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Reactions of Organouranium Compounds with Tetracyanoethylene and 7,7,8,8-Tetracyanoquinodimethane

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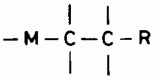
Abstract

Various organouranium(IV) complexes of the general type Cp_3UX ($Cp = \eta^5$-C_5H_5; $X = Cl$, CH_3, n-C_4H_9 and C_6H_5) react in toluene solution with tetracyanoethylene and even with 7,7,8,8-tetracyanoquinodimethane to give new triscyclopentadienyluranium keteniminates. Their NIR–Vis spectra seem to be typical of U(IV) compounds with trigonal bipyramidal coordination around the metal.

Introduction

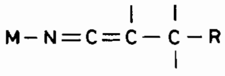
In the last decade, insertion reactions have played an important role in organouranium chemistry, in that their use provides facile and useful methods both for the synthesis of new and unusual organouranium compounds and for the studies of their reactivity and catalytic properties [1]. In fact several results have shown that polar molecules such as CO, CNR, SO_2, CO_2 and BH_3 can be inserted into U–X (X = alkyl, NEt_2 and H) bonds of organouranium complexes of the type Cp_3UX and Cp'_2UX_2 ($Cp = \eta^5$-C_5H_5, $Cp' = \eta^5$-C_5Me_5) [2–7] and into the U–H bond of Cp_3UAlH_4 [8], and that CO and CNC_6H_{11} can be inserted into the U=C double bonds of $Cp_3U{=}CHPR_3$ [9, 10]. Ethylene is reported to insert into $\{ThCp'_2(\mu\text{-}H)H\}_2$ and the same authors suggest that presumably it inserts into analogous organouranium hydrides [11]; however, no attention has been paid to the reactions of highly activated olefins.

On this basis we have turned our attention to the interaction of powerful electrophilic olefins such as tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) with organouranium compounds. In fact their reactivity, due to delocalization of the C=C π-electron density on the cyano substituents, is variable [12] and the literature contains several reports of complexes derived from their additions to M–R moieties, where M is either a transition metal [13] or a main group metal [14]. In particular, reactions of TCNE with M–R bonds can afford isomeric metal cyanoalkyls **I** and metal keteniminates **II**, corresponding to 1,2- or 1,4-insertion respectively.



$-M-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-R$

I



$M-N=C=\overset{|}{C}-\overset{|}{\underset{|}{C}}-R$

II

We have found that the reactions described here yielded a number of previously unknown keteniminato complexes formed by 1,4-addition of the olefins into U–C and U–Cl bonds.

Experimental

General Procedures

All operations were carried out with rigorous exclusion of oxygen and moisture in a dinitrogen-filled recirculating glove box. The solvents (toluene, CH_3CN, THF) were dried and purified by standard methods, and were stored in glove boxes.

Elemental analyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim, F.R.G.

Physical Measurements

Infrared spectra in the range 4000–400 cm^{-1} were recorded on a Perkin-Elmer 580B spectrophotometer using Nujol mulls between KBr discs in an air-tight holder sealed with an O-ring.

Electronic (NIR–Vis and UV) spectra were recorded at room temperature on a Cary 17 spectrophotometer using optical-quartz cells (10 mm).

Materials

The complexes Cp_3UCl [16] and Cp_3UR [17] (R = Me, Bu^n, Ph) were prepared as previously reported. TCNE (Janssen) was sublimed prior to use; TCNQ (Janssen) was recrystallized from ethylacetate.

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TABLE I. Elemental Analysis of Products of the Interaction between Cp_3UX with TCNE to Form Organouranium Keteniminates

Compound X	Analysis (%)									
	C		H		N		U		Cl	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Cl	42.26	42.61	2.53	2.52	9.39	9.47	39.88	39.65	5.94	5.81
Me	45.84	46.02	3.15	3.22	9.72	9.16	41.29	41.67		
Bu^n	48.55	48.60	3.91	3.79	9.06	8.67	38.48	38.04		
Ph	50.79	50.57	3.16	3.09	8.77	8.99	37.28	36.88		

Procedure and Characterization of the Products

Reactions with TCNE

A representative reaction of TCNE with complexes of general formula: $(\eta^5\text{-}C_5H_5)_3UX$ (X = Cl, Me, Bu^n, Ph) is described in detail. A solution of Cp_3UMe_3 (0.44 g, 1 mmol) and TCNE (0.128 g, 1 mmol) in 15 ml of toluene was stirred at room temperature. A brown solid almost immediately separated while the solution gradually cleared. After 24 h the mixture was filtered and the brown residue was washed several times with n-hexane, dried and analysed. Elemental analyses are reported in Table I. All new products exhibited essentially the same IR spectral patterns: (wavenumbers, cm^{-1}) 2201(s), 2122(vs), 1017(s), 791(vs).

Reaction with TCNQ

Cp_3UMe (0.448 g, 1 mmol) and TCNQ (0.204 g, 1 mmol) were stirred together overnight in 15 ml of THF. The brown solid formed was filtered and dried *in vacuo*. An elemental analysis was not obtained and the product was analysed by IR: (wavenumbers, cm^{-1}) 2183(s), 2101(vs), 1605(m), 1509(s), 1309(m), 1242(w), 1200(w), 1068(w), 1045(w), 1017(m), 919(br,m), 789(br,s), 728(w).

Results and Discussion

The reaction between equimolar amounts of Cp_3UX and TCNE in toluene at room temperature yields insoluble brown products the elemental analyses of which (Table I) indicate empirical formulae consistent with $Cp_3U(C_6N_4)X$. Their infrared spectra (in the 4000–400 cm^{-1} region) are identical and present the absorptions characteristic of η^5-bonded Cp rings (every vibration having its counterpart in spectra of Cp_3UX systems, Fig. 1) and two bands at 2200(s) cm^{-1} and 2123(vs) cm^{-1} that can probably be assigned to the C≡N and to the asymmetric N=C=C stretching modes respectively and point to the presence of a keteniminato linkage [13, 14]:

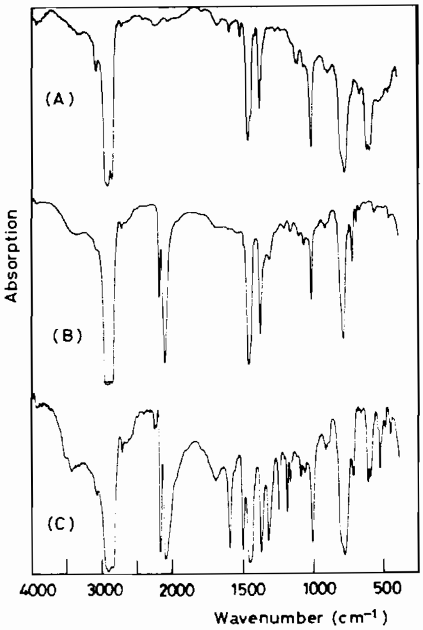
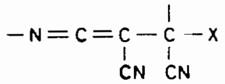


Fig. 1. IR spectra in Nujol mulls of: (A) Cp_3UCH_3; (B) $Cp_3UN{=}C{=}C(CN)C(CN)_2CH_3$; and (C) $Cp_3UN{=}C{=}C(CN)\text{-}C_6H_4C(CN)_2CH_3$.



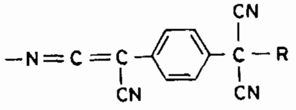
$$-N=C=\underset{CN}{C}-\overset{CN}{\underset{CN}{C}}-X$$

III

By comparison, $Ir(CO)P(C_6H_5)_3(C_6N_4){-}N{=}C{=}(CCN)(CCN)_2H$, the structure of which was resolved crystallographically, absorbs at 2200 and 2168 cm^{-1} [13c].

Analogously, Cp_3UR (R = Me, Bu) reacts with an equimolar amount of TCNQ giving a brown solid the IR spectrum of which presents bands due to η^5-bonded Cp rings, absorptions at 1605, 1509 cm^{-1} ($\nu(C\overset{\cdots}{-}C)$), 800 cm^{-1} ($\pi(C{-}H)$), and weak bands between 1245–1045 cm^{-1} ($\rho(C{-}H)$) that suggest the formation of a 1,4-substituted benzene ring;

these facts together with the absorptions at 2183(s) (ν(C=N)), 2101(vs) (ν_{as}(N=C=C)) and 1309(w) (ν_s(N=C=C)) indicate also in this case the presence of a keteniminato linkage as shown in **IV**.



IV

The new compounds are very slightly soluble in CH_3CN and THF giving intensely coloured red solutions the UV spectra of which present absorptions at 265 nm and 345 nm which have already been observed in the ketenimines [18]. Therefore spectroscopic evidence suggests that probably U–R and U–Cl bonds give uranium keteniminate complexes by 1,4-addition to TCNE or 1,6-addition to TCNQ.

Finally, their near IR and visible absorption spectra in THF or in CH_3CN are quite similar in both solvents and all differ from the spectra of the corresponding starting complexes (see Fig. 2). The most important features in the spectra of these new complexes, in comparison with the spectra of the parent Cp_3UX, are the strong absorption at 1530 nm and an alteration of the absorptions, characteristic of the pseudo-tetrahedral Cp_3UX systems, in the 1000–1050 nm region. Therefore, the spectra seem to be typical of U(IV) compounds with trigonal bipyramidal coordination around the central metal [19]. This observation, together with the low solubility and involatility, suggests that these complexes are oligomeric and are probably composed of linear –U–N–C–C–C–N chains linked by strong CN bridges; this in turn causes the resonance:

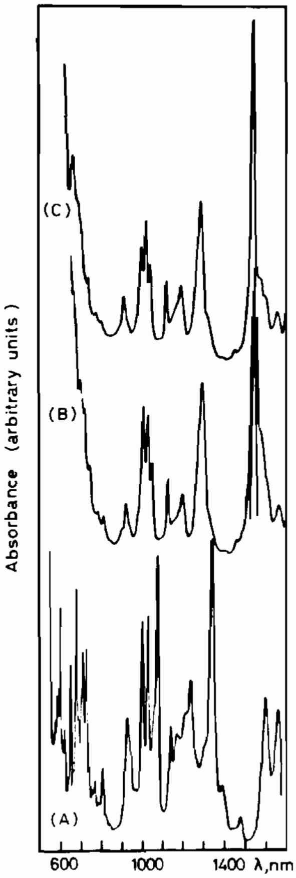
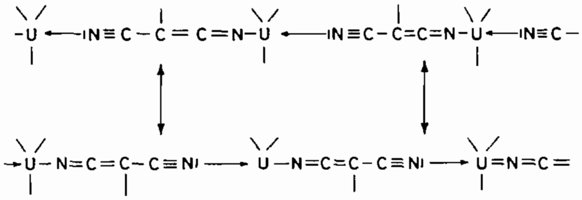
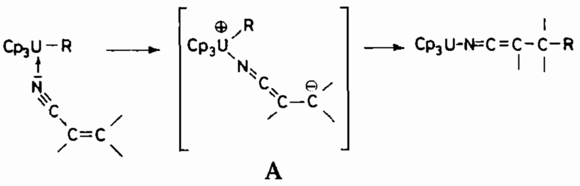


Fig. 2. NIR–Vis spectra of: (A) Cp_3UCH_3 in toluene solution; (B) $Cp_3UN{=}C{=}C(CN)C_6H_4C(CN)_2Bu$ in tetrahydrofuran solution; and (C) $Cp_3UN{=}C{=}C(CN)C(CN)_2Bu$ in tetrahydrofuran solution.



which leads to the stabilization of the products.

A possible reaction path for the formation of the new products described here is shown in Scheme 1. It would involve initial interaction of a cyano group on the U atom, followed by formation of a dipolar intermediate A and by subsequent nucleophilic attack of its negative terminus at R.



Scheme 1.

Therefore the interaction between Cp_3UX and TCNE or TCNQ can be regarded as a hard–hard interaction, where the hard Cp_3UX group accepts electron density from the relatively hard donor nitrile nitrogens of TCNE or TCNQ. In fact the electronic structures of these molecules are characterized by a build up of negative charge on the nitrile nitrogens relative to the olefinic carbon atoms [20]. This justifies the fact that 1,4-addition for TCNE (1,6-addition for TCNQ) occurs instead of the usual 1,2-addition as with unsaturated hydrocarbons; i.e., we think the formation of the hard base–hard acid keteniminato–uranium complex (due to the 1,4-addition) seems more probable than the corresponding soft base–hard acid cyanoalkyluranium complex (that could be formed by 1,2-addition).

Finally, we wish to add that $CH_3{-}CH{=}CH{-}CN$ does not react with Cp_3UX (X = Cl, alkyl group)[≠].

[≠] We have observed that $CH_3{-}CH{=}CH{-}CN$ reacts with Cp_3UAlH_4 giving a mixture of products the identification of which is still under investigation.

This inertness towards U–X bonds can probably be explained by the fact that acrylonitrile is less electrophilic than TCNE.

Acknowledgements

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