2$), but also with derivatives involving a formally genuine U–X two-electron bond (e.g. X = alkyl). Although the U–C bond of Cp$_3$U-alkyls is known to be photo- and thermo-chemically quite labile [30,39], "steric saturation" of the metal has occasionally been suggested to inhibit a facile incorporation of small unsaturated molecules by Cp$_3^f$MX systems [5]. This view has to be revised on the background both of convincing experimental facts and of the recently introduced "*SAS*-rule" [14–16].

As long as data for a detailed thermodynamic description [41] of the reaction

$$\mathrm{Cp_3UX + CO \rightleftarrows Cp_3U(\eta^2\text{-}COX)} \qquad (1)$$

are lacking, only the qualitative statement can be made that insertion products notably stabilized by structure **C** (i.e. X = CHPR$_3$, NR$_2$) tend to withstand subsequent CO extrusion at slightly elevated temperatures (ca. 60–80 °C), whereas decarbonylation is observed above room temperature in case of X = alkyl. CO-uptake around or below ca. 20 °C of Cp$_3$U-alkyls will therefore be only weakly exothermic. While the only precedent for a reversible carbonylation of an organo-*f*-element complex, Cp$^\star_2$U(η^2-CONMe$_2$)NMe$_2$ [1e], seems to arise mainly from steric congestion (cf. Table 1), the clear reversibility of eq. 1 is likely to have a different origin.

Table 8 lists the majority of complexes of the general type Cp$'_2$MXY, where M is either an *f*-element or a related "early transition metal", and X an usually carbonylation-inert extra ligand including Cp$'$ (Cp$'$ = Cp or Cp*) so far successfully carbonylated. It will be seen that the experimental conditions of facile Cp$_3$UX carbonylation match those of the majority of previously described CO-uptake reactions, and that there is a pronounced tendency to achieve ultimate stabilization by a variety of consecutive routes. Actually, the particular mode of final molecular stabilization

TABLE 8

GENERAL SURVEY OF CARBONYLATION CONDITIONS, AND FINAL MODES OF STABILIZATION, FOR VARIOUS COMPLEXES OF THE GENERAL TYPE Cp'_2MXY

No.	Constituents of Cp'_2MX fragment			Ligand(s) Y [a]	Reaction conditions [b]		Observed or assumed mode of ultimate stabilization [c]	Ref.
					T (°C)	t (h)		
1	Cp*	Th,U	–	$Y^{(1)} = Y^{(2)} = CH_3$	ca. −80	ca. 1.0	II	1a,1b
2	Cp*	Th,U	Cl	$CH_2Si(CH_3)_3$	ca. −80	0.3	III [d]	1b, 3a
3	Cp*	Th	OR	H	−40		CO-uptake reversible (II [e])	40
4	Cp*	Th	NMe_2	CH_3	"low temp"	0.2–1.5	(V ?)	1c,1d
5	Cp*	Th,U	NR_2	NR_2	0	2.0	IV	1e
6	Cp*	Zr	CH_3	CH_3	ca. 25		CO-uptake reversible [h]	22
7	Cp*	Th	Cl	$CH_2C(CH_3)_3$	ca. 25	0.2–1.5	(V ?), VI [f]	1b,1c,1e
8	Cp*	Th,U	–	$Y^{(1)} = Y^{(2)} = CH_2E(CH_3)_3$ (E = C, Si)	ca. 25	0.25	I	1a, 3a,3b
9	Cp	Zr	Cl	$CHP(C_6H_5)_3$	ca. 25	20	IV	38
10	Cp	U	η^5-Cp	$CHPR_2R'$	ca. 25	0.5	IV	7a,7b
11	Cp	U	η^5-Cp	R (= alkyl)	ca. 25	12–24	CO-uptake reversible	this work
12	Cp	U	η^5-Cp	$N(C_2H_5)_2$	ca. 25	12	IV	this work
13	Cp	Lu	THF [g]	$C(CH_3)_3$	ca. 25	48–72	VI [f]	2
14	Cp*	Th,U	η^2-$CONR_2$	NR_2	65	1.5	CO-uptake reversible; IV	1e
15	Cp*	Zr	η^2-$COCH_3$	CH_3	75	24	I	22
16	Cp*	Th,U	Cl	NR_2	95–100	1.5–2.0	IV, (V ?)	1e

[a] Of M–Y bond (s) undergoing carbonylation. [b] For quantitative carbonylation of Y [c] Numbers refer to the stabilization step depicted in Scheme 1. [d] 1,2-$SiMe_3$ migration. [e] At room temperature. [f] Formation of dinuclear system. [g] THF replaced by η^2-COR [h] Insertion product notisolable.

(Scheme 1) seems to depend in a subtle manner on the predominance of a few separate features, e.g.

(a) the steric bulk of the ligand sphere particularly within the most reactive ^{f}M–Y region of the organometallic reagent, as well as within the frequently even more congested (primary) product;

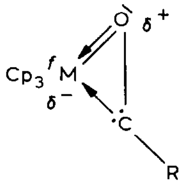
(b) the electronically-determined aptitude of the ^{f}M–Y bond to react with CO and related unsaturated species;

(c) any ancillary electronic influence of the non-carbonylated ligand(s) X, including a strengthening of both the U–O bond (by electron withdrawal) and of the oxycarbenoid ligand (by electron donation, e.g. structure **K**);

(d) the driving force of irreversible reaction steps following the primary CO-uptake, leading to further (electronic and/or steric) stabilization of the initial insertion product $Cp'_2M(\eta^2\text{-COY})X$ (see Scheme 1).

In accordance with the expectation that in most $Cp_3U(\eta^2\text{-COR})$ species the carbenoid centre must be effectively screened from a potential reactant by the three rather extended η^5-Cp ligands, neither dimerization of two $Cp_3U(\eta^2\text{-COR})$ moieties (step II of Scheme 1) nor the intramolecular 1,2-shift of a hydrogen atom (step III) or additional CO-uptake (step VI) have been observed at temperatures up to ca. 60 °C. Instead, exclusively clean decarbonylation (step VII) becomes predominant at elevated temperatures. Any important contributions of pathway V, which would likewise reduce the carbenoid character, can be ruled out from the NMR spectra in view of the virtual equivalence of all three Cp ligands down to 200 K.

On the other hand, according to some very recent results [4], the successfully carbonylated Cp_3Th-alkyls, $Cp_3Th(\eta^2\text{-COR})$, seem to clearly prefer typical carbene reactions (e.g. step II or II of Scheme 1) at elevated temperatures. Although any detailed explanation of the apparently different chemistry of $Cp_3{}^fM(\eta^2\text{-COR})$ systems involving ^{f}M = either U or Th must await further investigation, it may be argued that one reason could be the concerted influence of the three Cp ligands by which the U–O bond might be weakened more effectively than the corresponding Th–O bond. The oxygenophility of thorium even exceeds that of uranium, and so structure M, involving an extra O-to-^{f}M π-bond, will be more important in case of ^{f}M = Th, in addition to the structures **A**–**C**.



(M)

Mechanistic details of the CO-uptake of Cp_3UR are also still rather speculative. So far, all attempts to detect an intermediate species of trigonal bipyramidal geometry by NIR/VIS or ^{1}H NMR spectroscopy have so far failed not only in the case of CO, but also that of $NCCH_3$, as the electronically unsaturated Lewis base. Similar results have already been reported for the reaction of Cp_3UCH_3 with $LiCH_3$ [42].

Experimental

All manipulations were carried out with the rigorous exclusion of oxygen and moisture either in a dinitrogen-filled, recirculating glove box (Jahan, France) or by the usual Schlenk technique. Carbon monoxide (Carlo Erba) was purified by passage through two columns containing MnO (supported on vermiculite) and activated 4Å molecular sieves (BDH). The solvents (diethyl ether, toluene, n-hexane) were purified by refluxing over potassium in the presence of benzophenone as an oxygen indicator, followed by distillation under dinitrogen, and were stored in glove box.

Analytical method

Proton NMR spectra were recorded on FT-80 A (Varian) and WP 80 SY (Bruker) instruments, respectively, equipped with variable temperature accessories. The solutions of the samples (in degassed and anhydrous deuterated solvents) were prepared inside the glove box, and the tubes sealed in vacuo.

Infrared spectra in the range 4000–200 cm^{-1} were recorded on the Perkin–Elmer spectrophotometers 580 B or 577 using either KBr-pellets or Nujol mulls (between CsI disks in an air-tight holder sealed with an O-ring).

Electronic (NIR/VIS-) spectra were recorded at room temperature on a Cary 17 D spectrophotometer using optical-quartz cells (10 mm).

Mass spectra were recorded on a V.G. Organic Ltd. ZAB 2F spectrometer (*EI* 70 eV; probe temperature ca. 100 °C).

Elemental analyses and molecular weight determinations (see Table 9) were carried out by Dornis u. Kolbe, Mikroanalytisches Laboratorium, Mülheim (F.R.G.).

TABLE 9

ELEMENTAL ANALYSES AND EFFECTIVE MOLECULAR WEIGHTS, RESPECTIVELY, OF VARIOUS CARBONYLATED SYSTEMS

Product	Found (calcd.) (%)			Mol.Wt [a]
	C	H	N	
Cp_3UCOCH_3	42.35	3.92		945
	(42.85)	(3.78)		(473.3)
$Cp_3UCOC_2H_5$	43.67	4.49		436
	(44.08)	(4.08)		(490.4)
$Cp_3UCO(i\text{-}C_3H_7)$	44.93	4.50		450
	(45.24)	(4.36)		(504.4)
$Cp_3UCO(n\text{-}C_4H_9)$	45.98	4.52		
	(46.33)	(4.63)		
$Cp_3UCO(t\text{-}C_4H_9)$	46.01	4.58		
	(46.33)	(4.63)		
$Cp_3UCON(C_2H_5)_2$	45.05	4.72	2.74	
	(45.03)	(4.69)	(2.64)	
$Cp_3UCONCBH_3$	40.83	3.70	2.68	
	(40.73)	(3.59)	(2.79)	

[a] Effective molecular weight (cryoscopic in C_6H_6-soln.).

Synthesis of Cp_3UR

The Cp_3UR complexes ($R = CH_3$, $CH(CH_3)_2$, n-C_4H_9, t-C_4H_9) were prepared either as previously reported [30] or by our modified method described below for $Cp_3UC_2H_5$.

Cp_3UNEt_2 was made by our improved procedure [21].

$Cp_3UC_2H_5$

A solution of C_2H_5MgBr (2 m*M*) in diethyl ether (20 ml) was added very slowly at −70 °C to a stirred solution of Cp_3UCl (2 m*M*), in toluene (50 ml). The mixture was allowed to warm slowly to 20 °C during 2 h and then stirred at this temperature for ca. 12 h. The ether was removed under vacuum, and the resulting suspension was filtered then evaporated to dryness under vacuum. The analytically pure solid obtained was used without further purification. ^1H NMR spectrum (solvent C_6D_6, temp.: 27 °C, Δ in ppm relative to internal C_6D_5H): 10.32 (s, 15H, Cp); 19.80 (t, 3H); 196.83 (q, 2H).

Carbonylation reactions

Typical reactions were carried out in a 100 ml flask equipped with a rubber septum screw cap containing a solution of Cp_3UR (2 m*M*) in toluene (20 ml). The flask was evacuated by syringe, and carbon monoxide, in molar ratio 1/1.5, was then introduced by syringe at room temperature. The mixture was stirred for 6–12 h, then filtered from a small amount of insoluble material (less than 4%), and the solvent was removed under vacuum. The resulting solid was dried in vacuo for 2 h, and characterized. The yields were almost quantitative.

The tubes containing the samples dissolved in toluene-d_8, were sealed in vacuo, placed inside the probe of the Varian FT-80 A spectrometer, and spun for 15 min at the pre-adjusted temperature and the spectrum was recorded. It was recorded again after an interval of ca. 15 min, and this process was repeated, until no further change of the spectrum was observed. The probe temperature was then increased by 10 °C steps, and the previous procedure repeated. When the insertion/extrusion product ratio had reached ca. 30/70, the NMR-tube was transferred into a cryostat (Haake). After 24 h at a temperature of −5 °C the NMR-tube was replaced in the spectrometer probe, and the insertion/extrusion ratio measured. This procedure (alternate cooling and scanning) was repeated many times, but no further change of the initial insertion/extrusion ratio was observed (after 30 d the final ratio was 81/19).

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