Journal of Organometallic Chemistry, 295 (1985) 317–326
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE USE OF BULKY X-LIGANDS IN THE SYNTHESIS OF NEW Cp_2MX_2 COMPOUNDS ($M = U^{IV}$; Th^{IV}; $Cp = \eta^5$-C_5H_5)

G. PAOLUCCI

Dipartimento di Chimica, Facoltà di Chimica Industriale, Università di Venezia, Calle Larga S. Marta 2137, Venezia (Italy)

P. ZANELLA and A. BERTON

Istituto di Chimica e Tecnologia dei Radioelementi, Area di Ricerca C.N.R., Corso Stati Uniti, 35100 Padova (Italy)

(Received April 19th, 1985)

Summary

Some new Cp_2MX_2 ($M = U^{IV}$; Th^{IV}) compounds, stable towards ligand redistribution, have been synthesized by using very bulky X-ligands such as *N,N'*-di-*p*-tolyltriazenide (triaz) and *N,N'*-di-*p*-tolylformamidide (form). Whereas $Cp_2Th(NEt_2)_2$ undergoes protolysis by Htriaz in refluxing toluene to give $Cp_2Th(triaz)_2$, under the same conditions there is no protolysis by Hform. A suggested coordination mode of the ligands around the central ions of the Cp_2UX_2 (X = triaz; form) and $Cp_2Th(triaz)_2$ is based on the ^1H NMR and mass spectrometric data.

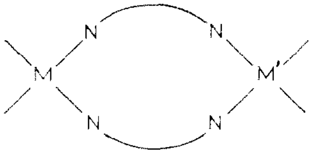
Introduction

In recent years interest in the chemistry of actinide organometallic compounds such as Cp_2MX_2 ($Cp = \eta^5$-cyclopentadienyl; $M = U^{IV}$; Th^{IV}) has grown markedly because of their high coordinative unsaturation [1], which implies interesting reactivity. Compounds such as Cp_2MX_2, stable towards intermolecular rearrangement reactions [2], have been made by using: (i) sterically hindered cyclopentadienyls (permethylated cyclopentadienyls [3], ring-bridged cyclopentadienyls [4], or cyclopentadienyls substituted with trimethylsilyl groups [5]), (ii) sterically hindered X-ligands (dialkylamides [6]; 8-hydroxyquinolinate [7]; borohydride [8]; acetylacetonate [9]; dihydrobis(pyrazolyl) borate or hydrotris(pyrazolyl) borate [10]); (iii) sterically hindered cyclopentadienyls and X ligands [5].

Adopting the second approach we chose as the sterically hindered X ligands some aza-pseudo-allyl systems, such as the isoelectronic *N,N'*-di-*p*-tolyl-triazenide (triaz) and *N,N'*-di-*p*-tolylformamidide (form). These ligands have been widely used in studies involving transition metals because of the variety of their coordination

0022-328X/85/$03.30

modes, which implies a potentially rich chemistry; it is known, that the triazenide and formamidide anions may act as monodentate [11,12], bidentate (chelate) [13], bridging [14], or orthometallate [15] ligands. In addition, in the monodentate form, the ligand (triazenide) may show fluxional behaviour both in solution [11,12,14f] and sometimes in the solid state [16]. Finally a new binuclear species (Rh–Hg), has been recently reported, containing two formamidide and/or triazenide groups, one of which chelates the rhodium atom while the other one bridges the Rh and Hg atoms, making possible a new dynamic process involving interchange between the chelating and bridging forms via a monodentate intermediate [17]. This behaviour could be very useful in the synthesis of new binuclear derivatives such as



(M = M' = actinide
or M = actinide and
M = transition metal)

We describe below the synthesis and characterization of some new organometallic complexes of general formula Cp_2MX_2 ($M = U^{IV}$; Th^{IV}; X = *N,N'*-di-*p*-tolyltriazenide; *N,N'*-di-*p*-tolylformamidide), and make tentative structural assignments on the basis of IR, ^1H NMR and mass spectrometric data.

Results and discussion

Because of the well known reactivity of the metal–nitrogen bonds of actinide amides towards molecules containing either acidic hydrogens or/and dipolar multiple bonds [18], we used the dicyclopentadienyl-uranium(IV) and -thorium(IV) bis(diethyl)amides as starting materials for the synthesis of Cp_2MX_2 complexes according to eq. 1.

$$Cp_2M(NEt_2)_2 + 2HY \rightarrow \underset{(\mathbf{1a}-\mathbf{1c})}{Cp_2MY_2} + 2HNEt_2 \qquad (1)$$

1a: M^{IV}; Y = *N,N'*-di-*p*-tolyl-triazenide. **1b**: $M = U^{IV}$; Y = *N,N'*-di-*p*-tolylformamidide. **1c**: $M = Th^{IV}$; Y = *N,N'*-di-*p*-tolyl-triazenide)

The inertness of $Cp_2Th(NEt_2)_2$ towards *N,N'*-di-*p*-tolylformamidine under the conditions in which it reacts with *N,N'*-di-*p*-tolyltriazene (refluxing toluene) may be due to a combination of factors, the lower acidity of the formamidinic than of the triazenic hydrogen, probably playing an important role.

The complexes **1a**, **1b** and **1c** are soluble in aromatic and insoluble in aliphatic hydrocarbons.

Spectroscopic data

The ligation mode of formamidide and triazenide ligands around the metal ions can be inferred from the IR and ^1H NMR data. Since the molecular weight measurements indicate that complexes **1a**, **1b**, **1c** are monomers, at least in solution, structures containing bridging ligands can be ruled out. Thus the ligands may be

TABLE 1

ANALYTICAL AND IR (4000–200 cm^{-1}) DATA OF **1a**, **1b**, AND **1c** COMPOUNDS

Compound	Analytical data (Found (calcd.) (%))				Molecular weight ^{a}	IR (cm^{-1}) ^{b}
	C	H	N	M		
1a	55.75	4.50	10.25	28.95	808	1608(mw), 1268(vs)
M = U^{IV}	(55.88)	(4.65)	(10.29)	(29.17)	(816)	1204(ms), 1176(m)
1b	58.90	4.85	6.85	29.00	803	1610(m), 1527(vs, b)
M = U^{IV}	(58.97)	(4.91)	(6.87)	(29.24)	(814)	1312(s), 1288(vs, b)
1c	56.26	4.64	10.25	–	794	1606(mw), 1268(vs),
M = Th^{IV}	(56.29)	(4.69)	(10.37)		(810)	1201(vs), 1175(ms)

[a] Taken in benzene solution at 36°C. [b] Only bands due to the *N*,*N*′-diaryl-triazenide and -formamidide linkage: mw = medium-weak, ms = medium strong, s = strong, vs = very strong.

present in the mono- or bi-dentate (chelate) forms. Triazenide transition metal complexes having the ligands in the monodentate form have been reported [12] to show characteristic IR absorption bands at 1150, 1190–1210, 1260–1300, and 1580–1600 cm^{-1}, whereas the chelated ligands show only two bands in the range 1260–1300, and 1580–1600 cm^{-1}. Complexes **1a** and **1c** each show a set of four bands, indicating the mono-dentate form (Table 1); there are then some minor differences between the two complexes as expected from the different ionic radii of the two metal ions. It has been reported [13] that complexes containing bidentate (chelate) formamidide ligands usually show bands at higher frequencies (10–30 cm^{-1}) than those of analogous monodentate formamidide complexes, probably owing to stronger donation of electron density from the two nitrogen atoms to the metal in chelate than in monodentate complexes. The bands due to the formamidide group of $Cp_2U(form)_2$ appear at 1610(m), 1527(vs), 1312(s), 1288(vs) and 1212(s) cm^{-1}, and can be tentatively assigned to the monodentate form, in agreement with the data reported for some other monodentate formamidide transition metal complexes.

The ^{1}H NMR spectra of the complexes **1a**, **1b** and **1c** are strongly indicative of the monodentate nature of the triazenide and formamidide ligands (see Tab. 2).

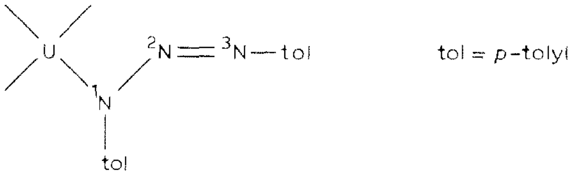
TABLE 2

^{1}H NMR DATA OF COMPLEXES **1a**, **1b**, AND **1c** (benzene-d_6 solutions; δ (ppm) from C_6D_5H as internal standard; *T* 27°C)

Compound	Cp ($\Delta\delta$) ^{a}	*ortho* ($\Delta\delta$)	*ortho′* ($\Delta\delta$)	*meta* ($\Delta\delta$)	*meta′* $\Delta\delta$)	Me ($\Delta\delta$)	Me′ ($\Delta\delta$)
1a	−3.33s ^{c}	−38.92d *J* 7.8 Hz	−10.90d *J* 7.8 Hz	10.68d *J* 7.9 Hz	4.04d *J* 7.9 Hz	−10.39s	−2.91s
	(−2.5)	(−38.87)	(−10.85)	(10.73)	(4.09)	(−10.34)	(−2.86)
1b	−3.86s	−34.86bd	−10.45bd	11.59bd	4.73bd	−10.45s	−2.08s
(CH = −23.86s) (−24.94)	(–) ^{b}	(−34.73)	(−10.32)	(11.72)	(4.86)	(−5.59)	(2.78)
1c	−0.83s	two broad AA′BB′ quartets centered at −0.05				−4.97s	−5.01s

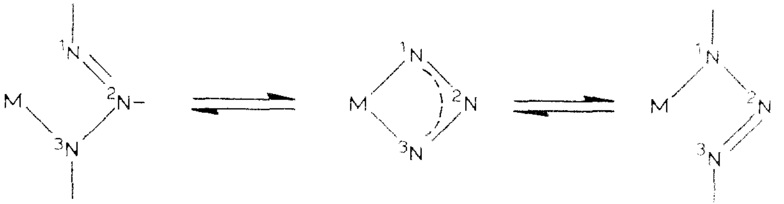
[a] $\Delta\delta$ = isotropic shift from the diamagnetic isostructural compound **1c**. [b] $\Delta\delta$ = isotropic shift from the free ligand. [c] s = singlet; d = doublet; bd = broad doublet.

The presence of the paramagnetic uranium(IV) atom, in the complexes **Ia** and **Ib**, spreads the ligand resonances over a range of about 50 ppm, facilitating their assignments by double resonance experiments. Thus the ^{1}H NMR spectrum of $Cp_2U(triaz)_2$ shows peaks due to the methyl protons at two very different frequencies (−2.91 and −10.39 ppm), another two for the *ortho* (−10.90 and −38.92 ppm) and also for *meta* (4.04 and 10.68 ppm) aromatic protons, and a singlet (−3.33) for the cyclopentadienyl protons. The integrations being in the ratio 6/6/4/4/4/4/10. The isotropic shifts of the aromatic protons reflect the effective spin transfer from the uranium(IV) central ion to the various position of the ligand and the sharpness of the signals suggests the presence of only one kind of triazenide ligand at room temperature. All these data are consistent with a monodentate form of the triazenide ligand:



In this form the *ortho* ($\Delta\delta$ −38.87) and *meta* ($\Delta\delta$ 10.73) aromatic protons, along with the *p*-CH_3 bonded to N(1), are much more influenced by the effects of the paramagnetic uranium(IV) ion than are the corresponding protons bonded to N(3).

Finally, while some triazenide complexes of transition metals are fluxional in solution [12,14f] $Cp_2U(triaz)_2$ shows no fluxionality in the range −80 to +80°C, thus excluding, in this temperature range, any possibility of equilibration between the chelate and monodentate triazenide forms (eq. 2).



(2)

Upon lowering the temperature there is a broadening of the lines without any coalescence of the signals such as could be expected for a chelate structure, in which the aromatic as well as the methyl protons are magnetically equivalent. $Cp_2U(triaz)_2$ shows a Curie–Weiss behaviour for the temperature dependent parmagnetism as can be seen in Fig. 1, the slope of the Cp curve being of opposite sign to that of the aromatic protons. Similar behaviour has been observed for some other organouranium(IV) derivatives [1].

From the analysis of the ^{1}H NMR spectrum of $Cp_2U(form)_2$ (Table 2) the same conclusions can be drawn as in the case of $Cp_2U(triaz)_2$ and $Cp_2Th(triaz)_2$.

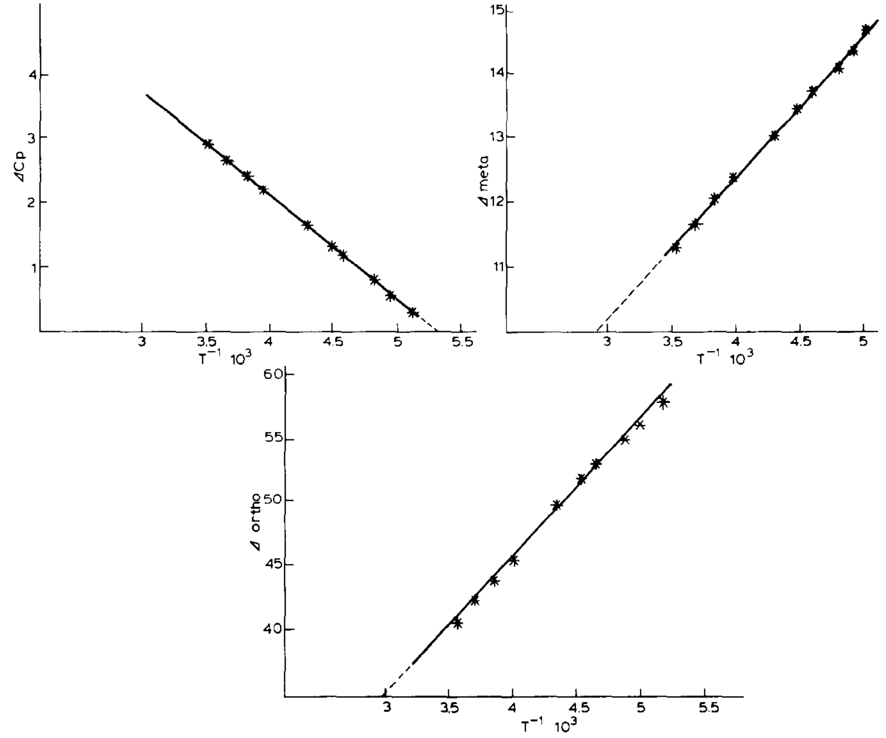
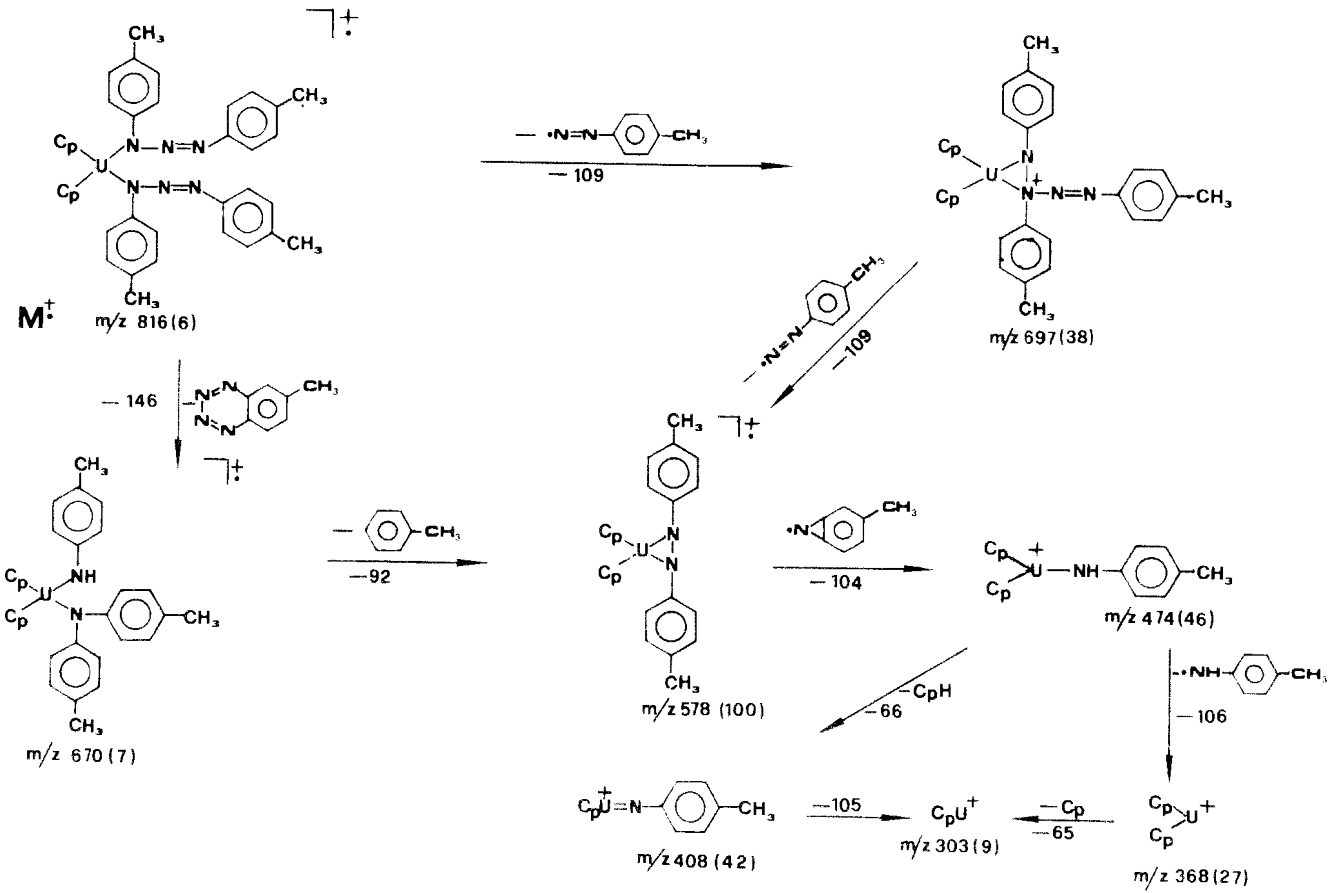


Fig. 1. Δ (ppm) vs. T^{-1} plots for all ^{1}H NMR shifts of $Cp_2U(triaz)_2$. Solvent: toluene-d_8, ref. to C_6D_5H (Δ > 0 = high field shift).

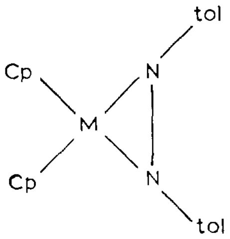
Mass spectra

The mass spectra of the complexes **1a**, **1b**, and **1c** (EI, 70 eV, *T* 100°C) show interesting differences in fragmentation patterns (see Schemes 1, 2, and 3). For compound **1a** the relative abundance of the molecular ion M^+ 816 *m/z* is quite low (6%) compared with that of the ion at 579 *m/z* (100%); this can be ascribed to increasing stability of the ions on passing from the molecular ion at 816 *m/z* (6%) through the ion at 697 *m/z* (38%) to the most abundant fragment at 578 *m/z* (100%), by progressive loss of the two ·N=N-tol radicals. This fragmentation pattern also strongly suggests a monodentate form of the triazenide ligand in compound **1a** as well as in **1c**. For **1c**, however, the relative abundances of the ions: M^+ 810 *m/z* (100%), 691 *m/z* (3%), 572 *m/z* (34%) are quite different from those observed for compound **1a** even though the fragmentation pattern is the same in both compounds.

It is noteworthy in both uranium(IV) and thorium(IV) triazenide upon electron impact in the gas phase form the species:



SCHEME 1. Fragmentation pattern of $Cp_2U(triaz)_2$ (EI, 70 eV, 100°C).

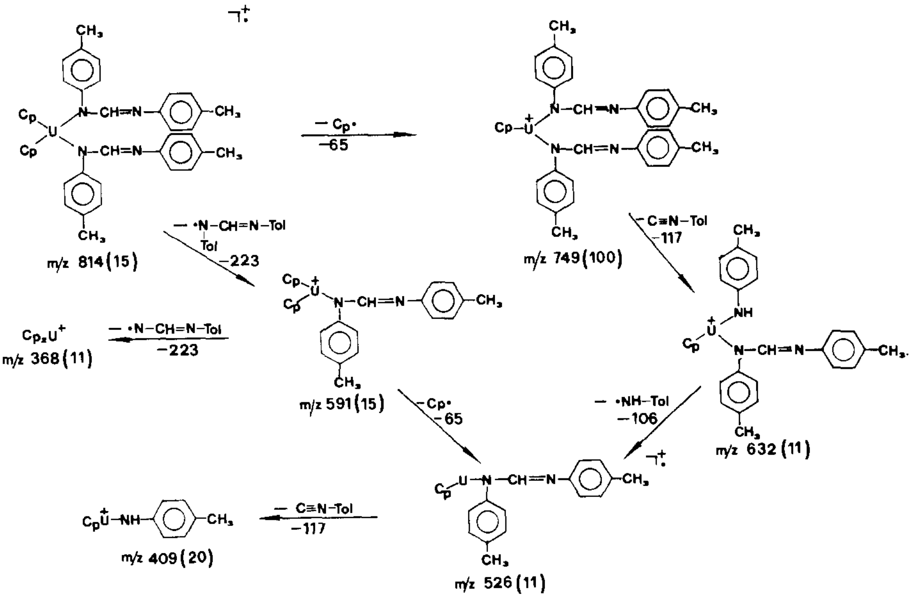


$\mathrm{M} = \mathrm{U}^{\mathrm{IV}} = 578 \quad m/z$

$\mathrm{M} = \mathrm{Th}^{\mathrm{IV}} = 572 \quad m/z$

which on the basis of their relative abundances have very high stabilities. This behaviour parallels that in the thermal decomposition of some monosubstituted triazenide metal complexes [13f] to amides.

Compound **1b**, on the other hand, behaves very differently, the primary fragmentation involving the loss of a Cp$^{\bullet}$ radical to give the most abundant fragment at 749 *m/z* (100%), and this by the loss of an isocyanide residue gives the ion at 632 *m/z* (11%). This last ion through two different fragmentations (the first involves the loss of tol-NH$^{\bullet}$ followed by that of tol-NC) gives the amido species at 409 *m/z* (20%). The second fragmentation gives rise to the Cp_2U^+ ion at 368 *m/z* (11%) by the successive loss of two formamidide fragments.

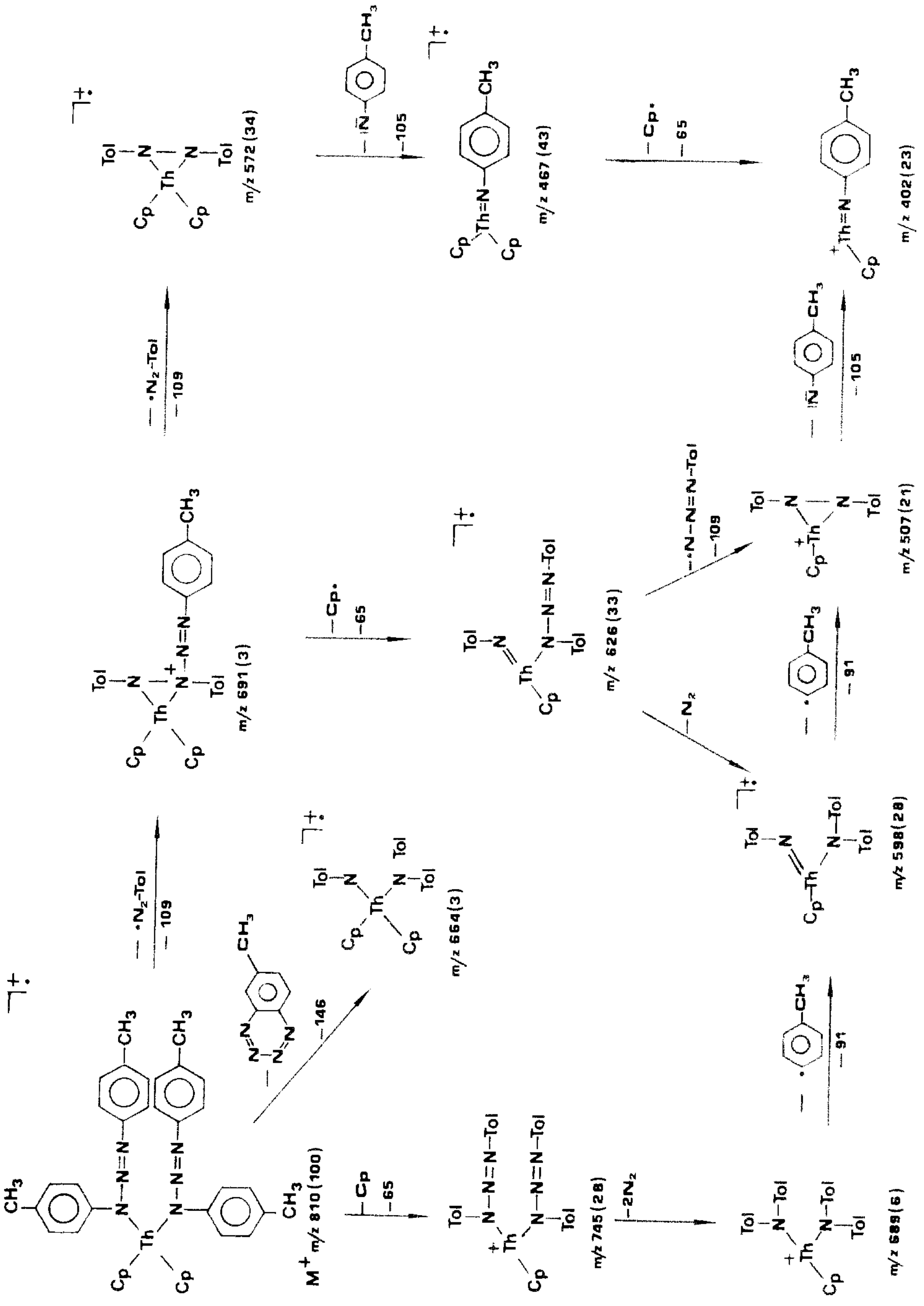


SCHEME 2. Fragmentation pattern of $Cp_2U(form)_2$ (EI, 70 eV, 100°C).

Experimental

Materials and methods

All manipulations involving organouranium and organothorium compounds were performed in a dinitrogen filled, recirculating glovebox (Jahan). *N*,*N*′-Di-*p*-tolyltriazene [19] and *N*,*N*′-di-*p*-tolylformamidine [20] were prepared by published procedures. $Cp_2(NEt_2)_2$ and $Cp_2Th(NEt_2)_2$ were synthesized as described previ-



SCHEME 3. Fragmentation pattern of $Cp_2Th(triaz)_2$ (EI, 70 eV, 100°C).

ously [18d]. Solvents (THF, diethyl ether, n-hexane, toluene) were purified by standard methods [21].

Analytical methods

Proton NMR spectra were recorded on a Varian FT-80A spectrometer equipped with a variable temperature accessory. Sample solutions (benzene-d_6, toluene-d_8) were sealed into the tubes in the glove-box. Infrared spectra were recorded on a Perkin-Elmer 580B spectrophotometer, using anhydrous Nujol mulls sandwiched between KBr plates in a holder made air-tight with an 0-ring seal.

Elemental analyses and molecular weight measurements (cryoscopic) were performed by the Dornis und Kolbe Mikroanalytisches Laboratorium, Mülheim, West Germany, or by Mr. A. Berton of our Institute.

*$Cp_2U(triaz)_2$ (**1a**)*

A solution of Htriaz (0.450 g, 2m*M*) in THF (10 ml) was slowly added at room temperature to a solution of $Cp_2U(NEt_2)_2$ (0.512 g, 1m*M*) in THF (30 ml). After 3 h stirring, the red solution was reduced in volume to ca. 10 ml and n-hexane (30 ml) was added. Dark red-brown crystals were formed (91% yield). Analysis: Found: C, 55.45; H, 4.45; N, 10.10; U, 28.85 $C_{38}H_{38}N_6U$ calcd.: C, 55.88; H, 4.66; N, 10.29; U, 29.17%. M.W. (benzene): Found: 807; calcd. 816.

*$Cp_2U(form)_2$ (**1b**)*

A solution of $Cp_2U(NEt_2)_2$ (0.512 g, 1 m*M*) in THF (10 ml) was slowly added at room temperature to a solution of Hform (0.448 g, 2 m*M*) in diethyl ether (25 ml). The solution immediately turned orange, and an orange product separated. After 12 h stirring the solid was filtered off and washed several times with diethyl ether (in which it is slightly soluble). The orange product was crystallized from THF/n-hexane (70% yield). Analysis: Found: C, 58.60; H, 4.75; N, 6.40; U, 28.95. $C_{40}H_{40}N_4U$ calcd.: C, 58.97; H, 4.91; N, 6.88; U, 29.24%. M.W. (benzene): Found: 805; calcd.: 814.

*$Cp_2Th(triaz)_2$ (**1c**)*

A solution of Htriaz (0.450 g, 2 m*M*) and $Cp_2Th(NEt_2)_2$ in toluene (50 ml) was refluxed for 4 h. The orange solution was evaporated to 10 ml under vacuum and then n-hexane (20 ml) was added. The yellow-orange precipitate was filtered off, washed several times with diethyl ether, (in which it is slightly soluble) and dried in vacuo (83% yield). Analysis: Found: C, 55.95; H, 4.40; N, 10.15. $C_{38}H_{38}N_6Th$ calcd.: C, 56.30; H, 4.69; N, 10.37%. M.W. (benzene): Found: 804; calcd.: 810.

References

1 T.J. Marks and R.D. Ernst, in Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, New York, Toronto, Sydney, Paris, Frankfurt, 1982, Vol. 6, p. 173–263.

2 R.D. Ernst, W.J. Kennelly, C.S. Day, V.W. Day, and T.J. Marks, J. Am. Chem. Soc., 101 (1979) 2656.

3 (a) P.J. Fagan, J.M. Manriquez, and T.J. Marks, in T.J. Marks and R.D. Fischer (Eds.), Organometallics of the *f*-Elements, Dordrecht, 1979, chap. 4, and ref. reported therein; (b) P.J. Fagan, J.M. Manriquez, E.A. Maata, A.M. Seyam, and T.J. Marks, J. Am. Chem. Soc., 103 (1981) 6650; (c) P.J. Fagan, J.M. Manriquez, S.H. Vollmer, C.S. Day, V.W. Day, and T.J. Marks, ibid., 103 (1981) 2206.

4 T.J. Marks, Adv. Chem. Ser., 150 (1976) 232; (b) C.A. Secaur, V.W. Day, R.D. Ernst, W.J. Kennelly, and T.J. Marks, J. Am. Chem. Soc., 98 (1976) 3713.

5 W.E. Hunter, and J.L. Atwood, Inorg. Chim. Acta, Abstr. 1st ICLA, Lanthanides and Actinides, A50 (1983) 80.

6 J.D. Jamerson and J. Takats, J. Organomet. Chem., 78 (1974) C23.

7 P. Zanella, G. Rossetto, and G. Paolucci, Inorg. Chim. Acta, 82 (1984) 227.

8 P. Zanella, G. de Paoli, G. Bombieri, G. Zanotti, and R. Rossi, J. Organomet. Chem., 142 (1977) C21.

9 K.W. Bagnall, J. Edwards, C.E.F. Rickard, and A.C. Tempest, J. Chem. Soc., Dalton Trans., (1979) 1321.

10 K.W. Bagnall, A. Beheshti, J. Edwards, F. Healty, and A.C. Tempest, J. Chem. Soc., Dalton Trans., (1979) 1241.

11 C.M. Harris, B.F. Hoskins, and R.L. Martin, J. Chem. Soc., (1959) 3728.

12 K.R. Laing, S.R. Robinson, and M.F. Uttley, J. Chem. Soc., Dalton Trans., (1974) 1205; (b) L.D. Brown and J.A. Ibers, Inorg. Chem., 15 (1976) 2788; (c) L. Toniolo, A. Immirzi, U. Croatto, and G. Bombieri, Inorg. Chim. Acta, 19 (1976) 209; (d) G. Bombieri, A. Immirzi, and L. Toniolo, Inorg. Chem., 15 (1976) 2428; (e) A. Immirzi, G. Bombieri, and L. Toniolo, J. Organomet. Chem., 118 (1976) 355; (f) G. Bombieri, A. Immirzi, and L. Toniolo, Transition Met. Chem., 1 (1976) 130.

13 (a) M. Corbett and B.F. Hoskins, J. Am. Chem. Soc., 89 (1967) 1530, (b) E. Pfeiffer, J. Kuyper and K. Vrieze, J. Organomet. Chem., 105 (1976) 371; (c) P.I. van Vliet, J. Kuyper and K. Vrieze, J. Organomet. Chem., 122 (1976) 99; (d) L.D. Brown and J.A. Ibers, Inorg. Chem., 15 (1976) 2788; (e) R. Graziani, L. Toniolo, U. Casellato, R. Rossi, and L. Magon, Inorg. Chim. Acta, 52 (1981) 119; (f) G.L. Hillhouse and J.E. Bercaw, Organometallics, 1 (1982) 1025.

14 (a) M. Corbett and B. Hoskins, J. Chem. Soc. Chem. Comm., (1968) 1602; (b) J.E. O'Connor, G.A. Janusonis and E.R. Carey, J. Chem. Soc. Chem. Comm., (1968) 445; (c) R. Hendriks, J. Kuyper and K. Vrieze, J. Organomet. Chem., 120 (1976) 285; (d) S. Candeloro de Sanctis, N.V. Pavel and L. Toniolo, ibid., 108 (1976) 409; (e) J. Kuyper, P.I. van Vliet and K. Vrieze, ibid., 105 (1976) 379; (f) L. Toniolo, G. Deganello, P.L. Sandrini and G. Bombieri, Inorg. Chim. Acta, 15 (1975) 11.

15 W. Bradley and I. Wright, J. Chem. Soc., (1956) 640.

16 A. Immirzi, W. Porzio, G. Bombieri, and L. Toniolo, J. Chem. Soc. Dalton Trans., (1980) 1098.

17 (a) P.I. van Vliet, M. Kokkes, G. van Koten and K. Vrieze, J. Organomet. Chem., 187 (1980) 413; (b) idem, ibid., 188 (1980) 301.

18 (a) A.L. Arduini, N.M. Edelstein, J.D. Jamerson, J.G. Reynolds, K. Schmid and J. Takats, Inorg. Chem., 20 (1981) 2470; (b) A.L. Arduini and J. Takats, ibid., 20 (1981) 2480; (c) A.L. Arduini, J.D. Jamerson and J. Takats, ibid., 20 (1981) 2474; (d) G. Paolucci, P. Zanella, G. Rossetto and R.D. Fischer, Abstr. 13èmes Journées des Actinides, Eilat, Israel, 1983; (e) G. Paolucci, G. Rossetto, P. Zanella, K. Yunlu and R.D. Fischer, J. Organomet. Chem., 272 (1984) 363; (f) G. Paolucci, P. Zanella, G. Rossetto and U. Croatto, Abstr. 1st ICLA, Inorg. Chim. Acta, Lanth. and Act., A25 (1983) 55.

19 Beilstein, 12, 919; 1, 419.

20 A.I. Vogel, A. Textbook of practical Organic Chemistry, 3rd ed., Wiley, New York, 1056, p. 626.

21 D.D. Perrin, W.L.F. Armarego and D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, 1980.