The $(CF_3)_2PCN$ and $(CH_3)_2PCl$ reactions are relatively clean cleavages, giving the expected products. The experiment with PF_5 was intended for fluorination of the SiH_3 group, as succeeded for disiloxanes.[4]

Trimethylsilylbis(trifluoromethyl)phosphine

Synthesis. The action of mercury upon $(CF_3)_2PI$ and $ISi(CH_3)_3$ favored the formation of $P_2(CF_3)_4$ more than in the $ISiH_3$ case: the conversion to $(CF_3)_2PSi(CH_3)_3$ never was complete; even though small portions of $(CF_3)_2PI$ were added to bring the total to 5 times the calculated amount, the conversion did not exceed 78%. However, this still is an efficient and fairly convenient synthesis, from reactants not too difficult to obtain. Purification is possible by repeated slow high-vacuum fractional condensations: $(CF_3)_2PSi(CH_3)_3$ condenses in a U trap at −55°, through which $P_2(CF_3)_4$ and $ISi(CH_3)_3$ pass more easily.

Boron Fluoride Cleavage. With equimolar BF_3, the cleavage of $(CF_3)_2PSi(CH_3)_3$ was completed during 48 hr at 25°; or with $2BF_3$, 5 hr sufficed. The results are expressed in mmol as follows

$$\begin{array}{cccc}
(CF_3)_2PSi(CH_3)_3 + & BF_3 \rightarrow & (CF_3PCF_2)_2 + & (CH_3)_3SiF \\
0.45 & 0.500 & 0.09 & 0.45 \\
 & \underline{-0.465} & & \\
 & 0.035 & & \\
0.47 & 0.97 & 0.12 & 0.47 \\
 & \underline{-0.85} & & \\
 & 0.12 & &
\end{array}$$

with the first experiment yielding also 0.10 $P_2(CF_3)_4$ and 0.06 $(CF_3)_2PH$ and the second respectively 0.03 and 0.18 of these.

Here the silane product was not subject to loss by decomposition, so that the relation to reaction 3 is more apparent. However, the yields of $(CF_3PCF_2)_2$ were not better. Again, BF_3 played a catalytic role.

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Registry No. $(CF_3)_2PSiH_3$, 53716-32-8; $(CF_3)_2PSi(CH_3)_3$, 21658-00-4; $ISiH_3$, 13598-42-0; $(CF_3)_2PI$, 359-64-8; $ISi(CH_3)_3$, 16029-98-4; BF_3, 7637-07-2; BCl_3, 10294-34-5; $B(OCH_3)_3$, 121-43-7; CH_3OBCl_2, 867-46-9; $(CH_3)_2PCl$, 811-62-1; $(CF_3)_2PCN$, 431-97-0; PF_5, 7647-19-0; CH_3CN, 75-05-8; CH_3NC, 593-75-9; $BrSiF_3$, 14049-39-9.

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Base Hydrolysis of Coordinated Benzonitrile. Reactions of Rhodium(III) and Iridium(III) Complexes

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Recent studies of the base hydrolyses of organonitriles coordinated to non-labile metal centers have included the acetonitrile–pentaammine complexes of Co(III),[2] Rh(III),[3] Ru(II),[3] and Ru(III)[3] ($M(NH_3)_5(CH_3CN)^{m+}$) and analogous benzonitrile complexes of Co(III)[4,5] and Ru(III).[3] Reported here are the base hydrolysis rates for benzonitrile complexes of rhodium(III) and iridium(III), thus allowing comparisons for a complete homologous series $M(NH_3)_5(C_6H_5CN)^{3+}$ where M is the tripositive metal ion of Co, Rh, or Ir. In an earlier paper we suggested that the nitrile hydrolysis rates are a reflection of the acidities of the respective metal centers and that such effects are functions of both electrostatic and electronic factors.[3] The pK_a values of the amide complexes provide one quantitative measure of the relative metal ion acidities and these are reported here for the benzamide[6] complexes of Rh(III) and Ir(III).

Experimental Section

Materials. Reagent grade chemicals and doubly distilled water were used throughout. $[Rh(NH_3)_5(C_6H_5CN)](ClO_4)_3$ was prepared according to Foust's procedure[7] (λ_{max} 235 nm, ϵ 2.04×10^4 M^{-1} cm^{-1}). $[Ir(NH_3)_5(C_6H_5CN)](ClO_4)_3$ was prepared similarly[8] by heating $[Ir(NH_3)_5OH_2](ClO_4)_3$ and benzonitrile together in dry dimethylacetamide and was recrystallized twice [λ_{max} 236 nm (ϵ 1.23×10^4 M^{-1} cm^{-1}), 283 nm (sh) (2.88×10^3), 255 nm (sh) (9.98×10^3); ν_{CN} 2280 (w) cm^{-1}, KBr disk].

Spectra of Benzamide Complexes. An accurately weighed sample of the appropriate benzonitrile complex was dissolved in ~10 ml of dilute NaOH. After hydrolysis was complete, the solution was diluted to a known volume at the desired pH and the uv spectrum was run on a Cary Model 14 spectrophotometer. $Rh(NH_3)_5(benzamide)^{3+}$: λ_{max} 235 nm (ϵ 1.29×10^4 M^{-1} cm^{-1}) (0.2 M $HClO_4$, 0.8 M $NaClO_4$). $Rh(NH_3)_5(benzamido)^{2+}$: 240 nm (sh) ($\epsilon$ 7.70×10^3) (pH 9, 1 M $NaClO_4$). $Ir(NH_3)_5(benzamide)^{3+}$: λ_{max} 229 nm (ϵ 8.70×10^3), 253 nm (sh) (ϵ 7.23×10^3) (1 M $HClO_4$). $Ir(NH_3)_5(benzamido)^{2+}$: λ_{max} 263 nm (ϵ 5.07×10^3), 218 nm (ϵ 8.78×10^3) (pH 7, 1 M $NaClO_4$).

pK_a Measurements. The benzamido complexes were generated in aqueous solution by base hydrolysis of the corresponding benzonitrile complex, and the solution was adjusted to pH ~6 with 1 M $HClO_4$. Solutions over a series of pH values were prepared[3] with [Rh(III)] = 7.2×10^{-5} M or [Ir(III)] = 1.4×10^{-4} M. The spectrum of each solution was recorded on a Cary Model 14 at 25°, and the pK_a values were determined by plotting absorbance against pH at 235 nm [Rh(III)] and 260 nm [Ir(III)]. The pK_a was calculated as the pH where the absorbance equaled $[\epsilon(B) + \epsilon(BH^+)][complex]/2)$.

Rate Studies. A stock solution of the benzonitrile complex was prepared in 1.0 M $NaClO_4$. Stock NaOH solutions (from 8×10^{-4} to 0.01 M) were also prepared at μ 1.0 M. Equal volumes of reactants at 25.0° were mixed in cylindrical 2.0-cm cells and absorbance *vs.* time was recorded at 236 nm on a Cary Model 118 equipped with a thermostated (25.0°) cell compartment. Rates for the iridium(III) complex were examined at five hydroxide concentrations and for the rhodium(III) complex at four concentrations. Triplicate runs were carried out at most concentrations.

Results and Discussion

The base hydrolysis products were characterized by their uv spectra which displayed reversible acid–base behavior in a manner analogous to that for previously studied Co(III)[4] and Ru(III)[3] complexes. The spectra were neither those of the corresponding aquo or hydroxo complexes nor those of the starting material. The molar extinction coefficients and general spectral features in the uv region are consistent with the π–π^* bands expected from coordinated benzamide. The pK_a values for the reversible acid–base behavior were 2.2 ± 0.1 and 2.4 ± 0.1 for the rhodium(III) and iridium(III) benzamide products, respectively. The iridium(III) product was isolated from a reaction solution of 25 mg of nitrile complex dissolved in ~3 ml of dilute sodium hydroxide. After hydrolysis the solution was neutralized with $HClO_4$ and saturated $NaClO_4$ solution was added dropwise. The white precipitate which appeared upon cooling was isolated by filtration, washed with ethanol and ether, and dried under vacuum (yield 8.5 mg). The uv spectrum and acid–base behavior was the same as that

Table I. Base Hydrolysis Rates of Coordinated Benzonitrile $M(NH_3)_5(C_6H_5CN)^{3+}$ and pK_a Values for Coordinated Benzamide, $M(NH_3)_5(C_6H_5CONH_2)^{3+}$

M	k_{OH},[a] M^{-1} sec^{-1}	pK_a[b]
Co(III)	18.2[c]	1.65[d]
Rh(III)	4.7	2.2
Ir(III)	2.1	2.4
Ru(III)	2.0×10^3 [e]	0.9[e,f]
Free ligand	7.2×10^{-6} [g]	~15 or higher[h]

[a] Rate constant for eq 1 at 25.0° and $\mu = 1.0\ M$ ($NaClO_4$) unless noted. [b] pK_a for eq 2 at 25.0° and $\mu = 1.0\ M$ ($NaClO_4$-$HClO_4$) unless noted. [c] 25.6°, ref 4. [d] $\mu = 1.0\ M$ ($LiClO_4$-HCl). [e] Reference 3. [f] $\mu = 2.0\ M$ ($NaClO_4$-$HClO_4$). [g] Extrapolated from higher temperature rate data reported for 50% aqueous acetone by K. B. Wiberg, *J. Amer. Chem. Soc.*, 77, 2519 (1955). [h] pK_a of free ligand is uncertain; values of ~15 and >19 have been reported: R. B. Horner and C. D. Johnson in "The Chemistry of Amides," J. Zabicky, Ed., Interscience, London, 1970, Chapter 3.

mentioned above. The ir spectrum showed no ν_{CN} stretch and was comparable to that of the Ru(III) homolog,[8] $[Ru(NH_3)_5(benzamido)](ClO_4)_2$ (benzamido bands at 1550 (s), 1295 (m), 1270 (s), and 700 cm^{-1} (m–s)). These observations indicate that the course of the base hydrolysis reaction is analogous to that reported previously for nitrile complexes[2-5] of Co(III), Rh(III), and Ru(III)

$$M(NH_3)_5(C_6H_5CN)^{3+} + OH^- \rightarrow M(NH_3)_5(C_6H_5CONH)^{2+} \qquad (1)$$

The acid–base spectral behaviors of the product solutions presumably reflect reaction of the coordinated benzamide (eq 2).

$$M(NH_3)_5(C_6H_5CONH_2)^{3+} \rightleftarrows M(NH_3)_5(C_6H_5CONH)^{2+} + H^+ \qquad (2)$$

Base hydrolysis kinetics were followed by absorbance changes at 235 nm, and linear first-order plots of ln $(A_t - A_\infty)$ *vs.* time were obtained. Observed rate constants were a linear function of $[OH^-]$ in accordance with the rate law

$$\frac{d[\text{amido complex}]}{dt} = k_{OH}[\text{nitrile complex}][OH^-] \qquad (3)$$

where k_{OH} has the values 4.7 ± 0.4 and 2.1 ± 0.2 M^{-1} sec^{-1} for the rhodium and iridium complexes, respectively (25.0°, μ = 1.0). These results are consistent with the second-order rate behavior observed with other systems.[2-5]

Examination of Table I shows that coordination to any of the 3+ metal ions markedly enhances the reactivity of benzonitrile toward base hydrolysis. This rate enhancement ranges from $\sim 3 \times 10^5$ for $Ir(NH_3)_5^{3+}$ to $\sim 3 \times 10^8$ for $Ru(NH_3)_5^{3+}$ and is paralleled by the dramatic enhancement in the acidities of the benzamide product coordinated to these 3+ metal ions. Given the marked differences from the free ligand reactivities the differences between the various M(III) complexes are relatively small. Of these the ruthenium(III)–benzonitrile complex is several orders of magnitude the more reactive toward base hydrolysis, a feature which has also been noted for the analogous acetonitrile complex[3] and has been attributed to the relative ability of the $4d^5$ Ru(III) center to act as a π acceptor.

It has been pointed out that when metal–ligand bond making or breaking is not a feature of the reaction of a coordinated ligand, there is little variation in rate constants over the series Co(III), Rh(III), and Ir(III).[10] This is also true for the reactions of interest here. Although the variations are small, the coordinated benzonitrile hydrolysis rates and the coordinated benzamide acidities follow the order Co(III) > Rh(III) > Ir(III) with the difference between Co(III) and Rh(III) greater in each case than between Rh(III) and Ir(III). Consideration of the M^{3+} ionic radii, Co^{3+} (0.53 Å) < Rh^{3+} (0.67 Å) < Ir^{3+} (0.73 Å),[9] supports the view that the rate differences for the nd^6, tripositive metal–benzonitrile complexes are largely due to the relative abilities of these metal ions to stabilize the developing negative charge on the nitrile nitrogen during the rate-determining step. Certainly, other variables must play roles in the overall bonding between the reacting ligands and the respective metal centers; for example, ligand field splitting energies (therefore ligand field stabilization energies) are much larger for Ir(III) than for Co(III). However, these other variables appear not to be large contributors to the free energies of activation for the base hydrolyses of the various benzonitrile complexes thus leaving the electrostatic differences to determine the relative reactivities.

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Registry No. $Rh(NH_3)_5(C_6H_5CN)^{3+}$, 46343-55-9; $Ir(NH_3)_5(C_6H_5CN)^{3+}$, 53783-43-0; $Rh(NH_3)_5(C_6H_5CONH_2)^{3+}$, 53702-61-7; $Ir(NH_3)_5(C_6H_5CONH_2)^{3+}$, 53783-44-1.

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Absolute Integrated Infrared Intensities of the Carbonyl and Thiocarbonyl Stretching Modes in η^5-$C_5H_5Mn(CO)_2(CS)$[1]

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Following the discovery of the first transition metal–thiocarbonyl complex by Baird and Wilkinson in 1966,[2] there has been considerable interest in the comparative bonding properties of the CO and CS ligands. Molecular orbital calculations,[3] photoelectron spectroscopy measurements,[4] and various other physiochemical data[5] suggest that CS is both a better σ-donor and a better π-acceptor ligand than CO. The utility of absolute integrated infrared intensity measurements is assessing the extent of π-electronic delocalization in the CO and N_2 groups of transition metal carbonyls and transition metal–dinitrogen complexes has now been well established.[6-18] We report here the results of the first intensity study for a CS stretching vibration in a transition metal–thiocarbonyl complex, *viz.*, η^5-$C_5H_5Mn(CO)_2(CS)$. This complex is particularly interesting because it is possible to make a direct comparison of the π-electronic properties of CO and CS in the same complex on the basis of the absolute infrared intensities of the CO and CS stretching modes.