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Isocyanide–Metal Complexes. I. Reactions of the Pentakis(*tert*-butyl isocyanide)cobalt Cation with Some Tertiary Phosphines and Arsines[1]

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The (*tert*-butyl isocyanide)cobalt(I) complex $[(t\text{-BuNC})_5\mathrm{Co}][\mathrm{PF_6}]$ reacts readily with various trivalent phosphorus and arsenic derivatives in boiling ethanol. Triphenylarsine thus reacts with $[(t\text{-BuNC})_5\mathrm{Co}][\mathrm{PF_6}]$ to give the monosubstituted derivative $[(t\text{-BuNC})_4\mathrm{CoAs(C_6H_5)_3}][\mathrm{PF_6}]$. Triphenylphosphine reacts with $[(t\text{-BuNC})_5\mathrm{Co}][\mathrm{PF_6}]$ to give the trans-disubstituted derivative *trans*-$[(t\text{-BuNC})_3\mathrm{Co[P(C_6H_5)_3]_2}][\mathrm{PF_6}]$. The chelating di(tertiary phosphines) $\mathrm{(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2}$ and *cis*-$\mathrm{(C_6H_5)_2PCH{=}CHP(C_6H_5)_2}$ react with $[(t\text{-BuNC})_5\mathrm{Co}][\mathrm{PF_6}]$ to give the disubstituted derivatives $[(t\text{-BuNC})_3\mathrm{Co(diphos)}][\mathrm{PF_6}]$. However, the nonchelating di(tertiary phosphine) *trans*-$\mathrm{(C_6H_5)_2PCH{=}CHP(C_6H_5)_2}$ reacts with $[(t\text{-BuNC})_5\mathrm{Co}][\mathrm{PF_6}]$ to give the biligate bimetallic derivative $[(t\text{-BuNC})_4\mathrm{Co}]_2[\textit{trans}\text{-}\mathrm{(C_6H_5)_2PCH{=}CHP(C_6H_5)_2}][\mathrm{PF_6}]_2$. The two tridentate ligands $\mathrm{[(C_6H_5)_2ECH_2CH_2]_2PC_6H_5}$ (E = P and As) react with $[(t\text{-BuNC})_5\mathrm{Co}][\mathrm{PF_6}]$ to give the trisubstituted derivative $[(t\text{-BuNC})_2\mathrm{Co(tridentate)}][\mathrm{PF_6}]$; the tri(tertiary phosphine) derivative of this type exhibits a temperature-dependent nmr spectrum in the methyl region. The tripod tetra(tertiary phosphine) $\mathrm{[(C_6H_5)_2PCH_2CH_2]_3P}$ reacts with $[(t\text{-BuNC})_5\mathrm{Co}][\mathrm{PF_6}]$ to give the tetraligate monometallic derivative $[(t\text{-BuNC})\mathrm{Co(tetraphos)}][\mathrm{PF_6}]$. However, the linear tetra(tertiary phosphine) $\mathrm{(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2}$ reacts with $[(t\text{-BuNC})_5\mathrm{Co}][\mathrm{PF_6}]$ to give the tetraligate bimetallic derivative $[(t\text{-BuNC})_3\mathrm{Co}]_2\mathrm{(tetraphos)[PF_6]_2}$. The hexa(tertiary phosphine) $\mathrm{[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2}$ reacts with $[(t\text{-BuNC})_5\mathrm{Co}][\mathrm{PF_6}]$ to give the hexaligate bimetallic derivative $[(t\text{-BuNC})_2\mathrm{Co}]_2\mathrm{(hexaphos)[PF_6]_2}$. The manganese(I) derivative, $[(t\text{-BuNC})_6\mathrm{Mn}][\mathrm{PF_6}]$, is much less reactive than $[(t\text{-BuNC})_5\mathrm{Co}][\mathrm{PF_6}]$ toward trivalent phosphorus ligands but does react with triphenylphosphine in boiling diglyme to give a low yield of the monosubstituted derivative $[(t\text{-BuNC})_5\mathrm{MnP(C_6H_5)_3}][\mathrm{PF_6}]$. The infrared spectra in the ν(CN) region and the proton nmr spectra, particularly in the methyl region, of these *tert*-butyl isocyanide derivatives are discussed.

Introduction

During the last decade reactions of numerous metal carbonyl derivatives with a wide variety of trivalent phosphorus and arsenic ligands have received considerable attention.[3,4] The formal similarity of isocyanide[5] and carbonyl ligands suggested that analogous extensive chemistry could be based on reactions of metal isocyanide complexes with trivalent phosphorus and arsenic ligands.

A characteristic of the substitution of carbonyl groups in metal carbonyls with trivalent phosphorus (and arsenic) derivatives is the strengthening of the metal–carbon monoxide bonds when the very strongly π-accepting metal carbonyl groups are replaced by the weaker trivalent phosphorus (and arsenic) π acceptors. In most cases this limits the number of carbonyl groups that can be replaced by trivalent phosphorus ligands when the metal carbonyl derivative is allowed to react with the ligand. The π-acceptor strengths of the alkyl isocyanide ligands are much less than that of carbon monoxide and approach those of the trivalent phosphorus (and arsenic) ligands. Therefore successive substitution of isocyanide ligands with trivalent phosphorus and arsenic ligands will not necessarily have a significant effect on the strengths of the metal–carbon bonds to the remaining isocyanide groups. This suggests that trivalent phosphorus (and arsenic) ligands will be able to displace more alkyl isocyanide ligands in metal isocyanide cations than metal carbonyl groups in isoelectronic metal carbonyl derivatives.

Reactions of metal carbonyls with trivalent phosphorus derivatives can be represented by the following general scheme

$$\mathrm{M(CO)}_n + \mathrm{R_3P} \longrightarrow \mathrm{M(CO)}_{n-1}\mathrm{PR_3} + \mathrm{CO}$$

If such reactions are carried out in open systems, the very volatile carbon monoxide will escape upon formation, thereby driving reactions of the above type to completion. Analogous reactions of metal isocyanide complexes can be represented by the following general scheme

$$\mathrm{(RNC)}_n\mathrm{M} + \mathrm{R_3P} \longrightarrow \mathrm{(RNC)}_{n-1}\mathrm{MPR_3} + \mathrm{RNC}$$

However, the alkyl isocyanide formed in this reaction is not normally very volatile and thus will not escape from reaction mixtures even when the reactions are carried out in open systems. The possibility that the alkyl isocyanide liberated in the above reaction will cause this reaction to reverse itself must therefore be considered as a factor which limits the degree of substitution of isocyanide ligands in metal isocyanide complexes with trivalent phosphorus and similar ligands. As more isocyanide groups in a metal isocyanide complex are replaced with tertiary phosphine and similar ligands, the concentration of liberated alkyl isocyanide will build up, thereby hindering further substitution of additional alkyl isocyanide ligands with trivalent phosphorus or related ligands. The relative nonvolatility of most alkyl isocyanide ligands thus serves to limit the possible degree of substitution of alkyl isocyanide ligands in their metal complexes with trivalent phosphorus and related ligands in a superficially similar manner to the unusually high π-acceptor strength of the carbon monoxide ligand.

This paper describes the reactions of the simple and readily available metal(I) isocyanide cations $[\mathrm{(RNC)_5Co}]^+$ and $[\mathrm{(RNC)_6Mn}]^+$ with different trivalent phosphorus and arsenic ligands. Poly(tertiary phosphines)

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(1) Portions of this work were presented at the XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., July 1971, Paper 186.

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TABLE I

REACTIONS OF PENTAKIS(*tert*-BUTYL ISOCYANIDE)COBALT(I) HEXAFLUOROPHOSPHATE WITH TRIVALENT PHOSPHORUS AND ARSENIC DERIVATIVES

Phosphine or arsine (g, mmol)	Quantity of $[(t\text{-BuNC})_5Co][PF_6]$, g (mmol)	Solvent (ml)	Temp, °C	Time, hr	Product	Yield, g (mmol)
Ph_3As (0.98, 3.1)	1.0 (1.62)	EtOH (50)	79	12	$[(t\text{-BuNC})_4CoAsPh_3][PF_6]$	1.1 (1.31)
Ph_3As (1.0, 3.2)	0.4 (0.65)	EtOH (50)	79	12	$[(t\text{-BuNC})_4CoAsPh_3][PF_6]$	0.43 (0.51)
Ph_3P (0.45, 1.72)	1.0 (1.62)	EtOH (50)	79	20	*trans*-$[(t\text{-BuNC})_3Co(PPh_3)_2][PF_6]$	0.9 (0.92)
Ph_3P (0.38, 1.45)	0.44 (0.71)	EtOH (50)	79	15	*trans*-$[(t\text{-BuNC})_3Co(PPh_3)_2][PF_6]$	0.6 (0.61)
Ph_3P (0.92, 3.5)	0.44 (0.71)	EtOH (50)	79	15	*trans*-$[(t\text{-BuNC})_3Co(PPh_3)_2][PF_6]$	0.65 (0.66)
Pf-Pf (0.2, 0.5)	0.62 (1.0)	EtOH (50)	79	12	$[(t\text{-BuNC})_3Co(\text{Pf-Pf})][PF_6]$	0.2 (0.23)
Pf-Pf (0.34, 0.85)	0.5 (0.81)	EtOH (50)	79	12	$[(t\text{-BuNC})_3Co(\text{Pf-Pf})][PF_6]$	0.5 (0.59)
Pf-Pf (1.6, 4.0)	0.62 (1.0)	$MeOCH_2CH_2OH$ (50)	126	12	$[(t\text{-BuNC})_3Co(\text{Pf-Pf})][PF_6]$	Not determined
cPf=Pf (0.34, 0.85)	0.5 (0.81)	EtOH (50)	79	12	$[(t\text{-BuNC})_3Co(\text{cPf=Pf})][PF_6]$	0.6 (0.71)
tPf=Pf (0.40, 1.0)	1.24 (2.0)	EtOH (50)	79	12	$[(t\text{-BuNC})_4Co]_2(\text{tPf=Pf})[PF_6]$	1.0 (0.68)
tPf=Pf (0.40, 1.0)	0.62 (1.0)	EtOH (50)	79	12	$[(t\text{-BuNC})_4Co]_2(\text{tPf=Pf})[PF_6]_2$	0.5 (0.34)
Pf-Pf-Pf (0.70, 1.31)	0.70 (1.13)	EtOH (50)	79	12	$[(t\text{-BuNC})_2Co(\text{Pf-Pf-Pf})][PF_6]$	0.74 (0.82)
Asf-Pf-Asf (0.63, 1.0)	0.62 (1.0)	EtOH (50)	79	12	$[(t\text{-BuNC})_2Co(\text{Asf-Pf-Asf})][PF_6]$	0.5 (0.50)
$P(\text{-Pf})_3$ (0.8, 1.2)	0.5 (0.81)	EtOH (50)	79	24	$[(t\text{-BuNC})CoP(\text{-Pf})_3][PF_6]$	0.6 (0.63)
Pf-Pf-Pf-Pf (0.67, 1.0)	1.24 (2.0)	EtOH (50)	79	10	$[(t\text{-BuNC})_3Co]_2(\text{Pf-Pf-Pf-Pf})[PF_6]_2$	0.5 (0.32)
$P_2(\text{-Pf})_4$ (0.47, 0.5)	0.62 (1.0)	EtOH (50)	79	10	$[(t\text{-BuNC})_3Co]_2P_2(\text{-Pf})_4[PF_6]_2$	0.5 (0.30)

and phosphine–arsines[6] were included as ligands in this study in order to explore the possibilities for chelating and/or bridging ligands in metal isocyanide complexes. *tert*-Butyl isocyanide was selected as the alkyl isocyanide ligand for the following reasons: (1) although *tert*-butyl isocyanide is a liquid, it gives crystalline complexes in most cases; (2) *tert*-butyl isocyanide is more readily handled and less malodorous than certain lower aliphatic isocyanides; (3) most importantly, the *tert*-butyl group gives a single sharp proton nmr resonance which provides an additional means for establishing structures and purities of *tert*-butyl isocyanide–metal complexes. The selection of the cations $[(RNC)_5Co]^+$ and $[(RNC)_6Mn]^+$ for this study of reactions of metal isocyanide derivatives with trivalent phosphorus and arsenic ligands enables a comparison to be made with the well-known[3,4] substitution chemistry of the isoelectronic metal carbonyls $Fe(CO)_5$ and $Cr(CO)_6$, respectively. Hexafluorophosphate salts were used throughout this work because generally they are stable and relatively easy to crystallize.

Experimental Section

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of organometallic compounds, and (c) admitting to evacuated vessels containing organometallic compounds.

Materials.—*tert*-Butyl isocyanide was prepared from *tert*-butylamine *via* *tert*-butylformamide.[7] The ligand 1,2-bis(diphenylphosphino)ethane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (abbreviated as Pf-Pf), was purchased from Arapahoe Chemical Co., Boulder, Colo. The ligandscis -1,2-bis(diphenylphosphino)ethylene, *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (abbreviated as cPf=Pf),[8] *trans*-1,2-bis(diphenylphosphino)ethylene, *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (abbreviated as tPf=Pf),[8] bis(2-diphenylphosphinoethyl)phenylphosphine, $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ (abbreviated as Pf-Pf-Pf),[6] bis(2-diphenylarsinoethyl)phenylphosphine, $[(C_6H_5)_2AsCH_2CH_2]_2PC_6H_5$ (abbreviated as Asf-Pf-Asf),[6] tris(2-diphenylphosphinoethyl)phosphine, $[(C_6H_5)_2PCH_2CH_2]_3P$ (abbreviated as $P(\text{-Pf})_3$),[9] 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (abbreviated as Pf-Pf-Pf-Pf),[6] and 1,1,4,4-tetrakis(2-diphenylphosphinoethyl)-1,4-diphosphabutane, $[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$ (abbreviated as $P_2(\text{-Pf})_4$),[10] were prepared by the cited published procedures.

Preparation of $[(t\text{-BuNC})_5Co][PF_6]$.—A solution of 1.2 g (5 mmol) of $CoCl_2\cdot 6H_2O$ in 20 ml of ethanol was treated with 6 ml (4.3 g, 52 mmol) of *tert*-butyl isocyanide. A solution of 1.5 ml of hydrazine hydrate (60% hydrazine) in 20 ml of ethanol was added dropwise to this reaction mixture. The color changed from blue to orange-yellow. About 10 to 15 ml of ethanol was then added to dissolve a precipitate which separated. The reaction mixture was then treated with a solution of 1 g (6.1 mmol) of ammonium hexafluorophosphate in 20 ml of ethanol. The solvent was then removed at 25° (25 mm). The solid which separated was filtered, washed repeatedly with water, and dried to give 3.0 g (97% yield) of golden-yellow $[(t\text{-BuNC})_5Co][PF_6]$, mp 113°. *Anal.* Calcd for $C_{25}H_{45}CoF_6N_5P$: C, 48.5; H, 7.3; N, 11.3. Found: C, 47.2; H, 7.2; N, 11.3. This procedure has been scaled up by a factor of 5 with equivalent results.

Reactions of $[(t\text{-BuNC})_5Co][PF_6]$ with Trivalent Phosphorus and Arsenic Ligands (Table I).—The indicated quantities (Table I) of $[(t\text{-BuNC})_5Co][PF_6]$, the trivalent phosphorus or arsenic ligand, and solvent (generally ethanol) were boiled under reflux for the indicated period of time. The reaction mixture was then concentrated under vacuum at room temperature to 10–20 ml and cooled to at least −15°. The yellow solid which separated was washed with a small volume of cold ethanol and dried to give the products indicated in Table I.

The properties, analytical data, and conductance data on the new compounds prepared by this method are given in Table II.

Preparation of $[(t\text{-BuNC})_6Mn][PF_6]$.—A mixture of 20 g (65 mmol) of anhydrous manganese(II) iodide (purchased from Research Organic/Inorganic Chemical Corp., Sun Valley, Calif.), 40 g (482 mmol) of *tert*-butyl isocyanide, and 200 ml of ethanol was warmed until all the manganese(II) iodide dissolved. Then 15 g (92 mmol) of solid ammonium hexafluorophosphate was added. After a few minutes of shaking, the $[(t\text{-BuNC})_6Mn][PF_6]$ began to precipitate. The reaction mixture was treated with gaseous sulfur dioxide for a total of 15 min. Solvent was then removed at 35° (35 mm). The residue was washed with four 50-ml portions of water and then with four 50-ml portions of benzene. The product was purified by recrystallization from hot ethanol to give 30 g (67%) of white $[(t\text{-BuNC})_6Mn][PF_6]$, mp ~250° dec. *Anal.* Calcd for $C_{30}H_{54}F_6MnN_6P$: C, 51.7; H, 7.8; N, 12.0. Found: C, 51.7; H, 7.7; N, 11.9.

Reaction of $[(t\text{-BuNC})_6Mn][PF_6]$ with Triphenylphosphine.—A mixture of 0.698 g (1 mmol) of $[(t\text{-BuNC})_6Mn][PF_6]$, 1.57 g (6 mmol) of triphenylphosphine, and 25 ml of diglyme (dimethyl ether of diethylene glycol; redistilled over lithium aluminum hydride) was boiled under reflux for 12 hr. The diglyme was then removed at ~50° (0.1 mm). The residue was extracted with 25 ml of ethanol. The filtered ethanol extract was concentrated to ~5 ml and then kept at room temperature for several weeks. A mixture of large yellow and small white crystals separated.

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[9] R. B. King, R. N. Kapoor, M. S. Saran, and P. N. Kapoor, *Inorg. Chem.*, **10**, 1851 (1971).

[10] R. B. King and M. S. Saran, *ibid.*, **10**, 1861 (1971).

TABLE II

PROPERTIES OF (*tert*-BUTYL ISOCYANIDE)COBALT(I) DERIVATIVES WITH TRIVALENT PHOSPHORUS AND ARSENIC LIGANDS

Compd[a]	Color	Mp,[b] °C	Elemental analyses,[c] % C		H		N		Molar conductance[d]
			Calcd	Found	Calcd	Found	Calcd	Found	
$[(t\text{-BuNC})_4\text{CoAsPh}_3][\text{PF}_6]$	Yellow	130	54.2	53.7	6.1	6.4	6.6	6.7	95 ± 6
trans-$[(t\text{-BuNC})_3\text{Co(PPh}_3)_2][\text{PF}_6]$	Yellow	232–236 dec	62.7	62.4	5.9	6.0	4.3	4.0	95 ± 5
$[(t\text{-BuNC})_3\text{Co(Pf-Pf)}][\text{PF}_6]$	Yellow	161–162 dec	57.8	57.5	6.0	6.0	4.9	4.8	92 ± 17
$[(t\text{-BuNC})_3\text{Co(cPf=Pf)}][\text{PF}_6]$	Yellow-orange	175–176 dec	58.0	58.3	5.8	5.9	4.9	4.9	99 ± 1
$[(t\text{-BuNC})_4\text{Co}]_2(\text{tPf=Pf})[\text{PF}_6]_2$	Orange	>155 dec	53.2	53.5	6.4	6.6	7.6	7.5	217 ± 31
$[(t\text{-BuNC})_2\text{Co(Pf-Pf-Pf)}][\text{PF}_6]$	Yellow	209–210 dec	58.6	57.9	5.6	5.5	3.1	2.9	92 ± 8
$[(t\text{-BuNC})_2\text{Co(Asf-Pf-Asf)}][\text{PF}_6]$	Yellow	173–174	53.3	53.0	5.2	5.2	2.8	2.8	94 ± 4
$[(t\text{-BuNC})\text{CoP(-Pf)}_3][\text{PF}_6]$	Yellow	236–238 dec	58.9	58.9	5.3	5.3	1.4	1.4	91 ± 3
$[(t\text{-BuNC})_3\text{Co}]_2(\text{Pf-Pf-Pf-Pf})[\text{PF}_6]_2$	Yellow	204 dec	54.7	54.4	6.1	6.2	5.3	5.3	206 ± 13
$[(t\text{-BuNC})_2\text{Co}]_2\text{P}_2(\text{-Pf})_4[\text{PF}_6]_2$	Yellow	206–208 dec	55.6	56.1	5.8	5.9	3.3	3.4	207 ± 17

[a] See the text for an explanation of the ligand abbreviations. [b] Melting points were determined in capillaries and are uncorrected. [c] Elemental analyses were performed by Mr. M. L. Kshatriya and Mr. W. W. Swanson at the University of Georgia. [d] Molar conductances were determined in ~0.0002 to 0.002 *M* acetone solutions at room temperature (~25°) using platinum electrodes and a Model 31 conductivity bridge manufactured by the Yellow Springs Instrument Co., Inc., Yellow Springs, Ohio.

These crystals were isolated by filtration. Careful washing with cold absolute ethanol removed the fine white crystals. Several of the yellow crystals were then separated mechanically to give a low yield of $[(t\text{-BuNC})_5\text{MnP(C}_6\text{H}_5)_3][\text{PF}_6]$. *Anal.* Calcd for $\text{C}_{43}\text{H}_{60}\text{F}_6\text{MnN}_5\text{P}_2$: C, 58.8; H, 6.9; N, 8.0. Found: C, 59.6; H, 6.9; N, 7.8.

Similar reactions of $[(t\text{-BuNC})_6\text{Mn}][\text{PF}_6]$ with the ligands $(\text{C}_6\text{H}_5)_3\text{As}$, Pf-Pf, cPf=Pf, P(-Pf)$_3$, and P$_2$(-PF)$_4$ in boiling diglyme failed to give any *tert*-butyl isocyanide–manganese(I) complexes containing the trivalent phosphorus or arsenic ligand. Instead, only unchanged $[(t\text{-BuNC})_6\text{Mn}][\text{PF}_6]$ was recovered.

Infrared Spectra (Table III).—Infrared spectra of all of the *tert*-butyl isocyanide metal complexes in the 2300–1700-cm^{-1} region (Table III) were measured in dichloromethane or chloroform solution and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated against the 1601-cm^{-1} band of polystyrene film.

TABLE III

ν(CN) INFRARED FREQUENCIES OF COBALT(I) AND MANGANESE(I) *tert*-BUTYL ISOCYANIDE COMPLEXES DISCUSSED IN THIS PAPER

Compd	ν(CN) frequencies, cm^{-1} (CH_2Cl_2 soln)
(A) Cobalt derivatives	
$[(t\text{-BuNC})_5\text{Co}][\text{PF}_6]$	2152 s, 2120 s
$[(t\text{-BuNC})_4\text{CoAsPh}_3][\text{PF}_6]$	2248 w, 2150 s, 2122 s
trans-$[(t\text{-BuNC})_3\text{Co(PPh}_3)_2][\text{PF}_6]$	2093 s, 2070 sh
$[(t\text{-BuNC})_3\text{Co(Pf-Pf)}][\text{PF}_6]$	2159 s, 2117 s, 2101 s
$[(t\text{-BuNC})_3\text{Co(cPf=Pf)}][\text{PF}_6]$	2160 s, 2114 s, br
$[(t\text{-BuNC})_4\text{Co}]_2(\text{tPf=Pf})[\text{PF}_6]_2$	2230 vw, 2153 s, 2122 s
$[(t\text{-BuNC})_2\text{Co(Pf-Pf-Pf)}][\text{PF}_6]$	2138 s, 2108 s
$[(t\text{-BuNC})_2\text{Co(Asf-Pf-Asf)}][\text{PF}_6]$	2138 s, 2108 s
$[(t\text{-BuNC})\text{CoP(-Pf)}_3][\text{PF}_6]$	2113 s
$[(t\text{-BuNC})_3\text{Co}]_2(\text{Pf-Pf-Pf-Pf})[\text{PF}_6]_2$	2156 s, 2113 s, br
$[(t\text{-BuNC})_2\text{Co}]_2\text{P}_2(\text{-Pf})_4[\text{PF}_6]_2$	2140 s, 2102 s
(B) Manganese derivatives	
$[(t\text{-BuNC})_6\text{Mn}][\text{PF}_6]$	2100 s, 2068 s
$[(t\text{-BuNC})_5\text{MnPPh}_3][\text{PF}_6]$	2166 w, 2093 s, 2059 s

Proton Nmr Spectra (Table IV).—The proton nmr spectra of all of the *tert*-butyl isocyanide metal complexes prepared in this work were measured in both chloroform-*d* and acetone-d_6 solutions and recorded at 100 MHz on a Varian HA-100 spectrometer. The spectra obtained in acetone-d_6 solution were generally far better than those obtained in chloroform-*d* solution. The chemical shift data listed in Table IV were all obtained from the spectra taken in acetone-d_6 solution and are reported in τ units.

In order to provide further confirmation of the stoichiometries of the complexes prepared in this work containing both *tert*-butyl isocyanide and trivalent phosphorus or arsenic ligands, the area ratios of the methyl resonances (from the *tert*-butyl isocyanide ligands) to the phenyl resonances (from the aryl groups in the trivalent phosphorus or arsenic ligand) were measured by integration. These values are also listed in Table IV as the ratio (area of the methyl resonance)/(area of the phenyl resonance). In all cases the observed values for this ratio were within 10% of the calculated values.

Discussion

A. Cobalt(I) Derivatives. (1) **General Comments.**—The pentakis(*tert*-butyl isocyanide)cobalt(I) salt $[(t\text{-BuNC})_5\text{Co}][\text{PF}_6]$ reacted with all of the trivalent phosphorus and arsenic derivatives used in this work upon boiling in ethanol solution for several hours. The products were yellow to orange solids which could be handled in the air. They were readily soluble in polar organic solvents such as dichloromethane, chloroform, and acetone but insoluble in hydrocarbon solvents. The stability of the cobalt(I) derivatives containing both trivalent phosphorus or arsenic and *tert*-butyl isocyanide ligands varied markedly. The derivatives of the di(tertiary phosphines), the linear tetra(tertiary phosphine) Pf-Pf-Pf-Pf, and triphenylarsine decomposed upon prolonged storage even at −10°. However, the derivatives of triphenylphosphine, the tri(tertiary phosphine) Pf-Pf-Pf, the tripod tetra(tertiary phosphine) P(-Pf)$_3$, and the hexa(tertiary phosphine) P$_2$(-Pf)$_4$ were stable upon prolonged storage at room temperature.

The infrared and proton nmr spectra were very useful for the characterization of the new cobalt(I) *tert*-butyl isocyanide derivatives. The infrared spectra of all of the cobalt(I) *tert*-butyl isocyanide complexes exhibited the expected strong bands around 2100 cm^{-1} arising from the ν(CN) frequencies of the coordinated *tert*-butyl isocyanide. The patterns of these ν(CN) frequencies corresponded to those expected for substituted trigonal-bipyramidal complexes and, for example, corresponded closely to the patterns of the ν(CO) frequencies of similarly substituted iron pentacarbonyl derivatives.[11] Unfortunately, the ν(CN) frequencies of these ionic (*tert*-butyl isocyanide)cobalt(I) derivatives could not be measured in saturated hydrocarbon solvents, which would have given the narrowest bands[12] and thus the most clearly resolved spectra. The spectra, therefore, had to be measured in dichloromethane or chloroform solution which made it impossible to observe reliably some of the very weak ν(CN) frequencies or to resolve closely spaced bands.

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(12) J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).

TABLE IV

PROTON NMR SPECTRA OF THE *tert*-BUTYL ISOCYANIDE–METAL COMPLEXES

Compd[a]	Proton nmr spectrum, τ			Integration Ratio $CH_3:C_6H_5$[d]	
	t-BuNC ligand[b] Methyl groups	R_3P or R_3As ligand[c]			
		C_6H_5	CH_2	Calcd	Found
$[(t\text{-BuNC})_5\text{Co}][\text{PF}_6]$	8.49				
$[(t\text{-BuNC})_4\text{CoAsPh}_3][\text{PF}_6]$	8.51 (1), 8.65 (1)	2.55–2.67		2.40	2.31
trans-$[(t\text{-BuNC})_3\text{Co}(\text{PPh}_3)_2][\text{PF}_6]$	9.29	2.44		0.90	0.83
$[(t\text{-BuNC})_3\text{Co}(\text{Pf-Pf})][\text{PF}_6]$	8.80	2.35 br, 2.50	7.27, 7.44	1.35	1.35
$[(t\text{-BuNC})_3\text{Co}(\text{cPf{=}Pf})][\text{PF}_6]$	8.86	2.49, 2.51		1.23[e]	1.32
$[(t\text{-BuNC})_4\text{Co}]_2(\text{tPf{=}Pf})[\text{PF}_6]_2$	8.50 (2), 8.68 (5), 8.97 (1)	2.42		3.27[f]	3.58
$[(t\text{-BuNC})_2\text{Co}(\text{Pf-Pf-Pf})][\text{PF}_6]$	8.85 (1), 8.93 (1)	2.1–2.9 m	7.32	0.72	0.69
$[(t\text{-BuNC})_2\text{Co}(\text{As-Pf-Asf})][\text{PF}_6]$	8.85	2.1–2.8 m	~7.5 br	0.72	0.77
$[(t\text{-BuNC})\text{CoP}(\text{-Pf})_3][\text{PF}_6]$	8.67	2.9	7.30, ~7.5 br	0.30	0.29
$[(t\text{-BuNC})_3\text{Co}]_2(\text{Pf-Pf-Pf-Pf})[\text{PF}_6]_2$	8.82	2.52–2.57	7.60 br	1.80	1.72
$[(t\text{-BuNC})_2\text{Co}]_2\text{P}_2(\text{-Pf})_4[\text{PF}_6]_2$	8.45 (1), 8.99 (1)	2.1–2.4, 2.5, 2.7–3.0	?	0.90	0.87
$[(t\text{-BuNC})_6\text{Mn}][\text{PF}_6]$	8.52				
$[(t\text{-BuNC})_5\text{MnPPh}_3][\text{PF}_6]$	8.46 (1), 8.69 (4)	2.4–2.6		3.00	3.00

[a] The ligand abbreviations are given in the Experimental Section. [b] All of these resonances were singlets. Relative intensities are given in parentheses. [c] The following abbreviations are used: m = multiplet, br = broad. [d] This refers to the ratio of the combined relative intensities of the resonances from the methyl protons of all of the *tert*-butyl isocyanide ligands to the combined relative intensities of all of the resonances arising from the phenyl protons of the trivalent phosphorus or arsenic ligand. [e] The calculated value of 1.23 for the $CH_3:C_6H_5$ ratio in $[(t\text{-BuNC})_3\text{Co}(\text{cPf{=}Pf})][\text{PF}_6]$ assumes that the resonance from the two vinyl protons of the cPf=Pf ligand is buried under the resonance from the 20 phenyl protons. If the resonance from these vinyl protons is located elsewhere, the calculated values for the $CH_3:C_6H_5$ ratio in this compound is 1.35. The signal-to-noise ratio in this nmr spectrum was insufficient for unambiguous location of the vinyl resonances of the cPf=Pf ligand. [f] The calculated value of 3.27 for the $CH_3:C_6H_5$ ratio in $[(t\text{-BuNC})_4\text{Co}]_2(\text{tPf{=}Pf})[\text{PF}_6]_2$ assumes that the resonance from the two vinyl protons of the tPf=Pf ligand is buried under the resonance from the 20 phenyl protons. If the resonance from these vinyl protons is located elsewhere, the calculated value for the $CH_3:C_6H_5$ ratio in this compound is 3.60. The signal-to-noise ratio in this nmr spectrum was insufficient for unambiguous location of the vinyl resonances of the tPf=Pf ligand.

The ν(CO) frequencies of metal carbonyl derivatives shift downward[11,13] upon successive replacement of the very strongly π-accepting carbonyl groups with the much weaker trivalent phosphorus or arsenic π acceptors because of the increased electron density on the metal atom for retrodative bonding to the remaining carbonyl groups. However, the π-acceptor strengths of the *tert*-butyl isocyanide and trivalent phosphorus or arsenic ligands are more nearly equal.[14] Therefore, successive replacement of the *tert*-butyl isocyanide ligands with trivalent phosphorus or arsenic ligands has very little effect on the electron density on the metal atom. This effect will make the retrodative bonding of the metal atom to the *tert*-butyl isocyanide ligands approximately the same regardless of the number of *tert*-butyl isocyanide ligands in the cation $[(t\text{-BuNC})_5\text{Co}]^+$ which are replaced with trivalent phosphorus or arsenic ligands. In accord with this idea, the ν(CN) frequencies in the (*tert*-butyl isocyanide)cobalt(I) cations change very little upon successive replacement of the *tert*-butyl isocyanide ligands with trivalent phosphorus or arsenic ligands. For example the single 2113-cm^{-1} ν(CN) frequency of the tetrasubstituted derivative $[(t\text{-BuNC})\text{CoP}(\text{-Pf})_3][\text{PF}_6]$ is very close to the 2151- and 2120-cm^{-1} ν(CN) frequencies of the unsubstituted $[(t\text{-BuNC})_5\text{Co}][\text{PF}_6]$.

The proton nmr spectrum of uncomplexed *tert*-butyl isocyanide exhibits a 1:1:1 triplet (J = 2.1 Hz) centered at τ 8.60 arising from the nine equivalent methyl protons split by the ^{14}N (I = 1) nucleus. In the octahedral manganese(I) complex $[(t\text{-BuNC})_6\text{Mn}][\text{PF}_6]$, the necessarily equivalent 54 protons of the six *tert*-butyl isocyanide ligands exhibit a sharp single proton nmr resonance indicating that splitting arising from nitrogen–hydrogen coupling is not a factor in the interpretation of the nmr spectra of complexed *tert*-butyl isocyanide. Apparently the electric field gradient around the quadrupolar ^{14}N nucleus is negligible in the free *tert*-butyl isocyanide ligand but appreciable in its metal complexes.

Interpretation of the nmr spectra of the *tert*-butyl isocyanide protons in the five-coordinate cobalt(I) derivatives is complicated by the possibility of stereochemical nonrigidity[15] which occurs in many five-coordinate structures. Thus the ^{13}C nmr spectrum of iron pentacarbonyl, with which the $[(t\text{-BuNC})_5\text{Co}]^+$ cation is isoelectronic, exhibits a single resonance even at temperatures as low as −63° despite the fact that the three equatorial carbonyl groups and the two axial carbonyl groups in iron pentacarbonyl are different.[16] Similarly, the salt $[(t\text{-BuNC})_5\text{Co}][\text{PF}_6]$ exhibited a single proton nmr resonance at ambient temperature suggesting equivalence of all *tert*-butyl isocyanide protons on the nmr time scale. However, cooling this solution caused this nmr resonance to split into two peaks with a chemical shift difference of about 0.08 ppm at −30° and 0.14 ppm at −60° and with the higher field resonance of distinctly lower relative intensity than the lower field resonance. This is consistent with the protons of the three equatorial and the two axial *tert*-butyl isocyanide ligands becoming nonequivalent on the nmr time scale at the lower temperatures. This shows that the cation $[(t\text{-BuNC})_5\text{Co}]^+$ is stereochemically nonrigid at ambient temperatures but becomes stereochemically rigid at lower temperatures. These observations indicate that complete interpretation of the nmr spectra of the five-coordinate cobalt(I) *tert*-butyl isocyanide derivatives discussed in this paper requires a temperature dependence study in order to evaluate the stereochemical rigidity of the particular five-coordinate system. Unfortunately, the limited solubility

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[13] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

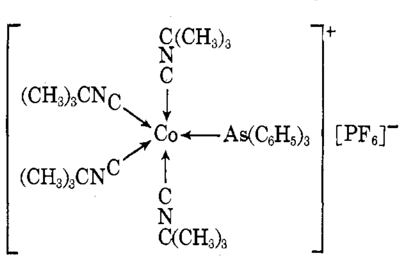
[14] M. Bigorgne, *Bull. Soc. Chim. Fr.*, 295 (1963).

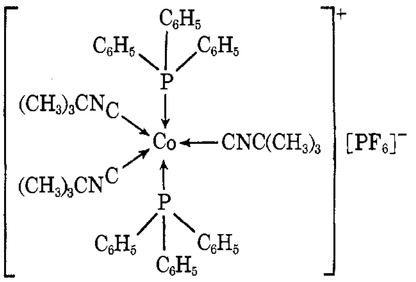
[15] E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970); P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687 (1971).

[16] (a) R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962); (b) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958).

of many of the five-coordinate cobalt(I) *tert*-butyl isocyanide derivatives in appropriate solvents, particularly below room temperature, and the limited stability of solutions of the cobalt complexes above room temperature restricted the scope of such temperature-dependence nmr studies.

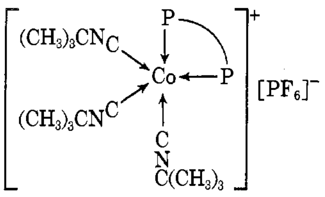
(2) **Derivatives of Monodentate Ligands.**—Triphenylarsine reacted with $[(t\text{-BuNC})_5Co][PF_6]$ in boiling ethanol to give only the monosubstituted derivative $[(t\text{-BuNC})_4CoAs(C_6H_5)_3][PF_6]$ even when 5 equiv of triphenylarsine for each equivalent of cobalt was used. The proton nmr spectrum of $[(t\text{-BuNC})_4CoAs(C_6H_5)_3][PF_6]$ exhibited two methyl resonances of equal relative intensities. This is consistent with formulation of $[(t\text{-BuNC})_4CoAs(C_6H_5)_3][PF_6]$ as a stereochemically rigid, equatorially substituted trigonal-bipyramidal derivative (I), which is the only one of the four possible isomers (considering both trigonal-bipyramidal and square-pyramidal coordination of the cobalt) which has the two *tert*-butyl isocyanide ligands of one type and the other two *tert*-butyl isocyanide ligands of another type as required by the nmr spectrum. The infrared spectrum clearly exhibited three of the four ν(CN) frequencies ($2\,A_1 + B_1 + B_2$) required for structure I. The missing ν(CN) frequency could easily be hidden among the two strongest ν(CN) frequencies at 2150 and 2122 cm^{-1}.

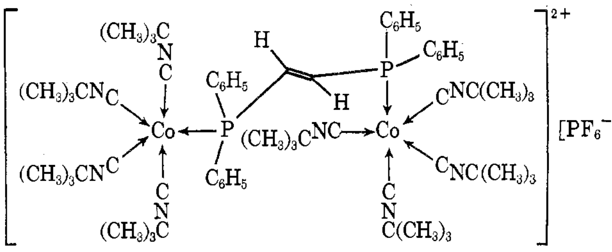

I


II

An attempt to prepare a monosubstituted triphenylphosphine derivative analogous to the above triphenylarsine derivative (I) by allowing 1 equiv of triphenylphosphine to react with 1 equiv of $[(t\text{-BuNC})_5Co][PF_6]$ gave instead the trans-disubstituted derivative *trans*-$[(t\text{-BuNC})_3Co[P(C_6H_5)_3]_2][PF_6]$ (II). The same trans-disubstituted derivative (II) was obtained when as many as 5 equiv of triphenylphosphine for each cobalt atom was used. The single strong ν(CN) frequency in the infrared spectrum of II confirms the trans configuration. The proton nmr spectrum of *trans*-$[(t\text{-BuNC})_3Co[P(C_6H_5)_3]_2][PF_6]$ exhibits the expected single methyl resonance in accord with the equivalence of the three *tert*-butyl isocyanide ligands. The nmr chemical shift of the *tert*-butyl isocyanide methyl protons in *trans*-$[(t\text{-BuNC})_3Co[P(C_6H_5)_3]_2][PF_6]$ was significantly higher (τ 9.29) than the nmr chemical shifts of the *tert*-butyl isocyanide methyl protons of any of the other complexes prepared in this work. This suggests that the aromatic rings of the two axial triphenylphosphine ligands shield the *tert*-butyl protons of the three equatorial *tert*-butyl isocyanide ligands.

(3) **Derivatives of Di(tertiary phosphines).**—The potentially chelating di(tertiary phosphines) $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ reacted with $[(t\text{-BuNC})_5Co][PF_6]$ in boiling ethanol to give the corresponding chelate (*i.e.*, biligate monometallic[17]) derivative $[(t\text{-BuNC})_3Co(\text{diphos})][PF_6]$. The infrared spectra of $[(t\text{-BuNC})_3Co(\text{Pf-Pf})][PF_6]$ exhibited three strong ν(CN) frequencies (2159, 2117, and 2101 cm^{-1}) in accord with its formulation as the cis isomer of type III. The infrared spectrum of $[(t\text{-BuNC})_3Co(\text{cPf}{=}\text{Pf})][PF_6]$ in the ν(CN) region (Table III) was similar to that of $[(t\text{-BuNC})_3Co(\text{Pf-Pf})][PF_6]$ except that the two lower ν(CN) frequencies were incompletely resolved and appeared as a broad band at 2114 cm^{-1}. The patterns of the infrared ν(CN) frequencies in the $[(t\text{-BuNC})_3Co(\text{diphos})][PF_6]$ derivatives (III) were very different from the single strong ν(CN) infrared frequency observed in the trans-disubstituted triphenylphosphine derivative *trans*-$[(t\text{-BuNC})_3Co[P(C_6H_5)_3]_2][PF_6]$.


III


IV

The proton nmr spectra of the two $[(t\text{-BuNC})_3Co(\text{diphos})][PF_6]$ derivatives of type III (Table IV) exhibited a single methyl resonance at τ 8.83 ± 0.03. Since the three *tert*-butyl isocyanide ligands in compounds of type III cannot be equivalent, this single nmr methyl resonance must indicate either a stereochemically nonrigid system or coincidentally identical shifts of the *tert*-butyl protons of the axial and equatorial *tert*-butyl isocyanide ligands in III. We feel that the latter possibility is much less probable since the nmr chemical shifts of the axial and equatorial *tert*-butyl groups in the triphenylarsine derivative $[(t\text{-BuNC})_4CoAs(C_6H_5)_3][PF_6]$ differ by more than 0.1 ppm. However, the single methyl nmr resonance in $[(t\text{-BuNC})_3Co(\text{cPf}{=}\text{Pf})][PF_6]$ from the *tert*-butyl isocyanide ligands remained unsplit at temperatures as low as −45°, suggesting that the stereochemical nonrigidity

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[17] R. B. King, *J. Coord. Chem.*, **1**, 67 (1971).

of this system is retained even at rather low temperatures.

In an attempt to prepare a compound with two chelating di(tertiary phosphines) bonded to a single cobalt atom, the reaction of excess $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ with $[(t\text{-BuNC})_5Co][PF_6]$ in the higher boiling 2-methoxyethanol was investigated. However, the only cobalt(I) *tert*-butyl isocyanide complex which could be isolated from the reaction mixture was $[(t\text{-BuNC})_3Co(\text{Pf-Pf})][PF_6]$.

The di(tertiary phosphine) *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ has its two phosphorus atoms located rigidly too far apart for both of them to bond to a single metal atom.[17,18] Reaction of this di(tertiary phosphine) with $[(t\text{-BuNC})_5Co][PF_6]$ in boiling ethanol gives the biligate bimetallic derivative $[(t\text{-BuNC})_4Co]_2(\text{tPf{=}Pf})[PF_6]_2$ in which the di(tertiary phosphine) bridges two cobalt atoms. The infrared spectrum of this complex in the ν(CN) region (Table III) resembled closely that of the monosubstituted triphenylarsine complex $[(t\text{-BuNC})_4CoAs(C_6H_5)_3][PF_6]$ (I) confirming the presence of monosubstituted $[(t\text{-BuNC})_4CoL]^+$ units in $[(t\text{-BuNC})_4Co]_2(\text{tPf{=}Pf})[PF_6]_2$. The proton nmr spectrum of $[(t\text{-BuNC})_4Co]_2(\text{tPf{=}Pf})[PF_6]_2$ (Table IV) was considerably more complex than that of $[(t\text{-BuNC})_4CoAs(C_6H_5)_3][PF_6]$; a possible rationalization of the observed 2:5:1 pattern in the methyl region of the nmr spectrum of the former complex is that one of the cobalt trigonal bipyramids has the phosphorus atom in the equatorial position and the other cobalt trigonal bipyramid has the phosphorus atom in the axial position which would lead to structure IV for $[(t\text{-BuNC})_4Co]_2(\text{tPf{=}Pf})[PF_6]_2$. The equatorially substituted cobalt atom in IV should give a methyl nmr pattern like that of $[(t\text{-BuNC})_4CoAs(C_6H_5)_3][PF_6]$ and the axially substituted cobalt atom in IV should exhibit two methyl nmr resonances in a 3:1 relative intensity ratio. If the methyl resonance of relative intensity 3 from the equatorial *tert*-butyl isocyanide ligands of the axially substituted cobalt atom coincides with one of the methyl resonances of relative intensity 2 from a pair of *tert*-butyl isocyanide ligands on the equatorially substituted cobalt atom, the observed 2:5:1 pattern of methyl nmr resonances is obtained.

(4) **Derivatives of Tridentate Ligands.**—The potentially tridentate ligands $[(C_6H_5)_2ECH_2CH_2]_2PC_6H_5$ (E = P or As) react with $[(t\text{-BuNC})_5Co][PF_6]$ in boiling ethanol to form triligate monometallic[17] derivatives of the type $[(t\text{-BuNC})_2Co(\text{tridentate})][PF_6]$. The infrared spectrum of each of these two complexes in the ν(CN) region (Table III) exhibits two strong bands of similar relative intensities and widths confirming the presence of two *tert*-butyl isocyanide ligands and indicating that at least one of these *tert*-butyl isocyanide ligands occupies an equatorial position of the cobalt trigonal bipyramid as in structure Va or Vb. The proton nmr spectrum of the phosphine–diarsine complex $[(t\text{-BuNC})_2Co(\text{Asf-Pf-Asf})][PF_6]$ exhibits a single methyl resonance whereas the proton nmr spectrum of the triphosphine complex $[(t\text{-BuNC})_2Co(\text{Pf-Pf-Pf})][PF_6]$ exhibits two methyl resonances of equal relative intensities (Table IV). However, upon heating a tetrachloroethylene solution of $[(t\text{-BuNC})_2Co(\text{Pf-Pf-Pf})][PF_6]$ to 70° or above, these two methyl resonances coalesce into a single resonance (Figure 1). These observations suggest that the limiting structure for the $[(t\text{-BuNC})_2Co(\text{tridentate})][PF_6]$ derivatives has the two *tert*-butyl isocyanide ligands slightly nonequivalent but that a dynamic process, which occurs at room temperature for the phosphine–diarsine derivative but only at 70° for the tri(tertiary phosphine) derivative, makes them equivalent. In structure Vb

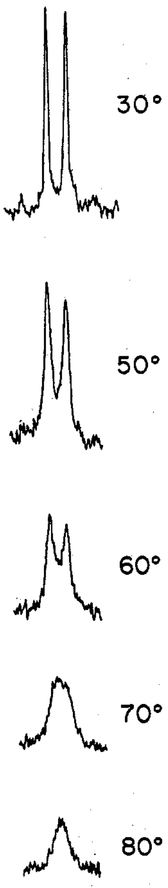
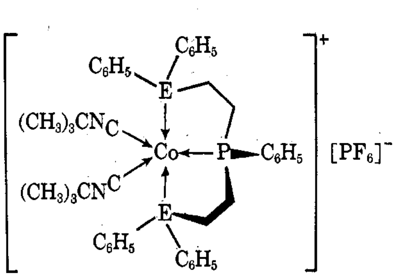
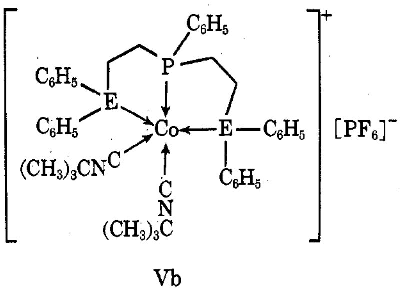


Figure 1.—Temperature dependence of the methyl resonances from the *tert*-butyl isocyanide ligands in $[(t\text{-BuNC})_2Co(\text{Pf-Pf-Pf})][PF_6]$.



Va



Vb

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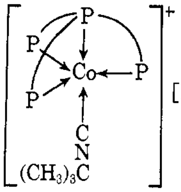
[18] (a) R. B. King, L. W. Houk, and P. N. Kapoor, *Inorg. Chem.*, **8**, 1792 1969); (b) R. B. King and A. Efraty, *ibid.*, **8**, 2374 (1969).

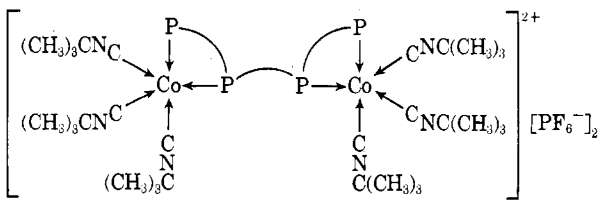
the two *tert*-butyl isocyanide ligands are nonequivalent because one occupies an equatorial and the other an axial position of the cobalt trigonal bipyramid. In structure Va the *tert*-butyl isocyanide ligands are slightly nonequivalent because the tetrahedral stereochemistry of the central phosphorus atom prevents the compounds from having a plane of symmetry which reflects one *tert*-butyl isocyanide ligand into the other without affecting the geometry of the chelate rings. Because of the very slight (0.08 ppm) nonequivalence of the methyl protons of the two *tert*-butyl isocyanide groups in $[(t\text{-BuNC})_2\text{Co(Pf-Pf-Pf)}][\text{PF}_6]$ as compared with the much larger nonequivalence (0.54 ppm) of the two types of methyl protons in the hexa(tertiary phosphine) complex $[(t\text{-BuNC})_2\text{Co}]_2\text{P}_2(\text{-Pf})_4[\text{PF}_6]_2$ (see below), we prefer to assign structures of the type Va to the complexes $[(t\text{-BuNC})_2\text{Co(tridentate)}][\text{PF}_6]$ assuming that the methyl protons in the equatorial and axial *tert*-butyl isocyanide ligands in a structure of the alternative type Vb would have a chemical shift difference around 0.5 ppm similar to that found in the hexa(tertiary phosphine) complex.

(5) **Derivatives of Tetra(tertiary phosphines) and Hexa(tertiary phosphines).**—The tripod tetra(tertiary phosphine) $[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2]_3\text{P}$ reacts with $[(t\text{-BuNC})_5\text{Co}][\text{PF}_6]$ in boiling ethanol to substitute four of the five *tert*-butyl isocyanide ligands with trivalent phosphorus atoms to give the tetraligate monometallic[17] derivative $[(t\text{-BuNC})\text{CoP(-Pf)}_3][\text{PF}_6]$ (VI). This was the most highly substituted derivative prepared during the course of this work. The compound $[(t\text{-BuNC})\text{CoP(-Pf)}_3][\text{PF}_6]$ (VI) exhibited the expected single ν(CN) infrared frequency and the single methyl nmr resonance arising from the single *tert*-butyl isocyanide ligand remaining bonded to the metal atom.

The reactions of the linear tetra(tertiary phosphine) $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ with $[(t\text{-BuNC})_5\text{Co}][\text{PF}_6]$ were also investigated. Attempts to prepare a compound of the type $[(t\text{-BuNC})\text{Co(tetraphos)}][\text{PF}_6]$ analogous to VI by the reaction of equimolar quantities of the linear tetra(tertiary phosphine) and $[(t\text{-BuNC})_5\text{Co}][\text{PF}_6]$ failed to give a pure product as indicated particularly by the complicated proton nmr spectra in the methyl region. However, the reaction of the linear tetra(tertiary phosphine) Pf-Pf-Pf-Pf with 2 equiv of $[(t\text{-BuNC})_5\text{Co}][\text{PF}_6]$ in boiling ethanol gave a tetraligate bimetallic derivative $[(t\text{-BuNC})_3\text{Co}]_2\text{(Pf-Pf-Pf-Pf)}[\text{PF}_6]_2$ (VII). The infrared (Table III) and proton nmr spectra in the methyl region (Table IV) of $[(t\text{-BuNC})_3\text{Co}]_2\text{(Pf-Pf-Pf-Pf)}[\text{PF}_6]_2$ were essentially identical with those of the $[(t\text{-BuNC})_3\text{Co(diphos)}][\text{PF}_6]$ derivatives confirming structure VII which may be regarded as two $[(t\text{-BuNC})_3\text{Co(diphos)}][\text{PF}_6]$ units joined by phosphorus–carbon and carbon–carbon bonds in the linear tetra(tertiary phosphine). These spectral data exclude the possibility that $[(t\text{-BuNC})_3\text{Co}]_2\text{(Pf-Pf-Pf-Pf)}[\text{PF}_6]_2$ contains one $(t\text{-BuNC})_4\text{Co}$ group and one $(t\text{-BuNC})_2\text{Co}$ group rather than two $(t\text{-BuNC})_3\text{Co}$ groups as in structure VII.

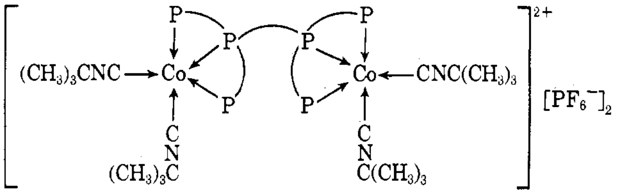


VI

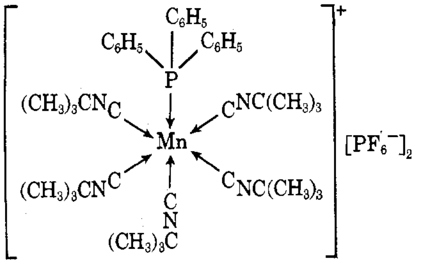


VII

The hexa(tertiary phosphine) $[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2]_2\text{PCH}_2\text{CH}_2\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2$ reacts with 2 equiv of $[(t\text{-BuNC})_5\text{Co}][\text{PF}_6]$ in boiling ethanol to give the hexaligate bimetallic derivative $[(t\text{-BuNC})_2\text{Co}]_2\text{P}_2(\text{-Pf})_4[\text{PF}_6]_2$. The infrared spectrum of this complex in the ν(CN) region (Table III) was very similar to that of the $[(t\text{-BuNC})_2\text{Co(tridentate)}][\text{PF}_6]$ derivatives discussed above (tridentate = Pf-Pf-Pf or Asf-Pf-Asf) indicating that the complex $[(t\text{-BuNC})_2\text{Co}]_2\text{P}_2(\text{-Pf})_4[\text{PF}_6]_2$ has structure VIII with two $(t\text{-BuNC})_2\text{Co}$ units rather than one $t\text{-BuNCCo}$ and one $(t\text{-BuNC})_3\text{Co}$ unit or one $(t\text{-BuNC})_4\text{Co}$ unit and the other cobalt atom bonded only to five of the six trivalent phosphorus atoms in the $\text{P}_2(\text{-Pf})_4$ ligand. The proton nmr spectrum of $[(t\text{-BuNC})_2\text{Co}]_2\text{P}_2(\text{-Pf})_4[\text{PF}_6]_2$ exhibits two methyl resonances at τ 8.45 and 8.99 of equal relative intensities. This pattern is very different from the nmr spectrum of the methyl protons in either $[(t\text{-BuNC})_2\text{Co(tridentate)}][\text{PF}_6]$ derivative where the compound containing the tri(tertiary phosphine) Pf-Pf-Pf exhibits two closely spaced methyl resonances of equal intensity which coalesce at about 70° (Figure 1) and the compound containing the phosphine–diarsine Asf-Pf-Asf exhibits a single methyl resonance even at ambient temperature. We therefore propose structure VIII for $[(t\text{-BuNC})_2\text{Co}]_2\text{P}_2(\text{-Pf})_4[\text{PF}_6]_2$ in which two of the *tert*-butyl isocyanide ligands are in axial positions and the other two in equatorial positions.



VIII



IX

B. **Manganese(I) Derivatives.**—The reactivity of the six-coordinate manganese(I) *tert*-butyl isocyanide complex $[(t\text{-BuNC})_6\text{Mn}][\text{PF}_6]$ toward trivalent phosphorus and arsenic ligands was considerably less than that of the five-coordinate cobalt(I) *tert*-butyl isocyanide complex [(*t*-BuNC)$_5$Co][PF$_6$] discussed above. Unchanged [(*t*-BuNC)$_6$Mn][PF$_6$] was the only manganese(I) complex recovered from its reactions with several of the trivalent phosphorus and arsenic ligands in boiling ethanol. Even in boiling diglyme the [(*t*-BuNC)$_6$Mn][PF$_6$] was recovered unchanged from its attempted reactions with all of the trivalent phosphorus ligands tried except for triphenylphosphine. This lower reactivity of [(*t*-BuNC)$_6$Mn][PF$_6$] relative to [(*t*-BuNC)$_5$Co][PF$_6$] is the expected trend for an octahedral complex relative to a trigonal–bipyramidal complex and is similar to the lower reactivity of Cr(CO)$_6$ relative to Fe(CO)$_5$.[19]

The reaction between [(*t*-BuNC)$_6$Mn][PF$_6$] and triphenylphosphine in boiling diglyme gave a low yield of the yellow crystalline monosubstituted derivative [(*t*-BuNC)$_5$MnP(C$_6$H$_5$)$_3$][PF$_6$] (IX) which had to be separated from unchanged [(*t*-BuNC)$_6$Mn][PF$_6$] by hand picking the crystals. The infrared spectrum of [(*t*-BuNC)$_5$MnP(C$_6$H$_5$)$_3$][PF$_6$] (IX) exhibited three ν(CN) frequencies in accord with the C_{4v} symmetry of the complex cation. The weak ν(CN) band at 2166 cm^{-1} may be assigned to the A$_1$ mode of the C_{4v} system. The remaining ν(CN) bands at 2093 and 2059 cm^{-1} are strong and may be assigned to the other A$_1$ mode and the E mode. The proton nmr spectrum of [(*t*-BuNC)$_5$MnP(C$_6$H$_5$)$_3$][PF$_6$] exhibited two methyl resonances with a 1:4 relative intensity ratio. The less intense resonance can be assigned to the nine methyl protons of the single axial *tert*-butyl isocyanide ligand and the more intense resonance can be assigned to the 36 methyl protons of the four equivalent equatorial *tert*-butyl isocyanide ligands.

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[19] R. B. King, "Transition Metal Organometallic Chemistry: An Introduction," Academic Press, New York, N. Y., 1969.

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Organometallic Transition Metal Derivatives Containing Fluorine. V. Some Perfluoro-1-methylpropenyl Derivatives of Metal Carbonyls and Metal Cyclopentadienyls[1,2]

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Reactions of various transition metal halide derivatives with perfluoro-1-methylpropenylsilver, C$_4$F$_7$Ag, in dichloromethane solution at room temperature give the corresponding perfluoro-1-methylpropenyl transition metal derivatives. Thus reactions of the metal pentacarbonyl bromides M(CO)$_5$Br (M = Mn and Re) with C$_4$F$_7$Ag give the volatile white crystalline C$_4$F$_7$M(CO)$_5$ (M = Mn and Re). Similarly, treatment of C$_5$H$_5$Fe(CO)$_2$I with C$_4$F$_7$Ag gives the volatile yellow crystalline C$_4$F$_7$Fe(CO)$_2$C$_5$H$_5$. Reaction of C$_5$H$_5$Cr(NO)$_2$Cl with C$_4$F$_7$Ag gives the volatile green crystalline C$_4$F$_7$Cr(NO)$_2$C$_5$H$_5$. Reactions of the fluorocarbon transition metal halides R$_f$Fe(CO)$_4$I (R$_f$ = C$_2$F$_5$, CF$_3$CF$_2$CF$_2$, and (CF$_3$)$_2$CF) and C$_5$H$_5$Co(CO)(R$_f$)I (R$_f$ = C$_2$F$_5$ and CF$_3$CF$_2$CF$_2$) with C$_4$F$_7$Ag give volatile pale yellow R$_f$Fe(CO)$_4$C$_4$F$_7$ (R$_f$ = C$_2$F$_5$, CF$_3$CF$_2$CF$_2$, and (CF$_3$)$_2$CF) and volatile yellow C$_5$H$_5$Co(CO)(R$_f$)(C$_4$F$_7$) (R$_f$ = C$_2$F$_5$ and CF$_3$CF$_2$CF$_2$), respectively. The infrared, fluorine nmr, and mass spectra of these new compounds are discussed.

Introduction

Within the last decade fluorocarbon transition metal derivatives have received considerable attention largely because of their stability relative to their hydrocarbon analogs.[3] Such compounds are prepared by the following general methods: (1) reactions of metal carbonyl anions with perfluoroacyl derivatives followed by decarbonylation; (2) nucleophilic substitution of fluoride with metal carbonyl groups by reactions of fluorinated olefins or aromatic compounds with metal carbonyl anions;[4] (3) addition of fluoroolefins, fluorinated alkynes, or perfluoroalkyl iodides to appropriate transition metal systems, particularly those in lower oxidation states; (4) reactions of metal halide derivatives with fluoroalkyl or fluoroaryl derivatives of electropositive metals such as lithium or magnesium. This repertoire of preparative methods in fluorocarbon transition metal chemistry has the following limitations: (1) the need of a sufficiently nucleophilic metal carbonyl anion for the reactions with perfluoroacyl derivatives, fluoroolefins, and fluorinated aromatic compounds (methods 1 and 2 above) or the need of an appropriately reactive low-oxidation-state derivative for the reactions with fluoroolefins, fluorinated alkynes, or perfluoroalkyl iodides (method 3 above); (2) the instability of many fluorocarbon derivatives of electropositive metals such as lithium or magnesium coupled with the high reactivity of organometallic derivatives of such electropositive metals which makes them able to effect undesirable side reactions (method 4). For these

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[1] For part IV of this series see R. B. King, R. N. Kapoor, and K. H. Pannell, *J. Organometal. Chem.*, **20**, 187 (1969).

[2] Portions of this work were presented to the Division of Fluorine Chemistry at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971; see Abstract FLUO-7.

[3] For a review article discussing fluorocarbon transition metal derivatives, see P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, **1**, 143 (1964).

[4] For a review of nucleophilic reactions of metal carbonyl anions with fluorocarbons, see M. I. Bruce and F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, **7**, 747 (1968).