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Contribution from the Dêpartement de Physico-Chimie,
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Formation of Reduced Species from Dichlorobis(pentamethylcyclopentadienyl)uranium(IV), Dichlorobis(pentamethylcyclopentadienyl)thorium(IV), Chloro(pentamethylcyclopentadienyl)magnesium(II), and Chloroisopropylmagnesium(II) by Pulse Radiolysis of Their Solutions in Tetrahydrofuran

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By use of the pulse radiolysis technique, the compound $(C_5Me_5)_2ThCl_2$ has been reduced by the solvated electrons (e^-_{THF}) created in tetrahydrofuran (THF) solution. The electronic spectrum of the transition species was attributed to a thorium(III) complex. These results are consistent with those obtained by electrochemistry; the reduction of thorium(IV) to thorium(III) occurred in the 2.32–2.8 V (vs. SCE) range under the experimental conditions. The interaction of e^-_{THF} with the complexes $(C_5Me_5)_2UCl_2$, $(C_5Me_5)MgCl$, *i*-PrMgCl, and $ZnCl_2$ led to uranium(III), magnesium(I), and Zn(I) species, respectively. Electronic spectra, disappearance rates, and the reaction order were established. The rate constants of reductions of $(C_5Me_5)_2UCl_2$, $(C_5Me_5)_2ThCl_2$, $(C_5Me_5)MgCl$, and *i*-PrMgCl are $(1.2 \pm 0.1) \times 10^{11}$, $(4.4 \pm 0.1) \times 10^9$, $(2.9 \pm 0.05) \times 10^9$, and $(0.7 \pm 0.1) \times 10^9$ M^{-1} s^{-1}, respectively.

Introduction

The reduction of chloro(cyclopentadienyl)uranium(IV) compounds (Cp_xUCl_{4-x}) is very well-known. In 1982, Mugnier et al.[1] reported the electrogeneration of the stable chlorotris(cyclopentadienyl)uranium(III) anion, and Finke et al.[2] reported that same year, a cyclic voltammetric and coulometric study of dichlorobis(pentamethylcyclopentadienyl)uranium. The corresponding stable anion of $(C_5Me_5)_2UCl_2$ has been identified,[1,2] but Finke et al.[2] noted that $(C_5Me_5)_2ThCl_2$ has not been reduced even out to −2.7 V (vs. SCE) on platinum or glassy-carbon electrodes. That same year, a photochemical synthesis of low-valent thorium and uranium organometallics was carried out. A photoinduced β-hydrogen elimination and $U(C_5H_5)_3$ formation mechanism was proposed to account for the photoreduction process.[3]

These results have prompted us to study the reduction of similar compounds, using pulse radiolysis in tetrahydrofuran (THF), which allows the creation in situ of a very strong reducing species, the solvated electron, e^-_{THF}.[4] In water, the redox potential of e^-_{aq} is 2.77 V (vs. H_2);[5] that of e^-_{THF} is unknown, and its use for organometallic compound reduction has not been developed.[6] However, its reducing power is probably at least as great as that of e^-_{aq}, so it was interesting to check if Th(IV) compounds could be reduced to those of Th(III). As we have previously obtained indirect proof that e^-_{aq} is able to reduce Th(IV),[7] we envisaged the reduction of these different compounds and the formation of a transient reduced species with an absorption spectrum possibly due to Th(III).

We also investigated the corresponding magnesium compound $(C_5Me_5)MgCl{\cdot}THF$ as well as *i*-PrMgCl and pentamethylcyclopentadiene itself. We extended our experiments to $ZnCl_2$ for reasons explained in the Results and Discussion.

Experimental Section

THF was purified by a procedure previously published.[4] The compounds $(C_5Me_5)_2UCl_2$, $(C_5Me_5)_2ThCl_2$, and $(C_5Me_5)MgCl{\cdot}THF$ were synthesized, and pentamethylcyclopentadiene was handled as described in the literature.[8] A concentrated (2 M) solution of *i*-PrMgCl was prepared as usual in dry diethyl ether and diluted in THF just prior to use.

The pulse experiments were carried out with a Febetron 707, which delivered pulses of 15-ns base duration of approximately 1.8-MeV electrons with doses from 50 to 90 krad. Transient species were detected by means of their absorption spectra. The setup has already been described.[6] For a normalized dose *D* of 100 krad, the values of the absorbances were obtained at different times after the pulse; they correspond to the product $G\epsilon lD$ × constant, where *G* is the yield of the species formed/100 eV of energy absorbed, ε is the molar extinction coefficient, and *l* is the optical path length (2.5 cm in our case.)

Electrochemical measurements on the air-sensitive thorium complexes were carried out at controlled temperatures (+20 or −35 °C) in millimolar solutions under argon, using a conventional three-electrode cell. The reference electrode was a saturated calomel electrode in saturated aqueous solution of KCl separated by a sintered-glass disk and connected to the working solutions by a junction bridge filled with the solution in question. The polarographic measurements were performed at a dropping-mercury electrode.[10] Measured half-wave potentials $E^{1/2}$ are reported vs. the saturated calomel electrode (SCE).

Solvents were rigorously dried and deoxygenated before use. Tetra-*n*-butylammonium hexafluorophosphate (background electrolyte) was recrystallized twice from 95% EtOH and dried 2 days at 100 °C under reduced pressure (10^{-2} Torr).

Results and Discussion

After it was verified that e^-_{THF} was formed in pure THF and that its disappearance rate was as previously found,[6] solutions of $(C_5Me_5)_2UCl_2$, 5×10^{-3} M, were submitted to pulse irradiation. The spectra observed at different times after pulse are shown in Figure 1. Immediately after the pulse, a quite stable peak appeared at 700 nm; its form remained unchanged during 4 μs after the pulse. However, 800 ms after the pulse, it gave way to two peaks at 660 and 750 nm, both stable during our detection time. Similar results were obtained with a 10^{-2} M solution, but its color was so intense that the transmitted light was too feeble for

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(1) Mugnier, Y.; Dormond, A.; Laviron, E. *J. Chem. Soc., Chem. Commun.* **1982**, 157.

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(9) It has been reported previously that Cp_2MCl_2 species (M = Ti) reacted with Hg to give Cp_2MCl and Hg_2Cl_2.[10] Nevertheless, such a reaction has not been observed in rigorously anhydrous experiments;[11,12] DMF or THF solutions of $(C_5Me_5)_2ThCl_2$, $(C_5H_5)_3ThCl$, and $(C_5Me_5)_2UCl_2$ were unchanged after shaking with mercury for days.

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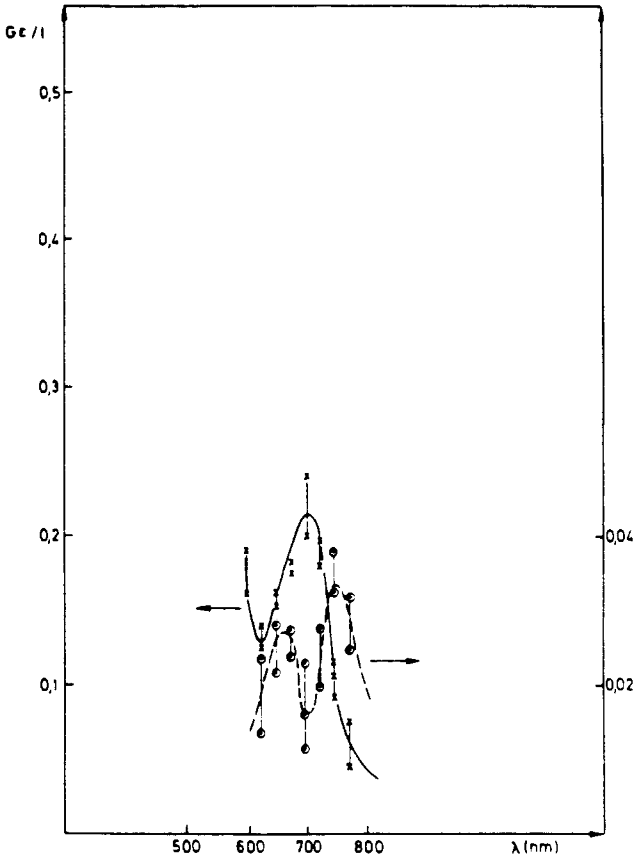

Figure 1. Spectra of the transient species obtained at different times after the pulse ((×) 4 μs and (○) 300 ms) for $(C_5Me_5)_2UCl_2$ (5×10^{-3} M).

measurements. The formation of the first species occured by an e^-_{THF} + $(C_5Me_5)_2UCl_2$ reaction, which was pseudo first order, and the reaction rate constant was found to be $(1.2 \pm 0.1) \times 10^{11}$ M^{-1} s^{-1}. (This value is corrected for the natural disappearance of e^-_{THF} in the absence of any solute and was determined with a $(C_5Me_5)_2UCl_2$ concentration of 2×10^{-4} M.) This reaction rate may be compared to the rate of reduction of UCl_4 (4.5×10^{10} M^{-1} s^{-1}).[6] This initially formed species undergoes further reaction, disappearing by a first-order reaction with a rate constant of 11.4 s^{-1}.

We suggest that the first peak corresponds to the anion $(C_5Me_5)_2UCl_2^-$, which undergoes Cl^- loss to yield $(C_5Me_5)_2UCl$. The spectrum of this second compound is similar in structure to that of UCl_3 (with shifted wavelengths) previously seen in UCl_4 reduction by e^-_{THF}.[6] As for the anionic compound, it would correspond to that already mentioned by Finke et al.,[2] but contrary to their results in THF or CH_3CN where Cl^- is not lost, it would be less stable under our conditions. It is noteworthy that the conditions for electroreduction of $(C_5Me_5)_2UCl_2$ are different from those of the radiolysis experiments; in the first case, a supporting electrolyte is added, and in the radiolysis experiment, a proton is formed simultaneously with each electron:

$$THF \rightsquigarrow THF^+ + e^-$$

$$e^- + THF \rightarrow e^-_{THF}$$

$$THF^+ + THF \rightarrow THF(-H) + THF(H)^+$$

In particular, it seems likely that the strong acid $THF(H)^+$ may contribute significantly to the disappearance of the anion.

The same types of experiments were carried out with a colorless solution of $(C_5Me_5)_2ThCl_2$, 1.05×10^{-2} M. A well-structured spectrum was immediately obtained after the pulse and presented four peaks at 470, 252, 600, and 650 nm (Figure 2). e^-_{THF} + $(C_5Me_5)_2ThCl_2$ was a pseudo-first-order reaction with a calculated second-order rate constant: $(4.4 \pm 0.1) \times 10^9$ M^{-1} s^{-1}, notably less than that of the uranium homologue. We suggest that this transient species is $(C_5Me_5)_2ThCl_2^-$. The decreases of the ab-

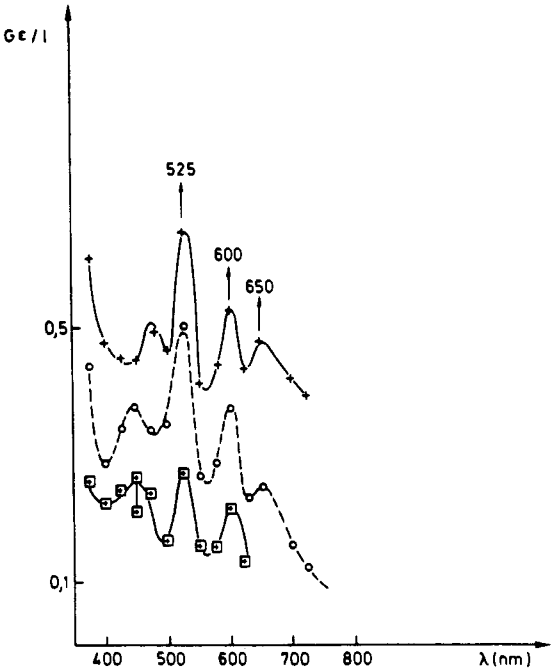

Figure 2. Spectra of the transient species obtained at different times after the pulse ((+) d_0, (○) 800 ns, (□) 2 μs) for $(C_5Me_5)_2ThCl_2$ (1.05×10^{-2} M).

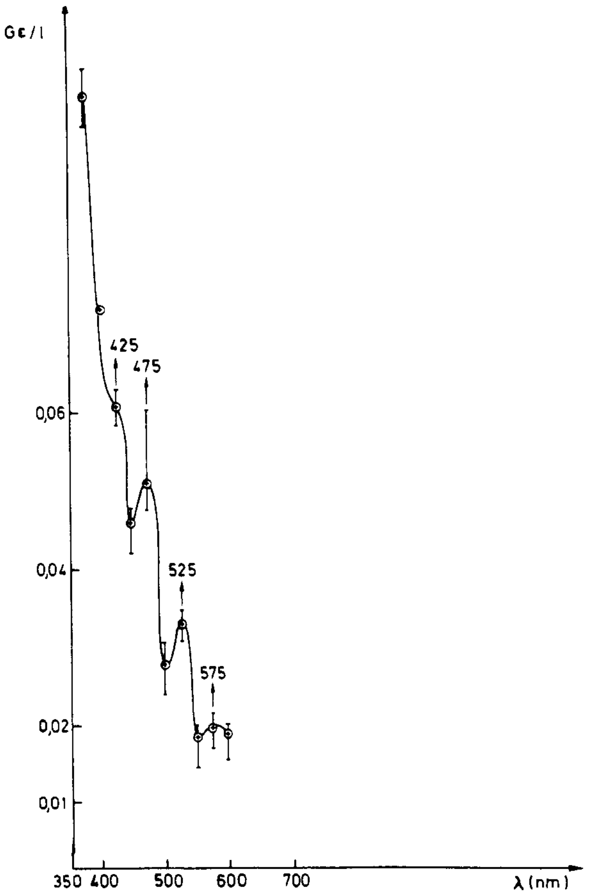

Figure 3. Spectrum of the transient species obtained for $(C_5Me_5)_2ThCl_2$ at 160 μs after the pulse.

sorption measured at three different wavelengths (600, 575, or 525 nm) are first order and have the same rate constant: $(1 \pm 0.07) \times 10^6$ s^{-1}. It led, after 160 μs, to a different spectrum (Figure 3). As the decrease of the initial absorption was first order, we suggest the loss of a Cl^- anion, giving $(C_5Me_5)_2ThCl$. This spectrum consists of four peaks at 425, 475, 525, and 575 nm, slightly different from that observed previously[3] (λ at 431, 477,

Table I. Electrochemical Reduction of Thorium(IV) Compounds at a Hg Electrode

compd	solvent	potential, V
$(C_5Me_5)_2ThCl_2$[21,22]	DMF	-2.45[23]
$(C_5Me_5)_2ThCl_2{\cdot}CNC_6H_{11}$[22]	DMF	-2.32[23]
$(C_5H_5)_3ThCl$	THF	-2.8[24]
$(C_5H_4C(CH_3)_3)_3THCl$	THF	0[25]

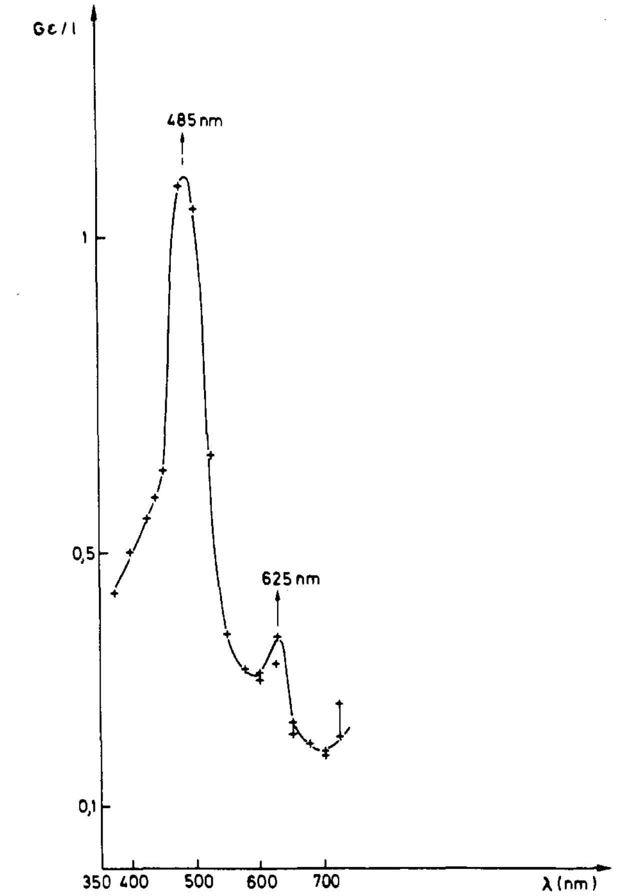

Figure 4. Spectrum of the transient species obtained at different times after the pulse for $(C_5Me_5)H$ (10^{-2} M) in THF.

and 572 nm) and attributed to $(C_5Me_5)_3Th$. Since the electrochemistry results show that Cp^- loss does not take place (see Table I), we assume that the primary anion loses a Cl^-. To provide evidence for or against this hypothesis, electrochemical reduction of thorium(IV) compounds was studied at a Hg electrode. (The mechanism of the electroreduction and the nature of the reduced species need further investigation and will be published in a future paper.) The first experiments are consistent with the pulse radiolysis findings. However, to ascertain that this spectrum corresponds to a reduced form of thorium(IV) and not, for example, of the ligand, we performed additional experiments. First, we examined the pentamethylcyclopentadiene, C_5Me_5H, and then two other magnesium compounds, $(C_5Me_5)MgCl{\cdot}THF$ and *i*-PrMgCl·THF, with the aim of obtaining the corresponding reduced derivatives and comparing their spectra with those of the thorium compound.

The transient spectrum obtained immediately after pulsing a 10^{-2} M solution of C_5Me_5H in THF is represented in Figure 4. This spectrum, with its intense narrow peak at 485 nm, is characteristic of an organic anion. A small absorption band also appears at 625 nm. The e^-_{THF} disappearance was pseudo first order, the second-order rate constant being $(4.4 \pm 0.1) \times 10^9$ M^{-1} s^{-1}. The anion spectrum decreases with time without any change by a second-order reaction with a slope equal to 5.7×10^7 s^{-1} cm^{-1}.

It is obvious that this spectrum is entirely different from the spectrum of the thorium compound. Of course, this is not proof of $(C_5Me_5)ThCl_2$ reduction, but if there was electron addition to the ligand, some similar absorptions bands would be expected in the reduced thorium compound.

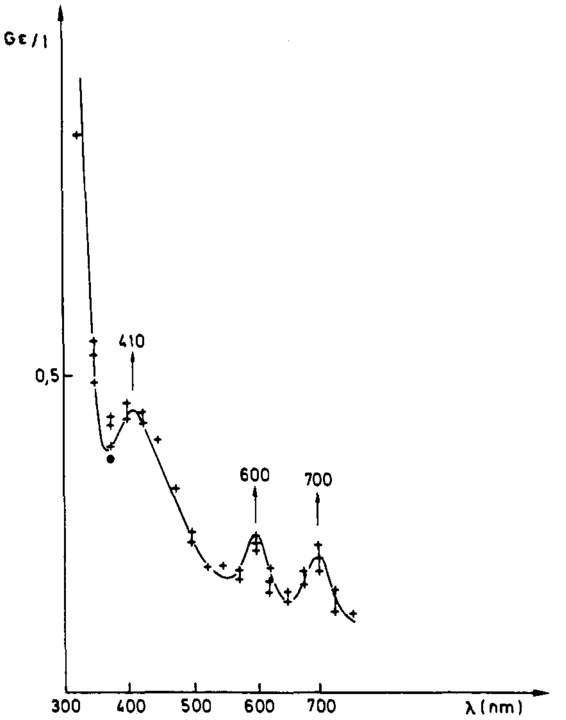

Figure 5. Spectrum of the transient species obtained for $(C_5Me_5)MgCl$ (10^{-2} M) in THF.

The absorbance curves of the transient species obtained by reaction of $(C_5Me_5)MgCl{\cdot}THF$ with e^-_{THF} are plotted at different times in Figure 5. Three peaks are present at 410, 600, and 700 nm, the most intense being at 410 nm. The disappearance of e^-_{THF} with this compound was pseudo first order, and the second-order rate constant k was $(2.9 \pm 0.05) \times 10^9$ M^{-1} s^{-1}. The three transient peaks disappear at different rates: at 410 nm, by a second-order reaction with a slope of 6.9×10^6 s^{-1}, and at 600 and 700 nm, by first-order processes, the rates for both being the same: $(1.5 \pm 0.2) \times 10^7$ s^{-1}. The peak at 410 nm may be due to a magnesium(I) transient, which disappears by disproportionation.

The existence of a low magnesium oxidation state has been a much debated topic. The formation of Mg^+ in γ-irradiated frozen Mg^{2+} solutions was claimed by Moorthy and Weiss[13] from ESR experiments. However, optical studies have shown[14] that the trapped electron is quite stable in 4 M $Mg(ClO_4)_2$ glass at 77 K. It is noteworthy that, as far as we know, no Mg(I) compound with organic ligands has been previously reported.

To elucidate the shape of this Mg(I) spectrum, we compared the results with those from another metal compound; we pulsed a 10^{-2} M THF solution of $ZnCl_2$ and also an aqueous solution of $ZnCl_2$. It is known that Zn(II) is reduced by e^-_{aq} and Zn(I) compound is formed, absorbing at 300 nm.[15]

The spectra obtained after pulsing either an aqueous or a THF Zn(II) solution are represented in Figure 6. The first spectrum is in good agreement with that reported in the literature. However, in THF, the spectrum presents two peaks: one at 320 nm, which is the most important, and a similar one at 425 nm. These absorption bands were absent after initially bubbling the solution with N_2O. Under argon, the peak at 320 nm was more stable than the second, as was the case for Mg(I) (cf. the peak at 410 nm). The 320-nm peak disappears by a second-order process, and the slope is 7.3×10^5 s^{-1}; at 425 nm, the reaction is first order, and the rate is 1.7×10^7 s^{-1}. In water, the formation rate of Zn(I) is 1.2×10^9 M^{-1} s^{-1}, and its disappearance is second order with a slope equal to 2.5×10^5 s^{-1}.

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(14) Buxton, G. V.; Gillis, H. A.; Klassen, N. V. *Can. J. Chem.* **1976**, *54*, 367.

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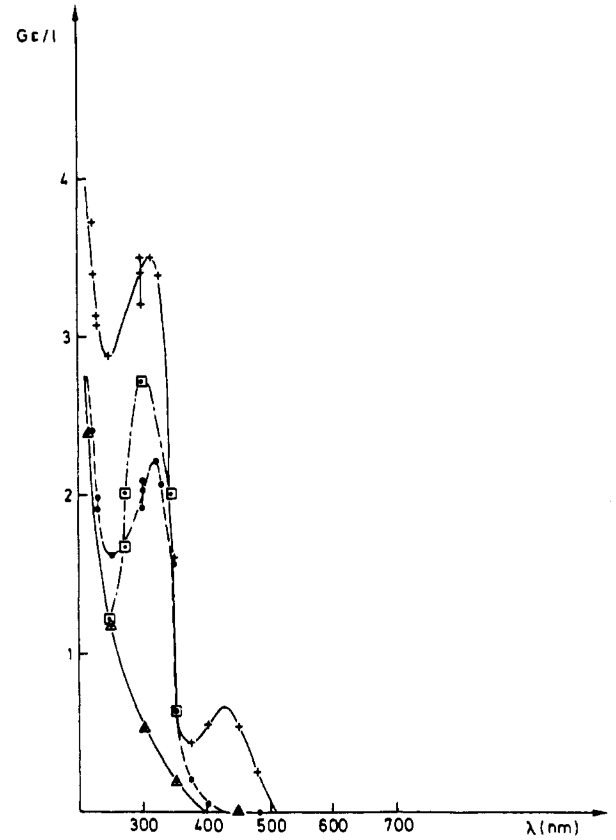

Figure 6. Spectra of the transient species obtained under different conditions: for $ZnCl_2$ (3×10^{-2} M), in THF, under argon ((+) d_0 and (•) 2 μs after the pulse and under N_2O ((▲)d_0); for $ZnCl_2$ (2×10^{-2} M) in water, under argon (◻).

These results seem to show that, in both cases, Zn(II) and Mg(II) reduction in THF leads to the simultaneous formation of two species.

Last, we checked whether another magnesium compound could also be reduced by e^-_{THF}. We chose *i*-PrMgCl. In Figure 7, the transient spectrum shows that a peak and a shoulder appeared respectively at 425 and 575 nm. A third absorption band began at 600 nm, the maximum probably being located in the near-IR region. The e^-_{THF} + *i*-PrMgCl reaction was pseudo first order, and its rate was $(0.7 \pm 0.1) \times 10^9$ M^{-1} s^{-1}.

The disappearance of the 425-nm peak was second order (4.53×10^6 s^{-1}); that of the 575 nm peak, first order (2.45×10^6 s^{-1}). From these experimental results, it is possible to conclude that the solvated electron in THF is able to reduce different organometallic compounds, giving reduced metallic species in unusual oxidation states.

The assignment of the optical spectrum (Figure 2) to f–f transitions of Th(III) may be discussed. Let us assume the electronic structure of Th(III) to be $5f^1$; we know that its fundamental spectroscopic term (^2F) is split by spin–orbit coupling into two levels $^2F_{5/2}$ and $^2F_{7/2}$ separated by $7\xi/2$ (ξ being the spin–orbit coupling); ξ for Th(III) is not known, but for Pa(IV), U(V), and Np(VI) the value has been estimated to be 1490, 1955, and 2405 cm^{-1}, respectively.[16] Thus, the expected transitions in the range 7000 cm^{-1} for uranium(V) are experimentally observed.[17] The crystal-field effects have been studied and theoretically analyzed in the case of high octahedral symmetry.[18] They are of the same order of magnitude as the spin–orbit coupling.

In low (or unknown) symmetry, higher energy bands are often observed and generally assigned to f–f transitions. For instance, for uranium(V), structured bands in the range 12000–16000 cm^{-1} were reported.[19,20]

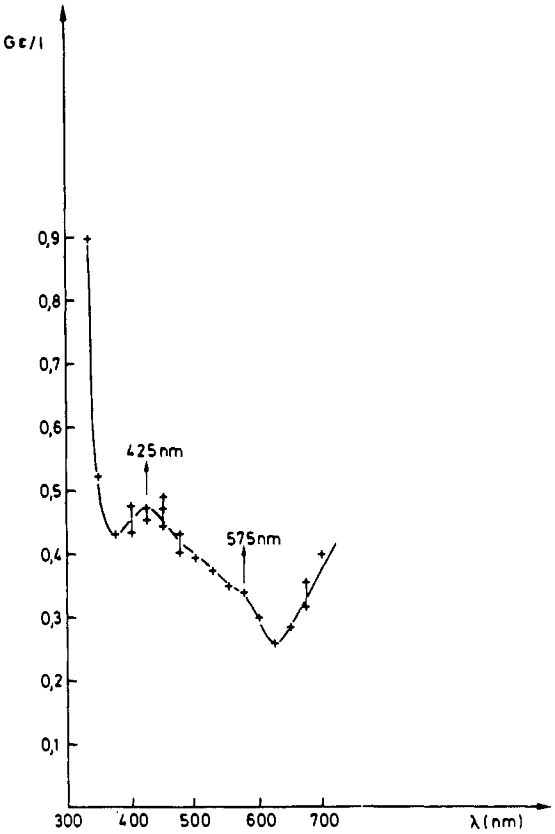

Figure 7. Spectrum of the transient species obtained for *i*-PrMgCl (2×10^{-2} M) in THF.

In the case of thorium(III), estimating ξ around 1400 cm^{-1} leads to calculated transitions around 5000 cm^{-1} (due to spin–orbit terms). However, the crystal-field parameters would allow transitions at higher energy. The structured band obtained by radiolysis is much more similar to a crystal-field transition than to a charge-transfer band and may reasonably be assigned to f–f transitions.

Conclusion

The results obtained show that in THF, different organometallic compounds may be reduced by e^-_{THF}, whose reducing power is equal or superior to that of e^-_{aq}, i.e. 2.7 V (vs. H_2). By pulse radiolysis of a THF–Th(IV) solution, we have indirect evidence of a thorium(III) oxidation state, in good agreement with electrochemical results.

Moreover, we have shown that species assigned to Mg(I) and

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(20) Grape, W.; Stumpp, E. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 137.

(21) $(C_5Me_5)_2ThCl_2$ reacted slowly with Bu_4NPF_6 ($t_{1/2}$ = 1 h) with a decrease of the reduction wave and formation of unidentified products. Addition of an excess of cyclohexyl isocyanide ((3–5)/1) stabilizes the complex $(C_5Me_5)_2ThCl_2 \cdot CNC_6H_{11}$ ($t_{1/2}$ = 12 h).[22]

(22) Reeb, P.; Mugnier, Y.; Dormond, A.; Laviron, E. *J. Organomet. Chem.* **1982**, *239*, C1.

(23) Any reduction waves were observed on the platinum electrode.

(24) Cyclic voltammograms (scan rates 50 mv/s–10 V/s) show an irreversible reduction peak on platinum-disk electrode at E_p = –2.5 V; the irreversibility of the reduction suggests that the anionic species loses a ligand. As loss of Cp^- does not take place (the oxidation wave $Cp^- \rightarrow Cp + e^-$ at –0.3 V has not been detected), the departing ligand is probably Cl^-.

(25) Surprisingly, $((C_5H_4)t\text{-}Bu)_3ThCl$ is not reducible on a platinum electrode at –3 V. When it is added to a THF solution of ferrocene, a significant enhancing of the reduction wave $FcH \rightarrow FcH^-$ ($E_{1/2}$ = –2.93 V) at –35 °C[26] is observed. This electronic transfer could be rationalized by the scheme

$$FcH^- + Cp'_3ThCl \rightarrow FcH + [Cp'_3ThCl]^- \xrightarrow{\text{very fast}} [Cp'_3Th] + Cl^-$$

(26) Mugnier, Y.; Moïse, C.; Tirouflet, J.; Laviron, E. *J. Organomet. Chem.* **1980**, *186*, C49.

Zn(I) may be produced in THF solution. Their spectra are not entirely understood, however, and again all the evidence for them is indirect.

The reduction rate constants of $(C_5Me_5)_2UCl_2$, $(C_5Me_5)_2ThCl_2$, $(C_5Me_5)MgCl\cdot THF$, and *i*-PrMgCl are $(1.2 \pm 0.1) \times 10^{11}$, $(4.4 \pm 0.1) \times 10^9$, $(2.9 \pm 0.05) \times 10^9$ and $(0.7 \pm 0.1) \times 10^9$ M^{-1} s^{-1}, respectively.

Acknowledgment. We thank Dr. Y. Mugnier for electrochemical measurements and helpful discussions.

Registry No. $(C_5Me_5)_2ThCl_2$, 67506-88-1; $(C_5Me_5)_2ThCl_2\cdot CNC_6H_{11}$, 109527-70-0; $(C_5H_5)_3ThCl$, 1284-82-8; $(C_5H_4C(CH_3)_3)_3ThCl$, 109527-71-1; $(C_5Me_5)_2UCl_2$, 67506-89-2; C_5Me_5H, 41539-64-4; $(C_5Me_5)MgCl\cdot THF$, 107495-40-9; *i*-$PrMgCl\cdot THF$, 109527-72-2; $ZnCl_2$, 7646-85-7; THF, 109-99-9.

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Synthesis and Structure of $Os_3(CO)_6[P(OMe)_3]_6$

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The cluster $Os_3(CO)_6[P(OMe)_3]$ (**1**) has been prepared (31% yield) as red-orange crystals from UV irradiation of $Os_3(CO)_8[P(OMe)_3]_4$ and excess $P(OMe)_3$ in heptane. The crystal structure of **1** was determined by X-ray crystallography at −60 °C and refined to $R = 0.041$ for 1021 observed reflections. The structure has precise 50% "Star-of-David" disorder; the phosphite ligands occupy the six equatorial sites of the Os_3 triangle. The $Os(CO)_2[P(OMe)_3]_2$ groups are twisted so that the molecule has D_3 symmetry. The Os–Os and two Os–P bond lengths are 2.927 (1), 2.229 (7), and 2.245 (6) Å, respectively. Spectroscopic properties (UV–vis, IR, NMR) of **1** are also reported.

Although the substitution of $Os_3(CO)_{12}$ by phosphorus donor ligands was first studied some 20 years ago,[1] it continues to be a topic of current research interest.[2] Usually the trisubstituted derivatives, $Os_3(CO)_9L_3$ (L = monodentate phosphorus ligand), are the most highly substituted complexes that can be prepared.[3] There are, however, some brief reports of the replacement of more than three CO ligands in $Os_3(CO)_{12}$ by chelate ligands with group 15 donor atoms.[1,4] Clusters of the type $Ru_3(CO)_8L_4$ are also known.[5,6]

We have reported the synthesis of $Ru[P(OMe)_3]_5$ from the photolysis of $Ru_3(CO)_{12}$ in hexane with excess $P(OMe)_3$.[7] In an extension of this work the corresponding reaction of $Os_3(CO)_{12}$ with $P(OMe)_3$ has been studied. Rather than mononuclear compounds, highly substituted derivatives of $Os_3(CO)_{12}$ may be isolated. Here we report the synthesis and crystal structure of the most highly substituted member of these clusters, $Os_3(CO)_6[P(OMe)_3]_6$. We have previously reported the preparation of $Os_3(CO)_7[P(OMe)_3]_5$ along with its novel fluxional properties.[8]

Experimental Section

The manipulation of compounds and the purification of solvents were carried out under a nitrogen atmosphere with use of Schlenk techniques. Heptane and toluene were refluxed over potassium and distilled before use; dichloromethane was similarly refluxed over P_2O_5 and distilled prior to use. Dodecacarbonyltriosmium was prepared by a literature method.[9] Trimethylphosphite, as obtained commercially, was transferred under nitrogen to a 500-mL round-bottom flask fitted with a Teflon valve; it was found to be pure by $^{31}P\{^1H\}$ NMR spectroscopy. The ultraviolet irradiation was carried out with a Hanovia 200-W lamp inside a water-cooled quartz jacket. The reactants were contained in a thick-walled Pyrex Carius tube (30 × 3 cm) fitted at one end with a Teflon valve. There was approximately 3 cm between the edge of the UV source and the edge of the reaction solution.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer; UV-visible spectra were recorded on a Varian Cary 210 spectrometer; the mass spectrum was recorded on a Kratos MS50 instrument (University of British Columbia, regional facility); and the NMR spectra were recorded on a Bruker WM400 instrument. An internal reference of $P(OMe)_3$ was used for the $^{31}P\{^1H\}$ spectrum of $Os_3(CO)_6[P(OMe)_3]_6$. The chemical shift of the ^{31}P resonance of the compound was then referenced to 85% H_3PO_4 ($\delta = 0$, downfield positive) by taking the ^{31}P resonance of $P(OMe)_3$ (1% in toluene–toluene-d_8 (5:1) at ambient temperature) as −140.2 ppm. The C/H microanalysis was performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University; the P microanalysis was carried out by Canadian Microanalytical Service Ltd., New Westminster, BC. The melting point was determined on a Gallenkamp apparatus with the sample in a sealed capillary under nitrogen.

Preparation of $Os_3(CO)_6[P(OMe)_3]_6$ (1). A Carius tube with $Os_3(CO)_{12}$ (0.50 g, 0.55 mmol), $P(OMe)_3$ (4 mL, ~34 mmol), and heptane (20 mL) was evacuated at −196 °C and the solution degassed with two freeze–pump–thaw cycles. The vessel and contents were then heated at 140–145 °C for 24 h. The tube was cooled slowly to −196 °C and evacuated; the solution was degassed with a freeze–pump–thaw sequence. The Carius tube was then warmed to just above room temperature so as to dissolve the precipitated orange solid (mainly $Os_3(CO)_8[P(OMe)_3]_4$). The solution was irradiated with ultraviolet light for 48 h, during which time an orange solid precipitated. The reaction solution and the solid were transferred to a Schlenk flask, and the orange solution was then removed. The remaining solid was washed with hexane (5 × 10 mL) and hexane–toluene (1:1 by volume, 3 × 5 mL) to afford analytically pure $Os_3(CO)_6[P(OMe)_3]_6$ (0.25 g, 31%). The compound may be recrystallized from toluene or CH_2Cl_2–hexane as red-orange prisms (mp 166.5–168 °C dec): UV-vis (CH_2Cl_2) 335, 412, 475 nm; IR (CH_2Cl_2) ν(CO) 2013 (vw), 1938 (s, br), 1881 (w) cm^{-1}; MS, *m/e* 1330 ($[M - P(OMe)_3 - 2Me]^+$); ^1H NMR (CD_2Cl_2, −54 °C) δ 3.53 (d, $J_{P-H} = 11.2$ Hz); ^1H NMR (toluene-d_8, 70 °C) δ 3.61 (d, $J_{P-H} = 10.9$ Hz); $^{13}C\{^1H\}$ NMR (CH_2Cl_2–CD_2Cl_2, 5:1, −57 °C) δ 203 (t, $J_{P-C} = 12.0$ Hz) $^{31}P\{^1H\}$

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