Carbonylation of the Alkyl Compounds [U(η-C_5H_4R)$_3$R′] and Rearrangement of the Acyl Derivatives [U(η-C_5H_4R)$_3$(η^2-COR′)] into C_6H_4RR'. Influence of R and R′ (Me, $\mathrm{Pr^i}$ or $\mathrm{Bu^t}$) and Role of the Solvent (Benzene or Tetrahydrofuran)†

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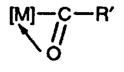
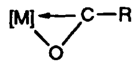
Carbonylation of the alkyl compounds [U(η-C_5H_4R)$_3$R′] **1** into the acyl derivatives [U(η-C_5H_4R)$_3$(η^2-COR′)] **2** exhibited pseudo first-order kinetics (*p*CO = 1 atm). The rate constants were dependent on R, following the order $\mathrm{Bu^t}$ < $\mathrm{Pr^i}$ < Me < H and varied with R′ in the unusual order $\mathrm{Pr^i}$ < Me < $\mathrm{Bu^t}$ < $\mathrm{Bu^n}$; for [U(η-C_5H_5)$_3$R′], $k(\mathrm{Bu^n}) = 2k(\mathrm{Bu^t}) = 4k(\mathrm{Pr^i})$. The rates were similar in benzene and in tetrahydrofuran. These results suggest that the migratory insertion of CO into the metal–carbon bond is not the rate-determining step. The rearrangement of the acyl complexes **2** afforded the alkylbenzene molecules C_6H_4RR', resulting from ring enlargement of a C_5H_4R ligand by incorporation of the CR′ fragment. This reaction exhibited first-order kinetics. Whatever the solvent, the rate constants were found to depend markedly on R′, increasing in the order $\mathrm{Bu^t}$ < $\mathrm{Pr^i}$ < $\mathrm{Bu^n}$ < Me. In benzene, the rates varied with R in the sequence H < Me < $\mathrm{Pr^i}$ < $\mathrm{Bu^t}$ whereas the opposite trend was observed in tetrahydrofuran. For a given solvent, the relative proportions of *meta*- and *para*-isomers of C_6H_4RR' were practically constant, whatever R and R′. These facts are best explained by a mechanism which involves a cyclopropyl intermediate resulting from addition of the oxycarbene group to the cyclopentadienyl ligand.

Acyl compounds of the early transition metals and f elements possess a very rich chemistry and many aspects of their synthesis, structure and reactivity appear unique and fascinating. In these complexes, both the carbon and oxygen atoms of the acyl ligand are bound to the metal and this η^2-co-ordination mode can be described by the two resonance structures **A** and **B**. Form **B** is likely to be responsible for the remarkable reactivity of the acyl group which reflects the carbene[1] or carbenium ion[2] character of the carbon atom. This property is manifest in a great variety of reactions such as insertion into metal–carbon,[3] metal–hydrogen[4] or carbon–hydrogen bonds,[5] coupling processes leading to monomeric and dimeric enediolates[6] or dimeric dienediolates,[2,7] and conversion into derivatives with ketone,[3] ketene,[8] carboxylate[9] or enolate ligands.[10] The electrophilic nature of the acyl carbon atom has also been noticed in the unusual rearrangement of the cyclopentadienyl compounds [Ta(η-C_5Me_4R)(η^2-COR′)Cl_3] (R = Me or Et, R′ = $\mathrm{CH_2Bu^t}$)[11] and [Ti(η-C_5Me_5)$_2$(η^2-COR′)] (R′ = Me or CH_2CMe_3)[12] which afforded the hexaalkylbenzene molecules C_6Me_4RR', resulting from ring enlargement of a C_5Me_4R ligand by incorporation of the alkylidene fragment CR′. We have found that the tris(cyclopentadienyl) uranium acyl complexes [U(η-C_5H_4R)$_3$(η^2-COR′)] (R, R′ = Me, $\mathrm{Pr^i}$ or $\mathrm{Bu^t}$) behave similarly, giving the substituted benzenes C_6H_4RR'.[13] In the present contribution, we will discuss the kinetic and selectivity patterns displayed by this rearrangement in two different solvents, benzene and tetrahydrofuran (thf), and for a range of alkyl R and R′ substituents.

The above acyl compounds have been synthesized in a classical way,[14] by insertion of CO into the U–C σ bond of the corresponding alkyl complexes [U(η-C_5H_4R)$_3$R′].[15] Such carbonylation reactions of f element alkyl derivatives have attracted much attention as they constitute interesting models for the activation and transformation of carbon monoxide. These reactions are likely to proceed by the intermediacy of CO adducts which are too labile to be observed by classical IR and NMR techniques.[16] In view of the very low affinity of lanthanide and actinide ions to form stable carbonyl complexes, one could expect that the first reversible addition of CO to the alkyl compound would play an important role in the formation of the acyl product. No data concerning this pre-equilibrium are available. It appeared that the uranium compounds [U(η-C_5H_4R)$_3$R′] reacted with CO in a manner quite distinct from that of their thorium analogues[16] and we will discuss here the differences in the carbonylation rates of these actinide complexes.



A



B

Results

The alkyl and acyl compounds [U(η-C_5H_4R)$_3$R′] and [U(η-C_5H_4R)$_3$(η^2-COR′)] are denoted by **1**(R, R′) and **2**(R, R′) respectively; for example, **1**(H, Me) and **2**(Me, $\mathrm{Pr^i}$) correspond respectively to [U(η-C_5H_5)$_3$Me] and [U(η-C_5H_4Me)$_3$(η^2-$\mathrm{COPr^i}$)]. All reactions were performed at 20 °C; the CO pressure was equal to 1 atm.

Carbonylation of the Alkyl Complexes [U(η-C_5H_4R)$_3$R′] **1**(R, R′).—Zanella and co-workers[15] first discovered that the complexes [U(η-C_5H_5)$_3$R′] (R′ = Me, $\mathrm{Bu^n}$, $\mathrm{Pr^i}$ or $\mathrm{Bu^t}$) could easily be carbonylated in benzene into the corresponding acyl derivatives which are stable in this solvent.[15] The velocities of these reactions were measured by monitoring the rate of disappearance of the cyclopentadienyl ^{1}H NMR signal of **1**(H, R′). For R′ = $\mathrm{Bu^n}$, $\mathrm{Pr^i}$ or $\mathrm{Bu^t}$, formation of the acyl product was complete in less than 24 h and plots of ln[**1**(H, R′)] *vs.* time were linear (Fig. 1). The pseudo first-order rate constants k_c for these reactions are listed in Table 1; they follow the order

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† *Non-SI unit employed:* atm ≈ 101 325 Pa.

$\mathrm{Bu^n} > \mathrm{Bu^t} > \mathrm{Pr^i}$ but do not vary considerably with R′ since $k_c(\mathrm{Bu^n}) = 2k_c(\mathrm{Bu^t}) = 4k_c(\mathrm{Pr^i})$. Carbonylation of the methyl derivative **1**(H, Me) did not go to completion and after 24 h, 90% of the complex was transformed into **2**(H, Me); conversion did not exceed 95% after 2 d. However, plots of ln[**1**(H, Me)] *vs.* time were linear over three half-lives and the rate constant k_c, which is similar to that determined for **1**(H, Bu^t), here refers to the rate of approach to the equilibrium position. In solution and in the absence of CO, **2**(H, Me) was readily decarbonylated to give back **1**(H, Me). Upon exposure to carbon monoxide, the benzyl compound **1**(H, CH_2Ph) was easily transformed into **2**(H, CH_2Ph) which was found to be unstable but, in contrast to the other acyl complexes (see later), decomposition of **2**(H, CH_2Ph) was not clean and gave unidentified products. In the early stages of the carbonylation of **1**(H, CH_2Ph), a straight line was obtained on plotting ln[**1**(H, CH_2Ph)] against reaction time and here again, the rate constant is similar to that measured for **1**(H, Bu^t).

The tris(methylcyclopentadienyl) uranium alkyl compounds **1**(Me, R′) (R′ = Me, Pr^i or Bu^t) were similarly converted into the corresponding acyl derivatives, with the same order of reactivity ($\mathrm{Bu^t} > \mathrm{Me} > \mathrm{Pr^i}$), but less rapidly than the non-substituted analogues **1**(H, R′) (Fig. 2). Thus, the reaction of **1**(Me, Me) or **1**(Me, Pr^i) was six times slower than the reaction of **1**(H, Me) or **1**(H, Pr^i) whereas **1**(Me, Bu^t) reacted twice as slowly as **1**(H, Bu^t). As in the case of **1**(H, Me), carbonylation of **1**(Me, Me) did not go to completion and the rate constant ($k_c = 1.9 \times 10^{-5}\ \mathrm{s^{-1}}$) corresponds to the initial stage of the reaction, over 2.5 half-lives of **1**(Me, Me). In contrast to **2**(H, R′), the acyl complexes **2**(Me, R′) slowly decomposed in benzene, giving the substituted toluene molecules C_6H_4MeR' (see later); only the two derivatives **2**(Me, Pr^i) and **2**(Me, Bu^t) could be isolated in a pure form.

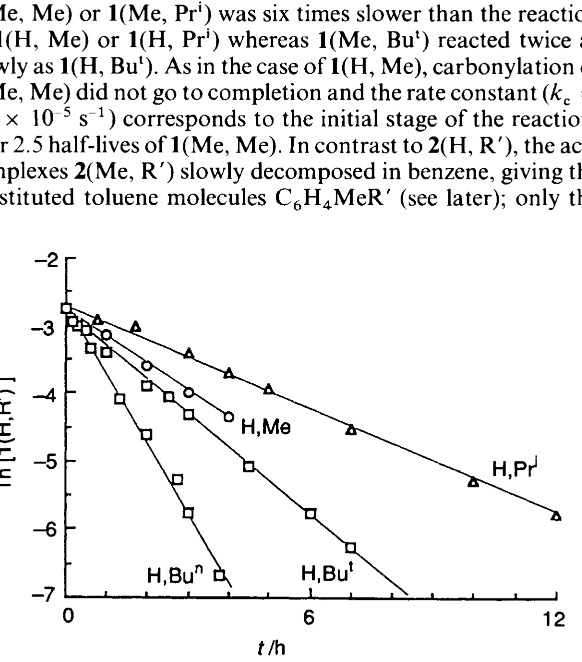


Fig. 1 Kinetic plot for the carbonylation of $[\mathrm{U}(\eta\text{-}C_5H_5)_3\mathrm{R}']$ **1**(H, R′) in benzene at 20 °C and 1 atm CO

Table 1 Pseudo first-order rate constants k_c for the carbonylation of $[\mathrm{U}(\eta\text{-}C_5H_4R)_3\mathrm{R}']$ **1**(R, R′) (pCO = 1 atm)

	$10^5\ k_c/\mathrm{s}^{-1\ a}$ at 20 °C	
R, R′	In benzene	In thf
H, Pr^i	7.1	7.1
H, Me	11.3	15.2
H, Bu^t	14.0	*b*
H, Bu^n	27.6	46.8
Me, Pr^i	1.1	1.8
Me, Me	1.9	2.2
Me, Bu^t	6.7	*c*
Pr^i, Me	0.9	0.7
Bu^t, Me	0.5	*d*

[a] Error limits at 95% confidence interval. [b] **1**(H, Bu^t) not stable in thf. [c] Not measured. [d] **1**(Bu^t, Me) reacted with CO to give unidentified uranium compounds.

Carbonylation of the series of methyl compounds **1**(R, Me) confirmed that the rates of CO insertion were dependent on R, decreasing in the order $\mathrm{H} > \mathrm{Me} > \mathrm{Pr^i} > \mathrm{Bu^t}$ (Fig. 2 and Table 1), and that the stability of the corresponding acyl products **2**(R, Me) decreased in the same order. Thus, reaction of **1**(Bu^t, Me) was achieved after 8 d but **2**(Bu^t, Me) was not detected, as it very rapidly transformed into a mixture of *tert*-butyltoluenes (see later).

The rates of these carbonylation reactions were not strongly affected when the benzene solvent was replaced by thf (Fig. 3 and Table 1); a slight enhancement was generally observed, which was more pronounced for the reaction of **1**(H, Bu^n) and **1**(Me, Pr^i), with rate constants being increased by a factor of 1.6. The relative influence of the substituents R and R′ on the reactivity of complexes **1** towards CO was identical to that found in benzene. None of the acyl complexes **2** was stable in thf.

Rearrangement of the Acyl Compounds $[\mathrm{U}(\eta\text{-}C_5H_4R)_3(\eta^2\text{-}\mathrm{COR}')]$ **2**(R, R′).—It has already been mentioned that the acyl complexes **2**(H, R′) are quite stable in benzene. The first signs of decomposition were visible after several days at 20 °C and the products then formed were not identified; no aromatic molecule could be detected. In thf, the compounds **2**(H, R′) decomposed to give the substituted benzene C_6H_5R' in almost quantitative yield. Formation of toluene, cumene or *tert*-butylbenzene was also observed when the corresponding alkyl complexes **1**(H, R′) were carbonylated in thf and the acyl intermediates **2**(H, R′) were detected in the case of R′ = Pr^i or Bu^t. Treatment of **1**(H, Bu^n) with ^{13}CO afforded, *via* the acyl complex $[\mathrm{U}(\eta\text{-}C_5H_5)_3(\eta^2\text{-}^{13}\mathrm{COBu^n})]$, a quantitative yield of *n*-butylbenzene in which the ^{13}C atom of the carbon monoxide was incorporated at the 1 position.[13] These reactions exhibited first-order kinetics ($-\mathrm{d}\ln[\mathbf{2}(\mathrm{H, R'})]/\mathrm{d}t = k_r$, Fig. 4), and the

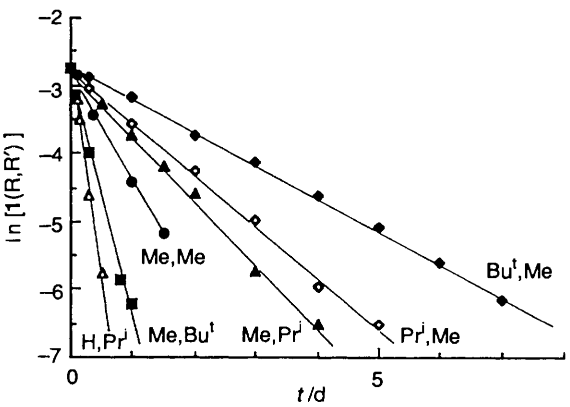


Fig. 2 Kinetic plot for the carbonylation of $[\mathrm{U}(\eta\text{-}C_5H_4R)_3\mathrm{R}']$ **1**(R, R′) in benzene at 20 °C and 1 atm CO

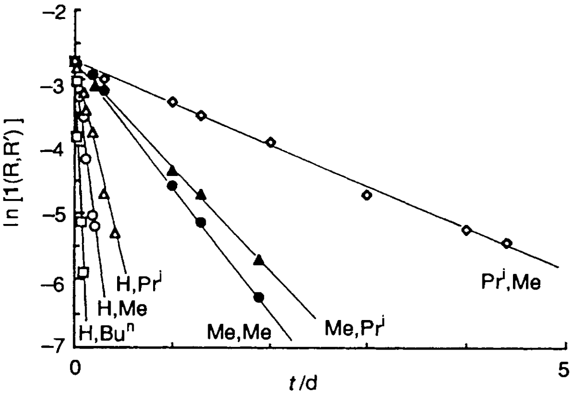


Fig. 3 Kinetic plot for the carbonylation of $[\mathrm{U}(\eta\text{-}C_5H_4R)_3\mathrm{R}']$ **1**(R, R′) in thf at 20 °C and 1 atm CO

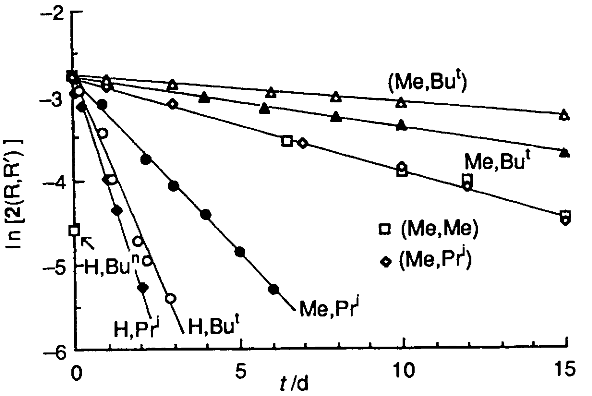


Fig. 4 Kinetic plot for the rearrangement of $[U(\eta\text{-}C_5H_4R)_3(\eta^2\text{-}COR')]$ **2**(R, R') at 20 °C in thf. In benzene denoted by parentheses

rate constants were found to depend markedly on R', decreasing in the order Me > Bu^n ≫ Pr^i > Bu^t (Table 2). The rearrangement of **2**(H, Me) was too rapid to be measured and there is at least a 10^3-fold increase in rate on proceeding from R' = Pr^i or Bu^t to R' = Me. Decomposition of the tris(methylcyclopentadienyl) uranium acyl complexes **2**(Me, R') proceeded much less rapidly than that of **2**(H, R'), but the same variation with R' was observed (Me > Pr^i > Bu^t). Not surprisingly, this decomposition required a longer period in benzene, especially in the case of the methyl derivative **2**(Me, Me); in the aromatic solvent, the rate constants followed the same variation with R' but were less dispersed than in thf. It is noteworthy that in benzene, the rates of rearrangement of the complexes **2**(R, Me) varied with R in the order Bu^t > Pr^i > Me > H whereas the opposite trend was observed in thf (Table 2).

This rearrangement of the acyl complexes **2**(R, R') gave a mixture of *meta*- and *para*-dialkylbenzene molecules C_6H_4RR' (R ≠ H); the *ortho* isomer was never detected by GLC or NMR spectroscopy. Whatever R and R', the relative proportions of *meta*- and *para*-isomers were practically constant, for a given solvent (Table 3). In thf, the ratio [*meta*]/[*para*] was equal to 0.5 whereas in benzene it was equal to 5 [2 for **2**(Bu^t, Me)]. As a consequence, the cross reactions of **2**(Me, Pr^i) and **2**(Pr^i, Me) afforded the same mixtures of cymenes, even if their kinetics were quite different; the distinct courses of the carbonylation reactions of **1**(Me, Pr^i) or **1**(Pr^i, Me), both leading to $C_6H_4MePr^i$ by the intermediacy of **2**(Me, Pr^i) or **2**(Pr^i, Me), is illustrated in Fig. 5.

During the rearrangement of complexes **2**(H, R') in thf, an NMR signal was visible at δ −21.31, which disappeared while a brown powder progressively precipitated. The latter was then insoluble in common organic solvents; elemental analyses of a sample were in reasonable agreement with the formula $[U(\eta\text{-}C_5H_5)_2O\cdot\text{thf}]$.[13] Similar observations could be made during the decomposition of **2**(Me, R') and **2**(Pr^i, Me) (see Experimental section). The organometallic product resulting from the transformation of **2**(Bu^t, Me) in benzene was soluble in this solvent and its ^{1}H NMR spectrum was identical to that of $[\{U(\eta\text{-}C_5H_4Bu^t)_2(\mu\text{-}O)\}_3]$.[17]

Discussion

Carbonylation of the Alkyl Complexes $[U(\eta\text{-}C_5H_4R)_3R']$ **1**(R, R').—The reasonable scenario which is generally accepted for the carbonylation of alkyl complexes such as **1**(R, R') is represented in Scheme 1.[16] Most of the lanthanide and actinide alkyl compounds react with CO to give the corresponding η^2-acyl derivatives[14] but the carbonyl complexes **C**, the likely intermediates in these transformations, could neither be isolated nor detected. The sole molecular carbon monoxide complex of an f element to have been observed in solution and solid phase is the U^{III} compound $[U(\eta\text{-}C_5H_4SiMe_3)_3(CO)]$, which is stable under CO pressure.[18] The second step of the carbonylation of complexes **1** (Scheme 1) should be the migratory insertion of CO into the metal–carbon σ bond, a reaction that has been extensively studied on a variety of d transition-metal systems.[19] The kinetic data for most of these CO insertions are in agreement with the sequence shown in Scheme 2, where the intermediate [M](COR') may be solvated (solv) or may possess an η^2-acyl group; the incoming ligand L may be CO itself.

By applying the steady-state approximation to this kinetic scheme, the expressions shown in equations (1) and (2) are

$$k_{obs} = \frac{k_2k_3[L]}{k_{-2} + k_3[L]} \qquad (1)$$

$$k_{obs}^{-1} = k_{-2}/(k_2k_3[L]) + k_2^{-1} \qquad (2)$$

Table 2 First-order rate constants k_r for the rearrangement of $[U(\eta\text{-}C_5H_4R)_3(\eta^2\text{-}COR')]$ **2**(R, R')

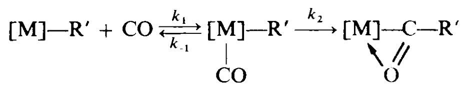
R, R'	$10^5\ k_r/s^{-1}$ [a] at 20 °C In benzene	In thf
H, Bu^t	*b*	1.1
H, Pr^i	*b*	1.4
H, Bu^n	*b*	640
H, Me	*b*	> 1500
Me, Bu^t	0.03	0.07
Me, Pr^i	0.13	0.48
Me, Me	0.13	> 30[c]
Pr^i, Me	1.5[d]	6[d]
Bu^t, Me	> 8[c]	*e*

[a] Error limits at 95% confidence interval. [b] Stable in benzene. [c] The acyl compound resulting from carbonylation of **1**(R, R') was not detected by NMR; for estimation of *k* limit, see Experimental section. [d] Rearrangement of **2**(Pr^i, Me) was concomitant with carbonylation of **1**(Pr^i, Me); for determination of k_r, see Experimental section. [e] **1**(Bu^t, Me) reacted with CO to give unidentified uranium compounds.

Table 3 Formation of the alkylbenzene molecules C_6H_4RR' from the reaction of $[U(\eta\text{-}C_5H_4R)_3R']$ **1**(R, R') and carbon monoxide. Reaction times and proportions of isomers

R, R'	*t*/d ([*meta*]/[*para*]) In benzene	In thf
H, Bu^n	*a*	0.1
H, Me	*a*	0.3
H, Pr^i	*a*	3
H, Bu^t	*a*	4
Me, Me	28 (5)	2 (0.5)
Me, Pr^i	28 (5)	7 (0.5)
Me, Bu^t	105 (5)	50 (0.5)
Pr^i, Me	6 (5)	4 (0.5)
Bu^t, Me	8 (2)	*b*

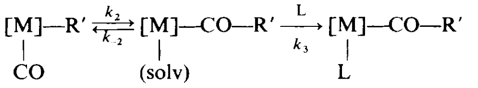
[a] The acyl compound is stable in benzene. [b] **1**(Bu^t, Me) reacted with CO to give unidentified uranium compounds.



$$[M]\text{—}R' + CO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\substack{|\\ CO}}{[M]\text{—}R'} \xrightarrow{k_2} [M]\text{—}\overset{}{C}(\text{=}O)\text{—}R'$$

C

Scheme 1



$$\underset{\substack{|\\ CO}}{[M]\text{—}R'} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\substack{|\\ (solv)}}{[M]\text{—}CO\text{—}R'} \xrightarrow[k_3]{L} \underset{\substack{|\\ L}}{[M]\text{—}CO\text{—}R'}$$

Scheme 2

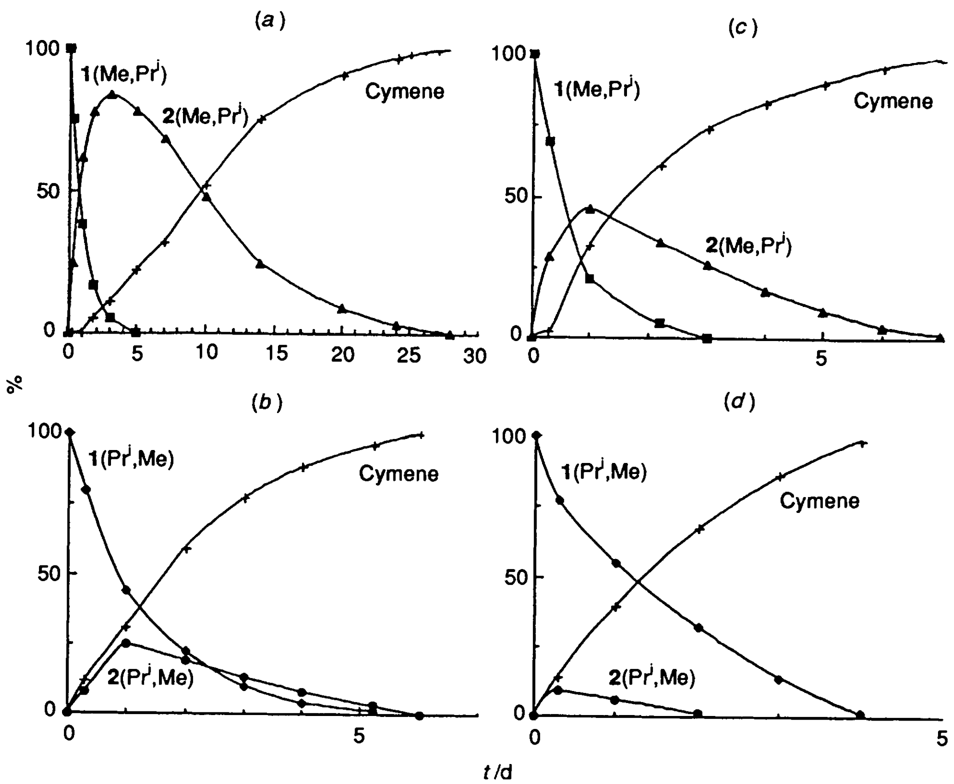


Fig. 5 Different courses of the cross reactions of **1**(Me, Pr^i) and **1**(Pr^i, Me) with CO: (*a*) and (*b*) in benzene, (*c*) and (*d*) in thf

obtained, where $k_{obs} = -d\ln[MR'(CO)]/dt = k[L]$. Even if the accurate determination of k_2 is often difficult, it has been noted that its value usually increases with the electron releasing capacity and/or the steric bulk of the alkyl group R'; the migratory aptitude of the alkyl group should also be related to the strength of the σ metal–carbon bond. The relative influence of these electronic, steric and energetic factors is difficult to appreciate and is not always well understood, but it is a general observation that CO insertion into a metal–isopropyl bond is much more facile than into a metal–methyl bond; benzylic complexes are rather unreactive. Such a trend has been found by Marks and co-workers[16] for the carbonylation in toluene of the thorium complexes [Th(η-$C_5H_5)_3$R'], the relative rates being 42 (Pr^i):1.0 (Bu^n):0.01 (Me): <0.01 (CH_2Ph).[16] Although the kinetic data do not allow, amongst others, determination of whether k_1 or k_2 in Scheme 1 is rate limiting, the above order is most consistent with insertion of CO into the Th–R' bond being the slow step. Application of the steady-state approximation to the concentration of **C** in Scheme 1 yields the rate law shown in equation (3), where $k_{obs} =$

$$k_{obs} = \frac{k_1 k_2}{k_{-1} + k_2} \tag{3}$$

$-d\ln[M\text{-}R']/dt = k[CO]$. If $k_2 \gg k_{-1}$, $k_{obs} = k_1$ and if $k_2 \ll k_{-1}$, $k_{obs} = Kk_2$ with $K = k_1/k_{-1}$. In the case of the thorium complexes [Th(η-$C_5H_5)_3$R'], the variation of k_{obs} with R' is similar to that expected for k_2, indicating that this variation is more important than that of the equilibrium constant *K*.

Carbonylation of the uranium compounds **1**(H, R') displayed quite different and unusual kinetic characteristics since in this series, the isopropyl derivative was the slowest to react, being approximately one quarter as reactive as **1**(H, Bu^t); the methyl complex exhibited an intermediate reactivity and even the benzyl compound could be carbonylated whereas the thorium analogue was inert under such conditions. These facts should reveal that here insertion of CO into the U–R' bond is not the rate-determining step. However, it seems unlikely that the rate constants k_c are exactly equal to k_1, because their dependence on the nature of the alkyl group R' is not typical (Bu^n > Bu^t > Me > Pr^i) and cannot be explained satisfactorily by steric or electronic factors; the values of k_2 and k_{-1} should be of the same order of magnitude and k_1 should be slightly inferior to k_c. The distinct reactivity towards carbon monoxide of the uranium and thorium compounds [M(η-$C_5H_5)_3$R'] can be accounted for by the following two reasons. The uranium–alkyl bond dissociation energies are invariably weaker than those of their thorium counterparts, by about 10–20 kJ mol^{-1},[20] and this difference should give rise to a more facile insertion of CO into the U–R' bond and a higher value of k_2. On the other hand, it is also conceivable that k_{-1} would be smaller for M = U, in relation with a higher kinetic stability of the intermediate **C** in Scheme 1. Theoretical calculations have shown that in [U(η-$C_5H_5)_3$(CO)] and [U(η-$C_5H_5)_3$(CO)]$^+$, the π back-bonding interaction is largely dominated by U 5f orbitals; this interaction is less important in the U^{IV} complex because only two f electrons are involved instead of three in the U^{III} compound, and also because the 5f orbitals are more contracted in the U^{IV} complex.[21] The thorium and uranium compounds [M(η-$C_5H_4R)_3$R'] have respectively a 5f^0 and 5f^2 ground configuration, and stabilization of the CO adducts **C** by metal to carbonyl π back-bonding would be disfavoured in the Th^{IV} compound which has no f electrons available.

The decrease in rates for the carbonylation of the ring substituted compounds **1**(R, Me) (H > Me > Pr^i > Bu^t) is also in agreement with k_1 being rate limiting and may be accounted for by the less easy approach of CO to the alkyl complex. The rates of these carbonylation reactions are not significantly affected by the solvent. It has often been observed that migratory CO insertion rates are strongly enhanced in donating, polar solvents, a fact that has been explained by co-ordinative solvent assistance and/or variations in solvent polarity.[19] Such phenomena would have no effect on k_{obs} if k_1 is rate limiting. On the other hand, the results show that co-ordination of CO to the alkyl compound is not impeded by competition with thf.

Rearrangement of the Acyl Compounds [U(η-C$_5$H$_4$R)$_3$(η^2-COR′)] **2**(R, R′).—The rearrangement of compounds **2**(R, R′) leading to the alkylbenzene molecules C$_6$H$_4$RR′, *via* deoxygenation of the COR′ group and insertion of the CR′ fragment into the cyclopentadienyl ligand C$_5$H$_4$R, is a further illustration of the oxycarbene character of such η^2-acyl complexes. This reaction now appears to be more general than might previously have been expected when similar transformations of peralkylcyclopentadienyl tantalum and titanium acyl compounds were discovered by Meyer and Messerle[11] and by De Boer and De White.[12] This rearrangement is likely to proceed by a concerted intramolecular process; no organic or organometallic product could be detected and the rates of the first-order reactions were not affected by varying the concentration of **2** (from 6×10^{-2} to 6×10^{-3} mol dm^{-3}). A mechanism is proposed in Scheme 3, where the intermediate or transition state **D**, resulting from addition of the carbene species to the cyclopentadienyl ligand, would rapidly give the final products.

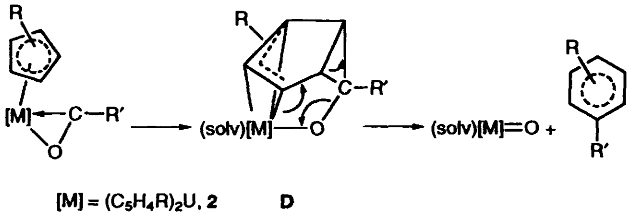
An alternative mechanism would involve acyl migration to the ring to form a cyclopentadienyl ketone complex **E** which would be readily deoxygenated; this possibility has been envisaged in the case of the aforementioned titanium complexes because formation of C$_5$Me$_5$(COMe) was observed during the rearrangement of [Ti(η-C$_5$Me$_5$)$_2$(η^2-COMe)(μ-OC)Mo(η-C$_5$H$_5$)(CO)$_2$].[12]

However, it is interesting that the ketone (or its complex **E**) could also be formed from intermediate **D**, as indicated in Scheme 4. The proportions of ketone and alkylbenzene molecules should then reflect the relative oxophilicity/reducibility of the metal centre, and it is not surprising that no ketone was detected during the transformation of the uranium complexes **2**(R, R′).

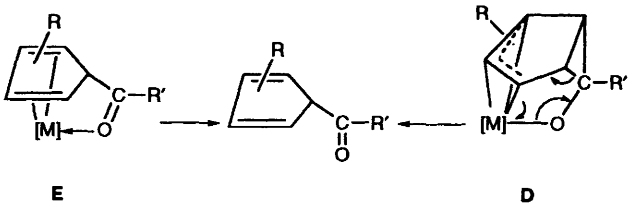
In benzene or thf, the rates of decomposition of **2**(R, R′) varied markedly with R′, decreasing in the order Me > Pr^i > Bu^t. Such a trend is easily accounted for by the influence of R′ on the reactivity of the electrophilic acyl carbon atom; the attack of the carbene species at the cyclopentadienyl ring will be facilitated by less sterically demanding and less electron donating R′ groups.

Acceleration of these reactions in thf can be explained by (*a*) stabilization of intermediate **D** by solvation and/or more likely (*b*) direct attack of solvent at the metal centre of **2**, leading to dissociation of the carbene species (S$_N$2 displacement) and its addition to the five-membered ring. This co-ordinative solvent assistance is particularly efficient for the non-substituted cyclopentadienyl compounds **2**(H, R′) which are stable in benzene. For the complexes **2**(Me, R′), the increase in rate of their decomposition by passing from benzene to thf is more pronounced for the methyl than for the isopropyl or *tert*-butyl derivatives, in agreement with the most facile approach of the co-ordinating solvent to the former. Therefore, the dispersion in rate constants with R′ groups (Me > Pr^i > Bu^t) is quite amplified in thf. Co-ordination of thf would also be favoured by smaller substituents on the cyclopentadienyl ligand and effectively, the rearrangement rates varied with R in the order H > Me > Pr^i. The opposite trend was observed in benzene because in the absence of solvent assistance, dissociation of the carbene species would correspond to a relief of the steric strain in **2** and would occur more readily with a bulky ring substituent.

The stereochemistry of the rearrangement of **2**(R, R′) is determined by the structure of intermediate **D** which results from addition of the carbene species to the cyclopentadienyl ligand. Not surprisingly, this addition does not take place on the more congested C–C bonds which are adjacent to the R substituent, and no *ortho* isomer of the dialkylbenzene molecules C$_6$H$_4$RR′ has ever been detected. In a given solvent, the two isomers of **D**, in which the R group occupies either the 1 or 2 position of the allyl moiety, and which give respectively the *meta*- and *para*-dialkylbenzene molecule, are in the same relative proportions whatever R and R′, as demonstrated by the constant ratio of the C$_6$H$_4$RR′ isomers. That interconversion of R and R′ in intermediates **D** does not affect their relative stabilities is well illustrated by the cross reactions of **2**(Me, Pr^i) and **2**(Pr^i, Me) or **2**(Me, Bu^t) and **2**(Bu^t, Me). In benzene, the isomer of **D** with the R substituent at the terminal site of the allyl fragment is the most stable and the reverse is true in thf, since in these two respective solvents, the *meta* or the *para* isomer of the aromatic molecule is formed predominantly. This difference of stereochemistry, which is obviously related to solvation and its electronic and steric effects, cannot be easily interpreted.[22]



Scheme 3



Scheme 4

In addition to the dialkylbenzene molecule, the rearrangement of **2**(R, R′) is expected to afford the oxo species [U(η-C$_5$H$_4$R)$_2$O]. It is only in the case of the transformation of **2**(Bu^t, Me) that the organometallic product, [{U(C$_5$H$_4$Bu^t)$_2$(μ-O)}$_3$], was characterized; the latter, which was previously obtained by thermolysis of the hydroxide compound [U(η-C$_5$H$_4$Bu^t)$_3$(OH)],[17] actually comes from the trimerization of [U(η-C$_5$H$_4$Bu^t)$_2$O]. The NMR signals which were observed during the reactions of **2**(R, R′) are likely to correspond to the intermediates [U(η-C$_5$H$_4$R)$_2$O] (R = H, Me or Pr^i), which would undergo rapid oligo- or poly-merization into insoluble products; similar behaviour of the putative species [M(η-C$_5$H$_5$)$_2$O] (M = Zr or Hf) has been reported.[23]

Conclusion

The carbonylation of the uranium alkyl compounds [U(η-C$_5$H$_4$R)$_3$R′] **1**(R, R′) exhibits pseudo first-order kinetics which are unusual and quite distinct from those of the thorium analogues, since the isopropyl complex is less reactive than the methyl or benzyl derivatives. The differences can be interpreted by considering that the migratory insertion of CO into the metal–carbon bond here is not the rate-determining step because of the weaker U–C bond dissociation energy and the greater stability of the CO adduct intermediate. Substitution of the cyclopentadienyl ligand induces a decrease in rate of carbonylation, which would reflect the less facile approach of CO to the alkyl compound. The transformation of the acyl compounds [U(η-C$_5$H$_4$R)$_3$(η^2-COR′)] **2**(R, R′) into the dialkylbenzene molecules C$_6$H$_4$RR′ is best explained by a mechanism which involves a cyclopropyl intermediate resulting from addition of the oxycarbene group to the cyclopentadienyl ligand. The electrophilic attack of the acyl carbon atom is more facile with smaller and less electron-donating R′ substituents and occurs at the less congested carbon–carbon bonds of the ring; thus the *ortho* isomer of C$_6$H$_4$RR′ was not detected. The relative proportions of *meta*- and *para*-isomers of C$_6$H$_4$RR′ indicate that in a given solvent, the structure of the intermediate is not affected by the nature of R and R′. The acyl complexes **2**(R, R′) are much less stable in benzene when the cyclopentadienyl ring is more substituted, a fact that could be explained by the tendency of the complex to relieve its steric strain by dissociation of the carbene species. However, the rearrangement of **2**(R, R′) is more rapid in thf but is then disfavoured by sterically demanding alkyl groups R which would impede the approach of the co-ordinating solvent.

These kinetic and stereoselectivity studies on the formation and rearrangement of the acyl complexes [U(η-$C_5H_4R)_3$(η^2-COR′)] indicate that these reactions are quite sensitive to the nature of the solvent, metal and ligand substituents and further illustrate the rich and varied chemistry of such η^2-acyl compounds.

Experimental

All manipulations were carried out under argon (< 5 ppm oxygen and water) using standard Schlenk-vessel and vacuum-line techniques or in a glove box. Deuteriated solvents were dried over Na/K alloy. The ^{1}H NMR spectra were recorded on a Bruker WP 60 (FT) or AC 200 instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). The GLC analyses were performed on an Intersmat IGC 120DFL apparatus equipped with an OV1 column.

Synthesis of the Alkyl Complexes **1**(R, R′).—Most of the compounds **1**(R, R′) were previously described: **1**(H, R′) (R′ = Me, Bu^n, Pr^i, Bu^t[24] or CH_2Ph[25]), **1**(Me, Me)[26] and **1**(Me, Bu^t);[27] these were classically prepared by treating the parent chloride [U(η-$C_5H_4R)_3$Cl] (R = H,[28] Me, Pr^i or Bu^t[29]) with the corresponding Grignard or alkyllithium reagent. The new derivatives **1**(Me, Pr^i), **1**(Pr^i, Me) and **1**(Bu^t, Me) were thus synthesized in almost quantitative yield by using MgPr^{i}Cl and LiMe in benzene and were characterized by their NMR spectra. (60 MHz, 30 °C, [$^2H_6$] benzene): **1**(Me, Pr^i), δ 3.29 and −2.80 (6 H + 6 H, s, C_5*H_4*Me), −8.10 (9 H, s, C_5H_4*Me*), −13.96 (6 H, d, *J* 6 Hz, CH*Me*$_2$), −184.8 (1 H, br, $w_{\frac{1}{2}}$ 50 Hz, C*H*Me$_2$); **1**(Pr^i, Me) δ 9.73 and −9.54 (6 H + 6 H, s, C_5*H_4*Pr^i), −4.70 (18 H, d, *J* 6, CH*Me*$_2$) −13.30 (3 H, spt, *J* 6 Hz, C*H*Me$_2$), −191.4 (3 H, br, $w_{\frac{1}{2}}$ 40 Hz, UMe); **1**(Bu^t, Me), δ 9.80 and −8.22 (6 H + 6 H, s, C_5*H_4*Bu^t), −6.63 (27 H, s, Bu^t), −191.9 (3 H, br, $w_{\frac{1}{2}}$ 50 Hz, UMe).

Carbonylation of the Alkyl Complexes **1**(R, R′).—The syntheses of the acyl compounds **2**(H, R′) (R′ = Me, Bu^n, Pr^i or Bu^t)[15] and **2**(Me, Bu^t)[27] have been previously reported. The new derivatives **2**(H, CH_2Ph), **2**(Me, Me), **2**(Me, Pr^i) and **2**(Pr^i, Me) were similarly prepared in benzene by treating the corresponding alkyl complexes **1**(R, R′) with CO (1 atm). These compounds are not stable in benzene and only **2**(Me, Pr^i) could be isolated in a pure form, after filtration and evaporation of the solution (85% yield). ^{1}H NMR (60 MHz, 30 °C, [$^2H_6$] benzene): **2**(H, CH_2Ph), δ 25.96 (2 H, s, CH_2), 17.56 (2 H, d, *J* 8, *o*-Ph), 11.57 (2 H, t, *J* 8, *m*-Ph), 10.00 (1 H, t, *J* 8 Hz, *p*-Ph), −11.22 (15 H, s, C_5H_5); **2**(Me, Me), δ 31.14 (3 H, s, COMe), −4.14 and −18.04 (6 H + 6 H, s, C_5*H_4*Me), −6.98 (9 H, s, C_5H_4*Me*); **2**(Me, Pr^i), δ 13.03 (1 H, spt, *J* 6, C*H*Me$_2$), 11.83 (6 H, d, *J* 6 Hz, CH*Me*$_2$), −5.15 and −14.42 (6 H + 6 H, s, C_5*H_4*Me), −9.51 (9 H, s, C_5H_4*Me*); **2**(Pr^i, Me), δ 33.13 (3 H, s, COMe), −0.91 and −15.22 (6 H + 6 H, s, C_5*H_4*Pr^i), −8.20 (18 H, d, *J* 6, CH*Me*$_2$), −16.62 (3 H, spt, *J* 6 Hz, C*H*Me$_2$).

The rates of these carbonylation reactions were determined by measuring the disappearance of **1**(R, R′). In a typical reaction, an NMR tube equipped with a Young Teflon valve was charged in the glove box with the alkyl complex (16 μmol, 7–10 mg) and the solvent (0.25 cm^3 of [$^2H_6$]benzene or [$^2H_8$]thf) was introduced *via* a syringe. The tube was adapted to the vacuum line, cooled at −50 °C, degassed and exposed to 1 atm of carbon monoxide. The tube was then removed from the vacuum line and allowed to warm at 20 °C in an air-conditioned room; the solution was stirred by attaching the tube perpendicular to the axis of an electrical rotor. The ^{1}H NMR spectra were recorded at appropriate time intervals and the concentration of **1**(R, R′) was determined by integration of the signals corresponding to the C_5H_4R ligand. Plots of ln[**1**(R, R′)] *vs.* time (Figs. 1–3) were fitted by standard linear regression techniques; the pseudo first-order rate constants are listed in Table 1. The error limits (> 95% confidence interval) were derived from the fitting procedure. Most experiments were repeated twice, with different initial concentrations of **1**(R, R′) and the results were reproducible.

Rearrangement of the Acyl Compounds **2**(R, R′).—The rates of rearrangement of **2**(R, R′) were determined by measuring the disappearance of the acyl complex; the first-order rate constants are listed in Table 2.

When **2**(R, R′) could be isolated pure in its solid form [**2**(H, R′) with R′ = Me, Bu^n, Pr^i or Bu^t and **2**(Me, R′) with R′ = Pr^i or Bu^t], a sample (16 μmol, 8–9 mg) was weighted in an NMR tube and dissolved in [$^2H_6$]benzene or [$^2H_8$]thf (0.25 cm^3). The spectra were recorded at appropriate time intervals and the concentrations of **2**(R, R′) and of the aromatic products were determined by integration of the corresponding signals. The rate constants were measured by plotting ln[**2**(R, R′)] *vs.* time (Fig. 4).

The other acyl complexes which were not stable enough to be isolated were prepared *in situ* by carbonylation of their alkyl precursor. The transformation of **1**(Me, Me) in benzene was complete after 2 d and the rate of rearrangement of **2**(Me, Me) could then be measured by plotting ln[**2**(Me, Me)]*vs.* time. Formation of **2**(Pr^i, Me) in benzene or thf was concomitant with its rearrangement (Fig. 5) and in this case, the rate constant of the rearrangement (k_r) was calculated by using the expression $[\mathbf{2}(\mathrm{Pr}^i, \mathrm{Me})] = [\mathbf{1}(\mathrm{Pr}^i, \mathrm{Me})]_0(k_c/k_r - k_c)\ (e^{-k_c t} - e^{-k_r t})$ where $[\mathbf{1}(\mathrm{Pr}^i, \mathrm{Me})]_0$ is the initial concentration of the alkyl complex and k_c the rate constant of its carbonylation.[30] The rearrangement of **2**(H, Me) or **2**(Me, Me) in thf and of **2**(Bu^t, Me) in benzene was more rapid than their formation and in this case, the inferior limit of k_r was estimated by using the expression $\beta_{max} = K^{K/1-K}$ where $\beta = [\mathbf{2}(R, R')]/[\mathbf{1}(R, R')]_0$ and $K = k_r/k_c$[30] and by assuming that **2**(R, R′) could be easily detected by NMR if its concentration had been superior to 5% of the initial concentration of **1**(R, R′).

The alkylbenzene products C_6H_4RR' resulting from the rearrangement of **2**(R, R′) have been identified by comparison of their NMR spectra and their GLC retention time with those of authentical samples. With the exception of [{U(η-C_5H_4-Bu$^t)_2$(μ-O)}$_3$] which was formed from **2**(Bu^t, Me) in benzene, the organometallic products resulting from the rearrangement of **2**(R, R′) were insoluble. However, paramagnetic NMR signals could be detected before precipitation of the brown powder; these resonances would be attributed to the oxo species [U(η-$C_5H_4R)_2$O] which would undergo rapid polymerization. ^{1}H NMR (60 MHz, 30 °C, [$^2H_8$]thf): R = H, δ −21.31; R = Me, δ 13.32 (6 H, s, Me), −34.99 and −38.22 (4 H + 4 H, C_5*H_4*Me); R = Pr^i, δ 5.70 (2 H, spt, *J* 6, C*H*Me$_2$), 3.98 (12 H, d, *J* 6 Hz, CH*Me*$_2$), −20.40 and −28.02 (4 H + 4 H, C_5*H_4*Pr^i).

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