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# Regiospecific Coordination of Ambidentate Tetrazoles to Cobalt Oximes

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Abstract: A series of complexes of the type $(n\text{-}Bu_3P)Co(DH)_2(5R\text{-tetrazolate})$ (DH is the monoanion of dimethylglyoxime; R = CF_3, CH_3, C_6H_5, $C_6H_5CH_2$, $(CH_3)_2N$, $4\text{-}FC_6H_4$, and $3\text{-}FC_6H_4$) have been prepared and characterized by conductance studies, elemental analyses, and ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and ^{19}F NMR spectroscopy. Quantum-mechanical calculations (MINDO/3) indicate that the N_1 nitrogens of the aromatic tetrazolate anion are slightly more nucleophilic than the N_2, yet in each complex the ambidentate tetrazolate anion is coordinated to cobalt via the N_2 nitrogen, showing that regiospecific coordination is sterically induced. This is in marked contrast to tetrazole complexes of platinum and palladium wherein both N_1 and N_2 bound tetrazoles are found in approximately equal abundances. These cobalt complexes react with alkyl halides such as CH_3I and $C_6H_5CH_2Br$ to produce exclusively 1,5-disubstituted tetrazoles. None of the isomeric 2,5-disubstituted tetrazole is detected in these reactions in marked contrast to the reactions of sodium tetrazolates or gold, palladium, or platinum tetrazolate complexes with alkyl halides which produce mixtures of the 1,5- and 2,5-disubstituted tetrazoles. The crystal structure of $n\text{-}Bu_3PCo(DH)_2(5\text{-}CF_3\text{-tetrazolate})$ was determined using three-dimensional X-ray diffraction techniques. The molecule crystallizes in the orthorhombic space group *Pbca* in a unit cell of dimensions $a = 12.040(2)$ Å, $b = 21.531(3)$ Å, $c = 23.536(4)$ Å, $\rho_{calcd} = 1.368$ g/cm^3, $\rho_{obsd} = 1.374$ g/cm^3. Refinement converged to 5.4% with 2525 independent reflections. The tetrazolato ring is coordinated to cobalt via N_2 and is planar. The Co-P bond (2.263 Å) is one of the shortest observed in $LCo(DH)_2X$ structures. The acute dihedral angle between the planes of the two glyoximato groups (10.4°) is among the largest dihedral angles observed in structures of this type. Surprisingly, the tetrazolato ring does not lie in the fold of the two glyoximato rings but is nearly normal to it. Thus, the regiospecificity of the alkylations of the coordinated tetrazolate with alkyl halides is sterically promoted.

Introduction

The anion that results when a 5-substituted tetrazole's tautomeric ring proton is attacked by a base has been found to possess two bonding modes (N_1 vs. N_2) that are virtually energetically equivalent.[2]
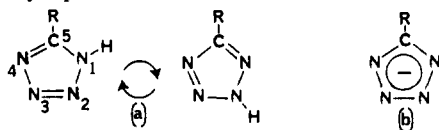

Tetrazole ring numbering scheme

Consequently, linkage isomers have been reported in solutions of 5-substituted tetrazolato ions coordinated to any of a number of transition-metal centers.[3,4] Treatment of this type of anion either as a sodium salt or a transition-metal complex with alkylating agents always produces mixtures of 1,5- and 2,5-disubstituted tetrazoles[3,5-12] in relative amounts that are affected by the electronegativity and size of the 5 substituent.[6,11] The family of tetrazoles is economically important because of the many practical applications of both a biological[13-20] and nonbiological[21] nature found for its members. For disubstituted tetrazoles, a major subclass with mainly medicinal and pharmacological applications, activity is usually

isomer dependent and requires separation procedures that may be difficult and costly. This is particularly true if the 1,5 isomer is the active one[13,16,17] because steric restrictions generally cause it to be formed in lower yield[5-12] than the 2,5 isomer. Thus far no successful method has been found for directly or indirectly producing the 1,5 isomer as the exclusive product. Blocking of the N_2 position by a *tert*-butyl group has been attempted but the N_1 position was also attacked even when the 5 substituent was relatively bulky.[22] Kozima et al.[8] did obtain high selectivity in formation of the 1,5 isomer by blocking the 2 position with tri-*n*-butyltin prior to alkylation but the 2,5 isomer was still formed in about a 10% average yield.

Marzilli et al.[23] prepared complexes of the type $PBu_3Co(DH)_2pur$, where pur is the anion of a purine-type base such as xanthine, and showed that the heterocyclic base was regiospecifically coordinated at the least hindered of two possible nitrogen bonding sites. Alkylation of the xanthine complex cleaved the heterocycle to yield an alkylated purine and halocobaloxime according to the equation

$$PBu_3Co(DH)_2pur + RX \rightarrow PBu_3Co(DH)_2X + R\text{-pur} \quad (1)$$
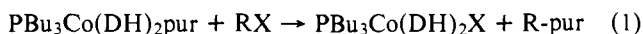
Identification of the alkylated ring site led to a deduction of the bonding mode in the purine complexes. The similarities in

electronic and structural properties of the tetrazole and purine families suggested the possibility of formation and alkylation of tetrazole cobaloxime complexes. Bending of the rigid dimethylglyoxime in the direction of the axial ligand *trans* to it may force coordination to occur exclusively at one of the two possible bonding sites. To investigate this possibility and that of subsequent alkylation of the complexes we prepared a series of complexes of the form $PBu_3Co(DH)_2$5-R-tetrazolate where R = CH_3, CF_3, $CH_2C_6H_5$, C_6H_5, 3-FC_6H_4, 4-FC_6H_4, and $N(CH_3)_2$. This series of tetrazoles includes 5 substituents which are both large and small, electron withdrawing and releasing. The complex of 5-(N,N-dimethylamino)tetrazolate has a third possible binding site, the exocyclic amine nitrogen.

The complexes are well suited to characterization by NMR and a complete analysis of the ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra is given. Each of these nuclei is expected to reveal whether or not a single binding site was utilized by a given tetrazole. Identification of the regiospecific binding site is possible directly from the ^{13}C and ^1H NMR spectra of complexes which have aromatic 5 substituents. These tetrazoles fall into the special class of heterocyclic biaryls. Many members of this class exhibit characteristic shieldings in the aromatic region of their ^1H[24-26] and ^{13}C NMR[27] spectra which are isomer dependent. Interpretation of these spectra not only has the potential of identifying the coordination site, but, because the shielding effects have been shown to be additive,[24] the chemical-shift assignments in the aromatic region may be predicted. Other cases where the mode of coordination of a heterocyclic ligand was determined on the basis of this phenomenon are rare.[8,28] Thus, this series of compounds provides an opportunity to further investigate these potentially useful additivity relationships and their utility in deducing the binding site of ambidentate heterocyclic biaryls. Thus, it should be possible to compare the relative abilities of ^{13}C and ^1H NMR to predict chemical shifts in systems where this phenomenon is thought to occur.

In addition, relatively little is known about factors affecting $\delta^{31}P$, $^nJ(^{31}P-^{13}C_n)$, and $\delta^{13}C_\alpha$ of coordinated organophosphines, and the trends exhibited by these parameters in the series of tetrazole complexes allow an evaluation of their relative sensitivity and significance in systems of this type.

Akylation of the complexes should reveal indirectly, as was found with Marzilli's purine complexes, through which nitrogen the tetrazole was coordinated and whether alkylation of the free or coordinated ligand occurred. Moreover, it was hoped that this type of reaction could be developed into a high-yield synthetic procedure for the exclusive preparation of 1,5-disubstituted tetrazoles. This hope was only partially realized. Alkylation of the coordinated tetrazole does proceed in high yield with the exclusive formation of 1,5-disubstituted tetrazoles. But, because the solubility properties of Bu_3P-$Co(DH)_2X$ and 1,5-disubstituted tetrazoles are very similar, their separation is difficult. Consequently this procedure does not yet show great synthetic promise. Results of an X-ray crystal structure of one of the 5-alkyltetrazole complexes, viz., n-$Bu_3PCo(DH)$5-CF tetrazolate, confirmed the validity of the deductions based on alkylation and spectroscopic results.

Experimental Section

Materials. Commercially available solvents, ligands, metal salts, etc., were reagent grade and used without further purification if they contained no spectroscopically detectable contaminants. Otherwise they were purified by standard techniques.[29]

Preparation of Compounds. A. 5-Substituted Tetrazoles. 5-Methyltetrazole,[30] 5-benzyltetrazole,[6] 5-phenyltetrazole,[30] 5-trifluoromethyltetrazole,[31] and 5-(N,N-dimethylamino)tetrazole[9] were prepared by published methods. 5-(4-Fluorophenyl)tetrazole and 5-(3-fluorophenyl)tetrazole were synthesized by treating the appropriate

substituted benzonitriles with trimethylammonium azide as described by Finnegan, Henry, and Lofquist.[32]

B. Disubstituted Tetrazoles. 1- and 2-benzyl-5-phenyltetrazole[6] and 1- and 2-methyl-5-phenyltetrazole[33] were prepared and separated by literature methods. 1-Methyl-5-(3- and 4-fluorophenyl)tetrazoles were synthesized from *m*- and *p*-fluorobenzamides,[34] phosphorus pentachloride, and hydrazoic acid following the procedure of Roberts, Fanta, and Martin.[35] After crystallization from benzene, the compounds were purified further by chromatography on silica gel (eluant was chloroform) followed by sublimation.

The infrared spectrum (CHCl₃) of 1-methyl-5-(3-fluorophenyl)tetrazole showed principal peaks at 1595, 1480, 1450 (shoulder), 1295, and 880 cm⁻¹ and its ^1H NMR spectrum (CDCl₃) consisted of a singlet (3 H) at δ 4.23 and a very broad, complex multiplet (4 H) at δ 7.0-7.7.

The infrared spectrum (CHCl₃) of 1-methyl-5-(4-fluorophenyl)tetrazole showed principal peaks at 1615, 1485, and 847 cm⁻¹, and its ^1H NMR spectrum (CDCl₃) consisted of a singlet (3 H) at δ 4.20 and two very broad, unsymmetrical multiplets (2 H apiece), one centered at δ 7.8 and the other at δ 7.28.

The 2-methyl-5-(3- and 4-fluorophenyl)tetrazoles were obtained by treating the sodium salt of 5-(3- or 4-fluorophenyl)tetrazoles with dimethyl sulfate in water. The resulting mixture of 1- and 2-methyl isomers was separated by chromatography on silica gel; the 2 isomers were eluted with benzene and the 1 isomers with chloroform. The relative amounts of the isomers in both cases were one part 1-methyl isomer to about four parts of the 2 isomer; the total yield of the two isomers was 80-90% of theory.

The infrared spectrum of 2-methyl-5-(3-fluorophenyl)tetrazole showed principal peaks at 1580, 1510, 1470 (shoulder), 1450, and 880 cm⁻¹, and its ^1H NMR spectrum consisted of a singlet (3 H) at δ 4.40 and a very broad, unsymmetrical multiplet (4 H) at δ 7.7.

The infrared spectrum (CHCl₃) of 2-methyl-5-(4-fluorophenyl)tetrazole showed principal peaks at 1615 (shoulder), 1600, 1455, 1155, 1095, and 844 cm⁻¹, and its ^1H NMR spectrum consisted of a singlet (3 H) at δ 4.40 and two unsymmetrical multiplets (2 H apiece) centered at δ 8.1 and 7.13.

C. Sodium Salts of the 5-Monosubstituted Tetrazoles. These could be easily obtained by dissolving equimolar amounts of the neutral tetrazole and NaOH in warm water and evaporating the solvent.

D. PBu₃Co(DH)₂Cl. This complex, a convenient starting material for all of the analogous tetrazole complexes, was prepared in two steps from CoCl₂·6H₂O as described by Marzilli[36] or by base exchange with $P(C_6H_5)_3Co(DH)_2Cl$,[37] the latter compound being prepared by the same two-step route as the PBu₃ analogue. Experience showed that the conditions used in the base exchange route were less prone to result in contamination by ion pairs of the type $[L_2Co$-$(DH)_2]^+[Co(DH)_2Cl_2]^-$.

E. LCo(DH)₂Cl. Eleven other complexes of this type were prepared by base exchange with $P(C_6H_5)_3Co(DH)_2Cl$[37] in ethanol including L = imidazole, 1-methylimidazole, 2-methylimidazole, 4-methylimidazole, pyridine, aniline, $(CH_3O)_3P$, $(CH_3)_2PC_6H_5$, $CH_3P(C_6H_5)_2$, $(p$-$ClC_6H_4)_3P$, and $(p$-$CH_3C_6H_4)_3P$. The complexes other than the imidazole complexes have been previously reported.[27] The yields, colors, and ^1H NMR spectral data for the new complexes are as follows. L = imidazole: brown powder, 95% yield; ^1H NMR (Me₂SO-d_6) δ 6.4-7.2 (m, 4 H, Im), 2.27 (s, 12 H, (DH)₂). L = 1-methylimidazole: brown crystals, 63% yield; ^1H NMR (CDCl₃) δ 6.6-7.2 (m, 3 H, Im), 3.57 (s, 3 H, 1mCH₃), 2.35 (s, 12 H, (DH)₂). L = 2-methylimidazole: brown powder, 91% yield; ^1H NMR (CDCl₃) δ 6.6-6.8 (m, 3 H, Im), 2.29 (s, 12 H, (DH)₂), 2.18 (s, 3 H, 1mCH₃). L = 4-methylimidazole: brown powder, 90% yield; ^1H NMR (CDCl₃) δ 6.1-7.0 (m, 3 H, Im), 2.28 (s, 12 H, (DH)₂), 2.01 (s, 3 H, 1mCH₃).

F. PBu₃Co(DH)₂(5-R-tetrazolate). The series of tetrazole complexes was prepared by anionic metatheses of PBu₃Co(DH)₂Cl.[36] A representative procedure went as follows: 1.5 g of PBu₃Co(DH)₂Cl (3 mmol) was dissolved with stirring and gentle heating in 25 mL of 80% CH₃OH. A second solution containing 3 mmol of Na⁺ 5-R-tetrazolate dissolved in 5 mL of warm H₂O was added dropwise to the first. The resulting solution was heated for about 30 min before more water was added in an amount that depended on the solubility of the product. The addition of water induced crystallization in each case except for the 5-benzyltetrazolate complex. The solutions containing crystals were refrigerated overnight, filtered with suction, washed with H₂O, and air dried. Addition of 50 mL of H₂O to the solution of 5-benzyl-

Table I. Physical Properties and Chemical Analyses of the [PBu₃Co(DH)₂-5-R-tetrazolate] Complexes[a]

R	description	dec point (θ), °C[b]	% yield[c]	empirical formula	calcd, %		found,[d] %	
					C	H	C	H
CH₃	yellow powder	180	48	$C_{22}H_{44}CoN_8O_4P$[e]	46.02	7.66	45.79	7.77
CF₃	brown plates	215	85	$C_{22}H_{41}CoF_3N_8O_4P$	42.04	6.58	42.18	6.59
C₆H₅CH₂	gold crystals	150	65	$C_{28}H_{48}CoN_8O_4P$	51.69	7.44	51.75	7.60
C₆H₅	brown crystals	185	97	$C_{27}H_{46}CoN_8O_4P$	50.94	7.28	51.11	7.36
3-F-C₆H₄	brown crystals	181	85	$C_{27}H_{45}CoFN_8O_4P$	49.54	6.93	49.26	7.24
4-F-C₆H₄	brown crystals	200	90	$C_{27}H_{45}CoFN_8O_4P$	49.54	6.93	49.65	7.12
(CH₃)₂N	yellow powder	180	90	$C_{23}H_{47}CoN_9O_4P$[f]	45.80	7.79	45.78	7.87

[a] Throughout the remainder of this paper the complexes will be abbreviated as follows: R = CH₃, [Me]; R = CF₃, [CF₃]; R = C₆H₅CH₂, [Bzl]; R = C₆H₅, [Ph]; R = 3-F-C₆H₄, [3F]; R = 4-F-C₆H₄, [4F]; R = (CH₃)₂N, [DMA]. [b] Decomposition points are uncorrected. [c] The yield is based upon the weight of (PBu₃)Co(DH)₂Cl used in the compound preparation. [d] Chemical analyses were performed by Chemalytics, Inc., Tempe, Ariz. [e] N: calcd, 19.51; found, 19.24. P: calcd, 5.39; found, 5.39. [f] N: calcd, 20.89; found, 20.86. P: calcd, 5.13; found, 5.40.

Table II. Crystal Data

formula: $C_{22}H_{41}CoF_3N_8O_4P$	$a = 12.040\ (2)$ Å
mol wt 628.6	$b = 21.531\ (3)$ Å
space group *Pbca*	$c = 23.536\ (4)$ Å
systematic absences	$V = 6106.3\ (1.8)$ Å³
$0kl\ (k = 2n + 1)$	$d_{calcd} = 1.368$ g cm⁻³
$h0l\ (l = 2n + 1)$	$d_{measd} = 1.374\ (8)$ g cm⁻³
$hk0\ (h = 2n + 1)$	$Z = 8$
$h00\ (h = 2n + 1)$	$\mu = 6.99$ cm⁻¹
$0k0\ (k = 2n + 1)$	$F(000) = 1156$
$00l\ (l = 2n + 1)$	

tetrazolate complex resulted in an oil which, upon cooling, sank to the bottom of the flask in a viscous, even layer. After several hours, traces of crystals could be seen which had formed from the top of the viscous mass. A small amount of these crystals was collected as the liquid was decanted through filter paper. The solid mass was dissolved in the minimum volume of a 90% DMF–10% H₂O solution and heated to 45 °C. Addition of water to the warm, filtered solution created an oil. Just enough 95% ethanol to dissolve the oil was added and then the solution was allowed to slowly evaporate. Seeding of the reduced solution followed by cooling resulted in glittering gold crystals. The product was isolated in essentially the same manner used with the other complexes. The complexes were usually pure enough to preclude recrystallization but each of them can be recrystallized from warm DMF–H₂O mixtures. Table 1 contains the physical properties, chemical analysis of each tetrazole complex, and the abbreviation scheme used throughout the remainder of this paper.

G. Attempted Preparation of Other LCo(DH)₂(5-R-tetrazolate) Complexes. Following a procedure similar to that given in F above, the LCo(DH)₂Cl [L = 1-methylimidazole, 2-methylimidazole, 4-methylimidazole, pyridine, aniline, (CH₃O)₃P, (CH₃)₂PC₆H₅, CH₃P(C₆H₅)₂, P(C₆H₅)₃, (*p*-ClC₆H₄)₃P, and (*p*-CH₃C₆H₄)₃P] complexes were each reacted with each of the Na⁺ 5-R-tetrazolates in 80% CH₃OH. In most cases decomposition occurred. Only four tetrazole complexes were isolated. PyCo(DH)₂(5-C₆H₅tet): brown crystals, 88% yield; ¹H NMR (CDCl₃) δ 7.2–8.6 (m, 5 H, py), 7.1–8.0 (m, 5 H, tetC₆H₅), 2.37 (s, 12 H, (DH)₂). CH₃P-(C₆H₅)₂Co(DH)₂(5-CH₃tet): brown crystals, 85% yield; ¹H NMR (CDCl₃) δ 7.2–7.7 (m, 10 H, P(C₆H₅)₂), 2.23 (s, 3 H, tetCH₃), 1.94 (d, 3 H, $J = 12$ Hz, PCH₃), 1.89 (d, 12 H, $J = 1.2$ Hz, (DH)₂. CH₃P(C₆H₅)₂Co(DH)₂(5-C₆H₅CH₂tet): yellow powder, 80% yield; ¹H NMR (CDCl₃) δ 7.1–7.7 (m, 10 H, P(C₆H₅)₂), 6.98 (s, 5 H, tetC₆H₅), 3.93 (s, 2 H, tetCH₂), 1.92 (d, 3 H, $J = 12$ Hz, PCH₃), 1.85 (d, 12 H, $J = 1.2$ Hz, (DH)₂). CH₃P(C₆H₅)₂Co(DH)₂[5-(4FC₆H₄tet)]: yellow powder, 90% yield; ¹H NMR (CDCl₃) δ 7.3–7.6 (m, 10 H, P(C₆H₅)₂), 6.7–8.0 (m, 4 H, tetC₆H₄F), 1.92 (d, 3 H, $J = 12$ Hz, PCH₃), 1.98 (d, 12 H, $J = 1.2$ Hz, (DH)₂). All four of these complexes appear to contain N₂-bound tetrazoles. See the Results and Discussion section for an explanation of this conclusion.

Physical Measurements. Nuclear Magnetic Resonance. The ¹H, ¹³C{¹H}, ³¹P{¹H}, and ¹⁹F{¹H} NMR spectra were recorded at 100.1, 25.2, 40.5, and 94.1 MHz, respectively, on a Varian XL-100-15 spectrometer operating in FT NMR mode with a Varian 620L computer. All proton and ¹³C{¹H} chemical shifts were recorded relative to internal Me₄Si. ³¹P{¹H} and ¹⁹F{¹H} NMR spectra were recorded relative to external 85% H₃PO₄ and external C₆F₆, respectively.

Conductivity Studies. Conductance studies were performed at 25 ± 0.1 °C with temperature regulation maintained by a Brinkmann Lauda K-2/R temperature controller. Conductance measurements were made using a Yellow Springs Instrument Co. conductivity cell Model 3403 and measured with an Industrial Instruments conductivity bridge Model RC16B2 adapted in house for use with either Heathkit Model E.U.W. 25 or Tektronix Inc. Type 310 oscilloscopes.

Experimental X-ray Diffraction. A crystal suitable for X-ray diffraction study (0.3 × 0.3 × 0.2 mm) was mounted on a Syntex P2₁ diffractometer. The cell dimensions (Table 11) and their standard deviations were determined by least-squares fit to the 2θ, ω, and χ settings for 12 independent reflections. Data were measured at room temperature using molybdenum graphite monochromatized radiation, a θ–2θ scan with speed of 2.0–29.3° min⁻¹, depending upon the intensity of a 2-s prescan, and a 2θ scan range of $(1.6 + 0.692 \tan \theta)°$ starting the scan from 0.8° below the calculated Kα₁ position. Background measurements were made at each end of the scan range for a time period equal to ¼ of the scan time with crystal and counter stationary. Reflections were measured in the *hkl* octant to $2\theta_{max} = 45°$. Three standard reflections were measured after every 100 reflections and their intensities showed deviations of less than 4% during the course of data collection; 2525 independent reflections were considered observed [$I > 3\sigma(I)$] and were used for solution and refinement after correction for background, Lorentz, and polarization effects. Absorption corrections were not made ($\mu = 6.99$ cm⁻¹).

Atomic coordinates were determined by direct methods and refined by least-squares techniques. Three cycles of refinement [function minimized, $\Sigma(|F_o| - |F_c|)^2$] of positional and anisotropic thermal parameters for the 39 nonhydrogen atoms gave $R = 6.7\%$ [$R = (\Sigma||F_o| - |F_c||/|F_o|)(100)$]. A difference Fourier map calculated at this stage allowed location of the 41 hydrogen atoms. The hydroxyglyoximato protons, however, were placed at calculated positions midway between the oxygen atoms. All other protons were placed as found. Positional parameters were varied for protons. Scattering factors for all atoms were taken from Cromer and Mann.[38] During the final cycles of refinement,[39] the Co and P form factor tables were corrected for the real and imaginary parts of the anomalous dispersion effect. Unit weights were used throughout. The final R was 5.4% and "goodness of fit" equals 2.8 [$((\Sigma w(F_o - F_c)^2/(NO - NV))^{1/2}$ where NO = 2446 observations and NV = 517 parameters].

Final atom positions are collected in Table 111, and derived angles and distances appear in Table 1V. The anisotropic thermal parameters and structure factor tables are available as supplementary material.

Results and Discussion

Thirteen different complexes of the type LCo(DH)₂Cl, where L was a variety of nitrogen and phosphorus donor ligands, were reacted with the sodium salts of seven different 5-substituted tetrazoles in 80% methanol solution with the intent of preparing LCo(DH)₂(5-R-tetrazolate) complexes. When L = Bu₃P, the cobalt tetrazolate complexes were each isolated in relatively high yield (48–97%). These seven complexes were easily crystallized, are highly soluble, and satisfied the overall objectives of this research. Among all the other attempts only four tetrazole complexes were easily isolated in high yield, namely, pyCo(DH)₂(5-C₆H₅tet), CH₃P(C₆H₅)₂Co(DH)₂(5-CH₃tet),　　CH₃P(C₆H₅)₂Co-

Table III. Fractional Coordinates with Standard Deviations

atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$	atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$
Co(1)	0.2540(1)	0.2661(1)	0.1465(1)	H(1)	0.418(5)	0.308(3)	0.213(2)
P(1)	0.1576(2)	0.3561(1)	0.1530(1)	H(2)	0.087(6)	0.218(3)	0.084(3)
N(1)	0.3850(5)	0.3086(2)	0.1308(2)	H(3)	0.144(7)	0.354(3)	0.249(3)
N(2)	0.2390(5)	0.2693(3)	0.0672(2)	H(4)	0.245(5)	0.399(2)	0.233(2)
N(3)	0.1264(5)	0.2200(2)	0.1639(2)	H(5)	0.112(7)	0.473(4)	0.202(3)
N(4)	0.2699(5)	0.2614(2)	0.2266(2)	H(6)	0.026(9)	0.440(5)	0.234(4)
N(5)	0.4212(6)	0.1793(2)	0.1040(2)	H(7)	0.054(5)	0.513(3)	0.296(3)
N(6)	0.3350(5)	0.1867(2)	0.1381(2)	H(8)	0.118(7)	0.450(4)	0.321(3)
N(7)	0.3075(6)	0.1341(3)	0.1625(3)	H(9)	0.214(5)	0.404(2)	0.070(2)
N(8)	0.3766(6)	0.0905(3)	0.1451(3)	H(10)	0.141(5)	0.445(3)	0.103(3)
O(1)	0.4588(4)	0.3250(2)	0.1705(2)	H(11)	0.296(6)	0.480(3)	0.157(3)
O(2)	0.1532(4)	0.2436(3)	0.0404(2)	H(12)	0.362(5)	0.430(3)	0.134(2)
O(3)	0.0580(4)	0.1970(2)	0.1244(2)	H(13)	0.358(8)	0.465(4)	0.038(4)
O(4)	0.3546(5)	0.2876(2)	0.2534(2)	H(14)	0.271(7)	0.524(3)	0.050(3)
C(1)	0.4081(6)	0.3158(3)	0.0763(3)	H(15)	−0.001(12)	0.310(7)	0.081(6)
C(2)	0.5197(8)	0.3400(4)	0.0573(5)	H(16)	−0.008(9)	0.312(5)	0.155(5)
C(3)	0.3222(7)	0.2927(3)	0.0402(3)	H(17)	−0.058(13)	0.398(7)	0.171(7)
C(4)	0.3287(11)	0.2960(5)	−0.0245(3)	H(18)	−0.041(7)	0.419(4)	0.096(4)
C(5)	0.1130(7)	0.2037(3)	0.2171(3)	H(19)	−0.196(8)	0.327(5)	0.098(4)
C(6)	0.0237(9)	0.1605(4)	0.2361(5)	H(20)	−0.221(12)	0.396(6)	0.108(5)
C(7)	0.1975(7)	0.2298(3)	0.2533(3)	H(21)	0.262(25)	0.493(13)	0.284(11)
C(8)	0.2006(10)	0.2200(5)	0.3170(3)	H(22)	0.230(16)	0.541(9)	0.268(9)
C(9)	0.4448(6)	0.1196(3)	0.1088(3)	H(23)	0.181(6)	0.553(3)	0.325(3)
C(10)	0.5375(8)	0.0880(4)	0.0807(4)	H(24)	0.395(13)	0.566(7)	0.111(6)
C(11)	0.2033(7)	0.4180(3)	0.1062(3)	H(25)	0.523(14)	0.524(7)	0.088(7)
C(12)	0.3060(7)	0.4545(3)	0.1206(3)	H(26)	0.447(10)	0.566(6)	0.054(5)
C(13)	0.3407(9)	0.4955(4)	0.0702(4)	H(27)	−0.201(10)	0.439(5)	0.058(5)
C(14)	0.4387(12)	0.5344(5)	0.0819(6)	H(28)	−0.160(12)	0.418(7)	0.023(6)
C(15)	0.0118(8)	0.3417(4)	0.1323(4)	H(29)	−0.278(13)	0.400(7)	0.034(6)
C(16)	−0.0586(11)	0.3874(7)	0.1107(7)	H(30)	0.555(9)	0.364(5)	0.086(5)
C(17)	−0.1641(9)	0.3742(5)	0.0869(7)	H(31)	0.554(10)	0.308(6)	0.051(5)
C(18)	−0.2063(17)	0.4032(13)	0.0470(9)	H(32)	0.511(9)	0.363(5)	0.036(5)
C(19)	0.1581(8)	0.3878(3)	0.2238(3)	H(33)	0.374(11)	0.270(6)	−0.038(5)
C(20)	0.0912(10)	0.4470(4)	0.2330(4)	H(34)	0.279(16)	0.288(9)	−0.039(7)
C(21)	0.1169(17)	0.4786(5)	0.2866(5)	H(35)	0.334(16)	0.334(8)	−0.042(7)
C(22)	0.2131(16)	0.5133(8)	0.2877(7)	H(36)	−0.030(11)	0.178(6)	0.231(6)
F(1)	0.5081(5)	0.0394(2)	0.0522(3)	H(37)	0.014(12)	0.127(7)	0.215(6)
F(2)	0.6145(6)	0.0704(4)	0.1129(3)	H(38)	0.048(13)	0.145(7)	0.267(7)
F(3)	0.5853(6)	0.1222(3)	0.0429(4)	H(39)	0.268(11)	0.202(6)	0.330(5)
				H(40)	0.195(12)	0.256(7)	0.336(6)
				H(41)	0.156(14)	0.200(8)	0.330(7)

$(DH)_2(5\text{-}C_6H_5CH_2tet)$, and $CH_3P(C_6H_5)_2Co(DH)_2[5\text{-}(4FC_6H_4tet)]$. By using the same NMR spectroscopic criteria discussed in the following sections it was concluded that the tetrazolate anions in each of these complexes were bound to cobalt via their N_2 nitrogens. Detailed spectroscopic and chemical characterization of the $(Bu_3P)Co(DH)_2(5\text{-}R\text{-}te$-trazolate) complexes was accomplished as discussed below.

^1H NMR. All of the $Bu_3PCo(DH)_2(5\text{-}R\text{-}tet)$ complexes exhibit a sharp, intense resonance at ca. δ 2.35 ppm due to the protons of the four equivalent oxime methyl groups, which appears as a narrow doublet due to phosphorus coupling ($J = 1.1\text{-}1.2$ Hz). The chemical shift of this resonance has been argued to depend upon changes in cobalt anisotropy,[40] electronic,[41] steric,[42,43] and anisotropic[44] interactions with the axial ligands for a wide variety of $LCo(DH)_2X$ complexes and found to vary over at least a 0.5-ppm range. Considering all of this, the narrow range of the oxime-methyl shifts exhibited in the cobaloxime tetrazoles is somewhat surprising: δ 2.30 ([Me]), 2.35 ([CF_3]), 2.24 ([Bz]), 2.36 ([Ph]), 2.38 ([3F]), 2.37 ([4F]), 2.34 ([DMA]). That only one oxime methyl signal was observed for each complex provides evidence for the existence of a single species in solution.[45] This is important for three reasons. First, PR_3 ligands are known to form ionic species such as $[(PR_3)_2Co(DH)_2]^+[Co(DH)_2X_2]^-$[46] and $[(PR_3)_2Co(DH)_2]^+X^-$,[47] especially in polar solvents such as methanol, which was used in the preparation of the tetrazole complexes. These types of species are detectable, even in trace

quantities, by the appearance of a triplet resulting from splitting of the oxime methyl resonance by the two mutually trans PBu_3 groups in the cationic half of the ion pair. Some batches of $PBu_3Co(DH)_2Cl$ contained impurities of this type and the absence of any such signals in the tetrazole complexes was taken as a preliminary indication of their purity. Second, the possibility of either tetrazole or phosphine dissociation from the complex, while not expected,[48] can be ruled out on this basis. Support for the absence of any ionic species, whether from tetrazole dissociation or ion-pair formation, was also found in the lack of any measurable conductance at 25 °C, even in highly dielectric solvents such as nitrobenzene. Finally, the steric consequences of N_1 and N_2 tetrazole coordination on the equatorial ligand system argue strongly against the possibility of identical shifts for the oxime methyl signals for the two linkage isomers. Thus, not only does there seem to be a single linkage isomer in each case but the narrow range of the oxime methyl shifts implies that all of the tetrazoles must be coordinated at the same position of their respective rings.

Spectra of complexes which have an NMR-observable group at the 5 position of the tetrazole ring support the case against a mixture of linkage isomers in any of these complexes as only single resonances were observed for the methyl protons in [Me], the methylene protons in [Bz], and the protons of the equivalent amino methyl groups in [DMA]. In the latter complex, the absence of splitting by the phosphorus of the amino methyl signal combined with its sharpness and chemical

Table IV. Relevant Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses[a]

Bond Lengths		Bond Lengths	
Co(1)–N(1)	1.860(6)	O(4)–H(1)	1.30(6)
Co(1)–N(2)	1.877(5)	O(1)–O(4)	2.456(7)
Co(1)–N(3)	1.875(6)	O(2)–H(2)	1.42(6)
Co(1)–N(4)	1.896(5)	O(3)–H(2)	1.10(6)
Co(1)–N(6)	1.979(6)	O(2)–O(3)	2.498(8)
Co(1)–P(1)	2.263(2)	N(6)–N(5)	1.321(9)
N(1)–O(1)	1.34(1)	N(5)–C(9)	1.320(9)
N(2)–O(2)	1.33(1)	C(9)–N(8)	1.340(10)
N(3)–O(3)	1.34(1)	N(8)–N(7)	1.320(10)
N(4)–O(4)	1.32(1)	N(7)–N(6)	1.312(9)
C(1)–N(1)	1.32(1)	C(9)–C(10)	1.46(1)
C(3)–N(2)	1.31(1)	C(10)–F(1)	1.29(1)
C(5)–N(3)	1.31(1)	C(10)–F(2)	1.26(1)
C(7)–N(4)	1.27(1)	C(10)–F(3)	1.29(1)
C(1)–C(3)	1.43(1)	Bond Angles	
C(5)–C(7)	1.44(1)	N(1)–Co(1)–N(2)	82.2(2)
C(1)–C(2)	1.51(1)	N(3)–Co(1)–N(4)	80.6(2)
C(3)–C(4)	1.53(1)	N(1)–Co(1)–N(4)	98.0(2)
C(5)–C(6)	1.49(1)	N(2)–Co(1)–N(3)	99.0(2)
C(7)–C(8)	1.51(1)	P(1)–Co(1)–N(1)	91.6(2)
P(1)–C(11)	1.814(8)	P(1)–Co(1)–N(2)	89.2(2)
P(1)–C(15)	1.848(10)	P(1)–Co(1)–N(3)	91.1(2)
P(1)–C(19)	1.801(8)	P(1)–Co(1)–N(4)	91.8(2)
C(11)–C(12)	1.50(1)	N(6)–Co(1)–N(1)	89.2(2)
C(12)–C(13)	1.54(1)	N(6)–Co(1)–N(2)	88.8(2)
C(13)–C(14)	1.47(2)	N(6)–Co(1)–N(3)	88.2(2)
C(15)–C(16)	1.40(2)	N(6)–Co(1)–N(4)	90.2(2)
C(16)–C(17)	1.42(2)	Co(1)–P(1)–C(11)	115.6(3)
C(17)–C(18)	1 24(3)	Co(1)–P(1)–C(15)	109.0(3)
C(19)–C(20)	1.52(1)	Co(1)–P(1)–C(19)	112.6(3)
C(20)–C(21)	1.47(2)	C(11)–P(1)–C(15)	104.6(4)
C(21)–C(22)	1.39(3)	C(11)–P(1)–C(19)	106.4(3)
O(1)–H(1)	1.17(6)	C(15)–P(1)–C(19)	108.0(4)

[a] Refer to Figure 4 for the crystallographic atom numbering scheme.

shift (δ 2.89) all point to coordination of an endocyclic ring nitrogen rather than the exocyclic amine nitrogen.

The most important aspect of the ¹H NMR spectra is found lin the aromatic region of [Ph], [3F], and [4F]. The tetrazole rings in these complexes exhibit interannular conjugation with their 5-Ph substituents. This phenomenon is manifested by a deshielding of the protons and shielding of the carbons ortho to the tetrazole ring (relative to the values of the corresponding parameters in unsubstituted benzene). Though explanations of the factors contributing to the effect seem to be as plentiful as the number of specific systems in which it has been observed, the one condition which all investigators agree must exist is the mutual coplanarity of the aromatic rings.[24] The key fact is that this coplanarity is maintained only when the tetrazole ring is N_2 substituted or, in this case, N_2 coordinated. The effect is diminished or disappears entirely when a substituent on the N_1 position of the tetrazole sterically induces rotation about the tetrazole–phenyl bond away from coplanarity. Table V contains chemical-shift data for the phenyl protons of [4F] and [Ph] as well as the data for some N_1- and N_2-alkyl derivatives of the corresponding free tetrazoles. The chemical shifts of the multiplets and the separation between them permit the unambiguous assignment of N_2 coordination of the tetrazole in [4F] and [Ph]. In [3F], the anisotropy caused by the meta-substituted fluorine causes the multiplets to overlap in a complex pattern. Figure 1 shows the ¹H NMR in the aromatic region of [3F], [4F], and [Ph] compared with the ¹H NMR of the N_1- and N_2-methyl substituted isomers of the corresponding free tetrazoles. It can be seen clearly that in each complex the splitting pattern is identical with that found in the 2-methyl-5-R-tetrazole.

Keeping in mind the qualitative nature of the data in Table V, some interesting observations can be made. For instance, the effects of substituents on the phenyl ring of the biaryl system have been found to be additive, to a certain extent, by Fraser and Haque.[24] They were able to predict the chemical shifts of the phenyl protons in compounds **7** and **9** (Table V) by adding the substituent effect of the nitro group to that of the substituted tetrazole ring. Numerical values for the effect of each substituent on the protons ortho and meta to it were simply defined as the difference between the shifts observed for each of these types of protons in the substituted benzene ring of the aryltetrazoles and the shift of benzene itself. Using the same procedure, predicted values were obtained for the isomeric N-methyl-5-phenyltetrazoles and for [4F]. The predicted values (Table V) agree quite well with the observed shifts, especially for [4F]. The largest deviation from additivity in our compounds is in the ortho protons of an N_1 isomer, **6,** where the observed value is 0.30 ppm downfield of what was predicted. Fraser and Haque[24] also claim that the electron-donating resonance effect of the tetrazole ring is manifested by downfield shifts of the ortho protons in going from an N_2 to the corresponding N_1 isomer. This behavior was said to be responsible for the shifts of **1** and **3**, though to a lesser degree than in **7** and **9**. Apparently this effect, if it exists at all, is of minor consequence in the 5-benzyltetrazoles since the meta protons of the N_1-substituted isomer are at higher field than those of N_2. Evidently, the aromatic ring of the benzyl group contributes additional shielding to the protons of the phenyl substituents on the tetrazole ring, especially those meta to the tetrazole. Finally, the phenyl protons in the complexed tetrazoles are slightly upfield of the corresponding values in the uncomplexed tetrazoles probably due to a weak, through-space effect of the equatorial ligand. It appears from these data that these additivity relationships should have general applicability in deducing the binding sites of potentially ambidentate heterocyclic biaryls.

¹³C NMR. A significant feature of the ¹³C NMR spectra is that in all of the complexes only one resonance appeared for each unique carbon. This substantiates our claim that a single mode of coordination exists between the tetrazole ring and Co. Table VI contains the chemical-shift values and $^nJ(P,C)$ coupling constants for the high-field region of the tetrazole complexes. The magnitude of the $^nJ(P,C)$ values and the relative shielding of the butyl carbons are consistent with those reported for other complexes containing the PBu₃ ligand.[50–53] Though the range of $^1J(P,C_\alpha)$ values is small, the magnitude of this parameter is seen to increase as the electron density of the tetrazole ring decreases and, hence, its trans labilizing ability decreases. This is consistent with Balimann and Pregosin's[53] observation that $^1J(P,C_\alpha)$ values of Pd^{II}- and Pt^{II}Cl₂L(PR₃) complexes are larger when the phosphine is trans to a group with a relatively small trans influence than vice versa.[53] Changes in $\delta^{13}C_\alpha$ are expected to parallel changes in $^1J(P,C_\alpha)$[54,55] but they do not. Despite the approximately 5 pK_a unit range of tetrazole acidities,[56] not only is it clear that the same donor atom is used throughout this series of complexes, but also the immediate environment of the metal remains essentially constant, consistent with the fact that all tetrazoles are N_2 coordinated and that the steric consequences of the different and remote 5 substituents are negligible.

Marzilli et al.[50] studied $^1J(P,C_\alpha)$ and $\delta^{13}C_\alpha$ in LCo(DH)₂X-type complexes where L included PBu₃ and X represented a large range of anionic ligands containing assorted donor atoms. Our results seem to support their conclusion that the estimation of through-bond electronic effects at nuclei close to a metal center using NMR shifts may be hazardous. However, their suggestion that a close parallel exists between the ability of X ligands to rehybridize metal centers and their charge-donating ability was not observed in our system.

Table V. [1]H Chemical Shifts of 5-Phenyltetrazole Derivatives

compd	no.	$\delta^1 H_o{}^{a,b}$	$\delta^1 H_{m,p}$	$\Delta\delta = ({}^1H_o - \delta^1 H_{m,p})$
1-CH$_3$,5-C$_6$H$_5$-tetrazole	1	7.64	7.64	0
1-CH$_2$C$_6$H$_5$,5-C$_6$H$_5$-tetrazole	2	7.53	7.28	0.25
2-CH$_3$,5-C$_6$H$_5$-tetrazole	3	8.13	7.41	0.72
2-CH$_2$C$_6$H$_5$,5-C$_6$H$_5$-tetrazole	4	8.17	7.43	0.74
[Ph]	5	7.96	7.28	0.68
1-CH$_3$,5-(4-FC$_6$H$_4$)-tetrazole	6	7.80 (7.50)^d	7.28 (7.32)	0.52 (0.18)
1-CH$_3$,5-(4-NO$_2$C$_6$H$_4$)-tetrazole^c	7	8.05 (7.85)	8.56 (8.59)	−0.51 (−0.74)
2-CH$_3$,5-(4-FC$_6$H$_4$)-tetrazole	8	8.10 (7.99)	7.13 (7.09)	0.97 (0.90)
2-CH$_3$,5-(4-NO$_2$C$_6$H$_4$)-tetrazole^c	9	8.21 (8.34)	8.21 (8.36)	0 (−0.02)
[4F]	10	7.94 (7.90)	7.01 (7.04)	0.93 (0.86)

^{a} All chemical shifts represent the center of gravity of the multiplet and are in parts per million downfield from internal Me$_4$Si for CDCl$_3$ solutions. ^{b} The phenyl protons are ortho (H$_o$) or meta and para (H$_{m,p}$) to the tetrazole ring. ^{c} Data taken from ref 24. ^{d} Values in parentheses are calculated from additivity relationships as described in the text.

Table VI. High-Field Proton Decoupled [13]C Chemical Shifts and $^nJ(P,C)$ Values of the [PBu$_3$Co(DH)$_2$-5-R-tetrazolate] Complexes

R	$\delta^{13}C(\text{ox-me})^a$	$\delta^{13}C_\alpha{}^b$	$^1J(P,C)^b$	$\delta^{13}C_\beta$	$^2J(P,C)$	$\delta^{13}C_\gamma$	$^3J(P,C)$	$\delta^{13}C_\delta{}^c$
CH$_3$	12.69	20.64	23.59	24.88	5.79	24.66	12.47	13.48
CF$_3$	12.65	20.82	24.26	24.80	5.82	24.53	12.57	13.38
CH$_2$C$_6$H$_5$	12.60	20.60	23.60	24.77	4.46	24.60	13.16	13.51
C$_6$H$_5$	12.73	20.66	24.11	24.81	5.74	24.62	12.70	13.52
3-F-C$_6$H$_4$	12.16	20.11	24.17	24.18	4.50	24.01	13.06	12.94
4-F-C$_6$H$_4$	12.72	20.66	23.87	24.77	3.68	24.59	12.50	13.48
N(CH$_3$)$_2$	12.64	20.63	23.59	24.84	4.45	24.66	13.18	13.54

^{a} Refers to the four equivalent methyl groups of the equatorial ligand; chemical shifts are in parts per million downfield from internal Me$_4$Si. ^{b}All coupling constants are in hertz; Co-P C$_\alpha$C$_\beta$C$_\gamma$C$_\delta$. ^{c} $^4J(P,C)$ in all of the complexes is $\approx$0.
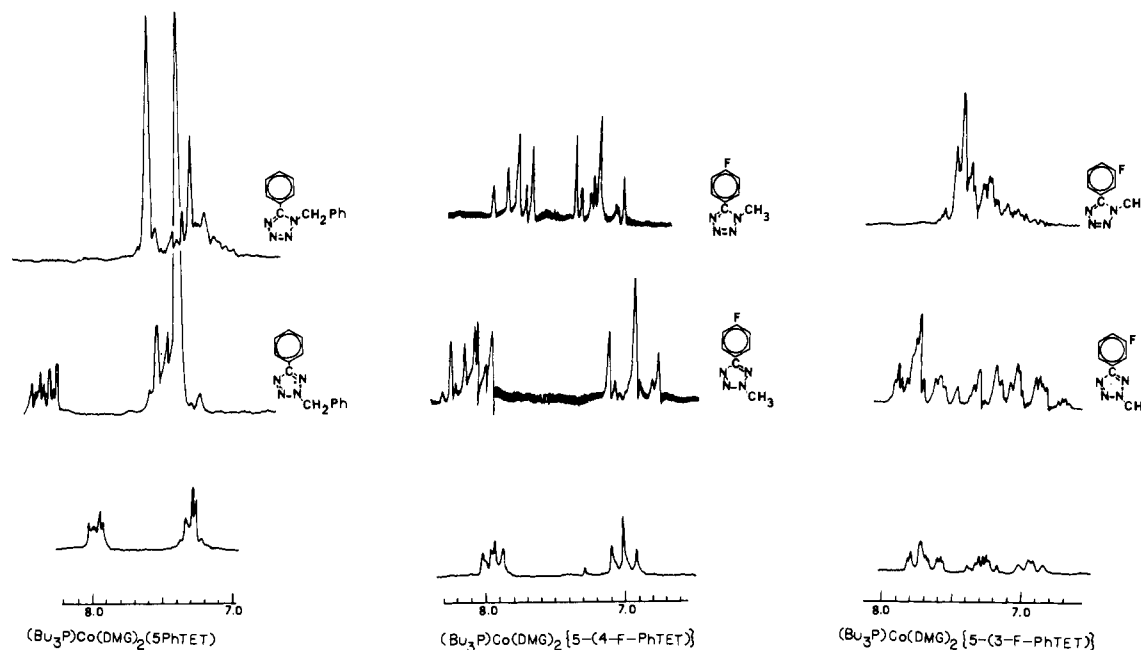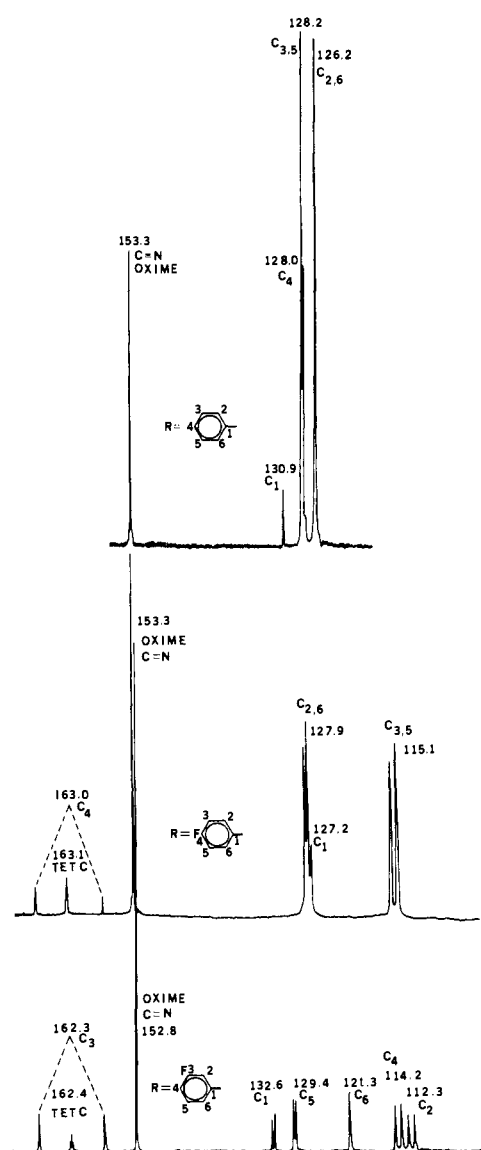

Figure 1. Low-field ^{1}H NMR spectra of 5-aryltetrazole derivatives.

Table VII contains $\delta^{13}C$, $^nJ(P,C)$, and $^nJ(C,F)$ data for the phenyl carbons in [Ph], [3F], [4F], and for free 5-phenylte-trazole and its N-methyl isomers, and Figure 2 compares the ^{13}C NMR spectra in the aromatic region of the 5-aryltetrazole complexes. For all the complexes, $\delta^{13}C$ of the oxime-imino carbon was found at 153.0 ± 1.0 ppm and, like the oxime methyl $\delta^{13}C$, did not correlate with the nature of the tetrazole substituent. The resonance due to the tetrazole ring carbon was not observed for all of the complexes. When this signal was seen, it was a very weak, poorly resolved multiplet of closely spaced lines. The chemical shifts for this carbon are relatively insensitive to the nature of the 5 substituent. This somewhat surprising result is found for uncomplexed tetrazoles as well, where the value for 5-phenyltetrazole (δ 140.2) can be com-

pared to δ 144.0 for tetrazole itself.[27] The splitting of the tetrazole carbon signal was observed to be ca. 3-3.5 Hz upon scale expansion. This value of $^4J(P,C)$ is interesting considering that $^4J(P,C) \simeq 0$ in the alkyl chains of both free[57] and complexed PBu$_3$.[54] Evidence supporting the nature of this coupling was found in the spectra of [3F] and [4F] (Figure 2). In the former, the expanded spectrum reveals an apparent triplet for the tetrazole ring carbon with a separation of $\approx$3 Hz between adjacent lines. This is consistent with approximately equal values of $^4J(P,C_{tet})$ and $^4J(C-F)$. The latter value of $\approx$3 Hz is very close to the 3.2 Hz found for $^4J(C-F)$ in fluoroben-zene.[58] In [4F] the tetrazole carbon is five bonds away from the fluorine substituent and the tetrazole-carbon signal exhibits four unsymmetrically spaced lines. One pair of lines is sepa-

Table VII. Low-Field $^{13}C\{^{1}H\}$ Chemical Shifts and $^{n}J(C,F)$ Values[a] of 5-Phenyltetrazole Derivatives

compd	$\delta^{13}C_{tet}$	$\delta^{13}C_1$[b]	$\delta^{13}C_2$	$\delta^{13}C_3$	$\delta^{13}C_4$	$\delta^{13}C_5$	$\delta^{13}C_6$
5-C₆H₅tet[c]	140.3	133.4	120.8	129.8	129.6	129.8	120.8
1-CH₃-5-C₆H₅tet[c]			128.1	128.8	130.8	128.8	128.1
2-CH₃-5-C₆H₅tet[c]			126.4	128.5	129.9	128.5	126.4
[Ph]		130.9	126.2	128.2	128.0	128.2	126.2
[3F][d]	162.4	132.6 (132.5)	112.3 (111.7)	162.3 (163.6)	114.2 (113.9)	129.4 (129.8)	121.3 (121.8)
	$^4J(C,F) = 3$	$^3J(C,F) = 8.6$	$^2J(C,F) = 23.5$	$^1J(C,F) = -243.9$	$^2J(C,F) = 21.3$	$^3J(C,F) = 8.1$	$^4J(C,F) = 1.4$
	$^4J(P,C) = 3$						
[4F][d]	163.1	127.2 (126.5)	127.9 (127.8)	115.1 (114.1)	162.5 (163.1)	115.1 (114.1)	127.9 (127.8)
	$^5J(C,F) = 1.2$	$^4J(C,F) = 3.3$	$^3J(C,F) = 8.1$	$^2J(C,F) = 21.6$	$^1J(C,F) = -246.0$	$^2J(C,F) = 21.6$	$^3J(C,F) = 8.1$
	$^4J(P,C) = 3$						

[a] All coupling constants are reported in hertz. [b] C_1 is the carbon bonded to C_5 of the tetrazole ring; values in parentheses are calculated from the additivity relationships as described in the text. [c] Data from ref 27. [d] Carbon-fluorine coupling constants, $^nJ(C,F)$, in fluorobenzene are $^1J(C,F) = -244.7$; $^2J(C,F) = 21.0$; $^3J(C,F) = 7.8$; $^4J(C,F) = 3.2$. See ref 58.

Figure 2. Low-field ^{13}C NMR spectra of 5-aryltetrazole complexes.

the aryltetrazoles and suggest that such interannula conjugations play a role in affecting ^{13}C coupling constants. In this regard it is somewhat surprising that the resonance of the tetrazole ring carbon shifts about 20 ppm downfield upon coordination while the phenyl ring carbons exhibit much smaller shifts (1.6–5.4 ppm). Thus, the effect of coordination at the N_2 nitrogen on the ^{13}C chemical shifts of the phenyl ring carbons in [Ph] is very nearly the same (with the exception of the carbon para to the tetrazole) as N_2-methylation. This observation adds further proof that interannular conjugation resulting from coplanarity of the phenyl and tetrazole rings is maintained in these complexes and, hence, that the tetrazole must be coordinated at the N_2 nitrogen.

The effect of a fluorine substituent on the chemical shifts of the phenyl carbons can also be seen in the data of Table VII. Once again, the values in parentheses represent predicted chemical shifts calculated from the substituent effects of fluorine and the tetrazolatocobaloxime moiety on the phenyl carbons in exactly the same manner as described in the discussion of ^1H NMR shifts. The fluorine substituent effect was derived from published ^{13}C data on fluorobenzene[59] and the data for [Ph] was used to obtain the effect of a coordinated tetrazole as a substituent. Confirmation of the assignment of each phenyl carbon in [3F] and [4F] was made by comparing the value of $^mJ(F,C)$ for a given carbon with the corresponding $^mJ(F,C)$ reported for fluorobenzene.[58] The excellent agreement for both [3F] and [4F] between the predicted (in parentheses) and the observed chemical shifts of each carbon in the phenyl ring is important in two respects. First, it demonstrates that additivity of substituent effects exists in the ^{13}C as well as in the ^1H NMR spectra. This additivity confirms that the tetrazole ring in both [3F] and [4F] is N_2 coordinated since the predicted values are partly based on the data of [Ph] which was shown to be N_2 coordinated. Second, it supports the claim of Begtrup that ^{13}C NMR spectra yield unambiguous results in contrast to the ^1H NMR spectra in the study of interannular conjugation in N- or C-phenylazoles. While the predicted shifts of the phenyl protons in [4F] agreed very well with the observed values, this success must be viewed as somewhat fortuitous. The chemical shifts of the phenyl protons were determined by estimating the center of gravity of the multiplet associated with each type of proton, a very qualitative approach which depends on adequate separation of well-defined multiplets and the absence of substituents possessing anisotropy or other special effects. The clearest example of the superiority of ^{13}C over ^1H in the study of interannular conjugation is the case of [3F]. As mentioned earlier, the anisotropy which results from the fluorine substituent meta to the tetrazole renders the aromatic proton resonances usless for analysis (see Figure 1) except by

rated by 3 Hz while the other pair is separated by slightly more than 1 Hz. This pattern is consistent with overlap of the $^4J(P,C)$ doublet with the smaller doublet which is attributed to $^5J(C,F)$. These highly unusual splittings indicate the large extent to which π electrons are delocalized over both rings in

simple visual comparison. [13]C spectroscopy, on the other hand, has afforded an empirical treatment which successfully predicted the chemical shift of each carbon in the phenyl ring. Thus, in the extreme case where substitution on the phenyl ring obscures the phenomenon in the ^{1}H NMR, the ^{13}C data should still be able to not only verify its existence but predict chemical shifts as well. Consequently, ^{13}C NMR should be of great value in determining the binding sites of potentially ambidentate heterocyclic biaryls.

^{19}F NMR. The ^{19}F nucleus is expected to be more sensitive to the presence of linkage isomers in the tetrazole complexes than any other nucleus investigated. This nucleus is not susceptible to the through-space effects which complicate the interpretation of proton shifts. In addition, our complexes each contain only one fluorine atom (or set of magnetically equivalent fluorines in the case of [CF3]). These facts, together with the extremely large range of chemical shifts exhibited by fluorine, make the use of ^{19}F NMR very attractive as supportive evidence for our conclusions. Beck et al.[60] have used the ^{19}F signal of 5-trifluoromethyltetrazole to determine that a single mode of coordination existed in transition metal–tetrazolato complexes formed via cycloaddition of coordinated azides.[60] We have also observed a single, sharp line (ca. 99 ppm downfield from C_6F_6) in the [19]F{[1]H} spectrum of [CF3]. The spectra of [3F] and [4F] each displayed only one multiplet which became a singlet upon proton noise decoupling (centered at ca. 47.8 ppm downfield from $\bar{C}_6F_6$) with the expected splitting patterns and $J(F,H)$ coupling constants. The results provide strong support for the existence of a single mode of coordination by the tetrazole.

^{31}P NMR. The ^{31}P NMR spectra of the tetrazole complexes consisted of a single, broad resonance for each complex. The best resolution obtained was a line width of 73 Hz (7.5 mm at a half-height of 50 mm). Despite this broadness, the chemical shifts were reproducible to 0.1 ppm. The chemical shifts, measured in CDCl3 and reported in parts per million downfield from external 85% H3PO4, follow: [CF3], δ 29.0; [3F], δ 26.9; [ϕ], δ 26.8; [4F], δ 26.7; [Bz], δ 25.6; [Me], δ 25.5; [DMA], δ 25.1. Our results agree with Balimann and Pregosin's study of Pd[II]- and Pt[II]Cl2L(PR3) complexes where they observed δ^{31}P to move upfield as the trans influence of L increased.[53]
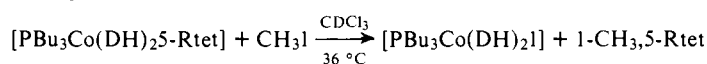
As the tetrazole ligand becomes less trans labilizing, the value of $^1J(P,C_\alpha)$ increases in magnitude and the ^{31}P signal moves to higher field. Since all the tetrazoles are coordinated via the N_2 position, the only significant difference between individual complexes in the series is the strength of the "electron pump" at the C5 position of the tetrazole ring. It is well known that $\delta^{13}C_\alpha$, $\delta^{31}P$, and $^1J(P,C_\alpha)$ are all intimately related to bond-angle changes at the phosphorus.[55] The substituent bond angles are strongly dependent on steric effects such as the size of the substituent and, in the case of Co–chelate systems, on the bulkiness of the other axial ligand. By utilizing only one phosphine with a homologous series of tetrazoles trans to it, the complexes of this system have all but eliminated a variation in steric effects, and a measure of the relative sensitivity of $\delta^{13}C_\alpha$, $\delta^{31}p$, and $^1J(P,C_\alpha)$ toward a purely electronic effect is possible. Thus, the tetrazole complexes show little change in the values of $\delta^{13}C_\alpha$, a small but finite variation in $^1J(P,C_\alpha)$, and a relatively large effect on $\delta^{31}P$.

The sensitivity of $\delta^{31}P$ is further demonstrated by its response to the rehybridization of Co which arises upon going from CH3Co(DH)2PBu3 to [Me]. The ^{31}P coordination chemical shift of the former[61] is 28 ppm compared to 57.8 ppm for [Me]. In the only other ^{31}P study of Co–chelate complexes with axial phosphines, Costa et al.[61] stated that, because the ^{31}P coordination chemical shifts they observed were in the range of other complexes, the possible effect of magnetic anisotropy due to the equatorial ligand was completely obscured. Reconsideration of their data, in conjunction with our results,

shows that this is incorrect. They observed a 2-ppm upfield shift on going from [CH3Co(DH)2PBu3] to [CH3Co{(do)(doh)-pn}PBu3]ClO4 (the latter is identical with (DH)2 except that one of the two OH···O bridges of (DH)2 is replaced by a trimethylene bridge). While the {(do)(doh)pn} complex bears a formal positive charge, this state is being approached as one goes from [DMA] to [CF3]. The upfield shift observed by Costa, being in the opposite direction to that expected on purely electronic changes at the Co center, as we have shown, is therefore attributable to anisotropic shielding by the equatorial ligand system. The $\Delta\delta^{31}P$ values observed by Costa for [CH3Co{(do)(doh)pn}PBu3]ClO4 (0 ppm) and for [C6H5Co{(do)(doh)pn}PBu3]ClO4 (+4 ppm) support this conclusion as well.[62] The difference in these two complexes, as far as the $\Delta\delta^{31}P$ is concerned, must be considered to be primarily inductive and the relative shifts are in accord with our results.
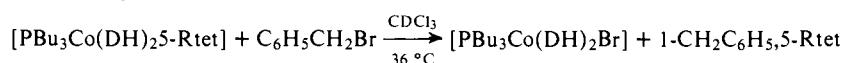
The broadness observed in the ^{31}P resonances of our complexes is assumed, as it was by Costa, to be caused by a quadrupolar relaxation mechanism induced by the [59]Co nucleus. Therefore a narrowing of the line width with an increase in temperature is expected. This follows as the quadrupolar relaxation rate, R_1, depends directly on the molecular correlation time, τ_c. As the temperature increases, the value of τ_c, an inverse function of molecular motion, decreases. This, in turn, will result in a decrease in the relaxation rate and a narrowing of the line width. Though line narrowing would also be seen if phosphine exchange were occurring, the possibility of this process is considered remote from the results discussed earlier and the known ability of PBu3 to displace every other phosphine from the coordination sphere of these types of complexes. It was, therefore, surprising to observe a small but definite broadening of the ^{31}P resonance upon increasing the temperature from 0 through 65 °C. The cause of this is uncertain. The only relaxation mechanism consistent with this behavior is spin rotation, and it has been shown that this mechanism, in general, becomes more important as a molecule becomes smaller and more symmetrical.[63] If this process were operative in our complexes, they would surely be the largest molecules yet reported to display it. Though the large size of our complexes is not in agreement with one of the conditions believed to generally exist in molecules displaying spin-rotation relaxation, it has also been suggested that molecules containing nuclei which have a wide range of chemical shifts may be prone to large spin-rotation interactions.[63] Considering the sensitivity of ^{31}P shifts to the subtle electronic changes in the tetrazole complexes, the existence of a spin-rotation relaxation mechanism has to be regarded as a possibility for the ^{31}P nucleus.

Alkylation Results. The NMR results alone do not conclusively establish the mode of coordination in complexes containing nonaryl 5 substituents but do provide strong evidence that a single linkage isomer is present. The N_2 coordination indicated for aryltetrazoles was expected because of the reported preference for N_2 attack by alkyl halides on 5-aryltetrazolate anions.[33] To confirm this assignment and to gain more information on the nonaryltetrazoles, solutions of each complex were treated with an excess of alkyl halide in an NMR tube. Several different alkyl halides were attempted in chloroform and nitrobenzene at room temperature. When the alkylation worked, a new signal would start to appear, usually within a few days, corresponding to the protons of the new ring substituent in the cleaved RN_1, 5-disubstituted tetrazole. Comparison of the chemical shift of this signal with the data previously reported allows the isomer to be immediately identified in most cases (Tables VIII and IX). For the alkylated tetrazoles which had not been previously prepared, the isomer could still be deduced. The important point is that, in each case where the alkylation worked, the product formed was *exclusively* the 1,5-disubstituted isomer. This is indirect evidence

Table VIII. Comparison of ^{1}H NMR Spectra of Isomeric Disubstituted Tetrazoles and the Products of the Reactions

$$[PBu_3Co(DH)_25\text{-Rtet}] + CH_3I \xrightarrow[36\ °C]{CDCl_3} [PBu_3Co(DH)_2I] + 1\text{-}CH_3,5\text{-Rtet}$$

| | reaction product | | free, disubstituted tetrazoles | | | |
| | | | 1,5 isomer | | 2,5 isomer | |
R	δR	δCH$_3$	δR	δCH$_3$	δR	δCH$_3$
CH$_3$	2.53	4.08	2.56	4.03	2.50	4.32
CF$_3$	a	4.27	a	4.30	a	b
CH$_2$C$_6$H$_5$	3.77	4.23	b	b	b	b
C$_6$H$_5$	7.47^c	4.07	7.64^c	4.15	8.13, 7.41^c	4.35
3-FC$_6$H$_4$	7.43^c	4.13	7.56^c	4.23	6.9–8.0^d	4.40
4-FC$_6$H$_4$	7.72, 7.17^c	4.23	7.80, 7.28^c	4.20	8.10, 7.13^c	4.40
N(CH$_3$)$_2$	3.00	3.90	3.00	3.87	b	b

^{a} R has no protons. Chemical shifts are downfield of internal Me$_4$Si for CDCl$_3$ solutions. ^{b} Data is unavailable. ^{c} Center of gravity of multiplet(s). ^{d} Broad, complex multiplet.

Table IX. Comparison of ^{1}H NMR Spectra of Isomeric Disubstituted Tetrazoles and the Products of the Reactions

$$[PBu_3Co(DH)_25\text{-Rtet}] + C_6H_5CH_2Br \xrightarrow[36\ °C]{CDCl_3} [PBu_3Co(DH)_2Br] + 1\text{-}CH_2C_6H_5,5\text{-Rtet}$$

| | reaction product | | free, disubstituted tetrazoles | | | |
| | | | 1,5 isomer | | 2,5 isomer | |
R	δR	δCH$_2$	δR	δCH$_2$	δR	δCH$_2$
CH$_3$	2.40	5.42	b	b	b	b
CF$_3$	a	5.60	a	5.60	a	5.73
CH$_2$C$_6$H$_5$	4.15	5.35	4.15	5.36	4.15	5.65
C$_6$H$_5$	c	5.55	7.53, 7.28^d	5.63	8.17, 7.43^d	5.73
3-FC$_6$H$_4$	c	5.57	b	b	b	b
4-FC$_6$H$_4$	c	5.53	b	b	b	b
N(CH$_3$)$_2$	2.90	5.40	2.98	5.50	3.05	5.57

^{a} R has no protons; chemical shifts are in parts per million downfield of internal Me$_4$Si for CDCl$_3$ solutions. ^{b} Data is unavailable. ^{c} Signal from R overlaps signal of aromatic protons in C$_6$H$_5$CH$_2$Br. ^{d} Center of gravity of multiplets.

Table X. Values of Angles of Fold and Cobalt Out-of-Plane Distances in Dimethylglyoximates Containing Phosphine Ligands

	compd	Co-P distance, Å	out-of-plane, Å	dihedral angle, deg	ref
I	n-Bu$_3$P-Co(DH)$_2$-tetrazole	2.263(2)	0.03	10.4	this work
II	n-Bu$_3$P-Co(DH)$_2$-py (C)	2.342(1)	0.03	4.4	65
III	n-Bu$_3$P-Co(DH)$_2$-xanthine (N)	2.285(2)	0.02	3.6	23
IV	Ph$_3$P-Co(DH)$_2$-CH$_3$	2.418(1)	0.112	13.6	68
V	Ph$_3$P-Co(DH)$_2$-Cl	2.327(4)	0.05	6.0	67
VI	Ph$_3$P-Co(DH)$_2$-NO$_2$	2.392(3)	0.04	7.7	66
VII	Chx$_3$P-Co(DH)$_2$-Cl	2.369(5)	0.100	15.7	68
VIII	pyCo(DH)$_2$(i-C$_3$H$_7$) (C)		0.022	4.3	72

that *all* of the tetrazoles were N$_2$ coordinated and that attack of the tetrazole ring occurred prior to its dissociation in every case.

Net atomic charges associated with each nitrogen of 5-methyltetrazolate and 5-(N,N-dimethylamino)tetrazolate were obtained by using MINDO/3 calculations.

	N$_1$	N$_2$	exocyclic N
5-CH$_3$tet$^-$	−0.3027	−0.1577	
5-N(CH$_3$)$_2$tet$^-$	−0.3150	−0.1402	−0.1895

Theoretically, the N$_1$ nitrogens are more nucleophilic than the N$_2$. For 5-N(CH$_3$)$_2$tet$^-$, N$_2$ sites are also less nucleophilic than the exocyclic nitrogen. Consideration of these results and the energetic equivalence of N$_1$ and N$_2$ substitution or coordination of tetrazole rings, as described in the Introduction, leads to the conclusion that regiospecific N$_2$ coordination in the cobalt oxime tetrazole complexes is due to steric restriction of the more nucleophilic, but also more hindered, N$_1$ binding site.

Complete alkylation results, including kinetics and mechanism, are the subject of a paper currently in preparation.

Discussion of the X-ray Crystallographic Results

1. General Geometry. Figures 3 and 4 show a perspective view of *trans*-bis(dimethylglyoximato)^N-2(5-trifluoromethyltetrazolato)(tri-n-butylphosphine)cobalt(III). Consistent with other structural investigations of bis(v-dioxime)cobalt(III) complexes (see references in Table X), coordination about the cobalt atom is roughly octahedral, but with distortion of the equatorial dimethylglyoximato ligands to accommodate the requirements of the most space filling of the trans ligands (PBu$_3$). The cobalt atom is displaced 0.03 Å toward the tri-n-butylphosphine group out of the plane of the four dimethylgyloxime nitrogen atoms (plane 1, Table XI). The average P(1)-Co(1)-N(equatorial) angle is 90.9° and the average N(6)-Co(1)-N(equatorial)^{64} angle is 89.1°. The N-Co(1)-N angles of the equatorial ligands are 82.2 (2) and 80.6 (2)° within the five-membered coordination rings and 98.0 (2) and 99.0 (2)° between those rings, consistent with observations in other structural determinations. The acute dihedral angle between the planes of the two glyoximato groups is 10.4°, the two planes being bent away from the tri-n-butylphosphine
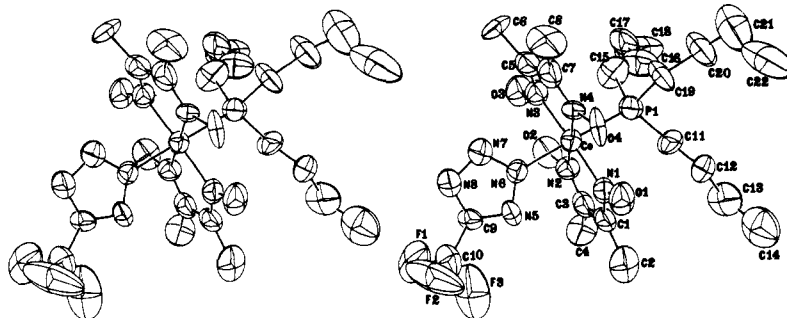
Figure 3. A view of PBu₃Co(DH)₂5-CF₃-tet complex.
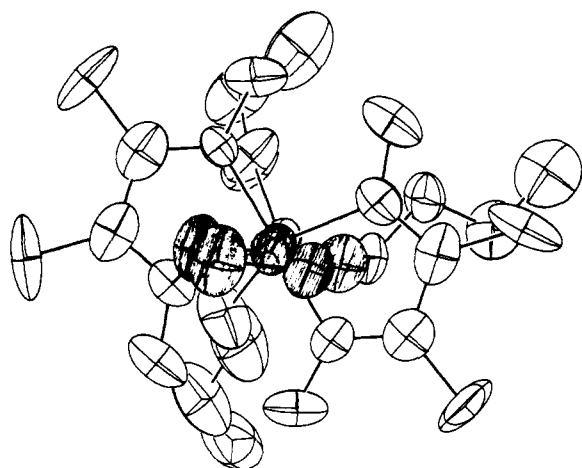
Figure 4. View of the PBu₃Co(DH)₂-tetrazole moiety down the Co-P bond.

Table XI. Equations of Least-Squares Planes and, in Brackets, Distances (Å) of Atoms from the Plane[a]

plane (1):	N(1)–(4)
	$-6.069x + 18.497y + 2.089z = 3.658$
	[N(1) −0.013, N(2) 0.013, N(3) −0.013,
	N(4) 0.013, Co(1) 0.030]
plane (2):	N(5)–(8), C(9)
	$7.445x + 4.474y + 17.839z = 5.792$
	[N(5) 0.002, N(6) 0.001, N(7) −0.004, N(8)
	0.005, C(9) −0.005, C(1) 0.020, C(5) −0.166]
plane (3):	Co(1), N(1)–(2), O(1)–(2), C(1)–(4)
	$-5.267x + 19.353y + 0.632z = 3.966$
	[Co(1) −0.062, N(1) 0.059, N(2) 0.028,
	O(1) 0.012, O(2) −0.034, C(1) 0.043,
	C(2) −0.089, C(3) 0.026, C(4) 0.016]
plane (4):	Cl(1), N(3)–(4), O(3)–(4), C(5)–(8)
	$-6.774x + 17.586y + 3.006z = 3.443$
	[Co(1) −0.043, N(3) 0.062, N(4) 0.007,
	O(2) 0.002, O(4) −0.025, C(5) 0.026,
	C(6) −0.070, C(7) 0.021, C(8) 0.020]

[a] The equations are referred to the crystal axes and x, y, and z are fractional coordinates.

group (I, Table X). Acute dihedral angles of 3.6 and 4.4° were observed in the structures of tri-*n*-butylphosphinebis(dimethylglyoximato)cobalt(III) xanthine[23] and pyridine[65] bound through nitrogen and carbon, respectively (III and II, Table X). Larger dihedral angles were observed in two structures having triphenylphosphinebis(dimethylglyoximato)cobalt(III) coordinated to a nitro group (7.7°)[66] and a chloride (6.0°)[67] (VI and V, Table X). A still larger angle of fold was in evidence in *trans*-bis(dimethylglyoximato)chlorotricyclohexylphosphinecobalt(III) toluene solvate (VII, Table X).[68] These increases of dihedral angle are paralleled by greater displacement of cobalt from the plane of the nitrogens of the equatorial ligand and by a lengthening of the Co-P bond (Table X).

It has been suggested that increased bulkiness of the phosphine ligand (cyclohexyl > phenyl > butyl) will dictate larger and larger angles of fold in those series where the trans ligand remains constant, but that in a series with a constant tri-R-phosphine ligand the space-filling properties of the opposite ligand, i.e., its ability to oppose deformation of the equatorial ligand, will be the dominant factor. The observation of a rel-, atively large angle (10.4°) in the title tetrazole structure as compared to 4.4° in the pyridine structure might thus be ascribed to the lessened opposition to deformation of the equatorial ligand offered by the five-membered tetrazole ring as compared to the six-membered pyridine ring. Other aspects of the structure suggest that the dominant effect is not steric (Discussion, part 5).[69]

2. Trans Effect. The cobalt-phosphorus bond (2.263 (2) Å) is one of the shortest observed in cobalt bis(dimethylglyoximato) structures. The trans effect has been well considered in complexes with relatively planar, equatorial ligands. In this structure, the shortness of the Co-P bond identifies *N*-2-(5-trifluoromethyltetrazole) as a slightly less powerful electron-donating ligand than xanthine, the trans Co-P bond being

0.022 Å longer in the xanthine complex. Both structures have shorter Co-P bonds than does the homologous C-bound pyridine complex (Co-P, 2.342 (1) Å), consistent with the observation that carbon-bonded ligands cause larger trans effects.

3. Hydrogen Bonding. Bis(dimethylglyoxime) structures have shown various modes of distribution of the hydrogen-bonded protons in the equatorial plane: (DH)(DH) symmetrical, (DH)(DH) asymmetrical, and (DH₂)(D).[23] In this determination, the protons were placed in (DH)(DH) symmetrical positions. They then refined to (DH)(DH) asymmetrical positions. Other determinations have assigned the longer Co-N and N-O distances of a
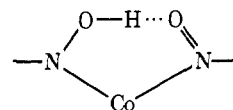
pair to the N-O-H group. This work does not clearly support that assignment.

4. Tri-*n*-butylphosphine. The tri-*n*-butylphosphine ligand has average P-C bonds (1.812 Å), average C-P-C angles (106.3°), and average Co-P-C angles (112.4°), consistent with phosphorus having tetrahedral coordination distorted by compression of the three alkyl groups away from the equatorial glyoxime ligands. Three anomalously short carbon-carbon distances give evidence of disorder in several carbon positions. Attempts to resolve the disorder, in terms of partial occupancy positions, were not stable to refinement. The other tri-*n*-butylphosphine structures (Table X) have also shown evidence of disorder in these groups.

5. *N*-2-(Trifluoromethyltetrazole). The planar tetrazole ring (SD 0.004) subtends an angle of 86.2° with the plane of the

equatorial nitrogen atoms. It coordinates to cobalt at N(6) and not at N(5). Unlike the xanthine and pyridine structures, where projection views down the P–Co bond show the plane of the trans ligand to be close to containing the line of fold of the two dimethylglyoximato rings (Figure 3, ref 23), the tetrazole ring in the title structure is situated such that its plane is nearly perpendicular to that line of fold (Figure 4). (C(1) and C(5) lie close to the plane of the tetrazole ring (plane 2, Table XI). Contact distances (Å) N(5)–N(1) (2.880 (8)), N(5)–N(2) (3.044 (9)), N(5)–C(1) (3.004 (9)), N(7)–N(3) (2.862 (10)), N(7)–N(4) (3.156 (10)), and N(7)–C(5) (3.068 (11)) are considerably shorter than van der Waals distances C–N (3.25 Å) and N–N (3.10 Å). In view of the relatively large angle of fold of the equatorial plane, the unexpected orientation of the tetrazole ring, and the short nonbonded contacts which might have been diminished by a different orientation of the ring or less folding, it is of interest to identify a positive or nonbonded attraction as the cause of these effects.

Interaction of the nucleophilic unshared pair of a nitrogen atom with a partially electron deficient center has been observed in the crystal structure of methadone base,[70] where nitrogen shows a nonbonded distance of 2.91 Å from a carbonyl carbon and the configuration of the molecule appears constrained to support that interaction. Evaluation of the geometry of a series of structures exhibiting this type of nonbonded interaction[71] shows that the shorter nonbonded distances may be correlated with deviation of bond angles at the electron-deficient carbon from sp^2 geometry toward an sp^3 configuration. In the title structure, the orientation of the tetrazole ring seems suitable for the interaction of N(7) with C(5) and N(5) with C(1) (Figure 3). In each dimethylglyoxime plane, the methyl carbon attached to C(5) or C(1) is the atom showing the greatest deviation from the plane, consistent with slight deviation of C(1) and C(5) from sp^2 geometry.

Supplementary Material Available: Listings of observed and calculated structure amplitudes and root mean square amplitudes of thermal vibrations (13 pages). Ordering information is given on any current masthead page.

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Transition Metal Arene Chemistry. 4.[1] Structural Studies of Cobalt Group Complexes

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Abstract: The molecular and crystal structures of $[\eta^6\text{-}C_6(CH_3)_6]_2Co^+PF_6^-$ (**1**) and of $[\eta^6\text{-}C_6(CH_3)_6]Rh[\eta^4\text{-}C_6H_2(CH_3)_6]^+PF_6^-$ (**2**) are described from an analysis of three-dimensional X-ray diffraction data. The cobalt salt, **1**, is orthorhombic, space group $Pnnm\text{-}D_{2h}^{12}$ (no. 58), with $a = 8.137$ (3) Å, $b = 10.738$ (4) Å, $c = 13.777$ (4) Å, and $Z = 2$. For the cationic cobalt complex, there is near D_{6h} symmetry with an eclipsed arrangement of the two hexahapto arene rings. Because all methyl substituents are bent away from the cobalt center there is no significant inter-ring nonbonded interaction. Consistent with the 20-electron character of this complex with the last two electrons residing in a degenerate metal–carbon antibonding orbital, the complex is paramagnetic and has relatively long cobalt–carbon bonds. The rhodium complex which was produced by Zn–HCl reduction of $[C_6(CH_3)_6]_2Rh^{2+}$ and previously described as a bis(hexamethylbenzene)rhodium⁺ complex is shown to be $[\eta^6\text{-}C_6(CH_3)_6]Rh[\eta^4\text{-}C_6H_2(CH_3)_6]^+$. The PF₆⁻ salt of the rhodium complex, **2**, is orthorhombic, space group $Pnna\text{-}D_{2h}^{16}$ (no. 62), with $a = 21.831$ (3) Å, $b = 13.401$ (2) Å, $c = 8.446$ (2) Å, and $Z = 4$. Partial hydrogenation of the one ring in the rhodium complex did not proceed through H₂ or H⁺ addition to the metal center of the precursor rhodium(II) bis(arene) complex because the two added hydrogen atoms are at exo ring positions. Presumably, the hydrogenation was effected by a heterogeneous process, i.e., at the zinc surface. This is the first crystallographic determination of an arene–rhodium complex and the structure exhibits several features of general significance in arene–metal chemistry.

Introduction

In a general study of transition metal arene complex chemistry, we seek structural and stereochemical definition of the mechanism by which transition metal bonds to aromatic hydrocarbons are formed and broken,[2] and of the mechanistic features of molecular transition metal complex catalysis of arene hydrogenation.[2b,3] A tetrahapto bonding of arene to metal has been suggested as a critical feature of the catalysis of arene hydrogenation by the d⁸ complex, $\eta^3\text{-}C_3H_5Co[P(OCH_3)_3]_3$.[3–5] For this reason, we have sought precise structural information about d⁸-metal arene complexes.

Literature reports posed interesting electronic and structural questions about d⁸ cobalt(I) bis(arene) complexes. A paramagnetic $[C_6(CH_3)_6]_2Co^+$ ion had been synthesized by the Fischer–Hafner procedure[6] and a diamagnetic $[C_6(CH_3)_6]_2Co^+$ ion reportedly[7] had been prepared from (mesityl)₂Co and 2-butyne. This apparent anomaly has been

resolved. Here we describe the crystal structure of the PF₆⁻ salt of the paramagnetic cation. In other studies, we have found that the (mesityl)₂Co and 2-butyne reactions produce no detectable bis(hexamethylbenzene)cobalt complex but rather a set of at least three cobalt(I) complexes. One has structure **3** with one hexahapto arene ligand and a tetrahapto penta-

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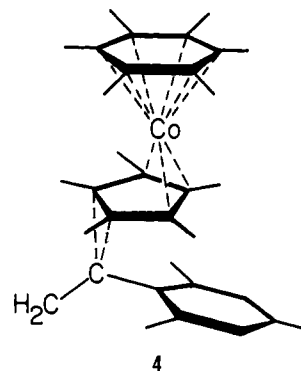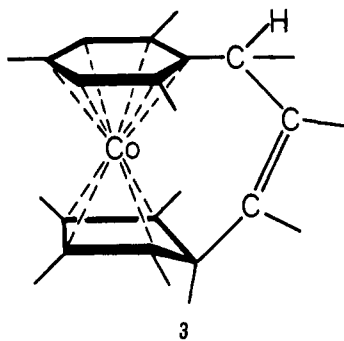
methylcyclopentadiene ligand. Preliminary X-ray diffraction results for another of these complexes indicate a solid-state structure in which a nonclassical carbonium ion has apparently been stabilized by interaction with a novel neutral (η^6-hexamethylbenzene)cobalt(η^3-pentamethylcyclopentadienyl) complex **4**. (In structures **3** and **4**, methyl groups are denoted by vectors from the contiguous carbon atoms.) However, the structural details have not yet been fully resolved for this system; complete structural descriptions of these relatively bizarre cobalt(I) complexes will be reported separately.[8]

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