Journal of Organometallic Chemistry, 345 (1988) 263–274
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Synthesis, crystal structures and ligand exchange reactions of some heptacoordinated acetylacetonate uranium(IV) complexes

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(Received October 23rd, 1987)

Abstract

The heptacoordinated uranium(IV) complexes $UCl_2(acac)_2L$ (L = THF, II; $OPPh_3$, III) and $CpUCl(acac)_2(OPPh_3)$ (IV) have been synthesized from $UCl_2(acac)_2(THF)_2$ (I).They are fluxional in solution, and undergo intermolecular ligand exchange reactions; in the presence of $OPPh_3$, III is in equilibrium with $UCl_2(acac)_2(OPPh_3)_2$ (V). The crystal structures of III and IV (as THF solvates) reveal pentagonal bipyramidal coordination with the oxygen ligands lying in the equatorial plane and Cl or Cp ligands in apical positions.

Introduction

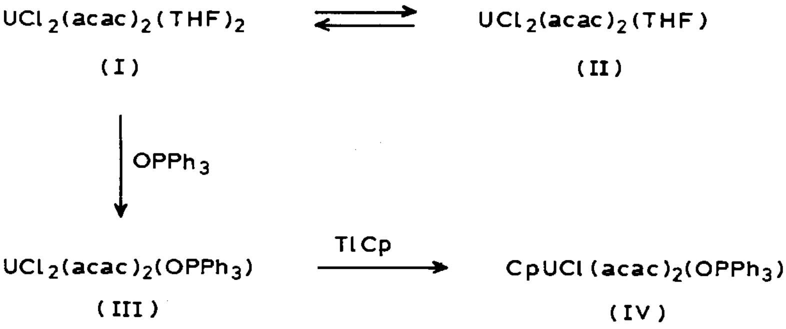
Heptacoordinate organotransition metal complexes generally undergo ready intramolecular rearrangements owing to the small energy differences between the possible coordination geometries [1]. It seemed to us of interest to determine the structures and study the dynamic behaviour of such compounds involving uranium(IV). These complexes are not common, but some of them have been characterized in the solid state [2,3]; solution studies have been carried out only for the acetylacetonate compound $CpU(acac)_3$ ($Cp = \eta$-C_5H_5, acac = $CH_3COCHCO$-$CHCOCH_3$) [4] and the $CpUCl_3L_3$ complexes that are intermediates in the substitution reactions of the octahedral $CpUCl_3L_2$ compounds [5]. We have prepared from $UCl_2(acac)_2(THF)_2$ (I) (THF = tetrahydrofuran) [6] the heptacoordinated uranium(IV) derivatives $UCl_2(acac)_2(OPPh_3)$ (III) and $CpUCl(acac)_2(OPPh_3)$ (IV), and we consider here the crystal structures and intra- and intermolecular ligand exchange reactions of these complexes.

0022-328X/88/$03.50

Results and discussion

Synthesis

The chemistry of the bis(acetylacetonato)dichlorouranium compound I has been studied previously by several groups [6,7]. The reactions we have observed, which differ somewhat from those previously reported, are summarized in Scheme 1.



Scheme 1

Evaporation of a toluene solution of I gave orange crystals of $UCl_2(acac)_2(THF)$ (II), which was made previously by stirring a suspension of I in pentane [7]. Addition of a stoichiometric amount of triphenylphosphine oxide to I gave $UCl_2(acac)_2(OPPh_3)$ (III), isolated as orange crystals; III reacted with TlCp to give green crystals of the monocyclopentadienyl compound $CpUCl(acac)_2(OPPh_3)$ (IV). The complexes were characterized by elemental analysis, X-ray crystallography, and NMR spectroscopy.

Synthesis of $UCl_2(acac)_2(OPPh_3)_2$ (V) from $UCl_4(OPPh_3)_2$ and some of cyclopentadienyluranium(IV) acetylacetonates, including $CpUCl(acac)_2$ and $CpUCl(acac)_2(OPPh_3)_2$, has been reported [7]; preparation of V from I has also been described [6]. All these complexes, as well as I [6], were, however, characterized only by their elemental analyses and their UV and IR spectra. We could not obtain crystals of V, which is in equilibrium with III in solution (vide infra), and we did not observe the formation of the cyclopentadienyl derivatives, which were expected to be unstable for steric reasons [8].

Crystal structures of THF solvates of III and IV

ORTEP [9] drawings of the molecules III and IV are shown in Figs. 1 and 2, respectively. Selected bond distances and angles are listed in Table 1 or indicated on Fig. 3. The structures of III and IV are very similar, and consist of discrete neutral molecules in which the U atom is seven-coordinate and in a pentagonal bipyramidal arrangement with exactly the same basal plane consisting of two acac ligands, acting as bidentate chelates, and one $OPPh_3$ ligand. There is no interaction between the THF solvate molecules and the uranium complexes: all the intermolecular contacts are greater than 3.52(5) Å in III (C(54)–C(33)) and 3.92(2) Å in IV (C(302)–C(18)). The pyramid axes, defined by the U atom and the apical positions (two Cl atoms in III, one Cl atom and one Cp ligand in IV), are essentially linear, and perpendicular to the pentagonal bases (III, Cl(1)–U–Cl(2) 177.8(4)°; IV, Cl–U–centroid of the Cp ring 178.2(6)°). The least-squares planes of the oxygen atoms show very small maximum deviations of these atoms from the plane (III, 0.15(2), −0.12(2) Å; IV,

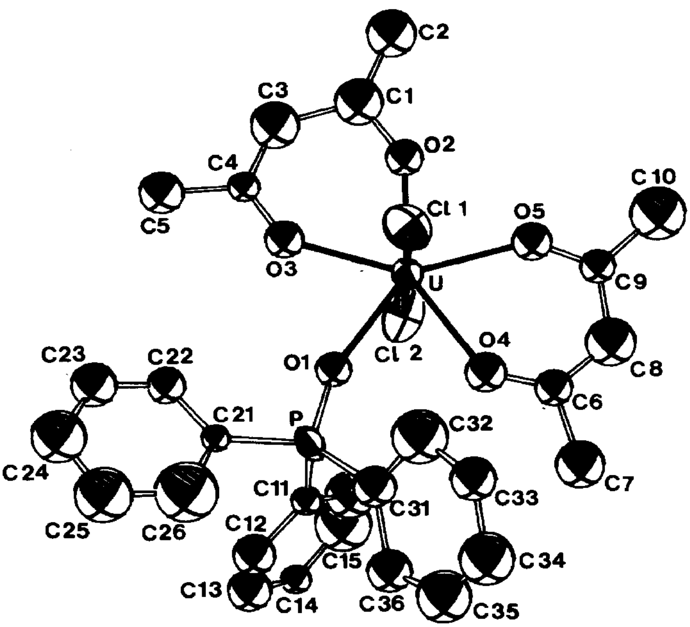


Fig. 1. View of molecule III indicating atom labelling.

0.06(1), −0.05(1) Å). The O–U–O equatorial bond angles ranging from 74.7 to 70.5° (III) and 72.3 to 70.1° (IV) are indicative of a fairly regular pentagon (the ideal value is 72°). The Cp ring, which has the usual planar geometry, is parallel to the equatorial plane, with the two pentagons twisted by 36° (Fig. 3). The U atom in IV is 0.228(1) Å from the pentagonal base on the Cp ring side, whereas it lies in the equatorial plane of III. The mean U–O(ketonate) bond lengths are identical in the two compounds (III, 2.32(4) Å; IV, 2.35(1) Å) as are the U–Cl and the U–O(PPh_3) bond lengths. The β-diketonate groups have the usual planar geometry; the folding angles along the O–O line are similar, namely 6(2) and 5(2)° in III and 8(3) and 5(1)° in IV. However, the two acac ligands are tilted on the same side of the equatorial plane in III, whereas they are on opposite sides in IV.

It is of interest to compare the structures of III and I ($UCl_2(acac)_2(THF)_2$ in which the U atom is in a dodecahedral environment (Fig. 3)). In this structure [10], the O atoms of the acac ligands form a planar trapeze perpendicular to a second trapeze defined by the two Cl and the two THF oxygen atoms. The latter atoms lie above and below the O(acac) plane at ±2.58(1) Å. The U,O(acac) planes are identical in compounds I and III, but the higher uranium coordination number in I leads to a bent Cl–U–Cl bond angle, considerably smaller (148.9(1)°) than the corresponding angle in III (177.8(4)°).

With the exception of the $[UCl(OPMe_3)_6]^{3+}$ cation, which has a capped octahedral structure [3], the few known examples of heptacoordinated uranium(IV) complexes [2] also have a pentagonal bipyramidal configuration. It is noteworthy that the two-electron donor ligands of these compounds always lie in the equatorial plane of the bipyramid, as is commonly observed in the heptacoordinated dioxouranium(VI) complexes, in which the linear uranyl group provides the rigid axis [11].

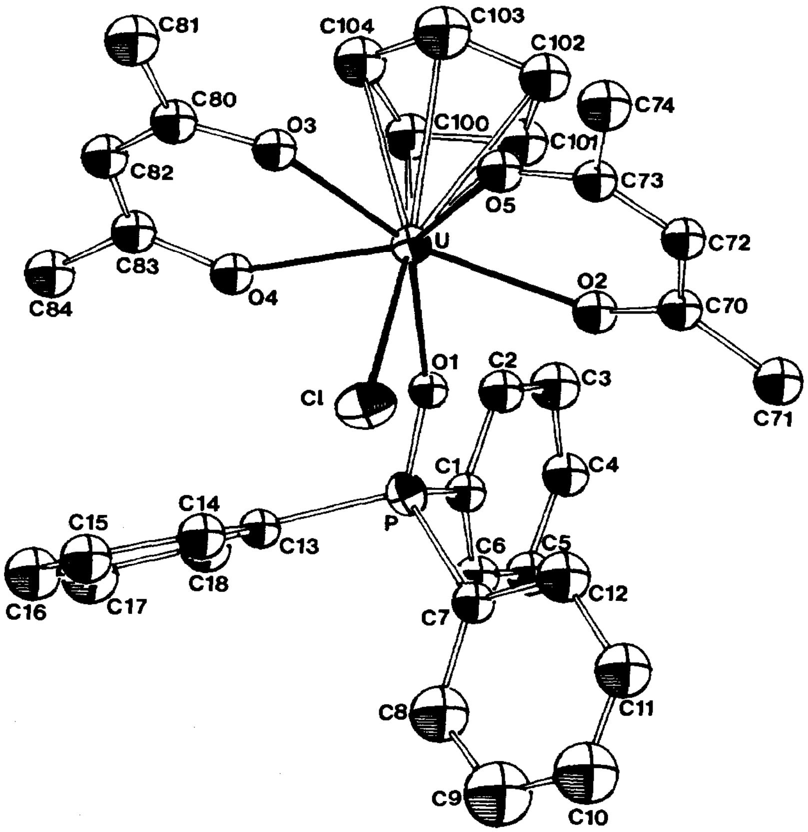


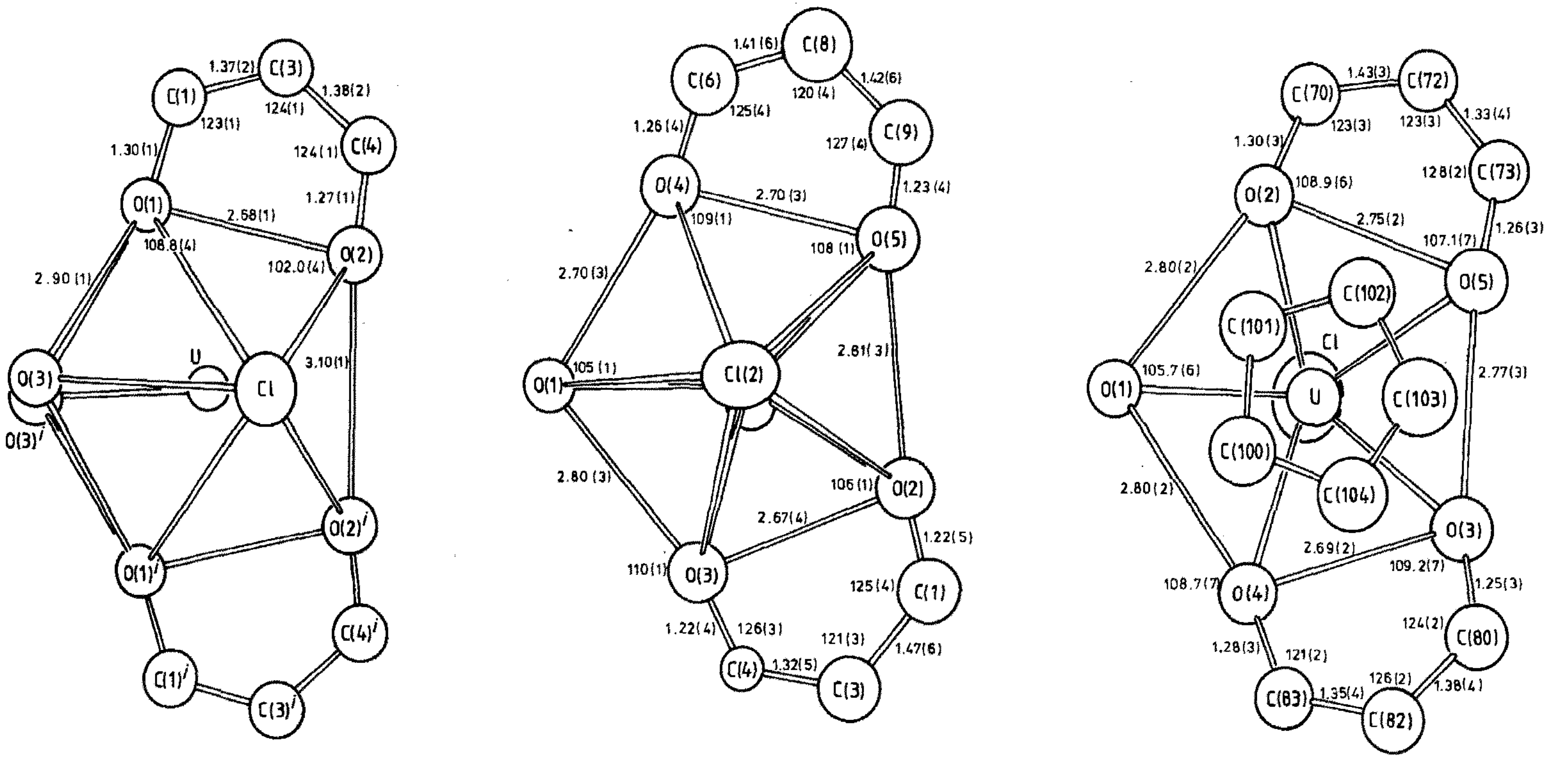
Fig. 2. View of molecule IV showing atom labelling.

Table 1

Selected bond distances (Å) and angles (°): environment of the U atom

$UCl_2(acac)_2(OPPh_3)$ (III)		$CpUCl(acac)_2(OPPh_3)$ (IV)	
U–O(1)	2.32(1)	U–O(1)	2.40(1)
U–O(2)	2.32(2)	U–O(2)	2.34(1)
U–O(3)	2.29(2)	U–O(3)	2.34(1)
U–O(4)	2.33(1)	U–O(4)	2.35(1)
U–O(5)	2.33(2)	U–O(5)	2.36(1)
U–Cl(1)	2.605(8)	U–Cl	2.662(8)
U–Cl(2)	2.629(8)	U–C(π-bonded) [a]	2.79(1)
Cl(1)–U–Cl(2)	177.9(2)	U–1 [b]	2.53(3)
		Cl–U–1	178.2(6)
O(1)–U–O(3)	74.0(5)	O(1)–U–O(2)	72.1(5)
O(1)–U –O(4)	71.3(5)	O(2)–U–O(5)	71.3(5)
O(3)–U–O(2)	70.8(6)	O(1)–U–O(4)	72.3(5)
O(20–U–O(5)	74.0(6)	O(3)–U–O(4)	70.1(5)
O(4)–U–O(5)	70.6(6)	O(3)–U–O(5)	72.3(5)

[a] Average values and related standard deviations calculated with the formulas $d_{av} = \Sigma_i/\sigma_i^2/\Sigma_i 1/\sigma_i^2$ and $\sigma_{av} = (1/\Sigma_i 1/\sigma_i^2)^{1/2}$ where d_i is the individual distance U–C and σ_i their standard deviations [19]. [b] 1 is the centroïd of the cyclopentadienyl ring.



(I)

(III)

(IV)

Fig. 3. View of the uranium environment in compounds I, III and IV. Projection on the pentagonal bases: in I, marked atoms (*i*) are related to the unmarked atoms by the diad axis.

Table 2

^{1}H NMR spectra of the complexes [a]

Compound	T (° C)	Ligands	
		acac	other
I	30	57.20(s,2H,CH) 18.15(s,12H,CH_3)	$-$5.84(br,8H,β-THF) $-$12.99(br,8H,α-THF)
II	30	51.35(s,2H,CH) 12.81(s,12H,CH_3)	$-$14.12(br,4H,β-THF) $-$25.64(br,4H,α-THF)
III	$-$30	48.52(s,2H,CH) 20.23(s,12H,CH_3)	6.86(t,7.6,3H,p-Ph) 5.74(d of t,7.6 and 3.0,6H,m-Ph) $-$5.26(d of d,12.0 and 7.6,6H,o-Ph)
IV	$-$30	50.55(s,2H,CH) 32.85(s,6H,CH_3) [b] $-$4.65(s,6H,CH_3) [b]	4.85(m,9H,p- and m-Ph) $-$3.90(d of d,12.0 and 7.6,6H,o-Ph) $-$32.63(s,5H,Cp)

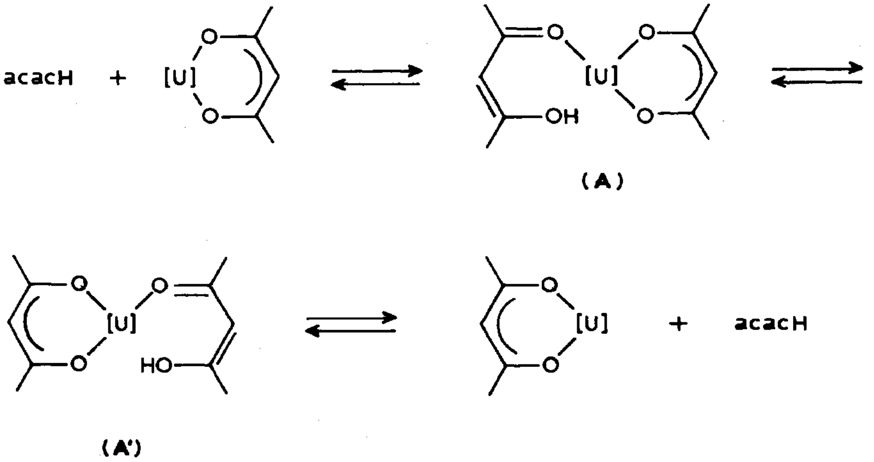
[a] In $CDCl_3$, except for IV which was in toluene-d_8; δ relative to TMS (multiplicity, J in Hz, intensity, assignment). [b] Spin saturation transfer observed between these two signals.

Ligand exchange reactions

The ^{1}H NMR spectral data for the complexes are listed in Table 2. Paramagnetic induced shifts and decoupling experiments allowed us to determine the positions of the signals from the various different phenyl hydrogens as well as their coupling constants [5]. As is usual for octa- and heptacoordinated compounds [1], complexes I–IV are fluxional in solution. The slow limit spectra of compounds I–III could not be observed, indicating that there are rapid intramolecular rearrangements of these complexes, even at low temperature. However, the spectrum of IV at 10 ° C, exhibits two signals from the acetylacetonate groups, and this is consistent with the crystal structure of the complex. Exchange between the methyl groups was revealed at 10 ° C by spin saturation transfer experiments [12]; coalescence occurred at about 65 ° C and a new broad signal was visible in the spectrum (3.80 ppm) at 110 ° C. The relative rigidity of IV can be attributed to steric factors; the dynamic behaviour of the compound is similar to that of CpU(acac)$_3$, which in solution at low temperature also adopts a pentagonal bipyramidal configuration [4].

The ^{1}H NMR spectra of I in the presence of 2–3 equivalents of THF showed broad resonances corresponding to tetrahydrofuran; the signals are shifted towards the diamagnetic region with increased concentrations of free ligand. This behaviour, which indicates rapid exchange between free and coordinated THF ligands of I, is not surprising since the complex readily dissociates reversibly in solution to give II. Variations in the NMR chemical shifts, signal broadening, and/or spin saturation transfer experiments indicated that complexes I–IV also exchange their acac ligands with free acetylacetone. Such reactions presumably proceed by the associative mechanism (Scheme 2) previously proposed for the intermolecular ligand exchange reactions of the tetrakis(β-diketonato)uranium(IV) compounds [13].

We assume that octacoordinated intermediates A and A′ are involved; they would be readily accessible from the coordinatively and sterically uncongested complex II, and therefore from I. The possibility of forming octacoordinated complexes from III was confirmed by NMR spectroscopic observation of the



Scheme 2

reversible addition of triphenylphosphine oxide to give $UCl_2(acac)_2(OPPh_3)_2$ (V) (see Experimental):

$$\underset{(III)}{UCl_2(acac)_2(OPPh_3)} + OPPh_3 \rightleftarrows \underset{(V)}{UCl_2(acac)_2(OPPh_3)_2}$$

This equilibrium was shifted towards the formation of V by addition of more triphenylphosphine oxide or by concentrating the solution. Unfortunately no crystals of V suitable for X-ray diffraction could be obtained.

Along with its intramolecular motion, complex IV undergoes much less facile exchange reactions of its acac and $OPPh_3$ ligands with the corresponding free molecules. These reactions could not be observed by NMR studies below 0 °C, and no intermediate could be detected.

Experimental

Microanalyses were carried out by the Analytical Laboratories at Engelskirchen (F.R.G.). The infrared spectra were recorded on a Perkin–Elmer 782 instrument and the ^1H NMR spectra on a Bruker W60 (FT) instrument. Deuterated solvents were dried over molecular sieves (3 Å). The paramagnetic chemical shifts were calculated with respect to tetramethylsilane ($\delta = 0$ ppm); positive values denote shifts to low field. The NMR spectra are given in Table 2.

All experiments were carried out under argon by standard Schlenk techniques or in a glove box. Evaporation was under reduced pressure. The THF, toluene, and n-hexane were distilled from sodium. $OPPh_3$ (Schuchardt) was used without purification; TlCp [14] and $UCl_2(acac)_2(THF)_2$ [6,7] were prepared by published methods.

Syntheses

$UCl_2(acac)_2(THF)$ (II)

The volume of a solution of I (250 mg) in toluene (5 ml) was reduced to half by evaporation. Orange crystals of II were immediately formed; these were filtered off and dried under vacuum (115 mg, 52%). The product was identical to that prepared as described in ref. 7.

$UCl_2(acac)_2(OPPh_3)$ (III)

$OPPh_3$ (118 mg) was added to a solution of I (277 mg) in THF (10 ml). After 10 min, the brown solution was evaporated to dryness to give an orange solid (330 mg). The NMR spectrum showed that the product was pure enough to be used without further treatment. An analytical sample was prepared by recrystallisation from $CDCl_3$/hexane. Analysis: Found: C, 42.52; H, 3.74; Cl, 9.25; P, 4.03. $C_{28}H_{29}Cl_2O_5PU$ calc: C, 42.80; H, 3.69; Cl, 9.04; P, 3.95%.

$CpUCl(acac)_2(OPPh_3)$ (IV)

TlCp (106 mg) was added to a solution of III, prepared in situ from I (256 mg) and $OPPh_3$ (110 mg) in THF (15 ml). The mixture was stirred for 3 h and filtered. The green solution was evaporated to small volume and hexane was added. The solution was kept for 3 d at 4 ° C and the green crystals then filtered off and dried under vacuum. The NMR spectrum of IV (toluene-d_8, -30 ° C) showed small additional resonances (the intensity of which varied with the preparation of the NMR tube) at ≈ 7.3 (free $OPPh_3$) and -11.15 ppm (unidentified compound). Analysis: Found: C, 48.85; H, 4.42; Cl, 4.22; P, 3.87. $C_{33}H_{34}ClO_5PU$ calc: C, 48.86; H, 4.19; Cl, 4.38; P, 3.82%.

X-Ray analysis

X-ray studies were carried out on the solvated compounds, $UCl_2(acac)_2(OPPh_3) \cdot THF$ and $CpUCl(acac)_2(OPPh_3) \cdot THF$, obtained by crystallisation from THF/hexane solutions. Single crystals were introduced into thin-walled Lindeman glass tubes in an inert-atmosphere drybox and studied with an Enraf–Nonius CAD4 automatic diffractometer. Cell dimensions were obtained by a least-squares refinement of the setting angles of the 25 reflections with θ between 8 and 12°. Intensities were corrected for Lorentz polarization and empirical absorption (III, based on ψ scans [15]; IV, using DIFABS [16]). The structures were solved by the heavy-atom method and refined by full-matrix least-squares (F). Only the U, P and Cl atoms were refined anisotropically. H atoms were included in the refinement at calculated positions (C–H 0.95 Å, B 5 Å^2); they were not refined but constrained to ride on their C atoms. The solvent molecule, found in the final difference Fourier synthesis, was introduced in the least-squares refinement for III, but just included in the structure factors calculations for IV, with thermal parameters arbitrarily fixed at 15 Å^2. The absolute structure was determined for III. All calculations were performed on a PDP 11/23 Plus computer with the Enraf–Nonius Structure Determination Package [17]. Analytical scattering factors for neutral atoms [18] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 3. Final positional parameters are listed in Tables 4 and 5 for compounds III and IV, respectively.

Lists of structure factors, anisotropic thermal parameters and H atoms coordinates are available from the authors.

Exchange reactions between acac ligands of complexes I–IV and acetylacetone

The NMR spectrum of a $CDCl_3$ solution ($6.5\ 10^{-2}$ M) of I in the presence of 1.8

Table 3

Crystallographic data and experimental details

	III	IV
Crystal data		
Cryst. dimensions (mm)	0.35×0.25×0.15	0.5×0.3×0.15
Color	orange	green
Cryst. system	orthorhombic	triclinic
Space group	$P2_12_12_1$	$P\bar{1}$
a (Å)	8.850(3)	9.133(3)
b (Å)	18.189(8)	11.112(2)
c (Å)	21.726(3)	19.390(4)
α (°)		92.45(1)
β (°)		94.24(2)
γ (°)		108.71(2)
V (Å^3)	3497(3)	1854(2)
Z	4	2
D_{calc} (Mg m^{-3})	1.63	1.589
μ(Mo-K_α) (mm^{-1})	4.64	4.30
Data collection		
Radiation	Mo-K_α (λ 0.71073 Å)	Mo-K_α
θ limits (°)	2–25	2–25
Scan type	$\omega/2\theta$	$\omega/2\theta$
Monochromator	graphite	graphite
Reflections measured		
h	0,8	−7,7
k	0,17	−9,9
l	0,20	0,18
Reflections collected		
total	1993	1732
unique	1909	1647
with $I > 3\sigma(I)$	1239	1303
Temperature (K)	295	295
Final values		
$R(F)$	0.046	0.040
$R\omega(F^2)(\omega = 1)$	0.049	0.048

eq. of acetylacetone was recorded at 30 °C. The THF resonances were shifted to −2.84 and −6.29 ppm. Irradiation of the methyl signal of I (δ 17.74 ppm) caused a decrease in the intensity of the methyl signal of acacH (δ 0.04 ppm) to 95% of its original value. Similar experiments were conducted with complexes II–IV. For each compound are shown, in order, the temperature (° C), the ratio [compound]/[acacH], and the residual intensity of the methyl acacH signal when the methyl signal of the compound was irradiated: II: 30, 0.5, 5%. III: 30, 0.4, 5%; IV: 10, 1, 55%.

Reaction of III with $OPPh_3$; formation of $UCl_2(acac)_2(OPPh_3)_2$ (V)

Addition of $OPPh_3$ (2.1 mg) to a solution of III (5.9 mg) in $CDCl_3$ (0.25 ml) gave V ([III]/[V] = 80/20) identified by NMR: V δ ($CDCl_3$, 30 °C): 42.94 (s, 2H, CH), 10.50 (s, 12H, CH_3), 7.8–5.6 (m, *m*- and *p*-Ph and free $OPPh_3$), −2.60 (dd, J 12.0 and 7.6 Hz, 12H, *o*-Ph). The ratio [III]/[V] was 5/95 after addition of an excess of $OPPh_3$ (8 mg). An unidentified product, which gave a signal from an *ortho*-H of the

Table 4

Fractional atomic coordinates, equivalent or isotropic thermal parameters and their e.s.d.'s for $UCl_2(acac)_2(OPPh_3)\cdot THF$ (III)

Atom	x	y	z	B (Å^2) [a]
U	0.7765(1)	0.54517(5)	0.42466(5)	3.06(2)★
Cl(1)	0.9141(8)	0.4498(5)	0.4944(3)	6.2(2)★
Cl(2)	0.6464(8)	0.6445(4)	0.3546(4)	5.1(2)★
P	0.7628(8)	0.3965(3)	0.3042(3)	3.5(2)★
O(1)	0.800(2)	0.4587(9)	0.3464(6)	3.1(3)
O(2)	0.902(2)	0.637(1)	0.4779(9)	4.5(5)
O(3)	1.000(2)	0.5713(8)	0.3756(8)	3.7(4)
O(4)	0.552(2)	0.4794(8)	0.4175(9)	4.3(4)
O(5)	0.618(2)	0.5783(9)	0.5058(9)	4.7(5)
C(1)	1.022(3)	0.674(2)	0.472(1)	4.9(7)
C(2)	1.062(4)	0.728(2)	0.523(1)	7(1)
C(3)	1.127(3)	0.665(1)	0.424(1)	4.7(6)
C(4)	1.109(2)	0.613(1)	0.381(1)	2.3(5)
C(5)	1.219(3)	0.608(1)	0.331(1)	5.5(7)
C(6)	0.422(3)	0.477(1)	0.443(1)	4.8(7)
C(7)	0.310(3)	0.421(1)	0.419(1)	6.7(8)
C(8)	0.384(3)	0.519(1)	0.494(1)	5.0(8)
C(9)	0.484(3)	0.566(1)	0.522(1)	4.6(7)
C(10)	0.430(3)	0.610(2)	0.580(1)	7.9(9)
C(11)	0.659(2)	0.431(1)	0.242(1)	1.9(5)
C(12)	0.673(3)	0.403(1)	0.181(1)	5.2(8)
C(13)	0.584(3)	0.437(2)	0.130(1)	6.0(8)
C(14)	0.491(3)	0.489(1)	0.142(1)	3.8(6)
C(15)	0.469(3)	0.521(2)	0.200(1)	5.5(8)
C(16)	0.559(3)	0.490(1)	0.247(1)	5.0(7)
C(21)	0.936(3)	0.357(1)	0.275(1)	3.5(6)
C(22)	1.064(3)	0.404(2)	0.274(1)	4.8(7)
C(23)	1.188(3)	0.372(1)	0.244(1)	5.7(8)
C(24)	1.192(3)	0.304(1)	0.220(1)	5.8(8)
C(25)	1.067(3)	0.259(2)	0.222(1)	5.9(8)
C(26)	0.941(3)	0.283(2)	0.248(2)	6.4(9)
C(31)	0.663(3)	0.323(1)	0.342(1)	3.3(6)
C(32)	0.685(3)	0.312(1)	0.403(1)	5.4(8)
C(33)	0.601(3)	0.256(1)	0.429(2)	5.8(7)
C(34)	0.508(3)	0.215(2)	0.398(1)	6.0(9)
C(35)	0.479(4)	0.220(2)	0.336(2)	6.8(9)
C(36)	0.554(3)	0.280(2)	0.308(2)	6.5(9)
O(6)	0.431(4)	0.410(2)	0.676(2)	16(1)
C(51)	0.641(5)	0.397(2)	0.636(2)	12(1)
C(52)	0.574(5)	0.425(2)	0.690(2)	13(2)
C(54)	0.387(4)	0.361(2)	0.626(2)	10(1)
C(55)	0.528(5)	0.347(3)	0.599(2)	14(2)

[a] ★ means: $B_{eq} = 4/3\Sigma_i\Sigma_j\beta_{ij}\vec{a}_i\vec{a}_j$.

phenyl group at −3.77 ppm, was also formed in ca. 20% yield during the reaction. After dilution of the solution (1/50), the NMR spectrum indicated the presence of only III and free $OPPh_3$. The IR spectrum of the solid obtained by evaporation showed a P–O stretching frequency at 1060 cm^{-1} (no free $OPPh_3$).

Table 5

Fractional atomic coordinates, equivalent or isotropic thermal parameters, and their e.s.d.'s for CpUCl-$(acac)_2(OPPh_3)\cdot$THF (IV)

Atom	x	y	z	B (Å^2) [a]
U	0.1145(1)	0.22714(8)	0.34269(7)	3.31(3)★
Cl	−0.0354(7)	0.1194(5)	0.2212(4)	5.6(3)★
P	0.2436(6)	0.4939(5)	0.2190(4)	3.7(2)★
O(1)	0.229(1)	0.402(1)	0.2738(8)	3.1(3)
O(2)	0.329(1)	0.193(1)	0.2961(9)	4.1(3)
O(3)	−0.119(1)	0.123(1)	0.3886(9)	3.9(3)
O(4)	−0.044(1)	0.357(1)	0.3406(9)	3.8(3)
O(5)	0.110(1)	0.017(1)	0.3623(9)	4.3(3)
C(1)	0.409(2)	0.632(2)	0.240(1)	3.4(5)
C(2)	0.479(2)	0.644(2)	0.309(1)	4.1(5)
C(3)	0.618(2)	0.749(2)	0.328(2)	5.1(6)
C(4)	0.674(2)	0.835(2)	0.282(1)	4.4(6)
C(5)	0.605(2)	0.825(2)	0.216(1)	4.4(6)
C(6)	0.472(2)	0.725(2)	0.199(1)	4.1(5)
C(7)	0.277(2)	0.429(2)	0.139(1)	3.8(5)
C(8)	0.243(3)	0.472(2)	0.072(2)	7.2(7)
C(9)	0.279(3)	0.423(3)	0.013(2)	9.7(9)
C(10)	0.342(3)	0.329(2)	0.014(2)	8.8(9)
C(11)	0.378(3)	0.287(2)	0.075(2)	6.6(7)
C(12)	0.337(2)	0.330(2)	0.142(2)	5.9(6)
C(13)	0.073(2)	0.540(2)	0.201(1)	3.4(5)
C(14)	0.080(2)	0.668(2)	0.206(1)	5.3(6)
C(15)	−0.062(3)	0.692(2)	0.190(2)	6.8(7)
C(17)	−0.200(2)	0.476(2)	0.170(1)	5.5(6)
C(16)	−0.196(3)	0.598(2)	0.178(2)	6.4(7)
C(18)	−0.064(2)	0.445(2)	0.181(1)	4.6(6)
C(70)	0.382(2)	0.099(2)	0.286(1)	3.9(5)
C(71)	0.521(2)	0.128(2)	0.244(1)	5.0(6)
C(72)	0.319(2)	−0.020(2)	0.315(1)	4.0(5)
C(73)	0.191(2)	−0.051(2)	0.347(1)	4.0(5)
C(74)	0.128(2)	−0.183(2)	0.378(1)	6.0(7)
C(80)	−0.230(2)	0.153(2)	0.410(1)	4.4(6)
C(81)	−0.339(2)	0.050(2)	0.448(1)	6.1(7)
C(82)	−0.251(2)	0.270(2)	0.403(1)	4.5(5)
C(83)	−0.163(2)	0.366(2)	0.368(1)	4.1(5)
C(84)	−0.207(2)	0.481(2)	0.358(1)	5.1(6)
C(100)	0.252(2)	0.424(2)	0.443(1)	4.9(6)
C(101)	0.367(2)	0.370(2)	0.433(1)	5.1(6)
C(102)	0.330(2)	0.251(2)	0.458(1)	5.3(6)
C(103)	0.188(2)	0.231(2)	0.483(2)	6.5(7)
C(104)	0.143(3)	0.337(2)	0.479(2)	5.7(6)
C(300)	0.258	0.880	0.083	15.0
C(301)	0.349	0.870	0.025	15.0
C(302)	0.252	0.789	−0.018	15.0
C(303)	0.150	0.862	−0.051	15.0
O(304)	0.139	0.916	0.033	15.0

[a] ★ means: $B_{eq} = 4/3\Sigma_i\Sigma_j\beta_{ij}\vec{a}_i\vec{a}_j$.

Exchange reaction of coordinated and free $OPPh_3$ ligand of IV

The NMR spectrum of a solution of IV (7.9 mg) in toluene-d_8 (0.25 ml) in the presence of $OPPh_3$ (3 mg) was recorded at 10 °C. Irradiation of the signal of free $OPPh_3$ ($\simeq 6.9$ pm) caused a decrease in intensity of the *ortho*-phenyl hydrogen signal of IV to 25% of its original value.

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