of this uranocene is listed in Table I along with the experimental data from the three other actinide complexes studied. Karraker has noted that, although actinocenes with differing substituents on the cyclooctatetraene ligands have different crystal structures, compounds within each series are approximately isostructural.[9] The X-ray powder patterns obtained are of poor quality, probably because of radiation damage, and many of the lines are rather weak; nevertheless, the data in Table I suggest that the Pa and Pu complexes are isostructural with $Np(TMCOT)_2$. The three complexes are therefore suggested to have the same structure as $U(TMCOT)_2$.

Visible spectra were obtained for the three TMCOT compounds studied, and the results are presented in Table II. While the spectra for the Np and Pu compounds are complex, like that of a uranocene, the spectrum from $Pa(TMCOT)_2$ contains only a single band and resembles that of a thorocene. The data for this Pa complex provide the first case in which spectra for COT complexes of all of the first five actinides can be compared. Although no clear pattern is apparent, the bathochromic shift previously observed for actinocenes with electron-donating substituents[9,14] is also found in this study (Table III). This consistency again suggests that bonding is similar in these compounds of different actinides and that these spectra are related in type, probably ring-to-metal charge-transfer transitions. In addition, the consistent observation of a bathochromic shift of about 900–1400 cm^{-1} from COT to TMCOT complexes allows the prediction of a maximum at about 365 nm in the spectrum of $Pa(COT)_2$. This compound had previously[6,7] been characterized only by its IR spectrum and X-ray powder pattern.

Experimental Section

Starting Materials. K_2TMCOT was prepared by the reaction of TMCOT with potassium and was isolated as a yellow powder by removal of the solvent. The preparation of ${}^{237}Np(BH_4)_4$ and ${}^{239}Pu(BH_4)_4$[15] has been previously published. ${}^{231}PaCl_4$ was prepared[16] at Harwell, England, and used as received. Tetrahydrofuran was purified by distilling twice from $LiAlH_4$ and was freeze–pump–thaw degassed before use. Due to the air-sensitive and radioactive nature of these compounds, all synthetic work was performed under an argon atmosphere or in vacuo by using an inert-atmosphere glovebox or a vacuum line equipped with containment facilities.

Visible spectra were run on a Cary 17 spectrophotometer using THF solutions prepared and loaded into a stoppered glass cell in an argon-filled glovebox. X-ray powder patterns were obtained from samples loaded into quartz capillaries, sealed with grease in the glovebox, and flame sealed immediately after removal from the box. Cu radiation, with a Ni filter to remove the $K\beta$, was used, and exposure times varied from 8 to 12 h.

Reaction of $PaCl_4$ with K_2COT. In an argon-filled glovebox, 10.5 mg (0.0576 mmol) of K_2COT was added to a solution of 13.0 mg (0.0349 mmol) of $PaCl_4$ in 10 mL of THF. Removal of the solvent in vacuo gave a green residue which was heated to ca. 400 °C under high vacuum (10^{-6} torr). The brown sublimate was found to be nonradioactive.

Bis(η^8-tetramethylcyclooctatetraene)protactinium(IV), $Pa(TMCOT)_2$. A 25-mL reaction tube was loaded with 7.6 mg (0.032 mmol) of K_2TMCOT and 5.8 mg (0.016 mmol) of $PaCl_4$. The tube was sealed with a stopcock and evacuated to 10^{-6} torr. THF (16 mL) was transferred in vacuo onto the solids, and the mixture was allowed to warm slowly. After the solution thawed, the $PaCl_4$ dissolved, and the solution darkened. Removal of the solvent in vacuo gave a dark powder. A powder pattern of this material indicated the presence of KCl and the sandwich complex.

The powder was loaded into the left arm of an H-tube extractor, and the extractor was evacuated. THF (ca. 5 mL) was transferred onto the solids. After warming to room temperature, the solution was filtered into the right arm of the extractor. About 1–2 mL of the THF was distilled back into the left side by cooling the left arm in liquid nitrogen. The solution was again filtered into the right side and this process was repeated twice. Little colored material was extracted on the final cycle, and the solvent was removed in vacuo. The small amount of product was dissolved in the THF, and a visible spectrum was obtained.

Bis(η^5-tetramethylcyclooctatetraene)neptunium(IV), $Np(TMCOT)_2$. A reaction tube was loaded with 16.5 mg (0.069 mmol) of K_2TMCOT and evacuated to 10^{-6} torr. THF (5 mL) was added by vacuum transfer, and 9.4 mg (0.032 mmol)[17] of $Np(BH_4)_4$ was sublimed into the frozen mixture. As the solution thawed, the green color of $Np(BH_4)_4$ faded, and the solution turned a dark brown. The solvent was removed by vacuum transfer.

The dark powder was transferred to the H-tube and extracted with benzene in the manner described previously. A visible spectrum and a powder pattern were obtained from the product.

Bis(η^5-tetramethylcyclooctatetraene)plutonium(IV), $Pu(TMCOT)_2$. By use of the procedure used in the preparation of $Np(TMCOT)_2$, 15 mg (0.063 mmol) of K_2TMCOT and ca. 9 mg (0.03 mmol)[17] of $Pu(BH_4)_4$ were allowed to react in ca. 8 mL of THF. Extraction with THF using the H-tube gave 2.5 mg (0.004 mmol, 15%) of green product and an insoluble white powder that was identified as KBH_4 by its X-ray powder pattern. A powder pattern and a visible spectrum were obtained from the green product.

Acknowledgment. This work was supported in part by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-ENG-48. H.P.G.B. was a NATO Postdoctroal Fellow, 1977–1978. We also thank Dr. Norman Edelstein for valuable discussions and advice.

Registry No. $Pa(TMCOT)_2$, 73574-67-1; $Np(TMCOT)_2$, 12715-86-5; $Pu(TMCOT)_2$, 73587-37-8; K_2TMCOT, 56726-06-8; $PaCl_4$, 13867-41-9; $Np(BH_4)_4$, 66615-98-3; $Pu(BH_4)_4$, 66615-99-4.

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[17] Based on the vapor pressure of $Np(BH_4)_4$.

Contribution No. 2709 from the Central Research and
Development Department, E. I. du Pont de Nemours and
Company, Wilmington, Delaware 19898,
and the Department of Chemistry, University of Toronto,
Toronto, Ontario, Canada M5S 1A1

Equilibrium Thermodynamic and Activation Parameters for Isomer Exchange in $[MoI(CO)_2((CH_3)_2PC_2H_4P(C_2H_5)_2)_2]I$

P. J. Domaille* and S. S. Wreford

Received October 4, 1979

Recently, we reported that compounds of the type $MX(CO)_2(\text{unsymmetric, bidentate phosphine})_2{}^{n+}$ [M = Ta, n = 0; M = Mo, n = 1; X = Cl, Br, I; unsymmetric, bidentate phosphine = $Me_2PC_2H_4PEt_2$ (dmdepe) and others] exist as cis and trans isomers with respect to the unsymmetric ends of the chelate.[1] The isomer distributions were as expected for the Ta(I) derivatives, i.e., the less crowded trans isomer (eq 1) being favored (1.8/1 for **2** at 30 °C). However, although the Mo(II) ion should be smaller and have shorter M–P bonds than Ta(I), the isomer distribution in **1** appeared to be more nearly equal (1.2/1 at −30 °C).

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* To whom correspondence should be addressed at E. I. du Pont de Nemours and Co.

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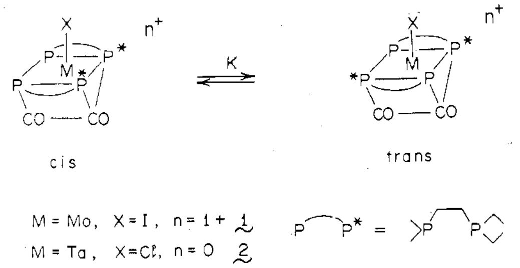
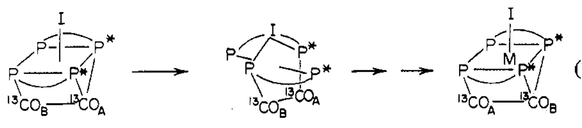
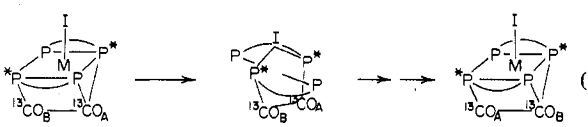


(1)

We noted that isomer exchange could be detected by both ^1H and ^{31}P NMR and probably occurred by a nondissociative mechanism, i.e., one in which both ends of the chelate remain attached throughout the exchange process. This suggestion was based on steric effects, on the barriers to exchange, and on the magnitude of $\Delta S^{\ddagger}$ for methyl-group exchange in $[MoI(CO)_2(dmpe)_2]I$. Further, on the basis of least motion calculations, we concluded that a likely path for ligand exchange in the monocapped trigonal-prismatic geometry corresponds to rotation of the unique edge about the M-capping ligand vector, a process involving passage through a pentagonal-bipyramidal transition state or intermediate (Figure 5, path I, of ref 1). For the complexes **1** and **2**, this process would be undetectable by ^{31}P or ^1H NMR. It would, however, be detectable by ^{13}C NMR, as it involves exchange of CO sites, which are chemically inequivalent in the cis isomer (eq 2 and 3).



(2)



(3)

To investigate the unexpected isomer distribution in **1** and to try to detect carbonyl-edge rotation, we have prepared the ^{13}C-labeled complex $[MoI(^{13}CO)_2(dmdepe)_2]I$ and have analyzed its dynamics by line-shape analysis of the ^{31}P and ^{13}C NMR spectra. Moreover, these measurements allow a more accurate determination of $\Delta S^{\ddagger}$ for isomer exchange.

Experimental Section

^{31}P and ^{13}C NMR spectra were obtained on a Bruker HFX-90 spectrometer interfaced with a Digilab FTS/NMR-3 data system and pulser. Low-temperature spectra were recorded by using CD_2Cl_2 as a solvent/lock while higher temperature runs used either CD_3CN or Me_2SO-d_6. For minimization of the possibility of systematic temperature differences between runs, the same probe–thermocouple–temperature controller arrangement was used for all variable-temperature ^{31}P and ^{13}C spectra. Temperature calibrations, performed prior to each run, were nearly identical for ^{31}P and ^{13}C inserts. A conservative estimate of the temperature reproducibility between different samples is ±2 °C.

$[MoI(^{13}CO)_2(dmdepe)_2]I$. To 20 mL of THF were added 1.77 g (4.24 mmol) of $MoCl_3 \cdot 3THF$,[2] 1.50 g (8.46 mmol) of dmdepe,[1] and 15 mL of 0.75% Na/Hg. The resulting suspension was stirred under an atmosphere of N_2 overnight. The dark solution was decanted, centrifuged, and evaporated to dryness. The residue was extracted with 50 mL of hexane; the extract was filtered through a layer of Celite and evaporated to dryness. The resulting 2.0 g (3.94 mmol) of oily solid had a mass spectrum consistent with that expected for $Mo(N_2)_2(dmdepe)_2$. This material was dissolved in 50 mL of heptane, and 20 mL of the yellow solution was placed in a 100-mL vessel, together with 3.0 mmol of 90% enriched ^{13}CO (Stohler). After the solution was heated at 90 °C for 24 h with vigorous stirring, it was decanted from the vessel and evaporated. Chromatography of the residue (Florisil, benzene eluant) afforded 216.4 mg (0.43 mmol) of *cis*-$Mo(^{13}CO)_2(dmdepe)_2$, identified by IR and mass spectral data. The carbonyl complex was dissolved in 20 mL of CH_2Cl_2 and treated with 0.38 mmol of I_2 in a manner similar to that described for the preparation of $[MoI(CO)_2(dmdepe)_2]I$.[1] An analogous workup and crystallization from CH_2Cl_2/methanol gave 184 mg of **1**, identified by IR, ^{31}P NMR, and ^{13}C NMR spectra and by comparison with the ^{12}C analogue.[1]

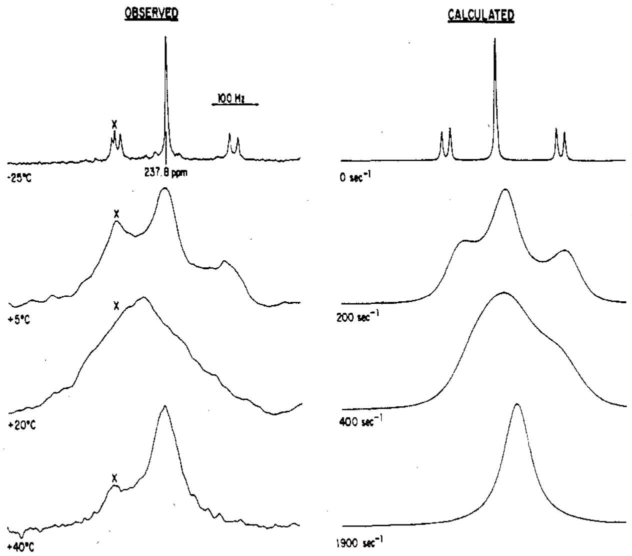


Figure 1. Observed and calculated $^{13}C\{^{31}P,^1H\}$ spectra of $[MoI(^{13}CO)_2(dmdepe)_2]I$ as a function of temperature. Simulated spectra are based on the three-site model of eq 5 with $k_1 = 0\ s^{-1}$. The symbol × represents a slight impurity.

Results and Discussion

Equilibrium Populations. Conventional $^{13}C\{^1H\}$ spectra of $[MoI(^{13}CO)_2(dmdepe)_2]I$ from −80 to −30 °C show a strong apparent quintet flanked by weaker and much more complex spin patterns. Broad-band ^{31}P decoupling simplifies the spectrum to a strong single line located almost midway between the A and B parts of an AB pattern (Figure 1). Undoubtedly, the strong line is the A_2' spin pattern of *trans*-**1** ($\delta_{A'}$ 237.8, −30 °C), and the AB spectrum is derived from the chemically inequivalent carbonyls of *cis*-**1** (δ_A 242.5, δ_B 231.4, $|J_{AB}| = 18$ Hz, −30 °C). As the temperature is increased from −80 to −30 °C, the $^{13}C\{^{31}P,^1H\}$ spectrum shows a gradual variation in the relative population of both isomers; the ratio *trans*-**1**/*cis*-**1** varies from 1.7/1 at −80 °C to 1.2/1 at −30 °C. A fit of the variable-temperature, slow-exchange data obtained in 5 °C increments gives[3] eq 4.

$$[\text{cis}]/[\text{trans}] = (3.3 \pm 2.1)\exp[(-660 \pm 50\ \text{cal mol}^{-1})/RT] \quad (4)$$

The derived value of $\Delta S^\circ = 2.2 \pm 1.4$ eu is not significant, but $\Delta H^\circ = -0.66 \pm 0.05$ kcal mol^{-1} shows the trans isomer to be more stable, presumably because of the relief of the steric interaction between the bulky ethyl groups. The absence of a significant entropy contribution to K and the larger trans/cis ratio observed in the case of Ta(I) imply an even more favorable trans energy relative to that of the cis isomer in these larger compounds. We interpret this to mean that ethyl–methyl steric interactions are also appreciable, and a larger metal center simply allows more freedom from steric crowding.

Dynamics. Independent analysis of the slow-exchange $^{31}P\{^1H\}$ NMR spectra yielded coupling constants almost

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(3) Error limits refer to 95% confidence limits.

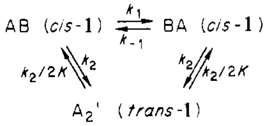
Table I. Activation Parameters[a] for $[MoI(CO)_2(dmdepe)_2]I$ from NMR Exchange Studies

	$^{13}C\{^{31}P, ^1H\}$[b]	$^{31}P\{^1H\}$[b]	$^1H\{^{31}P\}$[c]
$\Delta G^\ddagger$, kcal/mol (298 K)	13.50 (10)	13.60 (6)	13.5 (4)
$\Delta H^\ddagger$, kcal/mol	11.0 (20)	12.1 (13)	
$\Delta S^\ddagger$, cal/(mol K)	−8.4 (69)	−5.1 (46)	

[a] Uncertainties are 95% confidence limits in the last significant figure. Parameters are relative to the *cis*-**1** isomer since the rate constants used (k_2) refer to the forward reaction *cis*-**1** → *trans*-**1**. [b] This work. [c] Reference 1; uncertainty is the standard error from least-squares fit.

identical with those of the previous work.[1,4] The exchange-broadened spectra were fit to a two-site nonmutual-exchange model by using a complete density matrix approach.[5] Relative populations of the two isomers were fixed to values extrapolated from the slow-exchange spectra; thus, the rate constants were the only variables in the fits. Derived rate constants were fit to the Eyring equation[6] to obtain the activation parameters tabulated in Table I. This more rigorous treatment gives more accurate activation parameters than does the simple use of the Gutowsky–Holm[7] equation in ref 1.

The $^{13}C\{^{31}P,^1H\}$ NMR signals of **1** broaden above −30 °C and coalesce to a single line at about 20 °C. The exchange-broadened spectra were fit as a nonmutual-exchange problem by using the density matrix treatment described above.[5] The three-configuration model in eq 5 was used, where K is the equilibrium constant of eq 1.



Use of this model maintains an internal consistency with the rate constants used in the ^{31}P-exchange problem. Note that the model allows both carbonyl-edge rotation, k_1, and cis–trans exchange, k_2, to occur independently. The rates for cis–trans exchange were initially estimated from the rates obtained from the ^{31}P data, and the rate of carbonyl-edge rotation was varied to accommodate the spectra. Minimum deviations occurred when $k_1 \ll k_2$; larger values of k_1 produced calculated spectra which were markedly at variance with the experimental data. Subsequently, k_1 was fixed at zero, and the k_2 values were refined. A representative sample of experimental spectra and simulations is shown in Figure 1. A minor impurity in the downfield portion of the spectrum is evident but does not interfere significantly with the visual matching. Uncertainties in the rate constants were estimated from the range of values yielding acceptable comparisons.

These data establish that carbonyl-edge rotation of the type in eq 2 is slower than the process responsible for cis–trans exchange, if it occurs at all. That is, because carbonyl-edge rotation does not occur at an appreciable rate, we conclude that *any* mechanism based on the geometric transformation of path I of ref 1 is unlikely. It is important to note that the least motion transformation of path I simply depicts the equivalence of a unique edge rotation in a capped trigonal prism and an interchange of adjacent equatorial sites in a pentagonal bipyramid. The values for the activation parameters for cis–trans exchange from the independent ^{13}C and ^{31}P data are in good agreement. In both cases the magnitude of $\Delta S^\ddagger$ is consistent with a nondissociative, polytopal rearrangement.

Because of the inequality of competing rate constants, we conclude that multistep mechanisms, invoking path 1 of Figure 5 in ref 1, as suggested in the second step of Figure 6 of ref 1, are unlikely to be responsible for cis–trans exchange.[1,8] The simplest nondissociative mechanism capable of accounting for cis–trans exchange is a ligand twist of the bidentate phosphine.

Acknowledgment. The skilled technical assistance of G. Watunya and F. N. Schoch is gratefully appreciated. We thank Dr. Paul Meakin for discussions and the loan of the computer program PZDMX.

Registry No. *trans*-**1**, 65015-74-9; *cis*-**1**, 65058-47-1; $Mo(N_2)_2(dmdepe)_2$, 73544-69-1.

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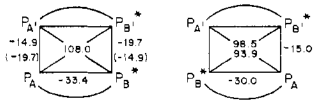
(4) Revised constants from ^{31}P data are



(5) The computer program PZDMX was kindly supplied by Dr. Paul Meakin. The general methods have been documented in several publications. See, for example: Meakin, P.; Muetterties, E. L.; Tebbe, F. N.; Jesson, J. P. *J. Am. Chem. Soc.* **1971**, *17*, 729 and references therein.

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Contribution from the Department of Chemistry,
The University of Chicago, Chicago, Illinois 60637

Synthesis of a Bis(pentamethylcyclopentadienyl) Derivative of Neodymium

Andrea L. Wayda and W. J. Evans*

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Bis(cyclopentadienyl)lanthanide chlorides $[(C_5H_4R)_2LnCl]_2$ and $(C_5H_4R)_2LnCl{\cdot}C_4H_8O$[1,2] (R = H, CH_3) are valuable synthetic precursors in organolanthanide chemistry.[3] Unfortunately, these complexes are not available for the early members of the lanthanide series, La–Nd, a result which excludes these metals from the derivative chemistry associated with $(C_5H_4R)_2LnCl$ precursors. If, as is often claimed,[1,4] syntheses of bis(cyclopentadienyl) chloride complexes of the larger lanthanides fail for steric reasons, then the use of a bulky substituted cyclopentadienyl ligand such as $C_5(CH_3)_5$[5] should allow the isolation of these important intermediates and their subsequent use in organolanthanide synthesis.

We have investigated this approach to bis(cyclopentadienyl)lanthanide chlorides and have succeeded in isolating and characterizing a crystalline bis(pentamethylcyclopentadienyl) complex of neodymium. Surprisingly, the isolated product is the lithium salt $[(C_5Me_5)_2NdCl_2][Li(C_4H_8O)_2]$ instead of the expected neutral species $[(C_5Me_5)_2NdCl]_2$.

Experimental Section

C_5Me_5H was prepared following the procedure of Bercaw and Threlkel.[6] LiC_5Me_5 was prepared by the reaction of C_5Me_5H and

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