(which was not observed) from the dependence on $[P(C_6H_5)_3]$ described by eq 13.

We thus conclude that the results of this investigation, together with our earlier observations, firmly establish the general features of the mechanism depicted by eq 1–3 for the $Pt(P(C_6H_5)_3)_3$-catalyzed oxidation of $P(C_6H_5)_3$. The detailed mechanisms of the individual steps, particularly of step 2, which we have previously interpreted in terms of a dissociative "oxygen insertion" sequence, *i.e.*

$$Pt(P(C_6H_5)_3)_2O_2 \xrightarrow{P(C_6H_5)_3} [Pt(OP(C_6H_5)_3)_2(P(C_6H_5)_3)] \xrightarrow{2P(C_6H_5)_3} Pt(P(C_6H_5)_3)_3 + 2(C_6H_5)_3PO^{2}$$

remain to be more fully elucidated.

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Nickel Complexes with Long-Chain Primary Amines

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Although methyl-, ethyl-, and propylamine readily form stable nickel(II) complexes,[1] isopropylamine does not.[2] We report the preparation and characterization of new complexes with higher alkylamine members, which clarify effects of chain length and branching on complex formation. The ligand system consists of straight-chain primary amines containing four through eight and eighteen carbon atoms, as well as isobutyl-, isopentyl-, and isohexylamine.

Experimental Section

Preparation of Compounds.—Ligands were distilled over BaO and charcoal immediately before use and diluted with *n*-hexane. Hydrated nickel perchlorate was dehydrated with 2,2-dimethoxypropane (DMP) and diluted with 1-butanol. This alcohol solution was distilled under reduced pressure to remove excess DMP and dehydration products, filtered, and added dropwise to ligand solution at 0° while stirring. Light blue solids formed, which were separated by filtration, washed with hexane, and dried in a moisture-free air stream. A chloroform–hexane mixture was used to dissolve *n*-octadecylamine.

Analyses.—Carbon–hydrogen analyses were obtained using a Coleman Model 33 analyzer in conjunction with a Mettler M-5 balance. Nickel was estimated as dimethylglyoximate, and per cent nitrogen for the octadecylamine complex was determined by Micro-Tech Laboratories, Skokie, Ill.

Physical Measurements.—Magnetic susceptibilities were determined at two field strengths by the Gouy method at room temperature. A Perkin-Elmer Model 457 grating spectrophotometer measured infrared spectra from 4000 to 250 cm^{-1} on samples mulled with Nujol and Fluorolube. A Cary Model 14 spectrophotometer marked electronic spectra from 3500 to 17,000 Å for mulled samples supported on filter paper and immersed in optical cells containing Fluorolube.

Results and Discussion

Elemental content clearly demonstrates the formation of hexakis-amine complexes in all cases (Table I). Poor results for isobutylamine reflect instability of that product. They all exhibit magnetic moments of 3.20 ± 0.05 BM (excessive magnetic dilution for *n*-octadecylamine prevented quantitative results with our equipment). Amine infrared bands appear more intense, sharper, and at lower frequencies after complexation, and T_d perchlorate frequencies remain intact. Visible–uv spectra of the complexes are remarkably similar in detail (Table II) and consist of three weak absorptions plus a shoulder. Minor band splitting is noted only for *n*-octadecylamine. Ligand field parameters[3] of $Dq = 1030\ \text{cm}^{-1}$ and $\beta \sim 900\ \text{cm}^{-1}$, obtained from mull spectra, closely match solution information for isobutylamine. Slight energy changes in solution as observed here are not uncommon.[4] This evidence shows the complexes are paramagnetic, six-coordinate species of O_h symmetry,[5] bound through amine nitrogen

TABLE I

ANALYTICAL AND MAGNETIC INFORMATION FOR $[Ni(ligand)_6](ClO_4)_2$

Ligand	% carbon		% hydrogen		% nickel		μ_{eff}, BM
	Calcd	Found	Calcd	Found	Calcd	Found	
n-$C_4H_9NH_2$	41.30	41.34	9.57	9.03	8.42	8.36	3.23
i-$C_4H_9NH_2$	41.30	40.28	9.57	9.25	8.42	7.29	Paramag
n-$C_5H_{11}NH_2$	46.16	45.91	10.09	9.65	7.52	7.63	3.22
i-$C_5H_{11}NH_2$	46.16	46.06	10.09	9.66	7.52	7.48	3.19
n-$C_6H_{13}NH_2$	49.99	49.64	10.51	9.99	6.78	6.62	3.24
i-$C_6H_{13}NH_2$	49.99	49.64	10.51	10.50	6.78	6.78	3.18
n-$C_7H_{15}NH_2$	53.16	53.12	10.76	10.50	6.18	6.16	3.21
n-$C_8H_{17}NH_2$	55.69	55.49	11.14	10.66	5.68	5.64	3.18
n-$C_{18}H_{37}NH_2$	69.15	69.35	12.48	12.34	(4.49)[a]	(4.60)[a]	Paramag

[a] These are figures for per cent nitrogen.

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TABLE II

ELECTRONIC SPECTRA FOR AMINE COMPLEXES

Complex	Solvent	Absorption bands, cm^{-1}
$[Ni(ligand)_6](ClO_4)_2$[a]	Mull	10,300
		12,800 sh
		17,000
		27,700
$[Ni(C_{18}H_{39}N)_6](ClO_4)_2$	Mull	10,300–10,700
		12,900 sh
		17,100
		27,800
$[Ni(n\text{-}C_4H_9NH_2)_6](ClO_4)_2$	$n\text{-}C_4H_9NH_2$	10,100 (5.3)[b]
		12,800 sh
		16,700 (7.4)
		27,200 (12.8)

[a] For all ligands except *n*-octadecylamine. [b] Molar absorptivities.

atoms,[6] and they contain ionic noncoordinated perchlorate.[7]

Two features arise from this work: (A) the chain length of the coordinating amine plays an insignificant role in deterring complex formation,[8] and (B) branching, although still a critical steric factor for isobutylamine, ceases to prevent complex formation with isopentylamine and beyond.

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Correspondence

The Raman Spectrum of $IF_6^+AsF_6^-$ in Hydrogen Fluoride Solution

Sir:

The vibrational spectrum of solid $IF_6^+AsF_6^-$ has previously been reported by us.[1] For IF_6^+ an unusual assignment of ν_2 (E_g) having a higher frequency value than ν_1 (A_1) was required to account for the observed intensities. Subsequently, Hardwick and Leroi proposed[2] a reversal of our original assignment based upon Urey–Bradley force field calculations. However, a comparison with the known spectra of a series of isoelectronic ions and molecules supported our original assignment.[3]

We have now resolved this controversy by recording the Raman spectrum of $IF_6^+AsF_6^-$ in HF solution. Since only ν_1 (A_1) should be polarized, it should be easy to distinguish between ν_1 (A_1) and ν_2 (E_g). As can be seen from Figure 1, the 711-cm^{-1} band is clearly polarized whereas the one at 732 cm^{-1} is depolarized, thus confirming our original assignment. Polarization characteristics are given qualitatively rather than quantitatively owing to internal reflections from the metal walls of the cylindrical sample container.

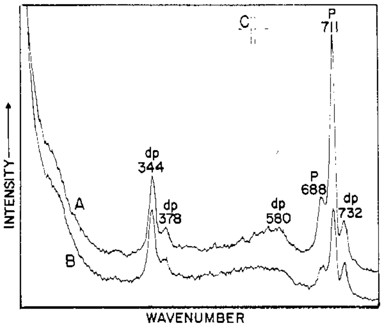

Figure 1.—Raman spectrum of $IF_6^+AsF_6^-$ in HF solution: traces A and B, incident polarization perpendicular and parallel, respectively; C indicates spectral slit width.

Comparison of the spectrum shown in Figure 1 with that[1] of solid $IF_6^+AsF_6^-$ shows a remarkable difference. In HF solution the bands due to AsF_6^- have suffered a considerable loss in relative intensity and also have become quite broad. This effect might be caused by interactions such as hydrogen bonding with the HF solvent. The fact that only AsF_6^- shows a pronounced change might be due to the acidic solvent HF interacting with the Lewis base, AsF_6^-, more readily than with the Lewis acid, IF_6^+. This parallels to some extent the general observation made for F^{19} nmr measurements on complex fluorides in HF solution. These show that rapid fluorine exchange occurs preferentially with the anions and not with the cations.[4]

Technique.—The preparation of $IF_6^+AsF_6^-$ has previously been described.[1] Hydrogen fluoride (from The Matheson Co.) was electrolytically dried.[5] The Raman spectrum was recorded using a Coherent Radiation Laboratories Model 52 Ar ion laser as a source of 1.3 W of exiting light at 5145 Å. The scattered light was analyzed with a Spex 1400 double monochromator, a photomultiplier cooled to about −25°, and a dc ammeter. Polarization measurements were carried out using a Model 310 polarization rotator from Spectra-Physics. A stainless steel cell with Teflon O rings and sapphire windows was used as a sample container. The design of this cell was similar to that of Gasner and Claassen.[6]

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