

Table I. Elemental Analysis of hfaPz^a and hfa-3-MePz^b Compounds of Actinide (IV) Ions

Compd	Color	% metal		% carbon		% hydrogen		% nitrogen		Mol wt ^c
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
Th(hfaPz) ₄	White	19.93	20.4	24.74	24.82	1.03	0.94	9.62	10.43	2000
U(hfaPz) ₄	Purple	20.27	20.4	24.61	24.77	1.03	1.02	9.57	9.83	2260
Np(hfaPz) ₄	Green	20.34	19.6							
Pu(hfaPz) ₄	Light red	20.41	19.4							
Th(hfa-3-MePz) ₄	White	19.01		27.42	26.99	1.64	1.34	9.22	9.58	1165
U(hfa-3-MePz) ₄	Blue-green	19.41	18.8	27.40	27.62	1.63	1.66	9.14	8.99	1260
Np(hfa-3-MePz) ₄	Green	19.34	20.7							
Pu(hfa-3-MePz) ₄	Green	19.48	18.3							

^a hfaPz is N₂C₃H₂OC(CF₃)₂. ^b hfa-3-MePz is CH₃N₂C₃HOC(CF₃)₂. ^c Benzene solution.

Table II. Magnetic Susceptibilities of Tetrakis(hexafluoroacetylpyrazole)actinide(IV) and Tetrakis(hexafluoroacetyl-3-methylpyrazole)actinide(IV) Compounds

Compd	Temp, range, °K	Θ, ^a °K	C, ^a emu-°K/mol	μ _{eff} , BM	χ, emu/mol
U(hfaPz) ₄	2.9-46		TIP ^b		(1.19 ± 0.05) × 10 ⁻²
Np(hfaPz) ₄	2.5-7.5	0.91	0.54	2.04	
	10-45	6.0	1.0	2.8	
Pu(hfaPz) ₄	2.5-20		TIP		(8.1 ± 0.8) × 10 ⁻³
U(hfa-3-MePz) ₄	2.8-40		TIP		(2.0 ± 0.03) × 10 ⁻²
Np(hfa-3-MePz) ₄	2.6-25	1.93	0.50	1.99	
	25-45	16	0.8	2.5	
Pu(hfa-3-MePz) ₄	2.6-50		TIP		(6.2 ± 0.8) × 10 ⁻³

^a Constants from the Curie-Weiss expression $\chi = C/(T + \Theta)$.

^b Temperature-independent paramagnetism.

II) are consistent with a site of low symmetry for the actinide(IV) ions. U⁴⁺ and Pu⁴⁺ compounds show only temperature-independent paramagnetism (TIP), and Np⁴⁺ compounds have a strong temperature-dependent paramagnetism. The expected magnetic behavior can be derived by a descent in symmetry from a cubic class crystal field model^{9,10} and the crystal structure.⁸

In this model, the U⁴⁺ ion would have singlets for its lowest crystal field levels, the Pu⁴⁺ ion will have a singlet level lowest for any crystal field symmetry, and the Np⁴⁺ compounds can only have Kramers doublets for crystal field levels. Singlet levels can have only TIP paramagnetism, and doublet levels will show temperature-dependent paramagnetism, in agreement with the magnetic susceptibility measurements. The persistence of TIP to 40-45°K for the U⁴⁺ compounds suggests a crystal field splitting on the order of several hundred reciprocal centimeters. The Np⁴⁺ ion would have a Γ₈ quartet level for a lowest crystal field level in cubic symmetry; the low site symmetry in these compounds will split the Γ₈ level into Γ₆ and Γ₇ doublets. The higher transition temperature for Np(hfa-3-MePz)₄ compared to that of Np(hfaPz)₄ suggests a stronger crystal field for the hfa-3-MePz chelates.

Registry No. Pu(hfaPz)₄, 40804-50-0; U(hfaPz)₄, 40904-28-7; Np(hfaPz)₄, 40904-27-6; Pu(hfa-3-MePz)₄, 40904-26-5; Th(hfa-3-MePz)₄, 40904-25-4; U(hfa-3-MePz)₄, 40904-24-3; Np(hfa-3-MePz)₄, 40904-23-2; 3-methylpyrazole, potassium salt, 40802-35-5; hexafluoroacetone, 684-16-2; potassium pyrazolide, 40802-36-6.

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pounds and advice on their preparation; to Karl Volz, Allan Zalkin, and D. H. Templeton of the Lawrence Berkeley Laboratory, University of California, for communicating the results of their single-crystal X-ray study in advance of publication; and to Sandra Slates, formerly of the Savannah River Laboratory, for assistance in gas chromatography experiments.

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Sulfur Dioxide and Carbon Disulfide Complexes of Osmium(II)

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In a previous communication^{1,2} we described the isolation of the complex OsH(CO)Cl(PCy₃)₂ (PCy₃ = tricyclohexylphosphine), a monomeric coordinately unsaturated molecule. This complex forms with pyridine (py) the compound OsH(CO)Cl(PCy₃)₂(py). We now report the reaction of OsH(CO)Cl(PCy₃)₂ with sulfur dioxide and carbon disulfide and present complete spectroscopic data on the prepared complexes. The reactions with these small molecules have not been studied in osmium metal chemistry.

Experimental Section

Materials. OsH(CO)Cl(PCy₃)₂ was prepared as previously described.^{1,2} All other reagents were analytical grade.

Preparation of OsH(CO)Cl(PCy₃)₂(SO₂)·C₆H₆. Sulfur dioxide was passed through a solution of OsH(CO)Cl(PCy₃)₂ (0.3 mmol) in 15 ml of benzene for 4 hr at room temperature. After evaporating the solution to 5 ml in a nitrogen atmosphere, the yellow precipitate was filtered off, washed with benzene, and dried *in vacuo*, mp (dec pt) 164°. *Anal.* Calcd for C₄₃H₇₃ClS₂O₃Os: C, 53.93; H, 7.68; Cl, 3.70; S, 3.35. Found: C, 53.98; H, 7.53; Cl, 3.66; S, 3.37.

Preparation of α-OsH(CO)Cl(PCy₃)₂(CS₂). OsH(CO)Cl(PCy₃)₂ (0.4 mmol) was added to 10 ml of carbon disulfide in an atmosphere of nitrogen. After evaporating the solution to 2 ml the yellow-brown crystals were filtered off and dried *in vacuo*, dec pt 140°. *Anal.* Calcd for C₃₈H₆₇ClS₂P₂OOs: C, 51.19; H, 7.57; Cl, 3.98; S, 7.19. Found: C, 49.96; H, 7.29; Cl, 4.55; S, 7.02.

Preparation of β-Os(CO)Cl(PCy₃)₂(HCS₂). Carbon disulfide (25 ml) was added to a solution of OsH(CO)Cl(PCy₃)₂ (0.6 mmol) in 40 ml of benzene in an atmosphere of nitrogen. After evaporating the solution to 5 ml, the brown crystals were collected, washed with benzene, and dried *in vacuo*, dec pt 194°. *Anal.* Calcd for C₃₈H₆₇ClS₂P₂OOs: C, 51.19; H, 7.57; Cl, 3.98; S, 6.67. Found: C, 50.94; H, 7.47; Cl, 4.05; S, 6.67.

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Table I. Major Infrared Absorption Bands (cm^{-1} in Nujol Mulls) of the Osmium Sulfur Dioxide and Carbon Disulfide Complexes

Complex	ν C-S or S-O	ν Os-Cl or Os-S	δ C-O ^a	ν C-O	Other bands
$\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{SO}_2) \cdot \text{C}_6\text{H}_6$	1284 s, 1109 s	364 s, 299 m, 276 w	604 s	1950 vs	2145 vw, 1910 vw, 1810 vw, 1480 m, 677 s
α - $\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{CS}_2)$	1510 s, 917 m, 790 w	307 m, 273 s	590 s	1920 vs	2170 vw, 1876 vw
β - $\text{Os}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{HCS}_2)$	917 s, 791 m	310 m, 274 s	592 s	1905 vs	2020 vw

^a L. Vaska, *J. Amer. Chem. Soc.*, **86**, 1943 (1964).

Table II. Mass Spectral Data (m/e above 800) of the Carbon Disulfide Complexes^a

Compounds	Mass peak, m/e	Composition	Rel intensity
α - $\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{CS}_2)$	884	$\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{CS}_2)$	8
	856	$\text{OsHCl}(\text{PCy}_3)_2(\text{CS}_2)$	10
	836	$\text{OsHCl}(\text{PCy}_3)_2\text{C}(\text{CS})$	16
	824	$\text{OsHCl}(\text{PCy}_3)_2(\text{CS})$	10
	808	$\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2$	100
β - $\text{Os}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{HCS}_2)$	884	$\text{Os}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{HCS}_2)$	10
	856	$\text{OsCl}(\text{PCy}_3)_2(\text{HCS}_2)$	8
	836	$\text{OsCl}(\text{PCy}_3)_2\text{C}(\text{HCS})$	10
	808	$\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2$	100

^a Only the lowest mass ion of a cluster is tabulated.

Physical Measurements. Magnetic susceptibilities were measured on a Gouy balance. A Perkin-Elmer 257 spectrophotometer was used for obtaining spectral data in the range 4000–650 cm^{-1} and a Hitachi EPI-L for the 700–200- cm^{-1} region, using the Nujol mull technique. The 70-eV mass spectra were recorded on a Varian-Atlas SM-1B double focusing instrument under low-resolution conditions. The samples were introduced into the mass spectrometer by a direct insertion system, $\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{SO}_2) \cdot \text{C}_6\text{H}_6$ at 150°, α - $\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{CS}_2)$ at 145°, and β - $\text{Os}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{HCS}_2)$ at 155°. Rapid heating and scanning were necessary in order to minimize thermal decomposition. The nuclear magnetic resonance spectrum of $\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{SO}_2) \cdot \text{C}_6\text{H}_6$ was determined with a Varian HA-100 nmr spectrometer. The sample was prepared by dissolving it in deuterated chloroform.

Results and Discussion

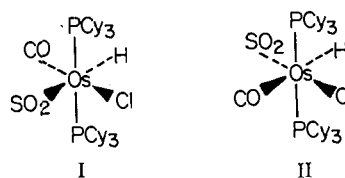
By passing sulfur dioxide over a benzene solution of $\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2$, yellow crystals were obtained which were analyzed for $\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{SO}_2) \cdot \text{C}_6\text{H}_6$. This complex is stable in a nitrogen atmosphere.

The ir spectrum (Table I) shows bands at 1950 ($\nu_{\text{C-O}}$), 1284 ($\nu_{\text{asym S-O}}$), and 1109 cm^{-1} ($\nu_{\text{sym S-O}}$). The SO stretching vibrations are in the same region as found for *S*-sulfinato complexes, indicating coordination through sulfur of the sulfur dioxide ($\nu_{\text{asym SO}}$ and $\nu_{\text{sym SO}}$ are reported for the complex $[\text{Ru}(\text{NH}_3)_4(\text{SO}_2)\text{Cl}]\text{Cl}$ at 1301, 1278, and 1100 cm^{-1} , respectively^{3,4}). The infrared spectrum showed bands at 677, 1480, and 1810 cm^{-1} which are characteristic of benzene. We found, in addition, very weak bands at 2145 and 1910 cm^{-1} . One of these bands may be assigned to $\nu_{\text{M-H}}$.

The sulfur dioxide complex was soluble enough in CDCl_3 for obtaining a nmr spectrum. The hydride resonance has been found as a 1:2:1 triplet arising from coupling of the hydride with two equivalent P nuclei [τ 16.2; $J(\text{P-H}) = 24$ Hz]. For the compound $\text{RuH}(\text{CO})\text{I}(\text{PPh}_3)_2(\text{CNR})$ the $J(\text{P-H})$ and τ are reported to be 20 Hz and 15.6, respectively.⁵

The mass spectrum shows the clusters $^{184}\text{OsH}(\text{CO})^{35}\text{Cl}(\text{PCy}_3)_2$ and $^{32}\text{SO}_2$ in high abundance. The parent ion could not be observed, suggesting decomposition of the complex in the mass spectrometer.

For this complex with five different ligands many octahedral structures are possible. The hydride resonance triplet indicates a trans position for the two phosphine groups. The chemical shift has been found at the lower part of the high-field region, indicating a ligand of high trans influence trans to hydrogen.^{6,7} From these data we conclude that one of the following structures is most probable.



Blake and Kubota⁸ have reported that the addition of nucleophiles in five-coordinated complexes of iridium is directed trans to hydrogen. From these data we would predict that configuration I is the expected structure for the SO_2 complex. We found an increase of the CO stretching frequency of 63 cm^{-1} for $\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{SO}_2)$ in comparison with $\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2$ ($\nu_{\text{CO}} 1887 \text{ cm}^{-1}$ ²). The increase of the ν_{CO} frequency is due to the effects of oxidative addition of SO_2 to Os.⁹

Reaction of $\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2$ in benzene solution or in the solid state with carbon disulfide gives complexes which analyze for $\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{CS}_2)$. These compounds are only slightly soluble in organic solvents.

The infrared spectrum of the CS_2 compound (α complex) prepared by addition of CS_2 to solid $\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2$ shows a $\nu_{\text{C-S}}$ band at 1510 cm^{-1} , indicating terminal coordination of the sulfur of the CS_2 molecule to the osmium atom.^{10,11} In addition $\nu_{\text{C-S}}$ bands were observed at 917 and 790 cm^{-1} , which points to the presence of β - $\text{OsCl}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{HCS}_2)$ in this product. The complex obtained in benzene solution (β complex) has two infrared bands at 917 and 791 cm^{-1} . These bands are much lower than the bands assignable to a π - CS_2 group^{12,13} and are comparable to those

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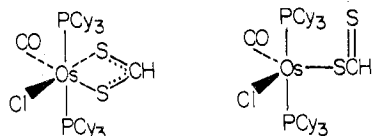
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found for $\text{Re}(\text{CO})_3(\text{DPE})(\text{HCS}_2)$, $\text{Mn}(\text{CO})_3(\text{DPE})(\text{HCS}_2)$, and $\text{Re}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{HCS}_2)$ ¹⁴⁻¹⁶ with DPE = diphenylphosphinoethane. In the region 2550–2600 cm^{-1} a ν S–H was not observed. From these data it is suggested that the β complex has one of the following structures.



In the mass spectra (Table II) of these carbon disulfide complexes, there is a cluster with the lowest fragment ion having m/e 884 which is in agreement with the lowest fragment ion $^{184}\text{Os}^{35}\text{Cl}(\text{CO})(\text{PCy}_3)_2(\text{C}^{32}\text{S}_2)$. The relative abundances of the peaks in this cluster agree with the calculated ratios. The described complexes are diamagnetic (measured between room temperature and -150°) indicating a low spin d^6 configuration. Distinguishing between the possible structures of these complexes with X-ray structure determination meets with difficulties because suitable crystals have not yet been obtained.

Registry No. $\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2$, 31177-20-5; $\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{SO}_2)$, 40583-39-9; $\text{OsH}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{CS}_2)$, 40583-40-2; $\text{Os}(\text{CO})\text{Cl}(\text{PCy}_3)_2(\text{HCS}_2)$, 40631-70-6.

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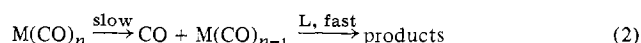
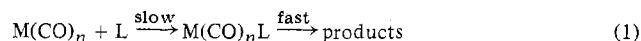
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Effect of Pressure on the Rates of Substitution Reactions of Metal Carbonyls

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The kinetics and mechanisms of the substitution reactions of metal carbonyls have been intensively studied during the last decade. The field has been reviewed by Werner.¹ Depending on choice of reaction conditions and substituting ligand, both first- and second-order rate laws have been found. Usually the activation entropies are positive when the first-order rate law applies and negative for second order. Rate laws and activation entropies provide the principal evidence for assigning either the associative mechanism (1) or the dissociative mechanism (2).



In recent years, especially for organic reactions, the volume of activation, ΔV^\ddagger , has proved to be a valuable criterion of

mechanism.^{2,3} It would be desirable to establish that the method also has utility for the study of inorganic reactions by choosing a group for which a great deal of mechanistic evidence already exists. Application of the method to the first-order decomposition reactions of metal carbonyls is especially promising owing to the fact that reactants and products are neutral molecules; thus, there can be no question of electrostrictive effects which often cloud and sometimes totally obscure the interpretation of activation volumes.

Reagents. Nickel tetracarbonyl was obtained from Matheson Gas Products. Chromium, molybdenum, and tungsten hexacarbonyl were obtained from Strem Chemicals, Inc. Triethyl phosphite was prepared by the method of Ford-Moore and Perry.⁴ Tri-*n*-butylphosphine was prepared by the method of Kauffman and Teter.⁵ Triphenylphosphine was obtained from Eastman Organic Chemicals. Tetraethylammonium azide was prepared by neutralization of tetraethylammonium hydroxide with aqueous hydrazoic acid. The solution was then evaporated to dryness under a stream of air.

Rate of Reaction of Nickel Tetracarbonyl with Triethyl Phosphite. Reaction mixtures were prepared by quickly combining cold heptane solutions of triethyl phosphite and nickel carbonyl to form 2 ml of solution which was 0.03 *M* in carbonyl and 0.15 *M* in phosphite. The solution together with a small magnetic stirring bar was placed in a 10-ml gas buret which was filled with mercury and inverted over mercury in a slightly larger test tube. These operations were performed within 1 min at a temperature below 0° . The reaction cell was then pressurized at 0° for 90 min. After depressurization, the stirring bar was agitated with an external magnet to expel CO, the inner and outer levels of mercury were equalized, and the volume of gas in the buret was recorded. The volume of gas after 10 half-lives was also recorded, and values of $\ln(V_\infty/V_\infty - V_t)$ were plotted against t . The mean deviation from the mean was 1.5%.

Rates of Reaction of Chromium and Molybdenum Hexacarbonyl with Triphenylphosphine. Cyclohexane solutions of chromium hexacarbonyl (6×10^{-3} *M*) and triphenylphosphine (2.4×10^{-2} *M*) were allowed to react for 3.75 hr at 124.0° , and the decrease in absorbance at 1983 cm^{-1} was measured. Solutions having corresponding concentrations of molybdenum hexacarbonyl and triphenylphosphine in 2,2,4-trimethylpentane were allowed to react for 4.0 hr at 103.0° , and the band at 1980 cm^{-1} was observed. The mean deviation of the mean of rate constants was 2.5%.

Rate of Reaction of Tungsten Hexacarbonyl with Tri-*n*-butylphosphine. The reaction was carried out under pseudo-unimolecular conditions using cyclohexane solutions 0.03 *M* in carbonyl and 0.3 *M* in phosphine. The 4-ml samples were allowed to react at 120.0° for various times from 2.5 to 4.0 hr. The reaction was followed by measurement of the volume of carbon monoxide as described in the case of nickel tetracarbonyl. The mean deviation from the mean was 3.0%.

Rate of Reaction of Chromium Hexacarbonyl with Azide Ion. Acetone solutions of chromium hexacarbonyl (3.37×10^{-2} *M*) and tetraethylammonium azide (3.37×10^{-2} *M*) were allowed to react for 1.5 hr at 24.0° . Analysis was performed by the volumetric method developed for nickel

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