

Contribution from the Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210**Stereochemistry and Exchange Processes in Five-Coordinate
Cobalt(I) Complexes Containing One of Three Triphosphine Ligands¹**DANIEL L. DuBOIS² and DEVON W. MEEK*

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Six extensive series of five-coordinate complexes of the types $[\text{Co}(\text{triphos})(\text{CO})_2]\text{X}$ and $[\text{Co}(\text{triphos})\text{L}(\text{CO})]\text{X}$ ($\text{X} = \text{BF}_4$, PF_6 ; $\text{L} = \text{P}(\text{OMe})_3$, PPh_2H , PPh_2Me , PEt_3 , PPh_3 ; $\text{triphos} =$ either bis(3-diphenylphosphinopropyl)phenylphosphine (ttp), bis(2-diphenylphosphinoethyl)phenylphosphine (etp), or 1,1,1-tris(diphenylphosphinomethyl)ethane (tripod- P_3)) were synthesized and their stereochemistry and dynamic behavior studied principally by $^{31}\text{P}\{^1\text{H}\}$ NMR. The details of the stereochemistry and exchange processes depend both on the monodentate ligand and on the triphosphine ligand. For example, the $[\text{Co}(\text{etp})\text{L}(\text{CO})]\text{X}$ and $[\text{Co}(\text{etp})(\text{CO})_2]\text{X}$ complexes are trigonal bipyramidal with the equatorial positions occupied by a carbonyl ligand and the two terminal phosphorus atoms of the triphosphine ligand; the axial positions are occupied by the central phosphorus atom and either a monophosphine or a carbonyl ligand, respectively. The $[\text{Co}(\text{ttp})\text{L}(\text{CO})]\text{X}$ complexes have square-pyramidal structures with L located at the axial position. A trigonal-bipyramidal structure is assigned to the dicarbonyl complexes $[\text{Co}(\text{ttp})(\text{CO})_2]\text{X}$. The complexes $[\text{Co}(\text{tripod-}\text{P}_3)\text{L}(\text{CO})]\text{X}$ are stereochemically nonrigid, whereas those of $[\text{Co}(\text{etp})\text{L}(\text{CO})]\text{X}$ are stereochemically rigid at room temperature. A large number of $^2J_{\text{PP}}$ coupling constants are presented for these complexes.

Introduction

The stereochemistry³⁻⁸ and intramolecular exchange processes^{3,7,8} of a number of five-coordinate complexes of cobalt(I) have been investigated. The preferred geometry in most cases appears to be based on a trigonal bipyramid,^{3,4,9} although square-pyramidal complexes are also known.^{5,10} In examples with monodentate ligands, the energy differences between the two limiting structures are small for $d^8 \text{ML}_5$ complexes;^{3,11} in addition, structures intermediate between the idealized trigonal-bipyramidal and square-pyramidal structures are fairly common.⁴ Six series of complexes of the types $[\text{Co}(\text{triphos})(\text{CO})_2]\text{X}$ and $[\text{Co}(\text{triphos})\text{L}(\text{CO})]\text{X}$ ($\text{triphos} =$ one of the three triphosphine ligands: bis(2-diphenylphosphinoethyl)phenylphosphine (etp),¹² bis(3-diphenylphosphinopropyl)phenylphosphine (ttp),¹² and 1,1,1-tris(diphenylphosphinomethyl)ethane (tripod- P_3);¹² $\text{L} = \text{P}(\text{OMe})_3$, PPh_2H , PPh_3 , PPh_2Me , and PEt_3 ; $\text{X} = \text{BF}_4^-$ or PF_6^-) have been studied and the results are reported herein. Subtle changes in the steric and electronic properties of the three triphosphine ligands cause variations in the stereochemistry of the five-coordinate cobalt(I) complexes, as has been observed for other metals.¹³⁻¹⁶ Recent preparations of efficient hydrogenation catalysts of cobalt containing two of the triphosphine ligands¹⁷ are additional incentives for studying the influence of different triphosphine ligands on the stereochemistry and exchange processes, since they are expected to be important in the mechanistic details of these catalysts.

Experimental Section

Physical Measurements. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra of the solid complexes were recorded on a Perkin-Elmer 337 spectrometer as Nujol mulls suspended between KBr plates. Infrared spectra of dichloromethane solutions of the compounds were recorded on a Beckman IR-9 spectrometer. Proton NMR spectra were recorded on a Varian A60-A, a Varian HA-100, or a Jeolco MH-100 spectrometer. Fourier-mode, proton-noise-decoupled ^{31}P NMR spectra were obtained on a Bruker HX-90 spectrometer that was equipped with a variable temperature probe. The ^{31}P NMR spectra were obtained on solutions of the samples using spinning 10-mm tubes, deuterated solvents for the internal lock, and 85% H_3PO_4 as an external standard. Positive chemical shifts are *downfield* from the H_3PO_4 standard. Conductance measurements were obtained as described previously.¹⁸

Materials. Organic solvents were reagent grade and were deoxygenated with either purified nitrogen or argon prior to use. Diphenylphosphine, diphenylmethylphosphine, triethylphosphine, and bis(2-diphenylphosphinoethyl)phenylphosphine were obtained from Pressure Chemical Co., Pittsburgh, Pa. Bis(3-diphenylphosphino-

propyl)phenylphosphine was prepared as described previously,¹⁹ and 1,1,1-tris(diphenylphosphinomethyl)ethane was obtained from Orgmet, Inc., East Hampstead, N.H. Trimethyl phosphite (Eastman Chemical Co.) was distilled from sodium under a nitrogen atmosphere. Preparation of the hydride complexes $\text{HCo}(\text{etp})\text{CO}$, $\text{HCo}(\text{ttp})\text{CO}$, and $\text{HCo}(\text{tripod-}\text{P}_3)\text{CO}$ will be described in another paper.¹⁷

Preparation of the Complexes. All reactions were carried out under nitrogen, using procedures that are detailed below for one or two complexes of each triphosphine ligand. The other preparations are summarized in Table I. Elemental analyses for the complexes are given in Table II.

(I) Preparations of $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]\text{BF}_4$ and $[\text{Co}(\text{etp})\text{L}(\text{CO})]\text{X}$ Complexes. (a) $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]\text{BF}_4$. Trimethyl phosphite (4 ml) and ammonium tetrafluoroborate (0.3 g) were added sequentially to a slurry of $\text{HCo}(\text{etp})\text{CO}$ (0.92 g) in methanol (70 ml). The reaction mixture was refluxed for 2 h, and the resultant yellow solution was filtered while hot. The filtrate was irradiated with ultraviolet light (350 nm) for 18 h. During the irradiation period the reaction flask was swept with nitrogen to remove the carbon monoxide. The volume of the resultant red solution was reduced to 20 ml and an oil precipitated when ca. 30 ml of ether was added. The solvent was decanted and the oil was washed sequentially with diethyl ether and water. The red oil was dissolved in methanol and red crystals were obtained from the solution by slowly adding ether, and cooling the resulting solution overnight in a refrigerator. The crystals were collected on a frit and dried *in vacuo*. Yield, 0.64 g, 47%.

(b) $[\text{Co}(\text{etp})(\text{CO})_2]\text{PF}_6$. Carbon monoxide was bubbled through a slurry of $\text{HCo}(\text{etp})\text{CO}$ (0.55 g) in refluxing ethanol (70 ml). On addition of ammonium hexafluorophosphate (0.3 g), the yellow crystals of $\text{HCo}(\text{etp})\text{CO}$ dissolved (ca. 15 min) to give a clear yellow solution. The resultant solution was refluxed an additional 10 min, and then the hot solution was filtered. The filtrate was cooled to room temperature, and its volume was reduced to ca. 20 ml *in vacuo*. The resultant yellow, microcrystalline product was collected on a filter and washed with three 10-ml aliquots of water and three 10-ml aliquots of diethyl ether. Yield, 0.57 g, 82%.

(c) $[\text{Co}(\text{etp})(\text{PEt}_3)_2]\text{BF}_4$. Triethylphosphine (0.5 ml) was added via a syringe to a refluxing slurry of $\text{HCo}(\text{etp})\text{CO}$ in ethanol (90 ml). On addition of ammonium tetrafluoroborate (0.3 g) the $\text{HCo}(\text{etp})\text{CO}$ dissolved (ca. 30 min) to give a yellow solution. The reaction solution was refluxed for 1 h and filtered while hot. The filtrate was cooled to room temperature and its volume was reduced *in vacuo* to ca. 20 ml. The resultant yellow crystals were collected on a filter and washed sequentially with diethyl ether (three 10-ml aliquots), water (three 10-ml aliquots), and diethyl ether (three 10-ml aliquots). Yield, 0.72 g, 89%.

(2) Preparations of $[\text{Co}(\text{ttp})\text{L}(\text{CO})]\text{X}$ Complexes. (a) $[\text{Co}(\text{ttp})(\text{CO})_2]\text{BF}_4$. Carbon monoxide was bubbled through a slurry of $\text{HCo}(\text{ttp})\text{CO}$ (0.28 g) in ethanol (50 ml). Ammonium tetrafluoroborate (0.15 g) was added, and the reaction mixture was refluxed for 2 h. The resultant clear, yellow solution was filtered while hot. The filtrate was cooled to room temperature, and its volume was

Table I. Reaction Conditions for the Preparation of [Co(triphos)L(CO)]X and [Co(triphos)(CO)₂]X Complexes^{1,2}

Product	HCo-(triphos)CO, g	NH ₄ X, g	L, ml	Solv, ml ^a	Reaction time, h	Yield, g (%)
[Co(etp)(CO) ₂]PF ₆	0.55	0.3		70 (e)	1/2	0.57 (82)
[Co(etp)(CO) ₂]BF ₄	1.00	0.4		80 (e)	3/4	0.94 (80)
[Co(etp)(P(OMe) ₃)CO]BF ₄	0.60	0.2	0.4	80 (m)	1/2	0.68 (85)
[Co(etp)(PPh ₂ H)CO]PF ₆	0.63	0.3	0.4	40 (e)	1/2	0.80 (84)
[Co(etp)(PPh ₂ H)CO]BF ₄ ^b	0.60	0.3	1.0	70 (m)	2	0.70 (81)
[Co(etp)(PPh ₃)CO]BF ₄	0.60	0.3	0.4 (g)	60 (e)	1/2	0.69 (74)
[Co(etp)(PPh ₂ Me)CO]BF ₄ ·EtOH	0.61	0.2	0.3	60 (e)	1/2	0.75 (80)
[Co(etp)(PEt ₃)CO]BF ₄	0.61	0.3	0.5	90 (e)	1	0.72 (89)
[Co(ttp)(CO) ₂]PF ₆ ^c	0.52	0.3		60 (e)	2	0.49 (75)
[Co(ttp)(CO) ₂]BF ₄	0.28	0.15		50 (e)	2	0.30 (91)
[Co(ttp)(PPh ₂ H)CO]BF ₄	0.72	0.4	0.6	80 (m)	4	0.55 (54)
[Co(ttp)(P(OMe) ₃)CO]BF ₄	0.43	0.3	0.5	50 (m)	5	0.41 (73)
[Co(tripod-P ₃)(CO) ₂]PF ₆ ^d	0.80	0.4		70 (e)	5	0.76 (77)
[Co(tripod-P ₃)(P(OMe) ₃)CO]BF ₄	0.55	0.3	0.4	80 (m)	3	0.54 (77)
[Co(tripod-P ₃)(PPh ₂ H)CO]BF ₄	0.60	0.4	0.5	70 (m)	24	0.33 (40)
[Co(tripod-P ₃)(PEt ₃)CO]BF ₄	0.70	0.4	0.5	70 (m)	24	0.64 (71)

^a (e) and (m) designate the solvents ethanol and methanol, respectively. ^b This complex required recrystallization from dichloromethane-ethanol and dichloromethane-benzene to remove excess diphenylphosphine. ^c This complex has also been prepared by a different procedure.^{19b} ^d The tetraphenylborate salt of this complex has also been prepared.^{20b}

Table II. Characterization Data for the [Co(triphos)L(CO)]X and [Co(triphos)(CO)₂]X Complexes^{1,2}

	Elemental Anal., %						ν(CO), cm ⁻¹		ΔM, Ω ⁻¹ cm ² /mol ⁻¹ ^a
	C		H		Co		Nujol mull	CH ₂ Cl ₂ soln	
	Calcd.	Found	Calcd.	Found	Calcd.	Found			
[Co(etp)(CO) ₂]PF ₆	54.42	54.20	4.19	4.07	7.42	7.22	1980, 2020	1983, 2028	79
[Co(etp)(CO) ₂]BF ₄	58.72	58.63	4.52	4.63	8.00	8.00	1980, 2020	1983, 2028	82
[Co(etp)(P(OMe) ₃)CO]BF ₄	54.83	54.60	5.09	5.12	7.08	7.26	1945	1953	84
[Co(etp)(PPh ₂ H)CO]BF ₄	63.11	63.20	4.96	5.02	6.59	6.39	1930	1939	69
[Co(etp)(PPh ₂ H)CO]PF ₆	59.26	59.48	4.66	4.65	6.18	5.98	1925	1939	67
[Co(etp)(PPh ₃)CO]BF ₄	65.59	65.90	4.98	5.16	6.07	6.29	1930	1940 isomer A 1959 isomer B	78
[Co(etp)(PPh ₂ Me)CO]BF ₄ ·EtOH	62.91	62.86	5.49	5.44	6.17	6.39	1930	1938	75
[Co(etp)(PEt ₃)CO]BF ₄	59.58	59.37	5.85	5.91	7.13	7.20	1930	1931	76
[Co(ttp)(CO) ₂]BF ₄	59.71	59.77	4.88	5.00	7.71	7.60	1940, 2000	1953, 2007	84
[Co(ttp)(P(OMe) ₃)CO]BF ₄	55.84	55.02	5.39	5.46	6.85	6.65	1920	1935	80
[Co(ttp)(PPh ₂ H)CO]BF ₄	63.80	63.77	5.24	5.16	6.39	6.27	1920	1931	82
[Co(tripod-P ₃)(CO) ₂]PF ₆	58.38	58.20	4.44	4.50	6.66	6.48	1953, 2026	1972, 2029	80
[Co(tripod-P ₃)(P(OMe) ₃)CO]BF ₄	58.59	58.41	5.24	5.30	6.39	6.16	1930	1931	84
[Co(tripod-P ₃)(PPh ₂ H)CO]BF ₄	65.87	65.99	5.12	5.20	5.98	6.00	1905	1918	81
[Co(tripod-P ₃)(PEt ₃)CO]BF ₄	62.90	62.81	5.94	5.87	6.43	6.36	1890	1911	82

^a Molar conductance values in ~10⁻³ M nitromethane solutions.

reduced to 15 ml. The resultant yellow, crystalline solid was collected on a filter, washed with water and diethyl ether, and dried in vacuo. Yield, 0.30 g, 91%.

(b) [Co(ttp)(P(OMe)₃)CO]BF₄. Ammonium tetrafluoroborate (0.3 g) was added to a slurry of HCo(ttp)CO (0.43 g) and trimethyl phosphite (0.5 ml) in methanol (50 ml). The reaction mixture was refluxed for 5 h to give a clear, red-orange solution. The solution was filtered while hot, and the volume of the filtrate was reduced to 20 ml. The orange, microcrystalline product was collected on a frit, washed with diethyl ether and water, and dried in vacuo. Yield, 0.41 g, 73%.

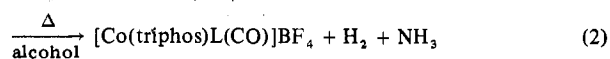
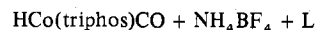
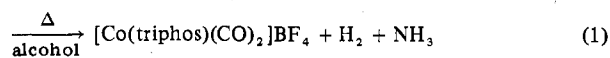
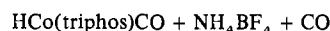
(3) Preparations of [Co(tripod-P₃)L(CO)]X Complexes. (a) [Co(tripod-P₃)(CO)₂]PF₆. This complex was prepared by a procedure similar to that used for the dicarbonyl complexes of etp and ttp. This compound has also been prepared by two other procedures.²⁰

(b) [Co(tripod-P₃)(PEt₃)CO]BF₄. Triethylphosphine (1 ml) was added to a slurry of HCo(tripod-P₃)CO (0.80 g) and ammonium tetrafluoroborate (0.5 g) in methanol (70 ml). The reaction mixture was refluxed 24 h and filtered while hot. The volume of the filtrate was reduced to 15 ml in vacuo, and the resultant orange powder was collected on a frit and washed sequentially with diethyl ether, water, and diethyl ether. Yield, 0.64 g, 71%.

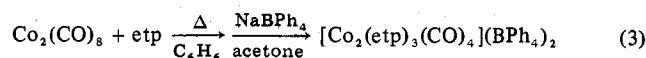
Results

Preparation and Characterization of the Complexes. Treatment of the hydride complexes HCo(etp)CO, HCo(ttp)CO, and HCo(tripod-P₃)CO with a weak acid (i.e., NH₄BF₄ or NH₄PF₆) in the presence of carbon monoxide or

a monodentate phosphine ligand provides a general synthesis for the complexes [Co(triphos)(CO)₂]X and [Co(triphos)L(CO)]X (eq 1-2). This route offers distinct advantages



over those that directly add the ligand to compounds such as Co₂(CO)₈. Difficulties (e.g., polymeric complexes) are often encountered when the polyphosphine ligand is added directly to a low-valent cobalt reagent (e.g., eq 3).²¹ Treatment of



HCo(triphos)CO with NH₄X is particularly useful for synthesis of the "mixed" complexes [Co(triphos)L(CO)]X, since such complexes are difficult to obtain by other synthetic procedures. The bisphosphite complex [Co(etp)(P(OMe)₃)₂]BF₄ may be obtained by irradiation of [Co(etp)(P(OMe)₃)CO]BF₄ in the presence of excess trimethyl phosphite. However, we were unable to obtain the analogous

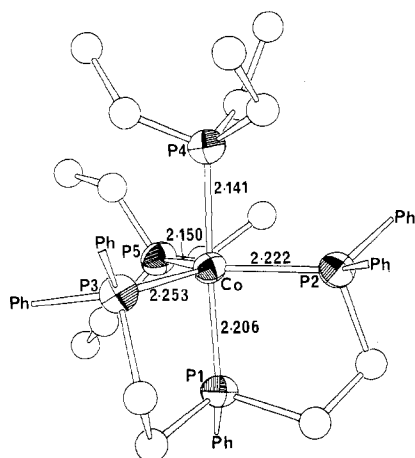


Figure 1. A perspective of the coordination geometry of the cation $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]^+$. The phenyl groups on the phosphorus atoms and the hydrogen atoms on the other atoms have been omitted for clarity.

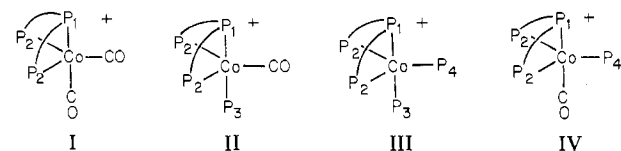
ttp complex by this procedure.

The yellow to orange complexes $[\text{Co}(\text{etp})(\text{CO})_2]\text{X}$ and $[\text{Co}(\text{etp})\text{L}(\text{CO})]\text{X}$ ($\text{X} = \text{BF}_4$ or PF_6) are stable indefinitely in the solid state, but their solutions are moderately sensitive to oxygen. In contrast, the analogous complexes $[\text{Co}(\text{ttp})\text{L}(\text{CO})]\text{X}$ and $[\text{Co}(\text{tripod-}P_3)\text{L}(\text{CO})]\text{X}$ are thermally unstable at 100°C in vacuo and slightly air sensitive even in the solid state.

The complexes $[\text{Co}(\text{triphos})(\text{CO})_2]\text{X}$ and $[\text{Co}(\text{triphos})\text{L}(\text{CO})]\text{X}$ have been characterized by conductivity measurements in nitromethane (Table II), elemental analyses (Table II), and infrared (Table II), proton NMR (Table III), and phosphorus-31 NMR spectra (Table IV). Infrared spectra (Nujol mulls) of all the $[\text{Co}(\text{triphos})\text{L}(\text{CO})]\text{X}$ complexes show only one carbonyl stretching frequency; the dicarbonyl complexes show two ν_{CO} absorptions, as expected for the symmetric and antisymmetric carbonyl stretching vibrations. Two ν_{CO} infrared bands are observed for a dichloromethane solution of $[\text{Co}(\text{etp})(\text{PPh}_3)(\text{CO})]\text{BF}_4$, and this is attributed to the formation of two isomers in solution (vide infra). In addition, the ^{31}P and ^1H NMR spectral data for the complexes $[\text{Co}(\text{etp})\text{L}(\text{CO})]\text{X}$, $[\text{Co}(\text{ttp})\text{L}(\text{CO})]\text{X}$, and $[\text{Co}(\text{tripod-}P_3)\text{L}(\text{CO})]\text{X}$ (Tables III and IV) indicate one monophosphine ligand and one triphosphine ligand is present in each complex. The fluxional nature of the $[\text{Co}(\text{tripod-}P_3)\text{L}(\text{CO})]\text{X}$ complexes prevented determination of phosphorus-phosphorus coupling constants for this series of complexes.

Stereochemistry of the Complexes

Complexes of the etp Ligand. Structures I-III show the stereochemistries that are assigned to the $[\text{Co}(\text{etp})(\text{CO})_2]\text{X}$, $[\text{Co}(\text{etp})\text{L}(\text{CO})]\text{X}$, and $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]\text{X}$ complexes, respectively. Structure IV is assigned to isomer B of $[\text{Co}(\text{etp})(\text{PPh}_3)\text{CO}]\text{BF}_4$. These assignments are based on (1) the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, (2) the ν_{CO} values from the infrared spectra of the complexes in solution and (3) the x-ray structural determination of $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]\text{BF}_4$ (Figure 1). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (and a simulated spectrum) of $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]\text{BF}_4$ is presented in Figure 2,²² the spectrum shows that the two terminal phosphorus atoms of coordinated etp are equivalent. As can be seen from structure



(I) the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, (2) the ν_{CO} values from the infrared spectra of the complexes in solution and (3) the x-ray structural determination of $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]\text{BF}_4$ (Figure 1). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (and a simulated spectrum) of $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]\text{BF}_4$ is presented in Figure 2,²² the spectrum shows that the two terminal phosphorus atoms of coordinated etp are equivalent. As can be seen from structure

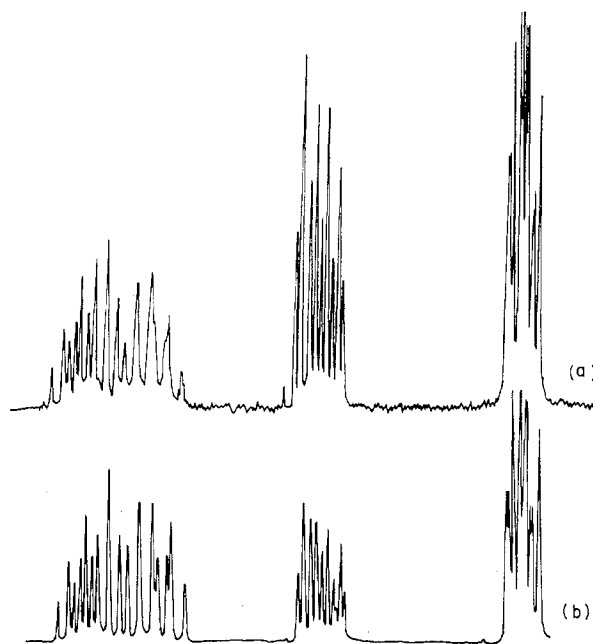


Figure 2. (a) The Fourier-mode $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]\text{BF}_4$ in dichloromethane at 257 K ; (b) the simulated spectrum of $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]\text{BF}_4$, using the parameters listed in Table IV and a value of 12 Hz for the line width at half-height. (See ref 22.)

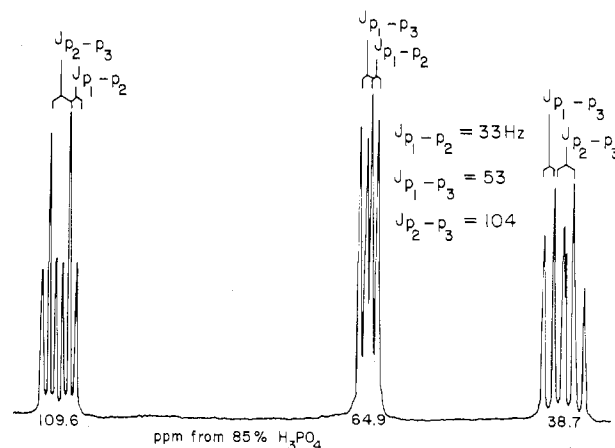


Figure 3. The Fourier-mode $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Co}(\text{etp})(\text{PEt}_3)\text{CO}]\text{BF}_4$ at 244 K in acetonitrile.

III and Table IV, the largest P-P coupling ($^2J_{P_1-P_3} = -193.5\text{ Hz}$) in $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]\text{BF}_4$ results from coupling of the two axial phosphorus atoms. The $\text{P}(\text{OMe})_3\text{-P}(\text{OMe})_3$ coupling is fairly large (136.5 Hz) for a $^2J_{\text{PP}}$ that involves a P-M-P angle of ca. 90° ; the other equatorial-axial $^2J_{\text{PP}}$ couplings are approximately 100 Hz (Table IV). Structurally related M-P and P-P coupling constants are generally larger for phosphite complexes than for phosphine complexes of transition metals;²³⁻²⁵ the same trend is observed in these cobalt(I) complexes (Table IV). The ^{31}P spectrum of $[\text{Co}(\text{etp})(\text{PET}_3)\text{CO}]\text{BF}_4$, which is typical of the etp series of complexes, is presented in Figure 3.

Structure II is related to $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]\text{BF}_4$ (structure III) by replacing the equatorial trimethyl phosphite ligand with a carbonyl ligand. The ^{31}P NMR data on $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)\text{CO}]\text{BF}_4$ (Table IV) are consistent with structure II since the coupling constants common to both $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]\text{BF}_4$ and $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)\text{CO}]\text{BF}_4$ are very similar. The relatively fixed phosphorus-phosphorus coupling constants within the $[\text{Co}(\text{etp})\text{L}(\text{CO})]\text{X}$ series (Table

Table III. Proton NMR Data for the $[\text{Co}(\text{triphos})\text{L}(\text{CO})]\text{X}$ and $[\text{Co}(\text{triphos})(\text{CO})_2]\text{X}$ Complexes^{a,b,12}

Compd	Chemical shift for each group of protons, τ				
	C_6H_5	CH_2	CH_3	C_2H_5	OCH_3
$[\text{Co}(\text{etp})(\text{CO})_2]\text{PF}_6$	2.5 (m)	7.2 (m)			
$[\text{Co}(\text{etp})(\text{CO})_2]\text{BF}_4$	2.5 (m)	7.2 (m)			
$[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)\text{CO}]\text{BF}_4$	2.21, 2.54 (m)	7.3-7.9 (m)			6.80 (d, 11)
$[\text{Co}(\text{etp})(\text{PPh}_2\text{H})\text{CO}]\text{PF}_6$	2.5, 2.9 (m)	7.7 (m)			
$[\text{Co}(\text{etp})(\text{PPh}_2\text{H})\text{CO}]\text{BF}_4$	2.5, 2.9 (m)	7.7 (m)			
$[\text{Co}(\text{etp})(\text{PPh}_3)\text{CO}]\text{BF}_4$	2.41, 2.67, 2.91, 3.21 (m)	6.7-8.4 (m)			
$[\text{Co}(\text{etp})(\text{PPh}_2\text{Me})\text{CO}]\text{BF}_4 \cdot \text{EtOH}$	2.5, 2.8 (m)	7.5-8.0 (m)	9.45 (d, 9)	8.77 (m), (EtOH)	
$[\text{Co}(\text{etp})(\text{PET}_3)\text{CO}]\text{BF}_4$	2.0, 2.45 (m)	7.4-8.1 (m)		8.71 (m), 9.21 (m)	
$[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]\text{BF}_4$	2.1, 2.6 (m)	7.2-8.0 (m)			6.7 (d, 10)
$[\text{Co}(\text{ttp})(\text{CO})_2]\text{PF}_6$	2.4, 2.8 (m)	6.6-8.4 (m)			
$[\text{Co}(\text{ttp})(\text{CO})_2]\text{BF}_4$	2.4, 2.8 (m)	6.6-8.4 (m)			
$[\text{Co}(\text{ttp})(\text{P}(\text{OMe})_3)\text{CO}]\text{BF}_4$	2.0, 2.5, 2.8, 3.06 (m)	6.8-7.8 (m)			6.54 (d, 11)
$[\text{Co}(\text{ttp})(\text{PPh}_2\text{H})\text{CO}]\text{BF}_4$	1.95, 2.45, 2.65 (m)	7.0-8.5 (m)			
$[\text{Co}(\text{tripod-}P_3)(\text{CO})_2]\text{PF}_6$	2.78 (s)	7.2 (m)	8.3 (m)		
$[\text{Co}(\text{tripod-}P_3)(\text{P}(\text{OMe})_3)\text{CO}]\text{BF}_4$	2.58, 2.78 (m)	7.26 (m)	8.16 (m)		6.70 (d, 11)
$[\text{Co}(\text{tripod-}P_3)(\text{PPh}_2\text{H})\text{CO}]\text{BF}_4$	2.68, 2.84 (m)	7.26 (m)	8.22 (m)		
$[\text{Co}(\text{tripod-}P_3)(\text{PET}_3)\text{CO}]\text{BF}_4$	2.5, 2.7 (m)	7.15 (m)	8.15 (m)	8.70 (m), 9.16 (m)	

^a Spectra recorded in nitromethane solutions. ^b Abbreviations used: s = singlet, d = doublet, m = multiplet. Separation (Hz) for doublets is given in parentheses.

IV) suggest that all these complexes have the same structural type, with the exception of isomer B of $[\text{Co}(\text{etp})(\text{PPh}_3)\text{CO}]\text{BF}_4$. When $[\text{Co}(\text{etp})(\text{PPh}_3)\text{CO}]\text{BF}_4$ is dissolved in dichloromethane, both ³¹P NMR and infrared spectra (ν_{CO} region) show the presence of two complexes. The spectra of isomer A are similar to those of the other $[\text{Co}(\text{etp})\text{L}(\text{CO})]\text{X}$ complexes; thus it is assigned structure II. Isomer B is assigned structure IV on the basis of the smaller and nearly equal values of ² $J_{\text{P}_1-\text{P}_4}$ and ² $J_{\text{P}_2-\text{P}_4}$ (47 and 55 Hz, respectively). Note in Table IV that all other etp complexes have phosphine-phosphine coupling constants equal to 107 ± 4 and 53 ± 4 Hz when the P-Co-P angles are ca. 180 and 90°, respectively. The relative amounts of the two compounds formed in solution are solvent dependent; isomer A predominates in acetonitrile, while the concentration of the two isomers is approximately equal in dichloromethane. The ³¹P NMR spectra show that the complexes $[\text{Co}(\text{etp})(\text{PPh}_2\text{H})\text{CO}]\text{X}$ and $[\text{Co}(\text{etp})(\text{PPh}_2\text{Me})\text{CO}]\text{BF}_4$ also isomerize in solution to give a small amount of a second isomer; however, the concentrations were too low in these cases to permit accurate measurement of the P-P coupling constants.²⁶ A similar type of isomerization involving two trigonal-bipyramidal structures has been proposed for $[\text{Co}(\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5)_4\text{CO}]\text{BPh}_4$.²⁷

The ν_{CO} values of the $[\text{Co}(\text{etp})\text{L}(\text{CO})]\text{BF}_4$ complexes in solution change as L is varied and produce the order: PPh_3 (isomer B) > $\text{P}(\text{OMe})_3$ > PPh_3 (isomer A), PPh_2H , PPh_2Me > PET_3 . This order parallels the order of increasing basicity of the monodentate phosphorus ligand, with the exception of isomer B of $[\text{Co}(\text{etp})\text{PPh}_3(\text{CO})]\text{BF}_4$. As the ν_{CO} frequency for isomer B occurs out of sequence, its structure is assigned as the trigonal-bipyramidal complex IV. The higher carbonyl stretching frequency observed for IV indicates that the M → CO back-bonding is much stronger in the equatorial position than in the apical position of the $[\text{Co}(\text{etp})\text{L}(\text{CO})]\text{X}$ complexes, as expected.^{5,28}

The relative intensities of the symmetric (higher frequency) and antisymmetric (lower frequency) stretching vibrations were used to calculate C-Co-C bond angles of 96 and 95° respectively for $[\text{Co}(\text{etp})(\text{CO})_2]\text{PF}_6$ and $[\text{Co}(\text{etp})(\text{CO})_2]\text{BF}_4$ in dichloromethane solutions.²⁹ These calculated bond angles are consistent with the trigonal-bipyramidal structure I.

Complexes of the ttp Ligand. The result of an X-ray structural determination of $[\text{Co}(\text{ttp})(\text{P}(\text{OMe})_3)\text{CO}]\text{BF}_4$ is shown in Figure 4.³⁰ The chemical shifts of ttp and the P-P coupling constants of $[\text{Co}(\text{ttp})(\text{PPh}_2\text{H})\text{CO}]\text{BF}_4$ indicate that the structure of the latter complex is also a square pyramid with PPh_2H occupying the apical position (e.g., VI). Although

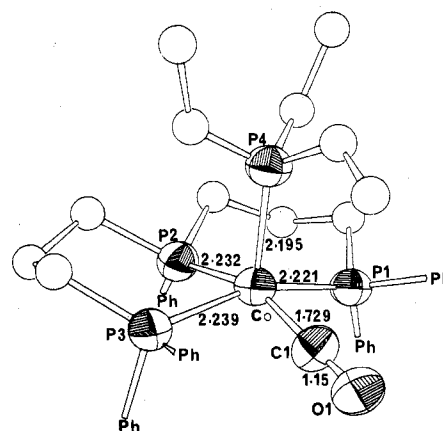
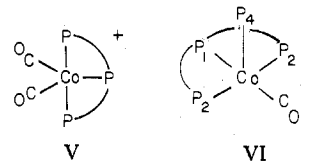


Figure 4. A perspective of the structure of $[\text{Co}(\text{ttp})(\text{P}(\text{OMe})_3)\text{CO}]^+$; the figure gives the bond distances in the coordination sphere. The phenyl groups on the phosphorus atoms are omitted for the sake of clarity.

the structure of $[\text{Co}(\text{ttp})(\text{P}(\text{OMe})_3)\text{CO}]\text{BF}_4$ in solution could differ from that in the solid, the infrared and electronic spectra suggest that a structural rearrangement does not occur.

The dicarbonyl cation $[\text{Co}(\text{ttp})(\text{CO})_2]^+$ is assigned structure V on the basis of a calculated C-Co-C angle of ca. 115°. ²⁹



This geometry is the most compatible of possible five-coordinate structures, since the expected C-Co-C angle is $\sim 120^\circ$. Additionally, the adjusted value of ² $J_{\text{P}_1-\text{P}_2}$ (vide infra) for $[\text{Co}(\text{etp})(\text{CO})_2]\text{X}$, ~ 76 Hz, is nearly identical with the 75 Hz value observed for $[\text{Co}(\text{ttp})(\text{CO})_2]\text{X}$. Comparable values might be expected for the two complexes, since ² $J_{\text{P}_1-\text{P}_2}$ for both I and V represents an axial-equatorial P-P coupling constant.

Complexes of the Tripod Ligand. The $[\text{Co}(\text{tripod-}P_3)\text{L}(\text{CO})]\text{X}$ complexes are fluxional at room temperature; only $[\text{Co}(\text{tripod-}P_3)(\text{PET}_3)\text{CO}]\text{BF}_4$ at -100°C gave a limiting spectrum. The spectral features are consistent with an AB_2X spin system which has $J_{\text{AB}} \gg \delta_{\text{A}} - \delta_{\text{B}}$ ^{31,32} (Figure 5), but the degeneracy of the spectrum has prevented a satisfactory analysis; thus, no detailed structural data are available from the phosphorus-31 NMR spectra of this series of complexes.

Table IV. Phosphorus-31 NMR Parameters for [Co(triphos)(CO)₂]X and [Co(triphos)L(CO)]X Complexes^{1,2}

Compd	δ^a	Assign	$J(\text{P-P})^b$	Assign ^c	Temp, °C	Solv
[Co(etp)(CO) ₂]PF ₆	122.4	PPh (t) ^{d,e}	48	PPh-PPh ₂ (1, 2)	Amb ^f	CH ₃ CN
	78.6	PPh ₂ (d)				
[Co(etp)(CO) ₂]BF ₄	122.6	PPh (t)	45	PPh-PPh ₂ (1, 2)		
	78.8	PPh ₂ (d)				
[Co(etp)(P(OMe) ₃)CO]BF ₄	150.0	P(OMe) ₃ (d-t)	211	PPh-P(OMe) ₃ (1, 3)	Amb	CH ₃ CN
	113.3	PPh (d-t)	88	PPh ₂ -P(OMe) ₃ (2, 3)		
	68.2	PPh ₂ (d-d)	38	PPh-PPh ₂ (1, 2)		
	115.4	PPh (d-t)	107	PPh-PPh ₂ H (1, 3)		
[Co(etp)(PPh ₂ H)CO]PF ₆	66.7	PPh ₂ (d-d)	54	PPh ₂ -PPh ₂ H (2, 3)	Amb	CH ₃ CN
	56.4	PPh ₂ H (d-t)	36	PPh-PPh ₂ (1, 2)		
	115.4	PPh (d-t)	107	PPh-PPh ₂ H (1, 3)		
	66.8	PPh ₂ (d-d)	56	PPh ₂ -PPh ₂ H (2, 3)		
[Co(etp)(PPh ₂ H)CO]BF ₄	56.6	PPh ₂ H (d-t)	36	PPh-PPh ₂ (1, 2)	Amb	CH ₃ CN
				P-H, 364 Hz		
[Co(etp)(PPh ₃)CO]BF ₄ Isomer A	108.4	PPh (d-t)	109	PPh-PPh ₃ (1, 3)	Amb	CH ₂ Cl ₂
	62.6	PPh ₂ (d-d)	49	PPh ₂ -PPh ₃ (2, 3)		
	49.4	PPh ₃ (d-t)	33	PPh-PPh ₂ (1, 2)		
Isomer B	105.9	PPh (d-t)	47	PPh-PPh ₃ (1, 4)	Amb	CH ₂ Cl ₂
	71.4	PPh ₂ (d-d)	55	PPh ₂ -PPh ₃ (2, 4)		
	39.5	PPh ₃ (d-t)	46	PPh-PPh ₂ (1, 2)		
[Co(etp)(PPh ₂ Me)CO]BF ₄	110.5	PPh (d-t)	108	PPh-PPh ₂ Me (1, 3)	Amb	CH ₂ Cl ₂
	63.5	PPh ₂ (d-d)	53	PPh ₂ -PPh ₂ Me (2, 3)		
	36.9	PPh ₂ Me (d-t)	37	PPh-PPh ₂ (1, 2)		
	109.6	PPh (d-t)	104	PPh-PEt ₃ (1, 3)		
[Co(etp)(PEt ₃)CO]BF ₄	64.9	PPh ₂ (d-d)	53	PPh ₂ -PEt ₃ (2, 3)	Amb	CH ₃ CN
	38.7	PEt ₃ (d-t)	33	PPh-PPh ₂ (1, 2)		
	156.2	P(OMe) ₃ (ba)	-193.5	PPh-P(OMe) ₃ (1, 3)		
	142.9	P(OMe) ₃ (ax)	95.3	PPh ₂ -P(OMe) ₃ (2, 3)		
[Co(etp)(P(OMe) ₃) ₂]BF ₄	108.0	PPh	41.0	PPh-PPh ₂ (1, 2)	-16	CH ₂ Cl ₂
	65.6	PPh ₂	136.5	P(OMe) ₃ - P(OMe) ₃ (3, 4)		
				PPh-P(OMe) ₃ (1, 4)		
				PPh ₂ -P(OMe) ₃ (2, 4)		
				PPh-PPh ₂ (1, 2)		
[Co(ttp)(CO) ₂]PF ₆	36.6	PPh ₂ (d) ^{d,e}	74	PPh-PPh ₂ (1, 2)	Amb	CH ₃ NO ₂
	-7.8	PPh (t)				
[Co(ttp)(CO) ₂]BF ₄	37.0	PPh ₂ (d)	75	PPh-PPh ₂ (1, 2)	Amb	CH ₃ CN
	-7.3	PPh (t)				
[Co(ttp)(P(OMe) ₃)CO]BF ₄	142.9	P(OMe) ₃ (d-t)	49	PPh-P(OMe) ₃ (1, 4)	-91	CH ₂ Cl ₂
	29.0	PPh ₂ (d-d)	18	PPh ₂ -P(OMe) ₃ (2, 4)		
	-6.0	PPh (t-d)	90	PPh-PPh ₂ (1, 2)		
	26.8	PPh ₂ (d-d)	46	PPh ₂ -PPh ₂ H (1, 4)		
[Co(ttp)(PPh ₂ H)CO]BF ₄	3.1	PPh ₂ H (d)	9	PPh ₂ -PPh ₂ H (2, 4)	-62	CH ₂ Cl ₂
	-8.2	PPh (t-d)	89	PPh-PPh ₂ (1, 2)		
				P-H, 317 Hz		
[Co(tripod-P ₃)(CO) ₂]PF ₆	24.1	PPh ₂			Amb	CH ₂ Cl ₂
[Co(tripod-P ₃)(PPh ₂ H)CO]BF ₄	52.9	PPh ₂ H			Amb	CH ₂ Cl ₂
	23.9	PPh ₂				
[Co(tripod-P ₃)(P(OMe) ₃)CO]BF ₄	143.1	P(OMe) ₃ (q)	12	PPh ₂ -P(OMe) ₃	-41	CH ₂ Cl ₂
	22.8	PPh ₂ (d)				
[Co(tripod-P ₃)(PPh ₂ Me)CO]BF ₄	34.8	PPh ₂ Me			Amb	CH ₂ Cl ₂
	19.1	PPh ₂				
[Co(tripod-P ₃)(PEt ₃)CO]BF ₄	36.0	PEt ₃			Amb	CH ₂ Cl ₂
	21.5	PPh ₂				

^a Ppm values relative to external 85% H₃PO₄. Values are estimated to be accurate to ±0.1 ppm, except for low-temperature values which are estimated to be accurate to ±0.2 ppm. ^b Coupling constants are accurate to ±2.5 Hz. ^c Numbers in parentheses designate couplings between phosphorus atoms numbered as shown in structures I-IV and VI. ^d Abbreviations used are: d = doublet, t = triplet, d-t = doublet of triplets, etc.; ax = axial, ba = basal. ^e The ³¹P resonance due to the PF₆⁻ anion is not reported in the table. ^f Amb = ambient operating temperature of the Bruker HX-90 spectrometer, ~33 °C.

The lower ν_{CO} values observed for the [Co(tripod-P₃)L(CO)]BF₄ complexes (compared with corresponding [Co(etp)L(CO)]X and [Co(ttp)L(CO)]X complexes) are consistent with the carbonyl group occupying an equatorial site (with strong π back-bonding) in the [Co(tripod-P₃)L(CO)]BF₄ complexes. In addition, the carbonyl stretching frequencies of the tripod-P₃ complexes resemble those of etp; for example, the ν_{CO} decreases with increasing basicity of the monophosphine L (Table II). The calculated C-Co-C bond angle of [Co(tripod-P₃)(CO)₂]PF₆ is 88°. The above data suggest that the [Co(tripod-P₃)(CO)₂]X and [Co(tripod-P₃)L(CO)]X complexes probably have distorted trigonal-bipyramidal structures (e.g., I and II). In other complexes of tripod-P₃, the P-M-P bond angles are usually ca. 92-95°. The C_{3v}

symmetry and steric constraints of tripod-P₃ are probably the major factors contributing to the fluxional nature of this series of complexes.

Correlations between Coupling Constants and Structure

An objective of this study was to establish an empirical relationship between the structures and the ²J_{P-P} values for phosphorus ligands at different sites of a trigonal bipyramid and a square pyramid. In contrast to the situation with square-planar and octahedral complexes,²³⁻²⁵ there is a dearth of information on the magnitudes of P-P coupling constants in nonfluxional five-coordinate complexes.^{3,36}

To facilitate comparisons of the ³¹P NMR data of [Co(etp)L(CO)]X and [Co(etp)(CO)₂]X with [Co(ttp)L(CO)]X

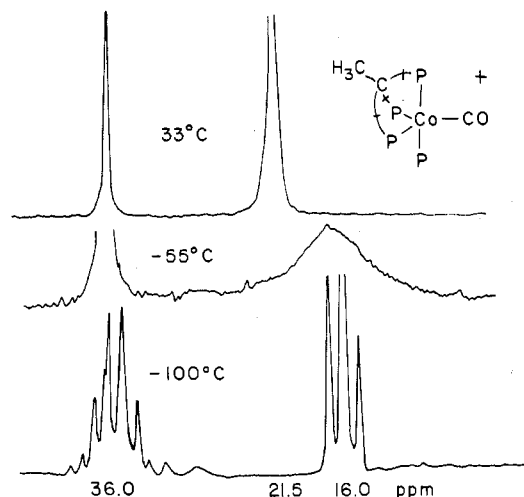


Figure 5. Fourier-mode $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[\text{Co}(\text{tripod-}\text{P}_3)(\text{PEt}_3)\text{CO}]\text{BF}_4$ in dichloromethane at the three temperatures listed. The ppm values are relative to external 85% H_3PO_4 , positive values being downfield from the standard.

Table V. $^2J_{\text{P-P}}$ Ranges Observed for Five-Coordinate Cobalt(I) Complexes

Trigonal Bipyramid			
	$J_{\text{Pa-Pa}}^a$	$J_{\text{Pa-Pe}}$	$J_{\text{Pe-Pe}}$
Phosphine-phosphine	$\sim 110^b$	47–75 ^b	$\sim 55^b$
Phosphine-phosphite	195–210 ^b	88–105 ^b	$\sim 110^b$
Phosphite-phosphite		100–150 ^{b-d}	$\sim 210^d$
Square Pyramid			
	$J_{\text{Pa-Pb}}$	$J_{\text{Pb-Pb-cis}}$	
Phosphine-phosphine	10–50 ^b	$\sim 90^b$	
Phosphine-phosphite	18–50 ^b		

^a Abbreviations used are: a = apical, b = basal, and e = equatorial. ^b This work. ^c Reference 3. ^d Reference 40.

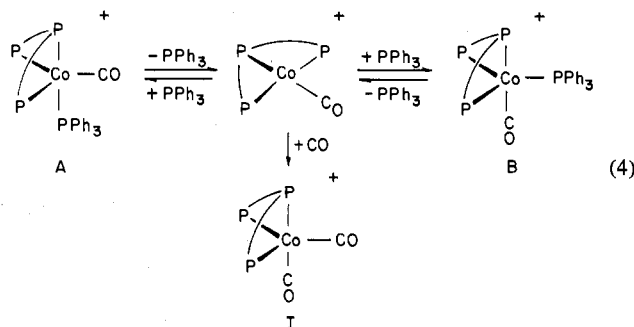
and $[\text{Co}(\text{ttp})(\text{CO})_2]\text{X}$, certain adjustments in the chemical shifts and coupling constants must be made for the etp complexes. Transition metal complexes of polyphosphine ligands containing a two-member connecting chain such as $-\text{CH}_2\text{CH}_2-$ or $-\text{OCH}_2-$ give $^2J_{\text{P-P}}$ values that are decreased from the corresponding $^2J_{\text{P-P}}$ values of similar monophosphine complexes by an amount equivalent to the $^3J_{\text{P-P}}$ value of the free polyphosphine ligand.^{37,38} To correct this effect, a value of ca. 30 Hz ($^3J_{\text{P-P}} \approx 29$ Hz for etp₃,³⁹ $^4J_{\text{P-P}} \approx 1$ Hz for ttp) should be added to the $^2J_{\text{P-P}}$ value reported for the etp complexes of Table IV. Table V summarizes the range of known $^2J_{\text{P-P}}$ values (corrected) for five-coordinate cobalt(I) complexes. The $^2J_{\text{P-P}}$ data indicate that it is possible to distinguish between trigonal-bipyramidal and square-pyramidal complexes, as long as a distinction is made between phosphine-phosphine, phosphine-phosphite, and phosphite-phosphite coupling. In practice this distinction should not be difficult. For example, the phosphine-phosphine coupling constants give ranges of $^2J_{\text{P-P}}$ that are different for the two structural types, although a small amount of overlap does occur between $J_{\text{Pa-Pe}}$ for a trigonal bipyramid and $J_{\text{Pa-Pb}}$ for a square pyramid. Clearly, more data are needed to define the $^2J_{\text{P-P}}$ ranges more accurately, but Table V lists tentative criteria.

Exchange Processes

Five-coordinate d^8 complexes containing monodentate^{3,7} and bidentate⁴¹ phosphine or phosphite ligands frequently undergo inter- and intramolecular exchange. Such exchanges play important roles in catalysis, as five-coordinate species are frequent intermediates. These cobalt(I) complexes have been

investigated to determine the relationships between their solution dynamics and the structures of the triphosphine ligands. The observed dynamic processes include intermolecular carbonyl exchange, intermolecular exchange of monophosphine ligand, intramolecular rearrangements, and facile interconversion of two isomers.

Exchange Processes in the etp Complexes. None of the $[\text{Co}(\text{etp})\text{L}(\text{CO})]\text{X}$ complexes, except $[\text{Co}(\text{etp})(\text{PPh}_3)\text{CO}]\text{BF}_4$, exhibit rapid intermolecular exchange of the monodentate phosphine on the phosphorus-31 NMR time scale at room temperature. When excess monophosphine was added to a solution of $[\text{Co}(\text{etp})\text{L}(\text{CO})]\text{X}$ the phosphorus-phosphorus coupling was retained and additional sharp peaks were observed at the resonance positions of the free ligand. The exception, $[\text{Co}(\text{etp})(\text{PPh}_3)\text{CO}]\text{BF}_4$, gives a set of products that are interrelated as shown in eq 4. Intermolecular exchange

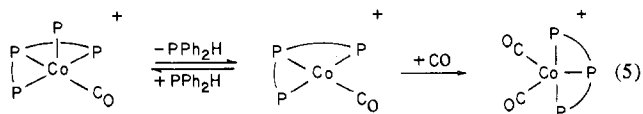


of triphenylphosphine is indicated by broadening of the phosphorus resonances when excess triphenylphosphine was added at room temperature. If the solution is cooled, sharp resonances for both coordinated and free PPh_3 are observed. Immediately after dissolution of $[\text{Co}(\text{etp})(\text{PPh}_3)\text{CO}]\text{BF}_4$ in dichloromethane two carbonyl bands are observed at 1940 and 1959 cm^{-1} . These two absorptions are assigned to two different compounds (isomers A and B) on the basis of the ^{31}P NMR spectrum (vide supra). Interconversion of isomers A and B takes place by dissociation of PPh_3 (eq 4), rather than by an intramolecular process common for complexes of monophosphines.³ Intermolecular exchange of PPh_3 is observed prior to any coalescing of the PPh_3 resonances of isomers A and B. Over a period of several days two new bands appear in the infrared spectrum at 1983 and 2028 cm^{-1} and slowly increase in intensity due to the formation of $[\text{Co}(\text{etp})(\text{CO})_2]\text{BF}_4$ (I of eq 4). The identity of I was confirmed by comparing its infrared and ^{31}P NMR spectra with those of an authentic sample of $[\text{Co}(\text{etp})(\text{CO})_2]\text{BF}_4$.

In contrast to monophosphine complexes of cobalt(I), these etp-Co(I) complexes are stereochemically rigid on the ^{31}P NMR time scale. The observation of two isomers for $[\text{Co}(\text{etp})(\text{PPh}_3)\text{CO}]\text{BF}_4$ and two distinct resonances for the two trimethyl phosphite ligands in $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]\text{BF}_4$ at room temperature shows that the monodentate phosphine ligands are not being permuted.

Exchange Processes in the ttp Complexes. A summary of the solution dynamics observed for $[\text{Co}(\text{ttp})(\text{PPh}_2\text{H})\text{CO}]\text{BF}_4$ in dichloromethane is shown in eq 5; it is similar to eq 4, which represents the equilibria for $[\text{Co}(\text{etp})\text{PPh}_3(\text{CO})]\text{BF}_4$. Intermolecular phosphine exchange was confirmed by a broadening of the ^{31}P resonances for the free ligand and the complex upon addition of excess diphenylphosphine. These resonances sharpened when the sample was cooled. Formation of the dicarbonyl complex (verified by ^{31}P NMR and infrared spectroscopy) is much faster in the case of $[\text{Co}(\text{ttp})(\text{PPh}_2\text{H})(\text{CO})]\text{BF}_4$ than for $[\text{Co}(\text{etp})(\text{PPh}_3)(\text{CO})]\text{BF}_4$. Facile dissociation of diphenylphosphine from $[\text{Co}(\text{ttp})(\text{PPh}_2\text{H})(\text{CO})]\text{BF}_4$ may explain our inability to isolate other possible members of the $[\text{Co}(\text{ttp})\text{L}(\text{CO})]\text{X}$ series. For example, an

attempt to prepare $[\text{Co}(\text{ttp})(\text{PEt}_3)(\text{CO})]\text{BF}_4$ gave the dicarbonyl complex in less than 50% yield, based on cobalt. Presumably, a bulky monophosphine ligands shifts the equilibrium in eq 5 to the right and results in the formation



of the more stable dicarbonyl complex. The trimethyl phosphite complex of ttp, $[\text{Co}(\text{ttp})(\text{P}(\text{OMe})_3)\text{CO}]\text{BF}_4$, does not exhibit rapid intermolecular exchange of the phosphite ligand; consequently, it does not form the dicarbonyl complex (at least in time periods comparable to those used for studying $[\text{Co}(\text{etp})(\text{PPh}_3)\text{CO}]\text{BF}_4$ and $[\text{Co}(\text{ttp})(\text{PPh}_3)\text{CO}]\text{BF}_4$). Our data do not permit a determination of the stereochemical rigidity of these complexes.

Exchange Processes for the Tripod- P_3 Complexes. In contrast to $[\text{Co}(\text{etp})(\text{PPh}_3)\text{CO}]\text{BF}_4$ and $[\text{Co}(\text{ttp})(\text{PPh}_2\text{H})\text{CO}]\text{BF}_4$, intermolecular carbonyl exchange is very slow for the $[\text{Co}(\text{tripod-}\text{P}_3)\text{L}(\text{CO})]\text{X}$ complexes even though intermolecular exchange of the monophosphine ligand has been observed by ^{31}P NMR to be rapid for all the monodentate phosphine ligands except $\text{P}(\text{OMe})_3$. All of the $[\text{Co}(\text{tripod-}\text{P}_3)\text{L}(\text{CO})]\text{BF}_4$ complexes exhibit rapid intramolecular exchange; only $[\text{Co}(\text{tripod-}\text{P}_3)(\text{PEt}_3)\text{CO}]\text{BF}_4$ gave a limiting ^{31}P NMR spectrum at -100°C . The temperature effects on the spectra of $[\text{Co}(\text{tripod-}\text{P}_3)(\text{PEt}_3)\text{CO}]\text{BF}_4$ (Figure 5) are not caused by an intermolecular process, since a sharp free ligand resonance is observed for all the tripod complexes at temperatures above those at which line broadening begins for the intramolecular process. Further evidence for a rapid intramolecular rearrangement is the observation that the trimethyl phosphite resonance of $[\text{Co}(\text{tripod-}\text{P}_3)(\text{P}(\text{OMe})_3)\text{CO}]\text{BF}_4$ appears as an incompletely resolved quartet at -41° ; the quartet indicates coupling to three equivalent phosphorus atoms. At lower temperatures the resonances of the $\text{P}(\text{OMe})_3$ complex broaden and then start to coalesce, but no limiting spectrum was obtained at -100°C . Rapid intramolecular exchange has been observed previously for $\text{Ni}(\text{tripod-}\text{P}_3)\text{C}_2\text{F}_4$ complexes by ^{19}F NMR.⁴² Presumably the constrained nature of the tripod- P_3 ligand causes the five-coordinate complexes to be nonrigid.

Summary. Cobalt(I) complexes of monodentate PR_3 and $\text{P}(\text{OR})_3$ ligands generally form nonrigid, trigonal-bipyramidal cobalt(I) complexes. In contrast, this study has shown that the cobalt(I) complexes of $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ (etp) are stereochemically rigid at room temperature. The coordination geometry adopted by the metal in the three series $[\text{Co}(\text{triphosphine})(\text{CO})_2]^+$, $[\text{Co}(\text{triphosphine})\text{L}(\text{CO})]^+$, and $[\text{Co}(\text{triphosphine})\text{L}_2]^+$ depends on whether the triphosphine ligand is $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ or $\text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)_2$. The change from square-pyramidal coordination geometry in $[\text{Co}(\text{ttp})(\text{P}(\text{OMe})_3)\text{CO}]^+$ to trigonal bipyramidal in $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]^+$ probably can be attributed to the decrease in "chelate bite" angle. As a consequence of the smaller "bite angle" in five-membered chelate rings, the central phosphorus atom must either be pulled in close to the metal in a square-pyramidal geometry or be free to adopt a coordination position more equivalent to those of the terminal phosphorus atoms, e.g., as in a trigonal-bipyramidal geometry I-IV.

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Registry No. $[\text{Co}(\text{etp})(\text{CO})_2]\text{PF}_6$, 60305-67-1; $[\text{Co}(\text{etp})(\text{CO})_2]\text{BF}_4$, 60305-68-2; $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)\text{CO}]\text{BF}_4$, 60305-70-6; $[\text{Co}(\text{etp})(\text{PPh}_2\text{H})\text{CO}]\text{PF}_6$, 60305-72-8; $[\text{Co}(\text{etp})(\text{PPh}_2\text{H})\text{CO}]\text{BF}_4$, 60305-74-0;

$[\text{Co}(\text{etp})(\text{PPh}_3)\text{CO}]\text{BF}_4$ (isomer A), 60305-76-2; $[\text{Co}(\text{etp})(\text{PPh}_3)\text{CO}]\text{BF}_4$ (isomer B), 60325-40-8; $[\text{Co}(\text{etp})(\text{PPh}_2\text{Me})\text{CO}]\text{BF}_4$, 60326-12-7; $[\text{Co}(\text{etp})(\text{PEt}_3)\text{CO}]\text{BF}_4$, 60305-78-4; $[\text{Co}(\text{etp})(\text{P}(\text{OMe})_3)_2]\text{BF}_4$, 60305-80-8; $[\text{Co}(\text{ttp})(\text{CO})_2]\text{PF}_6$, 60305-82-0; $[\text{Co}(\text{ttp})(\text{CO})_2]\text{BF}_4$, 60305-83-1; $[\text{Co}(\text{ttp})(\text{P}(\text{OMe})_3)\text{CO}]\text{BF}_4$, 60305-85-3; $[\text{Co}(\text{ttp})(\text{PPh}_2\text{H})\text{CO}]\text{BF}_4$, 60305-87-5; $[\text{Co}(\text{tripod-}\text{P}_3)(\text{CO})_2]\text{PF}_6$, 54003-37-1; $[\text{Co}(\text{tripod-}\text{P}_3)(\text{P}(\text{OMe})_3)\text{CO}]\text{BF}_4$, 60305-89-7; $[\text{Co}(\text{tripod-}\text{P}_3)(\text{PPh}_2\text{H})\text{CO}]\text{BF}_4$, 60305-91-1; $[\text{Co}(\text{tripod-}\text{P}_3)(\text{PEt}_3)\text{CO}]\text{BF}_4$, 60305-93-3; $[\text{Co}(\text{tripod-}\text{P}_3)(\text{PPh}_2\text{Me})\text{CO}]\text{BF}_4$, 60326-16-1; $\text{HCo}(\text{etp})\text{CO}$, 60305-94-4; $\text{HCo}(\text{ttp})\text{CO}$, 60305-95-5; $\text{HCo}(\text{tripod-}\text{P}_3)\text{CO}$, 59697-29-9; ^{31}P , 7723-14-0.

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Cobalt(II) Complexes Containing a 12-Membered Saturated Macrocyclic Ligand¹

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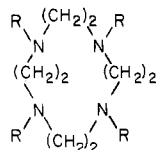
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A series of high-spin five- and six-coordinate macrocyclic cobalt(II) complexes whose stoichiometry is $\text{Co}(\text{tbcyclen})\text{X}_2 \cdot n\text{H}_2\text{O}$ (where tbcyclen is 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane and X is NO_3 , Cl, SCN, or $\text{Cl}-\text{ClO}_4$) have been prepared. On the basis of molecular models, conductivity, electronic spectra, and magnetic data it appears that the $\text{Co}(\text{tbcyclen})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ has a cis-octahedral geometry while all of the other complexes have a trigonal-bipyramidal geometry. The ligand tbcyclen stabilizes the divalent state of cobalt over the trivalent state. All attempts to oxidize $\text{Co}(\text{tbcyclen})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ by electrochemical means, by direct aeration, or by use of H_2O_2 have failed. (The stabilization of the divalent state by tbcyclen may be due to the weak ligand field strength of tbcyclen or to the fact that the bulky benzyl groups on the tbcyclen make it kinetically difficult to form the six-coordinate $\text{Co}(\text{III})$ -tbcyclen complexes.) These complexes are stable with respect to dissociation in acid-water solution but decompose rapidly in an acid solution containing both water and acetone.

Introduction

There has been considerable interest in the synthesis of macrocyclic metal compounds because of the structural similarity between these synthetic compounds and several biologically important metal complexes.² At present most of the published research has dealt with macrocyclic ligands containing at least 13 atoms in the ring.²⁻⁴ Most of these relatively large macrocyclic ligands form planar or trans-octahedral complexes and are considered strong-field ligands.²⁻⁴ It has been demonstrated that a 12-membered tetradentate macrocyclic ligand cannot form a planar complex with a divalent transition metal ion.⁵ This type of ligand should coordinate around the face of either an octahedron or a trigonal bipyramid. Collman and Schneider synthesized a series of cobalt(III) complexes with 1,4,7,10-tetraazacyclododecane (cyclen, Ia).⁶ On the basis of visible and infrared



Ia, R = H (cyclen)
 b, R = $\text{CH}_2\text{C}_6\text{H}_5$ (tbcyclen)

spectra, these cobalt(III) complexes of cyclen were assigned a cis-octahedral configuration. A crystal structure of $[\text{Co}(\text{cyclen})(\text{NO}_2)_2]\text{Cl}$ has confirmed that the cyclen is folded and that the NO_2^- groups coordinate in cis positions.⁷ Rosen and Busch⁸ showed that the nickel(II) complexes of the sulfur analogue of cyclen, 1,4,7,10-tetrathiacyclododecane, also had a cis-octahedral geometry. Kalligeros and Blinn⁹ prepared nickel(II) complexes of 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane (tbcyclen, Ib) and suggested that the geometry of such compounds is either cis octahedral or trigonal bipyramidal depending on the nature of the other univalent ligand group coordinated to the metal ion.

We are interested in preparing low-symmetry complexes which are likely to have weak highly strained metal to donor bonds. The cobalt(II) complexes of tbcyclen should have these attributes. Using x-ray data Itaka, Shina, and Kimura observed greater bond angle distortions from the expected values in the cobalt(III) complex of cyclen than from the analogous cobalt(III) complexes of ethylenediamine, diethylenetriamine,

and triethylenetetraamine. They attributed the additional angular distortion and strained rings in $[\text{Co}(\text{cyclen})(\text{NO}_2)_2]\text{Cl}$ to nonbonding repulsions. Most of these nonbonded repulsions were attributed to the interaction of hydrogen on the nitrogens with other hydrogen atoms on adjacent rings.⁷ Therefore it is reasonable to assume that substituting a relatively large benzyl group for the hydrogen atom on each nitrogen on cyclen should not reduce the degree of metal to nitrogen bond strain but should induce some additional steric strain. Molecular models of metal-tbcyclen complexes confirm the nonbonded interactions and suggest that these complexes should have lower symmetry than the cobalt-cyclen complexes in order to minimize the additional bond strain. Also, the use of cobalt(II), which is larger than cobalt(III) in $[\text{Co}(\text{cyclen})(\text{NO}_2)_2]\text{Cl}$, should increase the degree of metal to nitrogen bond strain.

Williams and Vallee have formulated a hypothesis about the nature of the environment around a metal ion in metalloenzymes to explain why the physical properties of these enzymes are different from those of synthetic coordination complexes.^{10,11} They suggested that the metal ion in the metalloenzyme is contained in an irregular geometry and the metal to donor bonds are strained. The combination of strained bonds and irregular geometry (entatic state) approximate the transition state for the reaction in which that enzyme is involved. Busch² has suggested that the metal ion can exist in the entatic state in a metalloenzyme because of the structural constraints of the proteins which inhibit the stepwise dissociation of the donor atoms from the metal ion ("multiple juxtapositional fixedness"). A macrocyclic ligand, likewise, inhibits the stepwise dissociation of the donor atoms from the metal ion.^{2,12-15} Although the Vallee and Williams hypothesis remains controversial^{16,17} and the entatic state environment has been shown to be unlikely with regard to several metalloenzymes,¹⁶ there still remains the question of whether an unusual coordination geometry accompanied by strained metal-to-donor bonds will result in complexes that will have unusual chemical and physical properties. The prime function of this research is to prepare and characterize complexes that are likely to have many of the properties of an entatic state environment. The cobalt(II) complexes of tbcyclen should contain strained metal to nitrogen bonds and should be kinetically stable because of the cyclic nature of the ligand. Therefore these complexes should show many at-