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Preparation and Fluxional Behavior of (1,2-Diazine)decacarbonyl-*triangulo*-triosmium

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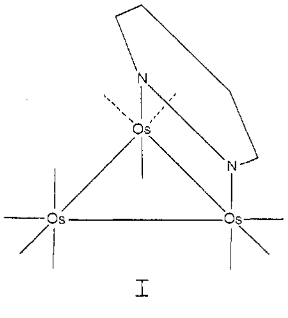
The reaction of $Os_3(CO)_{12}$ with pyridazine in the presence of trimethylamine oxide dihydrate proceeds smoothly and in high yield to form $(C_4H_4N_2)Os_3(CO)_{10}$. Infrared spectroscopy and carbon-13 NMR show the presence of only terminal carbonyl ligands in contrast to the analogous ruthenium compound which has three bridging carbonyls. Two complex exchange processes are observed in the variable-temperature carbon-13 NMR spectra. The low-energy process, with a coalescence temperature of about -30 °C, involves exchange of eight carbonyl ligands; we believe these to be the six equatorial carbonyl groups plus the two axial ones on the unique osmium atom. In the high-energy process ($T_c \approx 40$ °C) all ten carbonyl groups are scrambled to produce a one-line spectrum.

Introduction

The study of the stereodynamic behavior of $M_3(CO)_{12}$ molecules (M = Fe, Ru, Os) and their derivatives is an area of active interest. Although carbon-13 NMR has proven to be a powerful tool in studying fluxional metal carbonyls, it has provided no mechanistic information for the parent trinuclear carbonyls, $M_3(CO)_{12}$. $Fe_3(CO)_{12}$[1] and $Ru_3(CO)_{12}$[2] show only a single line in the carbon-13 NMR at the lowest temperatures studied (-150 and -100 °C, respectively). For $Os_3(CO)_{12}$[3] the activation energy is sufficiently high to allow the observation of axial–equatorial exchange on the NMR time scale. However, the high symmetry of $Os_3(CO)_{12}$ precludes the possibility of extracting any mechanistic information from the observed line shapes.

Through the study of suitably designed derivatives of $M_3(CO)_{12}$ molecules it is possible to obtain mechanistic information concerning carbonyl exchange. There are at least four processes that have been observed in $M_3(CO)_{12}$ derivatives and may therefore occur in the parent carbonyls as well. (1) There is scrambling of the equatorial carbonyl groups in $(C_4H_4N_2)Ru_3(CO)_{10}$,[4] $(C_6H_8)Os_3(CO)_{10}$,[5a] and $(C_7H_8)Os_3(CO)_{10}$.[5b] These processes involve the concerted opening and closing of three carbonyl bridges in the plane of the metal atoms. (2) There is scrambling of the six coplanar carbonyls on adjacent osmium atoms in $Os_3(CO)_{10}(PEt_3)_2$[6] and $Os_3(CO)_{11}PEt_3$.[6] The most likely mechanism here involves the concerted movement of two axial terminal carbonyls into bridging positions with subsequent bridge opening and a net exchange of one carbonyl between the osmium atoms.[6] (3) Localized axial–equatorial exchange has been observed on the unique ruthenium atom in $Ru_3(CO)_{10}(NO)_2$.[3] (4) There is scrambling of carbonyl groups in $[HFe_3(CO)_{11}]^-$[3] which proceeds by opening and closing of carbonyl bridges in a pairwise fashion as proposed for carbonyl scrambling in $Fe_3(CO)_{12}$.[1,7] Processes (3) and (4) were inferred only from the observation of a single carbon-13 NMR line as the slow-exchange limit was not reached in either case.[3] In an attempt to delineate further the exchange processes which occur in trinuclear metal carbonyls we have prepared and studied the 1,2-diazine derivative of $Os_3(CO)_{12}$, namely, $(C_4H_4N_2)Os_3(CO)_{10}$, I. We have found that this compound can be easily prepared in one step by using the oxidative decarbonylation method described by Shvo and Hazum[8] for preparing (diene)$Fe(CO)_3$ complexes and later by Shapley[9] for preparing $Rh_3(CO)_3(C_5H_5)_3$ and derivatives of $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$. Several comparisons will be made with the recently described ruthenium complex $(C_4H_4N_2)Ru_3(CO)_{10}$,[4] II, which differs in structure.



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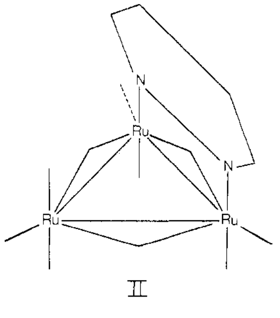

II

Experimental Section

Preparation of $(C_4H_4N_2)Os(CO)_{10}$. A slurry of $Os_3(CO)_{12}$ (100 mg, 0.11 mmol) and $(CH_3)_3NO \cdot 2H_2O$ (24.4 mg, 0.22 mmol) was prepared in 40 mL of THF under argon. To this mixture pyridazine (0.025 mL, 0.36 mmol) was added. After 4 h the solution was red-brown and the reaction was terminated. The solvent was then removed and the residue dried in vacuo overnight. The residue was dissolved in THF and filtered over Celite. Removal of solvent yielded approximately 90 mg of $(C_4H_4N_2)Os_3(CO)_{10}$. The infrared spectrum in CH_2Cl_2 shows carbonyl stretches at 2082, 2055, 2030, 2020 (sh), 2007, and 1978 cm^{-1}. A sample of $(C_4H_4N_2)Os_3(CO)_{10}$ was enriched to ca. 85% in ^{13}CO by stirring a THF solution of $(C_4H_4N_2)Os_3(CO)_{10}$ (80 mg) under 160 mL ^{13}CO (94%) in the presence of 5 mg of Pd/C for 48 h.

Carbon-13 NMR Spectra. These measurements were made on a Jeol-PS-100/Nicolet 1080 Fourier transform spectrometer operating at 25.0355 MHz and a spectral width of 5000 Hz. A 30° tilt angle and a repetition rate of 1.2 s were employed to collect 2048 scans per spectrum. Temperatures were measured by inserting a copper–constantan thermocouple into an NMR tube and reading the temperature on a Leeds–Northup 913 digital thermometer. For all spectra 95% tetrahydrofuran and 5% acetone-d_6 were used as the solvent.

Chemical shifts were measured from the downfield peak of THF and converted to the TMS scale using $\delta_{TMS} = \delta + 68.0$ ppm. Chemical shifts of the peaks in Figure 1 in the carbonyl region are as follows: A, 186.3 ppm; B, 184.6 ppm; C, 180.1 ppm; D, 178.7 ppm; E, 191.1 ppm; F, 185.9 ppm; $J_{^{13}C-^{13}C}(\text{trans}) = 33$ Hz.

Results and Discussion

Both the infrared and ^{13}C NMR spectra show that $(C_4H_4N_2)Os_3(CO)_{10}$ has a structure different from that of its ruthenium analogue, since the osmium compound has no bridging CO groups. The structure shown schematically as I is the only reasonable possibility. Presumably the longer metal-to-metal distance militates against the stability of CO bridges in the osmium compound.

Assignment of the NMR Spectra. The carbon-13 NMR spectra are shown in Figure 1 from -89 to +54 °C. The spectrum at -89 °C is in the slow-exchange limit; there are six carbonyl resonances in a ratio of 1:2:1:2:2:2, in accord with structure I. The two resonances of intensity 1 must be assigned to sites E and F; as a result of the high level of ^{13}C enrichment they appear predominantly as an AB multiplet, in accord with the expectation of observable coupling between a trans pair of ^{13}CO groups. Resonance A, which does not begin to broaden until 27 °C, is assigned to the CO groups trans to the pyridazine ring. The remaining resonances, B, C, and D,

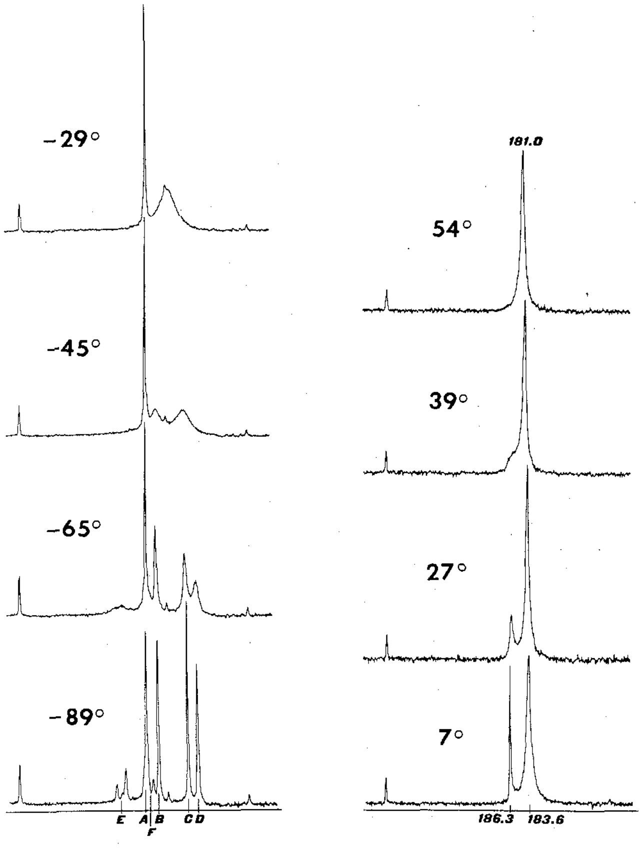

Figure 1. Carbon-13 NMR spectra in the carbonyl region from −89 to +54 °C. The small downfield peak is due to acetone. Chemical shifts for A, B, C, D, E, and F are given in the Experimental Section.

are due to the six equatorial carbonyl groups; the assignment of these resonances can be made from their relative rates of broadening as discussed below.

The lowest energy exchange process involves the scrambling of eight carbonyl groups whose resonances are labeled B, C, D, E, and F in Figure 1. These signals broaden and coalesce into a resonance at 183.6 ppm of relative intensity 8. We believe that these changes are best described as the result of two separate but simultaneous exchange processes, namely, in-plane cycling of the six equatorial carbonyls via a triply bridged intermediate and localized, axial–equatorial exchange on the unique osmium atom.

Thus, the equatorial carbonyl groups on the unique osmium atom will be exchanging not only with the other equatorial carbonyls but also with the axial carbonyl groups on that osmium atom, those giving rise to the multiplet labeled E, F. For this reason resonance D, which obviously broadens more rapidly than B or C, is assigned to the equatorial carbonyls on the unique osmium atom. Resonance C is seen to broaden more rapidly than B. In the process of in-plane cycling of the six equatorial groups, each of the two which are trans to each other across the Os–Os bond connecting the substituted metal atoms change their sites at every step, while only one of those which are cis changes in each step. Thus, the line for the trans ones should broaden more rapidly than that for the cis ones. Resonance C is therefore assigned to the two carbonyls "trans" to each other. Figure 2 shows the complete assignment of carbonyl ligands which follows from the above discussion. No conclusive assignment of E and F individually is possible.

Mechanism for Axial–Equatorial Exchange. In the molecules I and II there are three different types of axial carbonyl ligands. Each of these axial carbonyl groups in I may be exchanged with the equatorial carbonyl groups by a simple rotation of three mutually cis carbonyl ligands attached to one metal atom, two equatorial and one axial, as established for many $M(CO)_3$ fragments.[10-12] This mechanism is shown schematically in Figure 3. Let us consider its applicability in the cases of I and II.

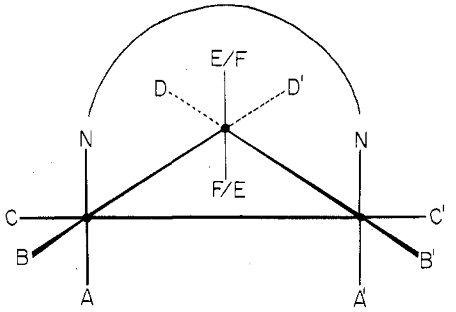

Figure 2. Schematic representation showing assignment of the carbonyl ligands in $(C_4H_4N_2)Os_3(CO)_{10}$.

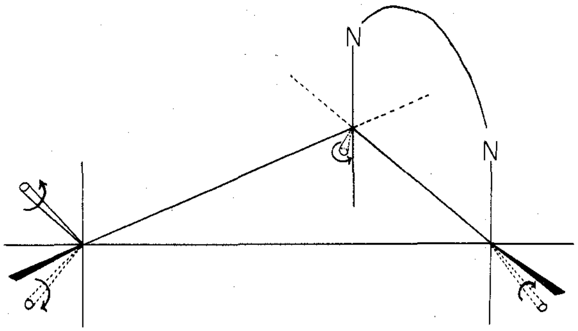

Figure 3. Proposed mechanism for axial–equatorial exchange in $(C_4N_2)M_3(CO)_{10}$ molecules (M = Ru, Os).

In the mechanism under discussion the two axial carbonyl groups on the unique metal atom do not scramble simultaneously as would be required by a concerted process, previously suggested for $Ru_3(CO)_{10}(NO)_2$,[3] involving all four carbonyls. Indeed it is possible that they may scramble at quite different rates. In I the relative rates of scrambling of E and F are not entirely clear since resonance F is partially obscured by resonance A. However, in II the analogous carbonyl groups were observed to scramble at distinctly different rates, which is consistent with the proposed mechanism.

Molecules I and II also differ in the relative rates of axial–equatorial exchange and the cycling of equatorial CO groups. For I these two processes occur essentially simultaneously with activation energies of approximately 10 kcal mol^{-1}. For II axial–equatorial exchange requires significantly higher activation energy than bridge–terminal exchange among the equatorial CO's (cycling of equatorial CO's) which occurs with an activation energy of only about 6 kcal mol^{-1}.[4] This is entirely consistent with the mechanism proposed in Figure 3 for axial–equatorial exchange since this mechanism *requires* that molecule II be transformed to an intermediate configuration without bridges (i.e., the ground-state structure of I) *before* axial–equatorial exchange can occur. The activation energy (ca. 6 kcal mol^{-1}) for in-plane cycling of CO groups in II suggests that the energy difference between the bridged and unbridged structures is ≤ 6 kcal mol^{-1}. The inversion of their relative stabilities on going from the ruthenium to the osmium compound is not surprising; since the energy favoring the bridged structure in the ruthenium case is not great, a rather small change in the relative energies of the two arrangements, upon going to the osmium case, serves to change the actual order of stability so that the unbridged structure becomes the preferred one.

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Registry No. $(C_4H_4N_2)Os_3(CO)_{10}$, 63833-62-5; $Os_3(CO)_{12}$, 15696-40-9; ^{13}C, 14762-74-4.

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Contribution from the Materials and Molecular Research Division,
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Syntheses and Optical and Magnetic Properties of Tetrakis(di-*n*-propylamido)uranium(IV), Tetrakis(di-*n*-butylamido)uranium(IV), Tetrakis(di-*n*-propylamido)thorium(IV), and Tetrakis(di-*n*-butylamido)thorium(IV), Volatile Liquid Amides

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The thorium and uranium alkylamides $M[N(CH_2CH_2CH_3)_2]_4$ and $M[N(CH_2CH_2CH_2CH_3)_2]_4$ (M = Th and U) have been prepared and isolated. These extremely air-sensitive compounds are liquids at room temperature and distillable under high vacuum at temperatures less than 100 °C. The proton magnetic resonance spectra, the optical spectra, and the temperature-dependent magnetic susceptibilities (T = 4.2–100 K) of the two uranium compounds are reported. The spectroscopic and magnetic properties of the uranium compounds are very similar to those of $U(N(C_2H_5)_2)_4$.

Introduction

Transition metal amides have been utilized as reactive intermediates in the synthesis of transition metal alkoxides, thiols, and organometallic derivatives.[1] Recently, we have reported many new uranium amides, which are not only useful as extremely reactive intermediates[2,3] but exhibit novel physical properties.[4-7] In the solid state, these new uranium compounds have exhibited monomeric,[6] dimeric,[4] trimeric,[5] and tetrametric[7] molecular units, with the U atoms being bridged by N atoms. The coordination about the U atom is four, five, or six in the crystals, while in solution the coordination about the U atom depends on the complexing ability of the solvent. In order to extend this work, we now report the preparation and isolation of the actinide amides $U[N(CH_2CH_2CH_3)_2]_4$ and $U[N(CH_2CH_2CH_2CH_3)_2]_4$ and their thorium analogues. These compounds are liquids at room temperature, and their physical and solution properties are markedly similar to those of $U(NEt_2)_4$[4,8] and $Th(NEt_2)_4$,[9] respectively.

Experimental Section

Solvents. All solvents were dried and deoxygenated by refluxing with sodium and benzophenone under purified argon.

Reagents and Synthesis. All reactions and manipulations were done either under vacuum or in a purified argon atmosphere. The amines were purchased from the Aldrich Chemical Co. *N*-Butyllithium was purchased from Alfa-Ventron Corp. and used as delivered.

$LiNR_2$. These compounds were prepared by the slow addition of the amine mixed with pentane (dried with KOH, then Drierite) to *n*-butyllithium in hexane at ice bath temperatures. The resulting precipitate was filtered and vacuum dried.

UCl_4 and $ThCl_4$. These compounds were purchased from ROC/RIC and used as delivered.

$U(N(CH_2CH_2CH_3)_2)_4$. UCl_4 (10 g, 0.0264 mol) and 11.2 g (0.105 mol) of $LiN(CH_2CH_2CH_3)_2$ were placed in a 250-mL Schlenk flask. Approximately 100 mL of diethyl ether was transferred into the flask under vacuum at liquid N_2 temperature. The heterogeneous mixture was warmed to room temperature and continuously stirred during the reaction. The reaction times varied from 24 h to 7 days. The formation of a characteristic green solution and a LiCl precipitate indicated the completion of the reaction. The solution was then filtered and the filtrate reduced to a high-viscosity liquid by vacuum evaporation. This residue was placed in a distillation apparatus and distilled between 40 and 50 °C at 10^{-4} mmHg, yielding a green liquid product. The yields for this compound and the others reported in this paper were about 30–40%. Anal.[10] Calcd for $U(N(CH_2CH_2CH_3)_2)_4$: U, 37.3; C, 45.1; N, 8.77; H, 8.77. Found: U, 37.58; C, 44.69; N, 8.63; H, 8.54.

$U(N(CH_2CH_2CH_2CH_3)_2)_4$. This compound was synthesized on the same scale as above but with the following minor changes. Reaction time was extended to 8 weeks. The characteristic green solution was not observed for at least 4 weeks. The sublimation temperature range was 90–100 °C. Temperatures above 110 °C caused noticeable decomposition, distilling over some volatile decomposition products. Anal. Calcd for $U(N(CH_2CH_2CH_2CH_3)_2)_4$: U, 31.73; C, 51.20; N, 7.47; H, 9.60. Found: U, 31.85; C, 50.95; N, 7.23; H, 9.51.

$Th(N(CH_2CH_2CH_3)_2)_4$. This compound was synthesized by the same method as above but with the following changes. Reaction time was at least 7 days. The reaction was complete when a slight yellow tinge to the diethyl ether solution appeared since the $ThCl_4$ and LiCl suspensions are virtually indistinguishable under these conditions. The sublimation temperature range was 60–70 °C at 10^{-4} mmHg, yielding a clear light yellow liquid. This compound appeared to be photosensitive for the product slowly darkened after distillation. Anal. Calcd for $Th(N(CH_2CH_2CH_3)_2)_4$: Th, 36.70; C, 45.57; N, 8.86; H, 8.86. Found: Th, 37.03; C, 45.16; N, 8.86; H, 8.86.

$Th(N(CH_2CH_2CH_2CH_3)_2)_4$. This compound was synthesized by the same method as above except with the following changes. Reaction time was 6 weeks. Sublimation temperature was 90–100 °C at 10^{-4} mmHg, and temperatures above 110 °C caused noticeable decomposition. The distillation produced a clear light yellow liquid, also sensitive to heat and light. Anal. Calcd for $Th(N(CH_2CH_2CH_2CH_3)_2)_4$: Th, 31.18; C, 51.60; N, 7.53; H, 9.68. Found: Th, 30.86; C, 51.32; N, 7.38; H, 9.51.

Physical Measurements. Proton magnetic measurements were obtained on a Varian T-60 spectrometer, a Varian NV-14 spec-