cyanate ion to form single atom bridges has been rationalized[21] in terms of the charge distribution in the ion.[9,23] Unlike the thiocyanate, selenocyanate, and azide ions, which have relatively high charge densities on both terminal atoms, the cyanate has, by far, the greater part of its charge localized on the nitrogen atom. Therefore, in the case of the $[Co(NH_3)_5NCO]^{2+}$ complex, remote attack by the reductant would be anticipated to be less favorable than the situations encountered with the other pseudohalide bridging groups.

The question as to what reactions actually take place still remains to be answered, however. In the case of the reaction with $[Co(CN)_5]^{3-}$, the most obvious hypothesis would be that the reaction proceeds *via* an outer-sphere electron transfer between $[Co(NH_3)_5NCO]^{2+}$ and $[Co(CN)_6]^{4-}$, which would yield $[Co(CN)_6]^{3-}$ directly. Another plausible explanation involves the formation of a $[(H_3N)_5Co\text{–}NCO\text{–}Co(CN)_5]^-$ bridged activated complex. This would lead to the formation of $[Co(CN)_5OCN]^{3-}$, which would most certainly be unstable, since the $[Co(CN)_5]^{2-}$ moiety is known to be a soft coordination center, *e.g.*, $[Co(CN)_5SCN]^{3-}$ is a stable S-bonded species,[15] whereas the cyanate ion is known to bond through its oxygen atom only to very hard Lewis acids, *e.g.*, Ti(IV),[24] Zr(IV),[24] Hf(IV),[24] Mo(III),[25] Re(IV),[25] and Re(V).[25] Expulsion of the unstable O-bonded cyanate could then lead to cyanide substitution, perhaps *via* an aquo intermediate, to yield $[Co(CN)_6]^{3-}$. Finally, the $[Co(CN)_6]^{3-}$ could result from a disproportion–oxidation reaction between $[Co(CN)_5]^{3-}$ and water with evolution of hydrogen. This is not very likely in the present case, since Poskozim has reported[26] that this reaction does not take place to any noticeable degree until the aqueous $[Co(CN)_5]^{3-}$ solution is heated, even with solutions of much higher concentration than that used in this study. It should be noted that the infrared spectrum of the product is identical with those of authentic samples of $K_3[Co(CN)_6]$, prepared either by Schlessinger's method[27] or by the reaction between $[Co(NH_3)_5CN]^{2+}$ and $[Co(CN)_5]^{3-}$.[17]

In the case of the reaction with chromium(II), the $[Cr(OH_2)_5OCN]^{2+}$ species resulting from a $[(H_3N)_5Co\text{–}NCO\text{–}Cr(OH_2)_5]^{4+}$ bridged activated complex would be susceptible to hydrolysis, especially in the strongly acidic solution employed in case (B), perhaps *via* a carbamato intermediate. It is also possible that the color changes observed are due to the oxidation of the chromium(II) by incipient oxygen, and, in case (B), the $[Co(NH_3)_5NCO]^{2+}$ complex simply decomposes in the acidic medium.

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Tris(trifluoromethyl)phosphine Chemistry of Nitrosylcobalt Tricarbonyl[1]

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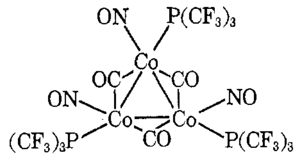
The isoelectronic analogy between nitrosylcobalt tricarbonyl and nickel tetracarbonyl makes it appropriate to compare their chemistry. An obviously expected similarity would be the successive displacement of 2CO by $2(CF_3)_3P$, the steric effect of which would preclude displacement of a third CO.[2,3] In fact, $(CF_3)_3PCoNO(CO)_2$ is formed from $CoNO(CO)_3$ not quite so easily as $(CF_3)_3PNi(CO)_3$ from $Ni(CO)_4$; then it is still harder to produce $[(CF_3)_3P]_2CoNOCO$, and a third-stage displacement of CO seems impossible.

A more subtle analogy concerns the decomposition of $[(CF_3)_3P]_2Ni(CO)_2$ at 25°, to form a deep red soluble material in which CO bridging between nickel atoms could be demonstrated by infrared peaks at 1878 and 1897 cm^{-1}.[4] The search for a somewhat similar polynuclear complex made up of $(CF_3)_3P$, Co, NO, and CO seemed significant because of the question whether NO or CO would be employed for bridge bonding between the cobalt atoms. In fact, the thermal decomposition of $(CF_3)_3PCoNO(CO)_2$ at 40° led to a dark brown, nonvolatile solid, soluble in the usual organic solvents and having the molecular formula $[(CF_3)_3PCoNOCO]_3$. The infrared spectrum of this included peaks at 1860 and 1826 cm^{-1}, assignable to bridging CO and terminal NO; there were no peaks in the terminal CO region (above 2000 cm^{-1} for Ni and Co carbonyls) nor in the 1500-cm^{-1} range characteristic of bridging NO. Reasonably assuming the molecular structure



it seems that, given equal opportunity, CO is better than NO for bridging between cobalt atoms.

Mononuclear Complexes

Formation.—Both of the new $(CF_3)_3P\text{–}Co$ complexes were made in a single quantitative experiment which determined their empirical formulas. The reactants $(CF_3)_3P$ and $CoNO(CO)_3$ were heated in a sealed glass tube for 10 hr at 120°; then the tube was opened to the Stock-type high-vacuum manifold. The free CO

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was removed through a −196° U trap, by an automatic Sprengel pump,[5] and measured. The remaining mixture was subjected to high-vacuum fractional condensation (using U traps at −78, −17, and 0°), for isolation of the main products and remaining reactants. The following reaction balance (with quantities in millimoles) summarizes the results

$$\begin{array}{lllll}
\mathrm{CoNO(CO)_3} & + \ \mathrm{(CF_3)_3P} & \longrightarrow \mathrm{CO} & + \ \mathrm{(CF_3)_3PCoNO(CO)_2} & + \\
\quad 0.604 & \quad 2.30 & \quad 0.93 & \quad 0.24 & \\
\underline{-0.024} & \underline{-1.38} & & & \\
\quad 0.580 & \quad 0.92 & & & \mathrm{[(CF_3)_3P]_2CoNOCO} \\
 & & & & \quad 0.34
\end{array}$$

The rate of the first-stage CO displacement was roughly indicated by the action of 0.410 mmol of $(CF_3)_3P$ upon 0.658 mmol of $CoNO(CO)_3$ in a sealed tube for 6 hr at 50°. The yield of $(CF_3)_3PCoNO(CO)_2$ was 0.218 mmol, and no $[(CF_3)_3P]_2CoNOCO$ could be detected. For a quantitative conversion of the 0.218-mmol product to the bis-phosphine complex, it was necessary to heat it for 12 hr at 102°, with 0.60 mmol of $(CF_3)_3P$.

Characterization.—The purity of each product was verified by its reasonable vapor tension curve (Tables I and II) and by its infrared and ^{19}F nmr spectra: neither was appreciably contaminated by the other or by the reactants. With purity recognized, the quantitative synthesis and the vapor phase molecular weight results (381 and 590 *vs.* calcd 383 and 593, respectively) sufficed to prove the molecular formulas.

TABLE I

VOLATILITY OF $(CF_3)_3PCoNO(CO)_2$

($\log P = 5.9542 + 1.75 \log T - 0.0045T - 2307/T$)

($t_{760} = 122°$; Trouton Constant = 22.1 eu)

	Temp, °C						
	−17.4	−12.5	−3.1	11.8	16.0	18.2	20.6
P_{obsd}, mm	1.00	1.44	2.82	7.48	9.56	10.90	12.52
P_{calcd}, mm	1.00	1.44	2.82	7.44	9.58	10.90	12.52

TABLE II

VOLATILITY OF $[(CF_3)_3P]_2CoNOCO$

($\log P = 6.6432 + 1.75 \log T - 0.0047T - 2772/T$)

($t_{760} = 165°$; Trouton Constant = 23.0 eu)

	Temp, °C					
	7.4	10.3	15.4	17.0	21.0	27.0
P_{obsd}, mm	0.52	0.68	0.96	1.08	1.44	2.32[a]
P_{calcd}, mm	0.53	0.67	0.97	1.08	1.44	2.15

[a] High value due to incipient evolution of CO.

The Trinuclear Complex

The trimer $[(CF_3)_3PCoNOCO]_3$ was formed in yields representing about 3% of a sample of $(CF_3)_3PCoNO(CO)_3$, stored in a sealed tube for 3 weeks at 40°. The only liberated ligand was CO. Higher temperatures or longer times led to some removal of NO and $(CF_3)_3P$, with formation of gray insoluble material.

The dark brown product, soluble in various organic solvents, was analyzed in two ways: by direct thermal decomposition to liberate CO and NO (but not the phosphine ligand as such) and by the action of iodine at 150° to liberate the phosphine ligand. The evolution of CO and NO was completed by moderate heating, and then flame heating gave no more. Results: 7.6% CO, 8.1% NO, 68% $(CF_3)_3P$, and, by difference, 16% Co (calcd: 7.9, 8.5, 67, and 16.4%, respectively). The osmometric molecular weight result (in benzene) was 1057 (calcd, 1063).

The infrared spectrum of the trimer (in cyclohexane) showed very strong C–F stretching peaks at 1140 and 1166 cm^{-1}, with a strong satellite at 1093 cm^{-1}, as well as the previously mentioned C–O bridge and N–O terminal stretching bands. These 1860- and 1826-cm^{-1} peaks were fairly sharp despite possible solvent effects. The absence of a second C–O stretching mode is ascribed to the symmetric character of the $(CoCO)_3$ pattern, for which the in-phase (A_1) mode would be weak, or even infrared inactive if this pattern is planar. The N–O units are too far apart for splitting due to in-phase *vs.* out-of-phase modes to be observable.[6]

The ^{19}F nmr spectrum of the trimer showed the expected doublet (J_{FP} = 91.3 cps) at 59 ppm upfield of Cl_3CF. The peaks were not seriously broadened by the cobalt quadrupole. For such results, the substance must be diamagnetic (as expected for the proposed structure, with d^{10} cobalt), in contrast to the probably analogous $[(C_6H_5)_3PCoNO(CO)_2]_3$,[7] wherein the d^9 cobalt would have oxidation state +1.

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Boron–Nitrogen Compounds. XXXI.[1,2] The Interaction of Boron Trihalides with Hexafluoroisopropylidenimine

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Boron–nitrogen compounds which are substituted with organofluorine derivatives are exceedingly rare. However, the recent discovery of hexafluoroisopropylidenimine[3] (hexafluoroacetone imine, $(CF_3)_2CNH$) and hexafluoro-2,2-propanediamine[3] ($(CF_3)_2C(NH_2)_2$) supplies two materials of potential value for the synthesis of fluorinated carbon–nitrogen–boron derivatives.

We have initiated an investigation of the borane chemistry of the two cited compounds and wish to report on the interaction of boron trihalides with hexafluoroisopropylidenimine.

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