istry,[7] applies to ylide–actinide compounds. While we, as of yet, have been unsuccessful in obtaining an organoactinide which contains only Ac–C σ bonds, the formation and stability of IV and V give hope that further $C_5H_5^-$ substitution can occur if the proper ylide system can be found. The ability of the lithiated ylides to displace $C_5H_5^-$ units from uranium also provides a pathway to complexes rich in Ac–C σ bonds which has not been available before.

Registry No. I, 77357-85-8; II, 77357-86-9; III, 67771-71-5; IV, 77357-87-0; V, 77357-88-1; $(\eta^5\text{-}C_5H_5)_3UCl$, 1284-81-7; $(\eta^5\text{-}C_5H_5)UCl_3\cdot 2THF$, 54674-00-9; $Li(CH_2)(CH_2)P(CH_3)(C_6H_5)$, 59983-61-8; $Li(CH_2)(CH_2)P(C_6H_5)_2$, 59983-62-9.

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Syntheses and Characterization of $(\eta^5\text{-}C_5H_5)_2U(NR_2)_2$ Compounds

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The reaction of 2 equiv of cyclopentadiene with $U(NPr_2)_4$ and $U(NPh_2)_4$ and the reaction of 1.5 equiv of cyclopentadiene with $U(NEt_2)_4$, generated in situ, gives the corresponding $Cp_2U(NR_2)_2$ complexes in good yields. However, $U(N\text{-}i\text{-}Pr_2)_4$ does not react with cyclopentadiene at room temperature and $U(NMe_2)_4$ gives mixture of $Cp_2U(NMe_2)_2$ and $Cp_3U(NMe_2)$. Excess cyclopentadiene also reacts with $Cp_2U(NEt_2)_2$ to produce $Cp_3U(NEt_2)$. The transamination reaction of $Cp_2U(NEt_2)_2$ with pyrrole and 2,3-dimethylpyrrole gives mixtures of products only; however, ethyl 3,4,5-trimethylpyrrole-2-carboxylate gives $Cp_2U[NC_4Me_3(COOEt)]_2$, and the reaction with 1 equiv of diphenylamine yields $Cp_2U(NEt_2)(NPh_2)$. It is argued that the reactivity sequence and the stability of $Cp_2U(NR_2)_2$ compounds are best explained by steric effect considerations. The spectral characteristics of the $Cp_2U(NR_2)_2$ complexes are presented which show that the compounds possess η^5-cyclopentadienyl moieties and monomeric solution behavior with no primary solvent interaction. In $Cp_2U[NC_4Me_3(COOEt)]_2$, additional interaction between uranium and oxygen of the carboxylate functionality is postulated.

Introduction

The synthesis of uranocene,[3] $U(COT)_2$, has rekindled interest in the field of organoactinide chemistry in general and organouranium complexes in particular. Although a large variety of complexes have been synthesized, a quick review of the now extant literature reveals a paucity of Cp_2UX_2-type complexes.[4] The logical entry into this area of chemistry, Cp_2UCl_2,[5] was shown to be incorrectly formulated,[6] and on the basis of best currently available evidences, it appears to be a mixture of Cp_3UCl and $CpUCl_3L_2$ (L = Lewis base).[6c] It is only recently that, by the clever use of the bulky pentamethylcyclopentadienyl ligand system, Marks et al. have succeeded in isolating $[C_5(CH_3)_5]_2UCl_2$[7] and utilized it as a versatile precursor to other $[C_5(CH_3)_5]_2UR_2$[8] complexes which have a very rich chemistry of their own.

Our approach to the synthesis of Cp_2UX_2 complexes was based on the expectation that, given a suitable ligand, a stable and authentic Cp_2UY_2 complex could obtain. Furthermore, if Y happens to be an easily displaceable ligand as well, the material would provide an entry into the elusive area of Cp_2UX_2 (X = some functional group) type compounds.

The utility of transition-metal amides as reactive intermediates has been recognized for years.[9] The reactivity of the metal–nitrogen bond toward molecules containing dipolar double bonds and acidic hydrogens can be exploited in an almost limitless fashion in order to prepare an amazing array of transition-metal complexes.[9] For our purposes, however, the reaction of cyclopentadiene with titanium group amides looked particularly interesting.[10] It was found that zirconium and hafnium amides cleanly gave $Cp_2M(NMe_2)_2$ complexes and this even in the presence of excess cyclopentadiene (eq 1). Since $U(NEt_2)_4$ has been known for a long time[11] and

$$M(NMe_2)_4 + \text{excess CpH} \rightarrow Cp_2M(NMe_2)_2 + 2HNMe_2 \qquad (1)$$
$$M = Zr, Hf$$

many new actinide amides have been synthesized recently,[12] the ramification of eq 1 for the synthesis of $Cp_2U(NR_2)_2$ compounds and their subsequent elaboration to other Cp_2UX_2-type complexes are clear.

The initial results of the substitution reaction using $U(NEt_2)_4$ and cyclopentadiene were encouraging.[13] The com-

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(1) Lawrence Berkeley Laboratory.

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(3) A. Streitwieser, Jr., and U. Müller-Westerhoff, *J. Am. Chem. Soc.*, **90**, 7364 (1968).

(4) T. J. Marks, *Prog. Inorg. Chem.*, **25**, 223 (1979), and references therein.

(5) L. Doretti, P. Zanella, G. Faraglia, and S. Faleschini, *J. Organomet. Chem.*, **43**, 339 (1972).

(6) (a) B. Kanellakopulos, C. Aderhold, and E. Dornberger, *J. Organomet. Chem.*, **66**, 447 (1974). (b) K. W. Bagnall, J. Edwards, and A. C. Tempest, *J. Chem. Soc., Dalton Trans.*, 295 (1978). (c) R. D. Ernst, W. J. Kennely, C. Secaur-Day, V. W. Day, and T. J. Marks, *J. Am. Chem. Soc.*, **101**, 2656 (1979).

(7) J. M. Manriquez, P. J. Fagan, and T. J. Marks, *J. Am. Chem. Soc.*, **100**, 3939 (1978).

(8) (a) J. M. Manriquez, P. J. Fagan, T. J. Marks, C. Secaur-Day, and V. W. Day, *J. Am. Chem. Soc.*, **100**, 7112 (1978). (b) J. M. Manriquez, P. J. Fagan, T. J. Marks, S. H. Vollmer, C. Secaur-Day, and V. W. Day, *ibid.*, **101**, 5075 (1979).

(9) (a) D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, **15**, 259 (1972). (b) D. C. Bradley and M. H. Chisholm, *Acc.* Chem. *Res.*, **9**, 273 (1976). (c) M. F. Lappert, P. P. Power, A. R. Sanger, and R. C. Srivastava, "Metals and Metalloid Amides: Synthesis, Structures, and Physical and Chemical Properties", Ellis Horwood Ltd., Chichester, and Wiley, New York, 1980.

(10) G. Chandra, A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, *J. Chem. Soc. A*, 2550 (1970).

(11) R. G. Jones, K. Karmas, G. A. Martin, and H. Gilman, *J. Am. Chem. Soc.*, **78**, 4285 (1956).

(12) (a) J. G. Reynolds and N. M. Edelstein, *Inorg. Chem.*, **16**, 2822 (1977). (b) J. D. Jamerson, Ph.D. Thesis, University of Alberta, 1974.

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

pound $Cp_2U(NEt_2)_2$ was prepared in reasonable yield and gave evidence as a useful precursor to other Cp_2UX_2 species. In this paper we report full details on the synthesis and physical properties of $Cp_2U(NEt_2)_2$ and related compounds. As well, the reactivity of $Cp_2U(NEt_2)_2$ toward other amines will be discussed. The reactivity of $Cp_2U(NEt_2)_2$ toward dipolar double bonds and molecules containing acidic hydrogens will form the basis of future reports.

Experimental Section

All reactions and manipulations were performed with use of Schlenk techniques under a static atmosphere of rigorously purified nitrogen or argon, with scrupulous exclusion of air and moisture. Solvents were dried by refluxing, under purified nitrogen, with the appropriate drying agent and were distilled immediately prior to use. The following reagents were prepared and purified according to published procedures: UCl_4[14] (also purchased from Research Organic/Inorganic Chemical Corp. and used as received), $U(NEt_2)_4$,[15] $U(NPr_2)_4$,[12a] and $U(NPh_2)_4$.[12b,16] Lithium dialkylamides, $LiNR_2$, were prepared by reaction of *n*-butyllithium (MC/B, 15% hexane solution) with the appropriate dialkylamine in hexane. The liquid dialkylamines were dried by distilling from potassium metal. Potassium diphenylamide ($KNPh_2$) was obtained by reacting clean potassium metal with freshly sublimed diphenylamide in refluxing benzene for 24 h. Ethyl 3,4,5-trimethylpyrrole-3-carboxylate was supplied by Professor D. Clive of this department and used as received.

Treatment of UCl_4 with 4 equiv of $LiNMe_2$ in THF gave, after concentration of the solution and precipitation of LiCl by the addition of hexane, $U(NMe_2)_4$ as a brown solid in 90% yield[12b] (Anal. Calcd: NMe_2 42.2. Found: NMe_2, 40.1). The reaction between UCl_4 and 4 equiv of LiN-*i*-Pr_2 in a mixture of THF/hexane required heating at 60–70 °C for 6 h to achieve complete conversion to $U(N$-*i*-$Pr_2)_4$, otherwise $U(N$-*i*-$Pr_2)_3Cl$ was the major component.[12b] $U(N$-*i*-$Pr_2)_4$, obtained in 55% yield, is a very dark, almost black, solid and is very soluble in all solvents including hydrocarbons. Although satisfactory analysis could not be obtained on this material, ^1H NMR spectrum of the material showed no other detectable species (−0.10 (d), CH_3; −6.00 ppm (br), CH).

Physical Measurements. Infrared spectra were recorded in the region 4000–250 cm^{-1} with a Perkin-Elmer 467 grating spectrometer. The complexes were studied as Nujol and Fluorolube mulls between potassium bromide plates. The samples were prepared in a glovebag filled with purified nitrogen. Proton magnetic resonance spectra were recorded on a Perkin-Elmer R-32, Varian NV-14, T-60, or A-60 Spectrometer. NMR spectra were obtained with the use of serum-stoppered or sealed NMR tubes. Mass spectra were recorded on an AEI-MS12 mass spectrometer operating at 70 eV and at temperatures just sufficient to record the data. Each sample was sealed in a capillary under nitrogen and admitted into the spectrometer by using a direct probe technique. The optical spectra were obtained on a Cary 17 spectrometer at room temperature. The solutions, 0.02 M, were placed in 0.5-cm Beckman cells in a drybox. The stopper seal was reinforced with silicone stopcock grease. All samples were run with a 0.5-cm solvent cell in the reference compartment.

Analyses and molecular weight determinations were performed by Analytische Laboratorien, D-5250 Engelskirchen, West Germany, on samples sent in glass tubes sealed under vacuum or in the Microanalytical Laboratory in the department at Alberta. Amine analysis was accomplished by hydrolyzing a known weight of the sample with 10% KOH, distilling the liberated amine into a known excess of sulfuric acid (ca. 0.1 M), followed by back titration with NaOH (ca. 0.1 M). Abbreviations used are as follows: COT = η^8-C_8H_8, Cp = η^5-C_5H_5, Me = CH_3, Et = CH_2CH_3, Pr = $CH_2CH_2CH_3$, *i*-Pr = $CH(CH_3)_2$, *n*-Bu = $CH_2CH_2CH_2CH_3$, Ph = C_6H_5.

Synthesis of $Cp_2U(NEt_2)_2$. UCl_4 (10.48 g, 27.6 mmol) and $LiNEt_2$ (8.79 g, 111 mmol) were placed in a 300-mL flask which was then wrapped in foil to exclude light. Into the flask was transferred 100 mL of Et_2O under vacuum at liquid-N_2 temperature. The reaction mixture was stirred at room temperature for 30 h and filtered and the solvent removed under vacuum. The resulting dark green oil was dissolved in 60 mL of pentane. To this solution, cooled to 0 °C, was added a solution of freshly distilled CpH (3.3 mL, 39.8 mmol) in 20 mL of pentane. The solution was stirred at room temperature for 7 h in a foil-wrapped flask. The gold-brown solution was then transferred to a jacketed Schlenk filter and cooled to −78 °C for 0.5 h, and the resulting gold flakes were filtered from the solvent. The solid was then washed with 15 mL of cold pentane and dried under vacuum to give 8.4 g of product (81% yield, based on the amount of cyclopentadiene used). The ^1H NMR spectrum of the compound showed that it contained 3% of $Cp_3U(NEt_2)$. The filtrate can be concentrated and cooled to yield more product which however also contains more of the impurity $Cp_3U(NEt_2)$.

The less than stoichiometric amount of cyclopentadiene used in the preparation is to take into account the possibility of some decomposition and losses of $U(NEt_2)_4$ which might occur during the in situ synthesis of $U(NEt_2)_4$. On the basis of several experiments, the optimum empirical ratio of cyclopentadiene to amide was found to be approximately 1.5:1.0. This ratio consistently gave good yields of $Cp_2U(NEt_2)_2$. In our hands, increasing this ratio toward the stoichiometric requirements resulted in an increase in the amount of $Cp_3U(NEt_2)$ formed.

$Cp_2U(NEt_2)_2$ will form small amounts of $Cp_3U(NEt_2)$ upon handling and storage. A convenient way of removing this impurity is to dissolve the sample in hexane and filter prior to use. The operation leaves behind the less soluble $Cp_3U(NEt_2)$ compound. This precautionary measure was routinely performed in subsequent reactions utilizing $Cp_2U(NEt_2)_2$ as precursor for other Cp_2UX_2 complexes. The purity of $Cp_2U(NEt_2)_2$ may be ascertained by recording the ^1H NMR spectrum of the compound. Anal. Calcd: NEt_2, 28.2. Found: NEt_2, 28.5.

$Cp_2U(NEt_2)_2$ cannot be purified by sublimation. Heating the compound at 120 °C and 10^{-4} mmHg produced a sublimate, but this was identified by ^1H NMR as being $Cp_3U(NEt_2)$.

Synthesis of $Cp_2U(NPr_2)_2$. In a 250-mL flask, 1.6 g (2.5 mmol) of freshly distilled $U(NPr_2)_4$ was placed. Then 100 mL of pentane was added under vacuum at liquid N_2 temperature. After the solvent addition was complete, 0.416 mL (5.0 mmol) of freshly distilled and degassed cyclopentadiene was added under vacuum. After the addition of cyclopentadiene was complete, the solution was allowed to warm to room temperature while stirring. A color change from the dark green of the amide to a dark golden brown of the Cp adduct was noticed shortly after the mixture has reached room temperature. Although no further color change was noticed, the reaction was continued for 24 h. At this time the reaction mixture was evaporated to dryness, giving a dark brown solid. Attempts to recrystallize the solid from pentane produced only slightly lighter precipitates. Spectral studies were done on these materials. The material sublimed with decomposition at 120 °C and 10^{-4} mmHg. The decomposition product was identified by ^1H NMR as being $Cp_3U(NPr_2)$.

Synthesis of $Cp_2U(NPh_2)_2$. Freshly distilled cyclopentadiene (0.30 mL, 0.24 g, 3.6 mmol) was added dropwise to a solution of 1.69 g (1.85 mmol) of $U(NPh_2)_4$ in 20 mL of THF. After the deep red solution stirred for 3 h at room temperature, the solvent was removed under vacuum to give a dark red solid. The solid was transferred to a Schlenk filter and washed with four 10-mL portions of pentane to yield 1.21 g (92.4%) of $Cp_2U(NPh_2)_2$. The purity of the sample was demonstrated by NMR spectroscopy and mass spectrometry.

Other Attempted Syntheses. $U(N$-*i*-$Pr_2)_4$ failed to react with cyclopentadiene at room temperature in pentane or in THF. The reaction between $U(NMe_2)_4$ and cyclopentadiene produced mixtures of $Cp_2U(NMe_2)_2$ and $Cp_3U(NMe_2)$ which were identified only by ^1H NMR spectroscopy.

Transamination Reactions Involving $Cp_2U(NEt_2)_2$. Preparation of $Cp_2U(NEt_2)(NPh_2)$. Diphenylamine (0.642 g, 3.79 mmol) was dissolved in 30 mL of hexane and was added to a solution of $Cp_2U(NEt_2)_2$ (1.94 g, 3.78 mmol) in 50 mL of hexane at room temperature. There was an immediate color change from golden brown to red. The reaction mixture was stirred at room temperature for 37 h. The solvent was removed under vacuum, giving an orange-red solid. Crystallization from toluene/hexane solvent mixture gave the pure product in 60% yield. Anal. Calcd for $C_{26}H_{30}N_2U$: C, 51.32; H, 4.97; N, 4.60; U, 39.11. Found: C, 51.13; H, 4.80; N, 4.47; U, 39.42. When this reaction was repeated with 2 equiv of diphenylamine, the expected $Cp_2U(NPh_2)_2$ did not form; instead, the monosubstituted complex precipitated out of solution as a microcrystalline red solid.

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(14) J. A. Hermann and J. F. Suttle, *Inorg. Synth.*, **5**, 143 (1957).

(15) J. G. Reynolds, A. Zalkin, D. H. Templeton, N. M. Edelstein, and L. K. Templeton, *Inorg. Chem.*, **15**, 2498 (1976).

(16) J. G. Reynolds, A. Zalkin, D. H. Templeton, and N. M. Edelstein, *Inorg. Chem.*, **16**, 1090 (1977).

When the reaction with 2 equiv of diphenylamine was carried out in benzene or THF, $Cp_2U(NPh_2)_2$ does obtain but mixed with $Cp_2U(NEt_2)(NPh_2)$ in the former solvent, or with $Cp_2U(NEt_2)(NPh_2)$, $CpU(NPh_2)_3$ and $Cp_3U(NPh_2)$ in the latter solvent system. No attempts were made to separate these mixtures.

Preparation of $Cp_2U[NC_4Me_3(COOEt)]_2$. A solution of $HNC_4Me_3(COOEt)$ (0.239 g, 1.32 mmol) in 3 mL of THF and 10 mL of hexane was syringed slowly into a solution of $Cp_2U(NEt_2)_2$ (0.372 g, 0.73 mmol) in 20 mL of hexane at room temperature. The solution was stirred for 24 h at the end of which time the solution was red-brown with a greenish tinge. The solvent was removed under vacuum and a yellow-brown solid was obtained. This solid was extracted with 10 mL of pentane for 24 h. The mixture was filtered, and the remaining green solid was dried under vacuum to give a yield of 48.2%. The green solid could be sublimed at 110 °C and 10^{-3} mmHg although the sublimation was not very efficient. Mass spectral data and an NMR spectrum confirmed that the green solid was $Cp_2U[NC_4Me_3(COOEt)]_2$.

Reaction of $Cp_2U(NEt_2)_2$ with Pyrrole and 2,5-Dimethylpyrrole. Attempts to exchange cleanly both diethylamido groups for NC_4H_4 and $NC_4H_2Me_2$ met with failure. The gold-brown solid obtained from the reaction with pyrrole was found to be a mixture of $Cp_2U(NC_4H_4)_2$ and $Cp_3U(NC_4H_4)$, while the reaction with dimethylpyrrole gave a mixture identified as $Cp_3U(NEt_2)$ and $Cp_2U(NEt_2)(NC_4H_2Me_2)$.

Results and Discussion

Reactions of $U(NR_2)_4$ with Cyclopentadiene. As expected from the known reactivity of metal amides,[9] the reaction of cyclopentadiene with certain uranium amides leads to the desired dicyclopentadienyl-bis(amido) derivatives, $Cp_2U(NR_2)_2$ (eq 2). However, contrary to transition-metal amides

$$U(NR_2)_4 + 2CpH \rightarrow Cp_2U(NR_2)_2 + 2HNR_2 \qquad (2)$$
$$R = Et, Pr, Ph$$

whose reactions were devoid of complications and succeeded even in the presence of excess cyclopentadiene, the success of the reaction with $U(NR_2)_4$ is a sensitive function of the amide used and the amount of cyclopentadiene employed.

Thus, in our hands, the reaction between $U(N\text{-}i\text{-}Pr_2)_4$ and cyclopentadiene in pentane or THF at room temperature does not give any noticeable reaction, and this we attribute to the severe steric congestion around the starting amido complex. On the other hand, the reaction between freshly prepared $U(NMe_2)_4$ and 2 equiv of cyclopentadiene invariably yields mixtures of $Cp_3U(NMe_2)$ and $Cp_2U(NMe_2)_2$, indicating that the NMe_2 group is apparently not bulky enough to stabilize $Cp_2U(NMe_2)_2$ against further reaction with cyclpentadiene and/or disproportionation, giving, among other things, $Cp_3U(NMe_2)$.[17] Even the diethylamide group is not bulky enought to completely suppress the formation of $Cp_3U(NEt_2)$. $Cp_2U(NEt_2)_2$ can be obtained pure and in good yield on the basis of the empirically derived conditions detailed in the Experimental Section. However, upon standing, the material apparently does disporportionate since the ^1H NMR spectra of old samples showed the presence of $Cp_3U(NEt_2)$. Similarly, attempted purification of $Cp_2U(NEt_2)_2$ by sublimation produced sublimaes which were mixtures of $Cp_2U(NEt_2)$ and $Cp_3U(NEt_2)$, as shown by ^1H NMR spectroscopy. Furthermore, and contrary to the reactivity of the titanium group amides where the reaction cannot be forced beyond the $Cp_2M(NR_2)_2$ stage,[10] it was also found that $Cp_2U(NEt_2)_2$ reacts with additional cyclopentadiene to give $Cp_3U(NEt_2)$. This observation is explicable in terms of the known propensity of uranium for high coordination numbers and the high stability of Cp_3UX-type compounds.[4,6,12b] The finding also indicates that even when previously isolated and pure uranium amides are used in reaction with cyclopentadiene, a strict adherence to the correct stoichiometry is necessary in order to obtain $Cp_2U(NR_2)_2$ derivatives. Such precautions were taken into account in the successful synthesis of $Cp_2U(NPh_2)_2$ and $Cp_2U(NPr_2)_2$.

Transamination Reactions Involving $Cp_2U(NEt_2)_2$. The amide exchange reaction has been shown to be a useful synthetic route in both transition-metal[9] and uranium[16] amide chemistry. It was of obvious interest to investigate whether this methodology could be applied to $Cp_2U(NEt_2)_2$, the most easily obtainable cyclopentadienylamido complex, and thus extend the number of known $Cp_2U(NR_2)_2$ derivatives. The reaction of $Cp_2U(NEt_2)_2$ with 1 or 2 equiv of diphenylamine in hexane at room temperature results in the precipitation of a red, microcrystalline solid which was shown to be $Cp_2U(NEt_2)(NPh_2)$. Attempts to obtain pure $Cp_2U(NPh_2)_2$, by carrying out the reaction in solvents where the monosubstituted complex is soluble, were met with failure. The reaction in benzene gave mixts. of $Cp_2U(NEt_2)$ and $Cp_2U(NPh_2)_2$; the mixtures obtained from THF also contained $CpU(NPh_2)_3$ and $Cp_3U(NPh_2)$.

Mixtures were also obtained from the reaction of $Cp_2U(NEt_2)$ and pyrrole (HNC_4H_4). The reaction with either 1 or 2 equiv of pyrrole in hexane or THF gave a gold solid which contained both $Cp_2U(NC_4H_4)_2$ and $Cp_3U(NC_4H_4)$, in variable amounts. The ^1H NMR spectrum shows peaks at 0.43, 7.66, and 31.06 ppm upfield from Me_4Si in a 10:4:4 ratio due to the dipyrrolide complex, a peak at 3.77 ppm is attributable to the Cp protons of $Cp_3U(NC_4H_4)$; few other small, unidentified peaks were also observed.

On the assumption that a more bulky ligand may result in the formation of a single product, 2 equiv of 2,5-dimethylpyrrole were combined with $Cp_2U(NEt_2)_2$ in hexane. The red crystalline material that is isolated exhibits a mass spectrum which contains fragments from $Cp_2U(NEt_2)(NC_4H_2Me_2)$ and $Cp_3U(NEt_2)$. The ^1H NMR spectrum corroborates this assignment [-7.08 (s, Me); -6.57 (q, CH_2); -1.28 (t, CH_3); 12.6 (s, H); 13.5 ppm (s, Cp) of $Cp_2U(NEt_2)(NC_4H_2Me_2)$ and 1.06 (t, CH_3); 11.86 (s, Cp) of $Cp_3U(NEt_2)$]. Hence the more bulky pyrrole only replaces one diethylamide group. Unfortunately, it does not eliminate ligand redistribution, and a pure product does not obtain.

That steric control can be overridden by apparent electronic effect is demonstrated by the even bulkier pyrrole derivative, ethyl 3,4,5-trimethylpyrrole-2-carboxylate. The reaction between 2 equiv of this ligand and $Cp_2U(NEt_2)_2$ in hexane results in the replacement of both diethylamide groups. There is no evidence for the monosubstituted compound in the mass spectrum. The ^1H NMR spectrum (vide infra) suggests that, in addition to U–N bonding, the carboxyl oxygen is coordinated to the uranium center as well. This extra interaction may account for the facile and exclusive formation of the disubstituted complex and may well be the reason for the suppression of the redistribution reaction with this combination of ligands.

Bonding and Structures of $Cp_2U(NR_2)_2$ Compounds. The ^1H NMR spectra of the complexes (Table I and Figure 1) exhibit sharp singlets for the cyclopentadienyl moieties and indicate the anticipated pentahapto bonding mode for these groups. This assignment is further corroborated by the infrared spectrum of the complexes. The characteristic frequencies in the 1600–400-cm^{-1} fingerprint region are listed in Table II.[18] As argued before,[19] the simple pattern is diagnostic of η^5-C_5H_5 moieties.

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(17) A qualitative ^1H NMR investigation in C_6D_6 of the original mixture showed that the initial Cp_3U/Cp_2U ratio increased with time, indicating that ligand redistribution in this system was happening.

(18) Supplementary material.

(19) (a) H. P. Fritz, *Adv. Organomet. Chem.*, **1**, 239 (1964). (b) E. Maslowsky, Jr., "Vibrational Spectra of Organometallic Compounds", Wiley-Interscience, New York, 1977, Chapter 3. (c) V. T. Aleksanyan and B. V. Lokshin, *J. Organomet. Chem.*, **131**, 113 (1977).

Table I. ^{1}H NMR Data of $Cp_2U(NR_2)_2$ Compounds

		resonances[a,b]			
compd	Cp	α	β	γ	others
$Cp_2U(NEt_2)_2$[c,f]	13.70 (s)	−8.78 (q)	−1.54 (t)		
$Cp_2U(NPr_2)_2$[d]	16.20 (s)	−7.20 (q)	−0.30 (m)	+1.64 (t)	
$Cp_2U(NPh_2)_2$[e]	18.21 (s)				−5.54 (d, *o*), −6.52 (t, *m*), −3.22 (t, *p*)
$Cp_2U(NEt_2)(NPh_2)$[c]	13.10 (s)	−6.86 (q)	−2.68 (t)		−9.31 (d, *o*), −8.04 (t, *m*), −5.62 (t, *p*)
$Cp_2U(NMe_2)_2$[e]	11.41 (s)	−14.77 (s)			
$Cp_2U(NEt_2)(NC_4H_2Me_2)$[c]	13.50 (s)	−6.57 (q)	−1.28 (t)		−7.08 (s, Me), 12.60 (s, H)
$Cp_2U[NC_4Me_3(COOEt)]_2$[c]	−3.4 (s)				−7.76, −5.47, −1.44, (s, Me) 12.5 (t, CH_3), 23.7 (q, CH_2)

[a] Chemical shifts in ppm from Me_4Si, positive numbers indicate shift to high field. [b] Key: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, *o* = ortho, *m* = meta, *p* = para. [c] $T = 35\ °C$. [d] $T = 37\ °C$. [e] $T = 44\ °C$. [f] $Cp_3U(NEt_2)$; Cp, 11.62 (s); α, −0.84 (q); β, 1.16 (t) ppm.

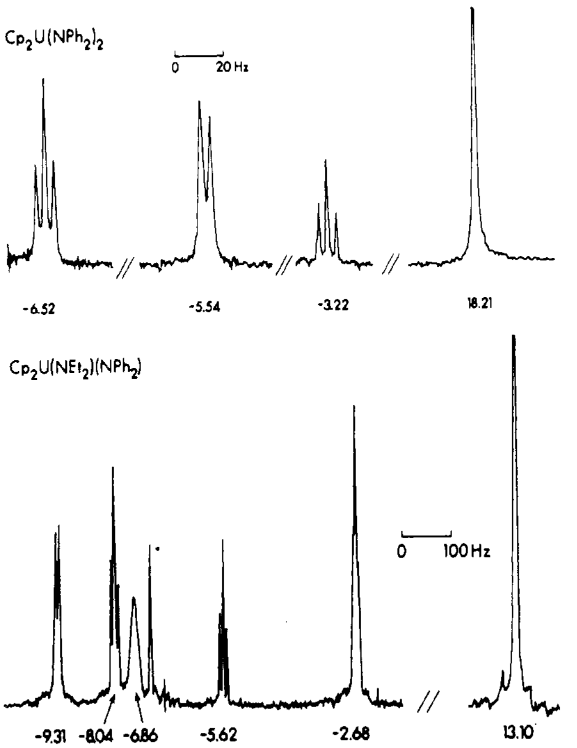

Figure 1. ^{1}H NMR spectra of $Cp_2U(NPh_2)_2$ and $Cp_2U(NEt_2)(NPh_2)$ in C_6D_6(*).

The ^{1}H NMR resonances are isotropically shifted due to the presence of the paramagnetic uranium(IV), $5f^2$, metal center. The paramagnetic chemical shifts arise from both dipolar and contact contributions.[20] The dipolar term is geometry dependent, so that in some cases, where the contact contribution to the isotropic shifts remains approximately constant, it is possible to correlate the NMR data with gross structural features. Marks et al.[21] have suggested that the constancy of the chemical shift of the Cp protons in a series of Cp_3UX compounds may be the result of similar molecular magnetic anisotropy arising from comparable structures. In the present complexes the cyclopentadienyl resonance is shifted upfield from the usual diamagnetic position, as expected for U–Cp compounds.[22] The similarity of the chemical shifts of the Cp protons for all the dicyclopentadienyl derivatives, except the carboxylate-substituted pyrrolide complex, is perhaps an indication that the angular, pseudo-tetrahedral-type structure usually found for Cp_2MX_2 (M = transition metal, X = monodentate ligand) type compounds is also possessed by the present complexes. The fact that the peak position of the Cp resonance for the compound $Cp_2U[NC_4Me_3(COOEt)]_2$ is considerably different than the other derivatives suggests that the coordination about the uranium center may include interaction with oxygen atoms of the carbonyl moieties. This assumed interaction is further supported by the large shifts observed for the methylene and methyl moieties of the carboxylate group.

The mass spectral data for $Cp_2U(NEt_2)_2$, $Cp_2U(NPh_2)_2$, and $Cp_2U(NEt_2)(NPh_2)$ are given in Table III,[18] and similar data and the major fragmentation processes in $Cp_2U[NC_4Me_3(COOEt)]_2$ are summarized in Table IV.[18] All complexes exhibit parent molecular ion peaks, and in the complexes $Cp_2U(NEt_2)_2$, $Cp_2U(NPh_2)_2$ and $Cp_2U(NEt_2)(NPh_2)$, the relative abundance of fragment peaks clearly indicates that the uranium–nitrogen bond is more easily broken than the uranium–cyclopentadienyl interaction. This pattern is different from the behavior of the inserted compounds, $Cp_2U(XYCNEt_2)_2$ or the carboxylate derivatives, $Cp_2U(XYCR)_2$ (X, Y = O or S).[23] These complexes, like $Cp_2U[NC_4Me_3(COOEt)]_2$, exhibit base peaks corresponding to cleavage of the uranium–Cp bonds. It would seem that uranium–nitrogen bonds which are unsupported (no interaction of the metal center with a functional group on the ligand) are more easily broken. The mass spectral behavior of the compound $Cp_2U[NC_4Me_3(COOEt)]_2$ is consistent with the suggestion that there is involvement of the ethyl carboxylate group with the uranium center.

The optical spectra of $Cp_2U(NEt_2)_2$ and $Cp_2U(NPr_2)_2$ in ether and benzene are listed in Table V.[18] The spectra are virtually identical in both solvents. This observation suggests that the solvent does not enter into the first coordination sphere of the uranium, as in some $U(NR_2)_4$ compounds containing relatively small amide functionalities.[15,16] It appears that the presence of two η^5-cyclopentadienyl groups in conjunction with two relatively bulky amido ligands is sufficient to saturate the coordination sphere enough that first-order solvent interactions do not occur.

Conclusions

$Cp_2U(NR_2)_2$ compounds have been obtained from the reaction of cyclopentadiene with $U(NR_2)_4$. Albeit the series is limited to a few complexes (R = Et, Pr, Ph), these molecules represent the first authentic and well-characterized Cp_2UX_2-type compounds where X is a monodentate ligand. The number of complexes can be increased slightly by amide exchange reactions on $Cp_2U(NEt_2)_2$. $Cp_2U(NEt_2)(NPh)_2$ and $Cp_2U[NC_4Me_3(COOEt)]_2$ were prepared this way. Unfortunately, both reactions, the amide substitution by cyclo-

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(20) R. D. Fischer in "NMR of Paramagnetic Molecules", G. N. LaMar, W. D. Horrocks, Jr., and R. H. Holm, Eds., Academic Press, New York, 1973, Chapter 13.

(21) T. J. Marks, A. M. Seyam, and J. R. Kolb, *J. Am. Chem. Soc.*, **95**, 5529 (1973).

(22) E. Cernia and A. Mazzei, *Inorg. Chim. Acta*, **10**, 239 (1974).

(23) A. L. Arduini, J. D. Jamerson, and J. Takats, *Inorg. Chem.*, following papers in this issue.

pentadienyl moieties and transamination, are often plagued by ligand redistribution reactions and concurrent formation of $Cp_3U(NR_2)$. $Cp_3U(NEt_2)$ also forms when $Cp_2U(NEt_2)_2$ is further reacted with cyclopentadiene. Thermal stability also appears to favor the tricyclopentadienyl derivatives since attempted sublimation of some of the products produced $Cp_3U(NR_2)$-type compounds. It is clear that steric factors are of utmost importance in this area of chemistry. The combination of two cyclopentadienyl groups and two amide moieties is sometimes sufficient to saturate the coordination sphere of uranium(IV) and stabilize the so formed Cp_2UX_2 species. However, given a chance, even those species rearrange or react to give the more favored Cp_3U containing complexes. $Cp_2U[NC_4Me_3(COOEt)]_2$ appears to be an exception. In this case, the postulated interaction between oxygen of the carboxylate functionality and uranium may account for the added stability. Indeed, as will be seen in the following papers, replacement of the amido gropus by potentially bidentate ligands results in the synthesis of relatively stable Cp_2UX_2 (X = R_2NCS_2, R_2NCOS, R_2NCO_2, RCO_2, RCOS) compounds.

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Registry No. $U(NMe_2)_4$, 53091-47-7; $U(NEt_2)_4$, 40678-59-9; $U(NPr_2)_4$, 63833-51-2; $U(NPh_2)_4$, 61900-16-1; $Cp_2U(NEt_2)_2$, 54068-37-0; $Cp_2U(NPr_2)_2$, 77507-87-0; $Cp_2U(NPh_2)_2$, 77507-88-1; $Cp_2U(NMe_2)_2$, 77507-86-9; $Cp_2U(NEt_2)(NPh_2)$, 77507-89-2; $Cp_2U[NC_4Me_3(COOEt)]_2$, 77507-90-5; $Cp_2U(NEt_2)(NC_4H_2Me_2)$, 77507-91-6; $Cp_3U(NEt_2)$, 77507-92-7; $Cp_2U(NC_4H_4)_2$, 77507-93-8; $Cp_3U(NC_4H_4)$, 77507-94-9; $Cp_3U(NMe_2)$, 77507-95-0.

Supplementary Material Available: Listings of characteristic infrared frequencies (Table II), mass spectral data (Tables III and IV), and the optical spectra (Table V) (4 pages). Ordering information is given in any current masthead page.

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Reactivity of Dicyclopentadienylbis(diethylamido)uranium(IV). Insertion Reactions

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$Cp_2U(NEt_2)_2$ reacts with CS_2, COS, and CO_2 to give insertion-type compounds of the formula $Cp_2U(XYCNEt_2)_2$ (X, Y = O or S; X = O, Y = S). Molecular weight data show that $Cp_2U(S_2CNEt_2)_2$ and $Cp_2U(OSCNEt_2)_2$ are monomeric in benzene; for $Cp_2U(O_2CNEt_2)_2$, polymeric behavior is indicated. Spectroscopic data are consistent with a bidentate coordination mode of the carbamate ligands and η^5-cyclopentadienyl moieties. The coordination geometry around the uranium can be described as pseudooctahedral with cyclopentadienyl groups occupying mutually cis positions. The variable-temperature ^1H NMR spectra of the molecules are indicative of dynamic solution behavior. It is shown that a combination of rapid metal-centered rearrangement with slow $C\overset{-}{\cdot\cdot}N$ bond rotation can adequately explain the observed spectra.

Introduction

The reactivity of the metal–nitrogen σ bond continues to occupy a central place in the chemistry of amido derivatives of the early transition metals, $M(NR_2)_n$.[1] These compounds have been shown to undergo substitution reactions with protic reagents and insertion reactions with molecules containing polar multiple bonds, thus providing unique synthetic intermediates for a wide variety of complexes of these transition elements. In contrast to this, the reactivity of actinide amides has remained largely unexplored even though initial work on their preparation was reported by Gilman as early as 1956.[2] However, as a result of renewed interest in the chemistry of actinide amides,[3] rapid progress in this field can be anticipated. Indeed the few reports already existing in the literature presage a chemistry comparable in diversity to that found with the analogous transition-metal compounds.

Insertion of CX_2 (X = O, S, Se) into the metal–nitrogen σ bonds of the tetrakis(amido)actinide(IV) complexes has been described by Bagnall and Yanir[4] as a means of obtaining thorium and uranium carbamates. We have shown that the tetrakis(amido) species, $U(NEt_2)_4$, will react with the weakly acidic hydrocarbon cyclopentadiene to yield the complex $Cp_2U(NEt_2)_2$.[5,6] This molecule, which contains labile uranium–nitrogen bonds, was expected to provide a versatile entry into the so far elusive organouranium chemistry containing the "Cp_2U" fragment.

In this first report on the reactivity on $Cp_2U(NEt_2)_2$, we detail our work on the insertion of CS_2, COS, and CO_2 into the uranium–nitrogen bonds, a reaction which produces the expected carbamates $Cp_2U(XYCNEt_2)_2$.

Experimental Section

Reagents and General Techniques. All reactions and operations were performed with the use Schlenk techniques under a static atmosphere of rigorously purified nitrogen.

Toluene, benzene, hexane, and pentane were dried by refluxing under purified nitrogen with the appropriate drying agent and were distilled prior to use. Pentane was also freeze–thaw–degassed before use. The compound $Cp_2U(NEt_2)_2$ was synthesized and purified according to published procedures.[6] Carbon disulfide (reagent grade, Anachemia) was refluxed over P_2O_5 and distilled. Dissolved oxygen was displaced by vigorously bubbling nitrogen through the liquid. Carbonyl sulfide (Matheson) was purified of H_2S contaminant by reaction with lead acetate. Carbon dioxide (glass flask assayed, research purity, Airco) was used as received.

Physical Measurements. Infrared spectra were recorded in the region 4000–250 cm^{-1} with a Perkin-Elmer 467 grating spectrometer. The complexes were studied as Nujol and Fluorolube mulls between potassium bromide plates. The samples were prepared in a glovebag filled with purified nitrogen.

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(1) D. C. Bradley and M. H. Chisholm, *Acc. Chem. Res.*, **9**, 273 (1976).

(2) R. G. Jones, G. Karmas, G. A. Martin, and H. Gilman, *J. Am. Chem. Soc.*, **78**, 4285 (1956).

(3) (a) J. G. Reynolds, A. Zalkin, D. H. Templeton, N. M. Edelstein, and L. K. Templeton, *Inorg. Chem.*, **15**, 2498 (1976). (b) J. G. Reynolds, A. Zalkin, D. H. Templeton, and N. M. Edelstein, *ibid.*, **16**, 599 (1977). (c) J. G. Reynolds, A. Zalkin, D. H. Templeton, and N. M. Edelstein, *ibid.*, **16**, 1090 (1977). (d) J. G. Reynolds and N. M. Edelstein, *ibid.*, **16**, 2822 (1977).

(4) K. W. Bagnall and E. Yanir, *J. Inorg. Nucl. Chem.*, **36**, 777 (1974).

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

(6) A. L. Arduini, N. M. Edelstein, J. D. Jamerson, J. G. Reynolds, K. Schmid, and J. Takats, *Inorg. Chem.*, preceding paper in this issue.

0020-1669/81/1320-2474$01.25/0