J. Am. Chem. Soc. **1989**, *111*, 3881–3886

Synthesis and Structure of a 17-Electron Tetrahedral Cobalt Complex, Bis(2,2′-biquinolyl)cobalt: Reactions of a New Co/Pyrrolyl Synthetic Intermediate[1]

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Abstract: The preparation of bis(2,2′-biquinolyl)cobalt [Co(biq)$_2$] has been carried out from two different cobalt intermediates produced via the metal vapor cocondensation technique. Accordingly, the compound was prepared by (a) the reaction of an isolable Co/pyrrolyl intermediate with 2,2′-biquinoline in pyrrole solution at room temperature and (b) the reaction of toluene-solvated cobalt atoms with 2,2′-biquinoline at low temperature. Co(biq)$_2$ crystallizes in space group $P2_1/c$ with four molecules per unit cell and was refined to a residual of 4.6%. The structure was determined from 3470 observed diffractometer data in the range $2\theta \leq 50.67°$ at ambient temperature. The cobalt atom is bonded to two chelating 2,2′-biquinolyl ligands in a distorted tetrahedral geometry. A short Co–N$_{av}$ distance of 1.952 (3) Å and a short C–C$_{av}$ distance of 1.429 (6) Å bridging the quinoline fragments in the biquinolyl ligands provide evidence for a substantial transfer of electron density from the cobalt atom to the π^* orbitals of the 2,2′-biquinolyl ligands. Reactions of the Co/pyrrolyl intermediate with cyclopentadienide, methylcyclopentadienide, 1,2-bis(diphenylphosphino)ethane, 2,2′-bipyridine, and 2,2′-biquinoline have resulted in the syntheses of cobaltocene, dimethylcobaltocene, hydridobis[1,2-bis(diphenylphosphino)ethane]cobalt, bis[bis(2,2′-bipyridyl)cobalt], and Co(biq)$_2$, respectively.

In a previous study a novel metalation reaction at the *N*-hydrogen of pyrrole was reported for iron and a useful Fe/pyrrolyl reagent was isolated.[2] This metalation reaction was then extended to the pyrrole functionality in $\alpha,\beta,\gamma,\delta$-tetraphenylporphine providing a high-yield synthesis for ($\alpha,\beta,\gamma,\delta$-tetraphenylporphinato)iron(II) and a low-yield (<2%) synthesis for ($\alpha,\beta,\gamma,\delta$-tetraphenylporphinato)cobalt(II).[3] Herein, we report the synthesis of a Co/pyrrolyl intermediate and the reactions of this intermediate with cyclopentadienide, methylcyclopentadienide, 1,2-bis(diphenylphosphino)ethane, and 2,2′-bipyridine to produce known compounds. In addition, a new complex, bis(2,2′-biquinolyl)cobalt [Co(biq)$_2$] was produced when the intermediate was allowed to react with 2,2′-biquinoline. Because few 2,2′-biquinolyl complexes have been reported and little is known concerning the bonding of a chelated 2,2′-biquinolyl ligand,[4] details of an X-ray structure determination of Co(biq)$_2$ are also reported. Moreover, a second synthetic route to the complex was developed analogous to the metal atom reactor preparation of bis[bis(2,2′-bipyridyl)cobalt] reported previously.[5,8]

Experimental Section

Reagents and Solvents. Manipulations of products, reagents, and solvents were carried out using conventional vacuum-line techniques or a drybox (Vacuum Atmospheres Dri Lab with Model HE-493 Dri Train) employing an argon atmosphere. Pyrrole was predried with CaSO$_4$, fractionally vacuum distilled over sodium, and was degassed by distillation under a dynamic vacuum into a liquid-nitrogen trap. Toluene and tetrahydrofuran were distilled over sodium and degassed. The 2,2′-bipyridine (Aldrich) was purified by sublimation. The 1,2-bis(diphenylphosphino)ethane (Aldrich) was recrystallized from benzene, and the 2,2′-biquinoline (Alfa) was recrystallized from ethanol/hexane.

Physical Measurements. UV/vis spectra were recorded on a Shimadzu UV 260 spectrometer. IR spectra were recorded on a Nicolet MX-S Fourier transform spectrometer. Mass spectra were recorded on a Hewlett Packard 5985B GC/MS (IP 70 eV, temperature scan of 30 °C/min from 30–300 °C) and a Du Pont 21-491 mass spectrometer (variable ionization potential). Samples for all physical measurements were prepared in a glovebox.

Metal Atom (Vapor) Reactor and Techniques. A Kontes-Martin Glass Co. Model No. K-927500 static metal atom reactor was employed. This apparatus has been described in detail previously.[6] A nichrome wire that was attached to the two reactor electrodes was wrapped around the ligand inlet section inside the reactor to enhance the introduction of solvent and reagent vapors.

Preparation of Co/Pyrrolyl Intermediate. Cobalt vapor 0.586 g/9.944 mmol) was codeposited for 2 h at −196 °C with 115 mL of dry, degassed pyrrole. The resulting frozen matrix was allowed to warm with stirring. Upon warming, the matrix turned from white to a very dark brown color and formed a dark brown solution. Also upon warming, the evolution of gas bubbles was observed. A sample of the gas was collected by filling and then flushing with nitrogen gas approximately 500 mL of the resulting gas mixture into a gas bag. A GC (HP 5880-A Refinery Gas Analyzer) analysis of the reactor head gas confirmed the presence of a small amount of dihydrogen. The dark brown reaction solution was suction filtered from the reactor through a medium-porosity frit. Vacuum stripping of the filtered dark brown solution resulted in 0.463 g of a brown solid.

Preparation of Co(biq)$_2$. (a) Reaction of Co/Pyrrolyl Intermediate and 2,2′-Biquinoline. The Co/pyrrolyl intermediate (0.351 g) and 2,2′-biquinoline (1.021 g) were mixed with 20 mL of pyrrole in an inert-atmosphere glovebox. The solution turned from brown to an intense green color within minutes and was filtered through a medium-porosity frit 1 h after mixing. High-quality crystals for X-ray structural analysis were

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(7) (a) Results obtained in our laboratory from a single-crystal X-ray diffraction study confirm the structure to be hydridobis[1,2-bis(diphenylphosphino)ethane]cobalt. Details to be reported in a later paper. (b) The first reported isolation of this hydride were: Zingales, F.; Canziani, F.; Chiesa, A. *Inorg. Chem.* **1963**, *2*, 1303. Sacco, A.; Ugo, R. *J. Chem. Soc.* **1964**, 3274.

(8) Butamina, K. N. Masters Thesis, The University of North Dakota, Grand Forks, ND, 1986. An X-ray structure determination has been carried out in our laboratory on crystals prepared by Klabunde and co-workers[5] by reacting 2,2′-bipyridine with a cobalt/toluene slurry. Although the complex was reported to be a monomer,[5] it exists as an 18-electron dimer bis[bis(2,2′-bipyridyl)cobalt] in the solid state. Reagen, W. K.; Butamina, K. N.; Radonovich, L. J., to be submitted for publication.

0002-7863/89/1511-3881$01.50/0

obtained by permitting the green solution to stand at room temperature for 72 h. The air-sensitive dark green crystals were isolated by decanting the mother liquor and drying under vacuum; yield 0.353 g (this corresponds to 9.28% by weight of available cobalt in the intermediate). UV/vis (benzene; λ_{max}): 787 (e, 10564), 700 (e, 10564), 787 nm (e, 16924). IR (benzene): 1340 (s), 1292 (m), and 796 (m) cm^{-1}. No NMR or EPR signals were detected. The crystals were sparingly soluble in pentane but very soluble in benzene, tetrahydrofuran, and pyrrole.

(b) Reaction of Co/Toluene Intermediate and 2,2′-Biquinoline. During a 1.5-h period 0.058 g (0.98 mmol) of Co metal was codeposited at −196 °C with 115 mL (1.08 mol) of dry, degassed toluene, yielding a yellow-brown matrix. The matrix melted and formed a reactive cobalt/toluene slurry when the reactor was warmed to −94 °C using an acetone/liquid-nitrogen slush. A saturated 2,2′-biquinoline (0.75 g/2.93 mmol) in toluene (100 mL/0.941 mol) solution was added dropwise to the stirred slurry (−94 °C) over a 30-min period. The reaction solution was allowed to warm to room temperature, and an intense dark green solution resulted. The solution was suction filtered from the reactor and stripped of solvent under dynamic vacuum, yielding an unpurified dark green solid. A UV/vis spectrum of this solid in benzene was identical with the green crystalline Co(biq)$_2$ synthesized from the Co/pyrrolyl intermediate.

Reaction of the Co/Pyrrolyl Intermediate and 1,2-Bis(diphenylphosphino)ethane. One-fourth (28 mL) of a pyrrole solution of the Co/pyrrolyl intermediate prepared by the cocondensation of 0.4804 g of cobalt and 115 mL of pyrrole vapors was reacted directly as a filtered solution from the metal atom reactor with 1,2-bis(diphenylphosphino)ethane (0.9910 g/2.487 mmol) at room temperature under an argon atmosphere. The reaction mixture changed from a dark brown to an amber-brown within several hours. After 24 h translucent red crystals were observed in the reaction vial. High-quality crystals were obtained by permitting the solution to stand at room temperature for 2 weeks. Red translucent crystals were isolated by decanting the mother liquor and drying under vacuum; yield 0.183 g (equivalent to 10.5% by weight of available cobalt in the intermediate). Mp: 264 °C. IR (paraffin oil; uncorrected): 1883 (m), 1584 (w), 1304 (w), 1094 (m), 1025 (w), 868 (m), 802 (s), 747 (m), 739 (s), 692 (s), 673 (w), 662 (m), 651 (w), 626 (m), 617 (w), 594 (m), 524 (s), 513 (s), 494 (s), and 484 (m) cm^{-1}. Results from a single-crystal X-ray study of this material confirm the structure to be hydridobis[1,2-bis(diphenylphosphino)ethane]cobalt.[7]

Reaction of the Co/Pyrrolyl Intermediate and 2,2′-Bipyridyl. One-fourth (28 mL) of a pyrrole solution of the Co/pyrrolyl intermediate prepared by the cocondensation of 0.4804 g of cobalt and 115 mL of pyrrole vapors was allowed to react directly as a filtered solution from the metal atom reactor with 2,2′-bipyridine (1.110 g/7.107 mmol) at room temperature under an argon atmosphere. The brown solution turned to a green-grey within minutes. The color change was consistent with that reported for the cobalt dimer bis(bis(2,2′-bipyridyl)cobalt). After 24 h the solution was filtered through a fine-porosity frit to remove any unreacted material. After 2 days a small quantity of uncharacterized red crystals were produced. The solution was decanted from the red crystals and stripped of solvent. The visible spectrum of the resulting solid redissolved in pyrrole was in good agreement with that previously reported for the cobalt dimer bis[bis(2,2′-bipyridyl)cobalt].[8]

Reaction of the Co/Pyrrolyl Intermediate and Sodium Cyclopentadienide or Sodium Methylcyclopentadienide. Tetrahydrofuran (10 mL/122.87 mmol), the Co/pyrrolyl intermediate (0.05 g), and an excess of sodium cyclopentadienide were combined at room temperature under argon. The solution gradually turned from a red-brown to a deep purple over a 24-h period. The solution was stripped of solvent under vacuum, and cobaltocene (0.015 g/79.4 × 10^{-3} mmol, equivalent to 9.3% by weight of available cobalt in the intermediate) was sublimed at 50 °C from the reaction product as a purple solid. The mass spectrum of the purple solid gave confirmation of cobaltocene. An analogous reaction with sodium methylcyclopentadienide resulted in a comparable amount of methylcobaltocene.

Crystal Structure of Co(biq)$_2$. A crystal prepared from the reaction of 2,2′-biquinoline with the Co/pyrrolyl intermediate and having dimensions of 0.50 × 0.67 × 0.47 mm was wedged in a thin-walled 0.5-mm-diameter glass capillary under an Ar atmosphere. Preliminary Weisenberg and precession photographs led to the determination of space group $P2_1/c$ (No. 14).[9] Lattice constants from the setting angles of 30 reflections determined on a Picker FACS-1 diffractometer at room temperature were a = 12.189 (2), b = 18.644 (3), c = 14.280 (2) Å, and β = 107.83 (1)°. This unit cell with Z = 4 provides a calculated density, at ~23 °C, of 1.307 g/mL. Intensity data were collected with Zr-filtered Mo Kα radiation within the range $2\theta \leq 50.67°$. A 2θ scan width of 1.6°, plus an allowance for spectral dispersion, was used, and background counts were of 20-s duration. A set of three standard reflections monitored every 100 data remained stable over the course of data collection. An approximate calculation of absorption effects suggested that the maximum error introduced on F_o was <3%. Thus, no absorption corrections were made.

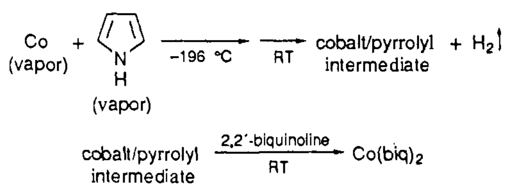
Intensity data were reduced to a set of $|F_o|$'s by application of Lorentz and polarization corrections (Lp).[10] Standard deviations were calculated according to

$$\sigma_F = [(C + k^2B + (0.02I)^2)/4|F_o|^2(Lp)^2]^{1/2}$$

where C and B are the count of the scan and backgrounds, respectively, k is the ratio of scan to background counting time, and I is the net intensity. Of the 5639 independent data collected, 3470 having $|F_o| > 3\sigma_F$ were taken as observed and utilized in the structure determination and refinement. Patterson and Fourier techniques were used to locate all non-hydrogen atoms in the asymmetric unit of structure.[11a] Isotropic full-matrix refinement[11b] was followed by anisotropic block diagonal refinement for the 46 non-hydrogen atoms. The 29 hydrogen positions were calculated at a fixed distance of 0.95 Å from their respective carbons and included in further refinement as fixed contributors with thermal parameters of 7 Å.[2] Neutral atom scattering factors[12] were used for all atoms, and anomalous dispersion[13] corrections were made for the cobalt atom at the end of the refinement. The pyrrole of solvation was treated as a five-carbon ring contributor in the refinement, and the five atoms were allowed to vary spatially and thermally. A discrepancy factor R between the calculated and observed structure factors of 6.8% and a weighted value R_w of 7.7% resulted. Further refinement proceeded smoothly and included the incorporation of empirical weights ($w = 1/\sigma^2$) where σ was calculated as defined previously.[14] The final refinement converged with R = 0.046, R_w = 0.060, and a goodness of fit of 1.17, with no significant change in any of the structural parameters previously obtained. The data to parameter ratio was 8.55:1. A final difference synthesis revealed the largest residual electron density was 0.30 e/Å^3 and the most negative value was −0.61 e/Å^3.

Results and Discussion

Synthesis of Co(biq)$_2$ and the Co/Pyrrolyl Intermediate. The first method



involved the room-temperature reaction of a new isolable Co/pyrrolyl intermediate with 2,2′-biquinoline. This reaction is an extension of earlier findings using iron vapor in the formation of an isolable Fe/pyrrolyl synthetic reagent.[2] Cobalt and pyrrole vapors were cocondensed simultaneously under a dynamic vacuum to form a frozen matrix, which was then warmed to room temperature forming the Co/pyrrolyl intermediate. Throughout the warm-up, the evolution of dihydrogen (GC analysis) was observed from the reaction mixture. In addition, the lack of an N–H stretch in the infrared spectrum of the reaction product is consistent with both the evolution of dihydrogen and a metalation reaction at the N-hydrogen of the pyrrole ring. Upon its formation in the metal vapor reactor, the intermediate remained soluble in pyrrole, but the degree of its resolubilization in this solvent after vacuum stripping was variable. Stable for months at room temperature under inert atmosphere, the intermediate is an air-sensitive dark

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(9) *International Tables for X-Ray Crystallography*; MacGillavry, C. H., Rieck, G. D., Eds.; Kynoch Press: Birmingham, England, 1962. This is a three volume set; Vol. I contains space group information, Vol. II contains mathematical principles, and Vol. III contains the information used in calculating the absorption coefficient.

(10) Program DIFFDATA, a Fortran program for data reduction, local version.

(11) (a) Zalkin, A. FORDAP, a Fortran crystallographic Fourier synthesis program, local version used. (b) Busing, W. R.; Martin, K. O.; Levy, H. A. Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1962. The function minimized was $w(|F_o| - |F_c|)^2$.

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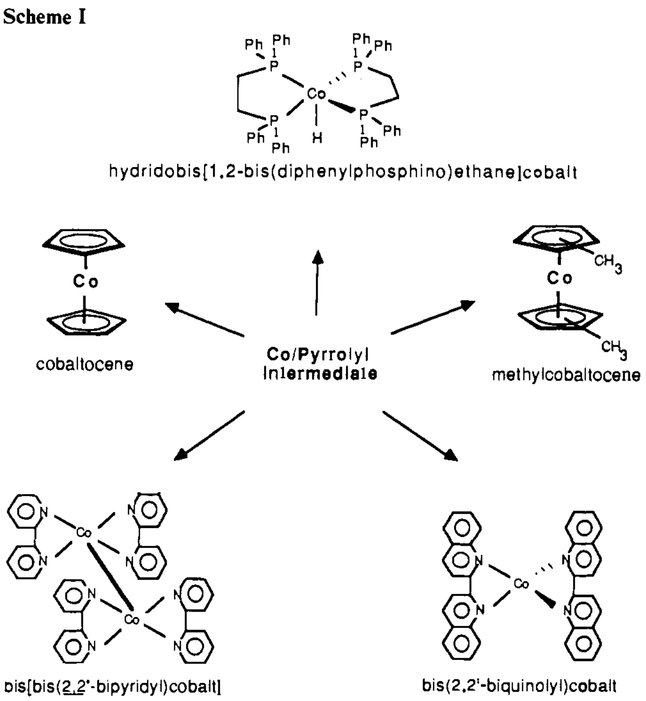
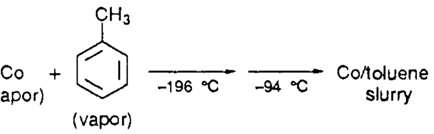
Scheme I



brown solid, which turns light brown upon air exposure. The isolable solid is a reactive and storable form of the Co/pyrrolyl intermediate, but the reactivity of the intermediate is greater if it is used directly from the reactor as a filtered pyrrole solution. Attempts to isolate a pure crystalline material by dissolving the filtered and vacuum-stripped reaction product in a variety of solvents followed by refrigeration were unsuccessful. Solvents attempted include pyrrole, tetrahydrofuran, toluene, and combinations of these.

The second method employed in the synthesis of Co(biq)$_2$ was analogous to that used in the preparation of bis[bis(2,2′-bipyridyl)cobalt]



$$\text{Co/toluene slurry} \xrightarrow[-94\ ^\circ\text{C}]{\text{2,2'-biquinoline}} \text{Co(biq)}_2$$

reported previously by Klabunde and co-workers.[5,8] We have substituted 2,2′-biquinoline for 2,2′-bipyridine in the reaction of a cobalt/toluene slurry at low temperature.

Reactions of the Co/Pyrrolyl Intermediate. Both the Co/pyrrolyl intermediate reported here and the cobalt/toluene slurry are useful intermediates to the formation of Co(biq)$_2$. As a pyrrole solution or as an isolable solid, the Co/pyrrolyl intermediate is of particular interest because it can be used at room temperature. It is also extremely reactive, usually forming products within minutes at room temperature under an inert atmosphere. The simple addition of an excess of 2,2′-biquinoline to a pyrrole solution of the Co/pyrrolyl intermediate at room temperature under an inert atmosphere resulted in the formation of Co(biq)$_2$. In addition, room-temperature reactions with cyclopentadienide, methylcyclopentadienide, 1,2-bis(diphenylphosphino)ethane, and 2,2′-bipyridine resulted in the isolable products, cobaltocene, methylcobaltocene, hydridobis[1,2-bis(diphenylphosphino)ethane]cobalt, and bis[bis(2,2′-bipyridyl)cobalt], respectively (Scheme I).

Similar to the Fe/pyrrolyl reagent previously reported, the reaction chemistry of the Co/pyrrolyl intermediate has been developed while its structural characterization remains inconclusive. The lack of a volatile component in the mass spectrum up to 300 °C and the slow resolubilization of the intermediate in pyrrole are properties consistent with an oligomeric or polymeric material. In addition, the lack of an N–H stretch in the infrared spectrum is consistent with metalation at the *N*-hydrogen of pyrrole. A possible structural model is a coordination polymer involving a π-pyrrolyl ligand that simultaneously functions as a σ-donor ligand. Indeed, as previously reported for a number of dimeric transition-metal complexes and a manganese trimer, the pyrrolyl ring can simultaneously fulfill both functions.[15] One possible model is depicted in Figure 1, which is similar to the model proposed for the Fe/pyrrolyl reagent.[2] The Co model differs by the inclusion of a Co–Co bond in order to maintain an 18-electron count.

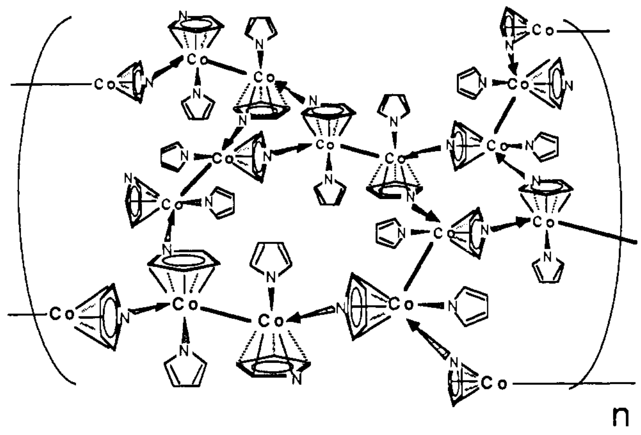


Figure 1. Possible model for the Co/pyrrolyl intermediate.

Thus far we have isolated Co(0), Co(I), and Co(II) complexes from the Co/pyrrolyl reagent. If the reagent contains Co(II), then the formation of a Co(0) complex, Co(biq)$_2$, would require the concomitant oxidation of some species. Two possibilities are the oxidation of pyrrolide ion to dipyrrole or, perhaps, a disproportionation reaction.

Unlike the vast number of cyclopentadienyl transition-metal complexes reported, the number of pyrrolyl complexes is very few.[2,16] This is somewhat surprising since pyrrolide is the closest heterocyclic analogue to the cyclopentadienide ligand. In the absence of other ligands, the propensity of pyrrolide to simultaneously act as a π-donor to one transition metal and as a σ-donor ligand to a second metal appears to be quite high. This type of bonding would lend itself to the formation of oligomeric and/or polymeric materials consistent with the physical properties observed for the cobalt- and iron/pyrrolyl intermediates. These materials may not have been anticipated in past attempted syntheses of π-pyrrolyl derivatives and might account for the fact that few complexes involving the pyrrolyl ligand exclusively have been isolated and characterized.[2,16d,f,l,r]

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Table I. Atomic Coordinates[a] in Bis(2,2-biquinolyl)cobalt Pyrrole

atom	10^4x	10^4y	10^4z	atom	10^4x	10^4y	10^4z
Co	1087.8 (5)	3848.2 (3)	3059.9 (4)	C_{17}	3072 (5)	5089 (3)	3289 (4)
N_1	203 (3)	3612 (2)	3946 (2)	C_{18}	2746 (4)	4997 (2)	4133 (3)
N_2	1864 (3)	4524 (2)	4106 (2)	C_{19}	−512 (4)	4611 (3)	1321 (3)
N_3	298 (3)	084 (2)	1687 (2)	C_{20}	−696 (5)	5136 (3)	1956 (4)
N_4	1886 (3)	3159 (2)	2478 (2)	C_{21}	−1482 (6)	5678 (3)	1615 (4)
C_1	553 (4)	3991 (2)	4811 (3)	C_{22}	−2119 (5)	5704 (3)	625 (4)
C_2	−30 (5)	3896 (3)	5527 (3)	C_{23}	−1959 (4)	5203 (3)	−3 (4)
C_3	−948 (5)	3461 (3)	5357 (4)	C_{24}	−1157 (4)	4648 (3)	309 (3)
C_4	−1340 (4)	3075 (3)	4467 (4)	C_{25}	−916 (4)	4132 (3)	−326 (3)
C_5	−2282 (5)	2610 (3)	4238 (4)	C_{26}	−97 (4)	3637 (3)	26 (3)
C_6	−2591 (5)	2216 (3)	3399 (5)	C_{27}	524 (4)	3610 (2)	1049 (3)
C_7	−1961 (4)	2270 (3)	2743 (4)	C_{28}	1416 (4)	3103 (2)	1481 (3)
C_8	−1038 (4)	2730 (3)	2924 (3)	C_{29}	1820 (4)	2580 (3)	946 (3)
C_9	−719 (4)	3148 (3)	3781 (3)	C_{30}	2659 (4)	2119 (3)	1410 (4)
C_{10}	1502 (4)	4466 (2)	4920 (3)	C_{31}	3173 (4)	2163 (2)	2445 (3)
C_{11}	2064 (5)	4845 (3)	5792 (3)	C_{32}	4053 (4)	1700 (3)	2982 (4)
C_{12}	2943 (5)	5282 (3)	5828 (4)	C_{33}	4522 (4)	1772 (3)	3962 (4)
C_{13}	3297 (4)	5392 (3)	4978 (4)	C_{34}	4145 (5)	2311 (3)	4466 (4)
C_{14}	4172 (5)	5869 (3)	4950 (4)	C_{35}	3281 (4)	2766 (3)	3971 (3)
C_{15}	4486 (5)	5955 (3)	4121 (5)	C_{36}	2769 (4)	2702 (2)	2955 (3)
C_{16}	3932 (6)	5547 (4)	3286 (4)				
Pyrrole of Solvation							
C_{37}	3862 (6)	4379 (5)	1369 (5)	C_{40}	−5379 (5)	3987 (4)	1709 (5)
C_{38}	−3660 (6)	3730 (4)	1827 (5)	C_{41}	−4969 (7)	4530 (4)	1300 (5)
C_{39}	−4543 (7)	3512 (4)	2004 (5)				
Hydrogens							
H_2	219.8	4140.3	6133.2	H_{20}	−275.7	5125.8	2633.6
H_3	−1343.3	3411.6	5834.9	H_{21}	−1594.4	6027.5	2045.2
H_5	−2712.4	2571.9	4690.0	H_{22}	−2666.3	6087.0	400.8
H_6	−3233.6	1895.3	3270.2	H_{23}	−2397.5	5240.8	−675.6
H_7	−2166.4	1986.4	2158.0	H_{25}	−1319.2	4128.1	−1003.8
H_8	−607.0	2769.9	2472.3	H_{26}	77.6	3299.1	−402.5
H_{11}	1802.2	4789.4	6351.6	H_{29}	1501.5	2554.0	255.8
H_{12}	3334.8	5521.9	6432.5	H_{30}	2906.2	1761.4	1046.9
H_{14}	4540.5	6134.8	5517.5	H_{32}	4336.1	1324.5	2660.5
H_{15}	5069.5	6285.1	4103.9	H_{33}	5097.2	1446.2	4313.3
H_{16}	4158.0	5578.6	2726.6	H_{34}	4496.9	2375.1	5152.1
H_{17}	2702.6	4820.4	2717.3	H_{35}	3021.5	3131.5	4326.0
Pyrrole of Solvation							
H_{37}	−3333.1	4643.0	1143.4	H_{40}	−6107.8	3986.0	1762.2
H_{38}	−2969.3	3495.1	1955.3	H_{41}	−5310.1	4922.3	1018.1
H_{39}	−4628.9	3072.9	2297.6				

[a] Estimated standard deviations are given in parentheses, and the coordinates are given as fractional coordinates.

Structure and Bonding. An ORTEP drawing of one molecule of the complex is shown in Figure 2.[17] Final positional parameters for the atoms are given in Table I, and their associated thermal parameters are given in the supplementary material. The asymmetric unit of structure contains one discrete molecule of $Co(biq)_2$ and one molecule of pyrrole solvent. The cobalt is coordinated to two chelating 2,2′-biquinolyl ligands through the nitrogen atoms of each ligand in an approximately tetrahedral geometry. The observed angle between the two CoN_2 planes if 86.5°, reflecting a small distortion from the tetrahedral value of 90°. The associated bond distances and angles for the asymmetric unit of structure are listed in Tables II and III, respectively.

The two biquinolyl ligands are not structurally equivalent. The biquinolyl ligands labeled I (quinoline groups A and B) and II (quinoline groups C and D) in Figure 3 differ significantly in the degree of rotation about the bonds bridging the quinoline fragments at the 2 and 2′ positions. Biquinolyl I has a 10.1° rotation about its C_1–C_{10} bridging bond, while biquinolyl II has a 3.7° rotation about its C_{27}–C_{28} bridging bond. Analysis of the intermolecular bonding interactions reveals a significant interaction between the pyrrole of solvation and both of the biquinolyl ligands. It appears that a larger number of relatively short interactions with the pyrrole of solvation is responsible for the greater rotation in biquinolyl I.

Analysis of biquinolyl I shows several points of interest. The angle between the adjacent pyridine ring fragments is 8.0° and the angle between the extreme phenyl ring fragments is 11.9°. In addition, the angle between the phenyl and the pyridyl ring of quinolyl A is 3.1° and that of quinolyl B is 1.8°. Analysis of biquinolyl II shows reduced but similar rotations. These deformations from planarity are consistent with an overall banana-shaped curvature of the biquinolyl ligands, which was previously observed in the X-ray structural analysis of bis(2,2′-biquinolyl)bis(μ-chloro)dimanganese(II).[4a] In addition, distortions from planarity of the quinolyl fragments in 2,2′-biquinolyl ligands in both manganese and nickel complexes were suggested to occur due to steric interactions.[4a,b] The observed results support this conclusion. The rotation about the bridging bonds in biquinolyl I and II and a summary of the intermolecular interactions are shown in Figure 3.

The observed stabilization of a tetrahedral 17-electron cobalt complex can be attributed to the steric requirements of the 2,2′-biquinolyl ligand, which preclude the formation of a square-planar complex. To demonstrate this, the observed bond parameters were used to create scaled bonding models (Figure 4) for hypothetical square-planar complexes of bis(2,2′-bipyridyl)cobalt and $Co(biq)_2$. Bond parameters used for the 2,2′-biquinolyl ligand in the hypothetical square-planar complex were those of biquinolyl II (Figure 3). In order to generate a square-planar geometry, biquinolyl II was duplicated and reflected through a mirror plane. The 2,2′-bipyridyl ligand was created by omitting the peripheral phenyl carbon atoms of the biquinolyl

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(17) Johnson, D. K. *ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*; Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

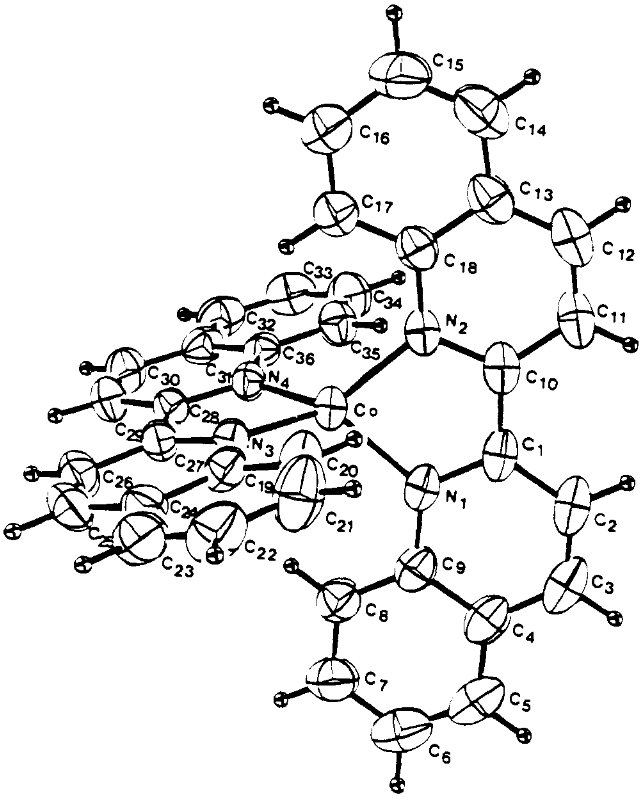


Figure 2. ORTEP drawing of one molecule of $Co(biq)_2$ as it exists in crystals of $Co(biq)_2{\cdot}C_4H_5N$. Hydrogen atoms are numbered according to their associated carbons and have been deliberately reduced in size for clarity.

Table II. Bond Distances (Å) in Bis(2,2′-biquinolyl)cobalt Pyrrole

atoms	distance	atoms	distance
Coordination Sphere			
$\mathrm{Co{-}N_1}$	1.948 (3)	$\mathrm{Co{-}N_3}$	1.951 (3)
$\mathrm{Co{-}N_2}$	1.962 (3)	$\mathrm{Co{-}N_4}$	1.945 (3)
Biquinolyl I			
$\mathrm{C_1{-}C_2}$	1.424 (5)	$\mathrm{C_{10}{-}C_{11}}$	1.413 (6)
$\mathrm{C_2{-}C_3}$	1.342 (7)	$\mathrm{C_{11}{-}C_{12}}$	1.334 (7)
$\mathrm{C_3{-}C_4}$	1.411 (7)	$\mathrm{C_{12}{-}C_{13}}$	1.423 (6)
$\mathrm{C_4{-}C_5}$	1.397 (7)	$\mathrm{C_{13}{-}C_{14}}$	1.399 (7)
$\mathrm{C_5{-}C_6}$	1.356 (8)	$\mathrm{C_{14}{-}C_{15}}$	1.361 (8)
$\mathrm{C_6{-}C_7}$	1.386 (7)	$\mathrm{C_{15}{-}C_{16}}$	1.402 (7)
$\mathrm{C_7{-}C_8}$	1.374 (6)	$\mathrm{C_{16}{-}C_{17}}$	1.353 (7)
$\mathrm{C_8{-}C_9}$	1.401 (6)	$\mathrm{C_{17}{-}C_{18}}$	1.390 (6)
$\mathrm{C_9{-}N_1}$	1.381 (5)	$\mathrm{C_{18}{-}N_2}$	1.382 (5)
$\mathrm{N_1{-}C_1}$	1.372 (5)	$\mathrm{N_2{-}C_{10}}$	1.368 (5)
$\mathrm{C_4{-}C_9}$	1.415 (5)	$\mathrm{C_{13}{-}C_{18}}$	1.398 (5)
$\mathrm{C_1{-}C_{10}}$	1.427 (6)		
Biquinolyl II			
$\mathrm{C_{19}{-}C_{20}}$	1.397 (6)	$\mathrm{C_{28}{-}C_{29}}$	1.417 (5)
$\mathrm{C_{20}{-}C_{21}}$	1.375 (7)	$\mathrm{C_{29}{-}C_{30}}$	1.345 (6)
$\mathrm{C_{21}{-}C_{22}}$	1.389 (7)	$\mathrm{C_{30}{-}C_{31}}$	1.421 (6)
$\mathrm{C_{22}{-}C_{23}}$	1.351 (7)	$\mathrm{C_{31}{-}C_{32}}$	1.406 (6)
$\mathrm{C_{23}{-}C_{24}}$	1.401 (6)	$\mathrm{C_{32}{-}C_{33}}$	1.347 (7)
$\mathrm{C_{24}{-}C_{25}}$	1.413 (6)	$\mathrm{C_{33}{-}C_{34}}$	1.393 (7)
$\mathrm{C_{25}{-}C_{26}}$	1.339 (6)	$\mathrm{C_{34}{-}C_{35}}$	1.369 (6)
$\mathrm{C_{26}{-}C_{27}}$	1.425 (5)	$\mathrm{C_{35}{-}C_{36}}$	1.398 (5)
$\mathrm{C_{27}{-}N_3}$	1.356 (4)	$\mathrm{C_{39}{-}C_{31}}$	1.415 (5)
$\mathrm{N_3{-}C_{19}}$	1.378 (5)	$\mathrm{C_{36}{-}N_4}$	1.379 (5)
$\mathrm{C_{24}{-}C_{19}}$	1.420 (5)	$\mathrm{N_4{-}C_{28}}$	1.366 (4)
$\mathrm{C_{27}{-}C_{28}}$	1.431 (5)		
Pyrrole of Solvation			
$\mathrm{C_{41}{-}C_{37}}$	1.352 (9)	$\mathrm{C_{39}{-}C_{40}}$	1.318 (8)
$\mathrm{C_{37}{-}C_{38}}$	1.36 (1)	$\mathrm{C_{40}{-}C_{41}}$	1.340 (9)
$\mathrm{C_{38}{-}C_{39}}$	1.25 (1)		

Table III. Bond Angles (deg) in Bis(2,2′-biquinolyl)cobalt Pyrrole

atoms	angle	atoms	angle
Coordination Sphere			
$\mathrm{N_1{-}Co{-}N_2}$	83.3 (1)	$\mathrm{N_2{-}Co{-}N_3}$	126.5 (1)
$\mathrm{N_1{-}Co{-}N_3}$	120.2 (1)	$\mathrm{N_2{-}Co{-}N_4}$	124.2 (1)
$\mathrm{N_1{-}Co{-}N_4}$	125.2 (2)	$\mathrm{N_3{-}Co{-}N_4}$	82.9 (1)
Biquinolyl 1			
$\mathrm{C_1{-}N_1{-}C_9}$	119.2 (3)	$\mathrm{C_5{-}C_4{-}C_3}$	123.7 (4)
$\mathrm{C_1{-}N_1{-}Co}$	112.8 (2)	$\mathrm{C_5{-}C_4{-}C_9}$	118.3 (4)
$\mathrm{C_9{-}N_1{-}Co}$	127.9 (2)	$\mathrm{C_6{-}C_5{-}C_4}$	121.9 (4)
$\mathrm{N_1{-}C_1{-}C_2}$	119.8 (4)	$\mathrm{C_5{-}C_6{-}C_7}$	119.8 (4)
$\mathrm{N_1{-}C_1{-}C_{10}}$	115.8 (3)	$\mathrm{C_8{-}C_7{-}C_6}$	120.6 (4)
$\mathrm{C_2{-}C_1{-}C_{10}}$	124.4 (4)	$\mathrm{C_7{-}C_8{-}C_9}$	120.2 (4)
$\mathrm{C_3{-}C_2C1}$	121.2 (4)	$\mathrm{C_8{-}C_9{-}C_4}$	119.2 (4)
$\mathrm{C_2{-}C_3{-}C_4}$	120.2 (4)	$\mathrm{N_1{-}C_9{-}C_4}$	121.4 (4)
$\mathrm{C_3{-}C_4{-}C_9}$	118.0 (4)	$\mathrm{N_1{-}C_9{-}C_8}$	119.4 (3)
$\mathrm{C_{10}{-}N_2{-}C_{18}}$	118.5 (3)	$\mathrm{C_{18}{-}C_{13}{-}C_{12}}$	123.3 (4)
$\mathrm{C_{10}{-}N_2{-}Co}$	113.0 (2)	$\mathrm{C_{15}.C_{14}{-}C_{13}}$	121.3 (4)
$\mathrm{C_{18}{-}N_2{-}Co}$	128.4 (2)	$\mathrm{C_{14}{-}C_{15}{-}C_{16}}$	119.1 (4)
$\mathrm{N_2{-}C_{10}{-}C_{11}}$	120.9 (4)	$\mathrm{C_{17}{-}C_{16}{-}C_{15}}$	120.7 (4)
$\mathrm{N_2{-}C_{10}{-}C_1}$	114.7 (3)	$\mathrm{C_{16}{-}C_{17}{-}C_{18}}$	120.6 (4)
$\mathrm{C_{11}{-}C_{10}{-}C_1}$	124.4 (3)	$\mathrm{N_2{-}C_{18}{-}C_{17}}$	118.8 (3)
$\mathrm{C_{12}{-}C_{11}{-}C_{10}}$	120.5 (4)	$\mathrm{N_2{-}C_{18}{-}C_{13}}$	121.6 (3)
$\mathrm{C_{11}{-}C_{12}{-}C_{13}}$	120.3 (4)	$\mathrm{C_{17}{-}C_{18}{-}C_{13}}$	119.6 (4)
$\mathrm{C_{18}{-}C_{13}{-}C_{14}}$	118.6 (4)		
Biquinolyl 2			
$\mathrm{C_{27}{-}N_3{-}C_{19}}$	118.6 (3)	$\mathrm{C_2.C_{23}{-}C_{24}}$	121.9 (4)
$\mathrm{C_{27}{-}N_3{-}Co}$	112.9 (2)	$\mathrm{C_{23}{-}C_{24}{-}C_{25}}$	124.1 (4)
$\mathrm{C_{19}{-}N_3{-}Co}$	128.1 (2)	$\mathrm{C_{23}{-}C_{24}{-}C_{19}}$	118.3 (4)
$\mathrm{N_3{-}C_{19}{-}C_{20}}$	119.5 (3)	$\mathrm{C_{25}{-}C_{24}{-}C_{19}}$	117.5 (4)
$\mathrm{N_3{-}C_{19}{-}C_{24}}$	122.0 (3)	$\mathrm{C_{26}{-}C_{25}{-}C_{24}}$	120.3 (3)
$\mathrm{C_{20}{-}C_{19}{-}C_{24}}$	118.5 (4)	$\mathrm{C_{25}{-}C_{26}{-}C_{27}}$	120.7 (4)
$\mathrm{C_{21}{-}C_{20}{-}C_{19}}$	121.2 (4)	$\mathrm{C_{26}{-}C_{27}{-}C_{28}}$	124.1 (3)
$\mathrm{C_{20}{-}C_{21}{-}C_{22}}$	119.9 (4)	$\mathrm{N_3{-}C_{27}{-}C_{26}}$	120.8 (3)
$\mathrm{C_{23}{-}C_{22}{-}C_{21}}$	120.1 (4)	$\mathrm{N_3{-}C_{27}{-}C_{28}}$	115.1 (3)
$\mathrm{C_{28}{-}N_4{-}C_{36}}$	118.8 (3)	$\mathrm{C_{32}{-}C_{31}{-}C_{30}}$	123.4 (4)
$\mathrm{C_{28}{-}N_4{-}Co}$	113.0 (2)	$\mathrm{C_{36}{-}C_{31}{-}C_{30}}$	117.7 (4)
$\mathrm{C_{36}{-}N_4{-}Co}$	127.9 (2)	$\mathrm{C_{33}{-}C_{32}{-}C_{31}}$	121.1 (4)
$\mathrm{N_4{-}C_{28}{-}C_{29}}$	120.7 (3)	$\mathrm{C_{32}{-}C_{33}{-}C_{34}}$	120.4 (4)
$\mathrm{N_4{-}C_{28}{-}C_{27}}$	114.9 (3)	$\mathrm{C_{35}.C_{34}{-}C_{33}}$	120.3 (4)
$\mathrm{C_{29}{-}C_{28}{-}C_{27}}$	124.4 (3)	$\mathrm{C_{34}{-}C_{35}{-}C_{36}}$	120.7 (4)
$\mathrm{C_{30}{-}C_{29}{-}C_{28}}$	120.8 (3)	$\mathrm{C_{35}{-}C_{36}{-}C_{31}}$	118.7 (3)
$\mathrm{C_{29}{-}C_{30}{-}C_{31}}$	120.1 (3)	$\mathrm{N_4{-}C_{36}{-}C_{35}}$	119.5 (3)
$\mathrm{C_{32}{-}C_{31}{-}C_{36}}$	118.9 (4)	$\mathrm{N_4{-}C_{36}{-}C_{31}}$	121.8 (3)

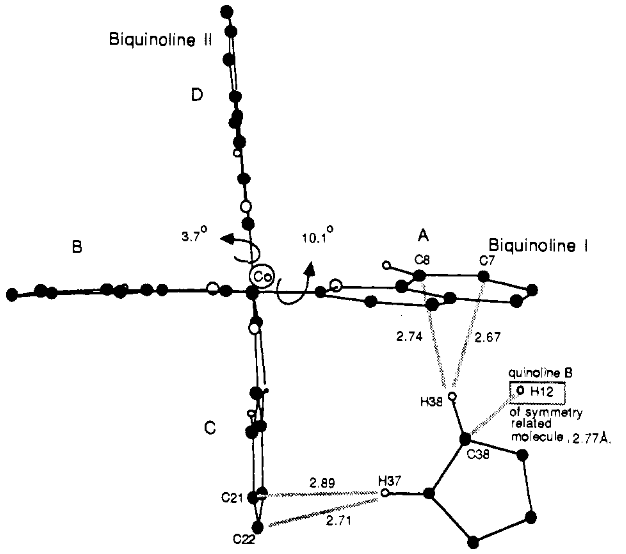


Figure 3. Scaled drawing showing the important nonbonded interactions between the biquinolyl ligands and the pyrrole of solvation.

ligand. The models reveal the important steric interactions resulting from two 2,2′-bipyridyl or two 2,2′-biquinolyl ligands adopting a square-planar geometry about a cobalt atom when the Co–N distances are 1.95 Å and the C–H distances are 1.0 Å. The severe overlap of the two biquinolyl ligands as they approach the same coordination plane can be clearly seen in this model. Four pairs of carbon atoms would overlap to the extent of occupying

Table IV. Comparison of Some 2,2'-Biquinolyl Bond Parameters[a]

param[b]	this work	uncomplexed 2,2'-biquinoline[c]	$[(C_{18}H_{12}N_2)MnCl_2]_2$[d]	$[(C_{18}H_{12}N_2)NiCl_2]_2$[e]	$(C_{18}H_{12}N_2)NiBr_2$[e]
C_2–$C_{2'}$	1.429 (6)	1.492 (3)	1.458 (5)	1.483 (3)	1.494 (9)
C–N_{av}	1.373 (5)	1.347 (2)	1.354 (6)	1.367 (2)	1.353 (8)
C–C_{av}	1.391 (8)	1.407 (2)	1.399 (7)	1.397 (3)	1.40 (1)
M–N_{av}	1.952 (3)		2.241 (2)	2.038 (2)	1.992 (5)

[a] All distances are in angstroms. [b] The C_2–$C_{2'}$ distance refers to the bond between individual quinoline ring fragments. [c] Reference 21. [d] Reference 4a. [e] Reference 4b.

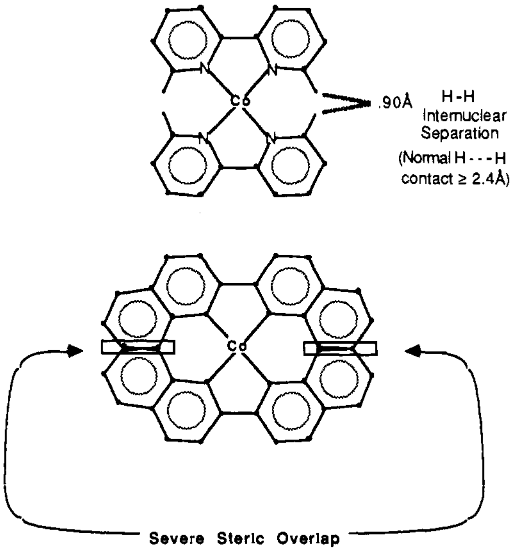


Figure 4. Hypothetical square-planar complexes of bis(2,2'-bipyridyl)cobalt and $Co(biq)_2$.

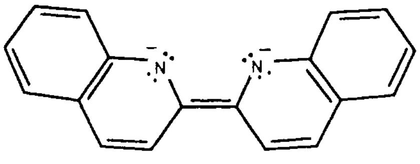
the same regions of space. This observation is consistent with the absence of any metal complex reported in the literature incorporating a square-planar configuration of two 2,2'-biquinolyl ligands.

The model for square-planar bis(2,2'-bipyridyl)cobalt also shows a significant steric interaction but not nearly as serious as the analogous 2,2'-biquinolyl complex. It predicts an internuclear separation of approximately 0.90 Å for the α-hydrogens between the two 2,2'-bipyridyl ligands. Since the normal van der Waals radius of a hydrogen atom is 1.2 Å, the configuration must distort to relieve this steric strain.[18] This result is consistent with the existence of complexes incorporating distorted square-planar geometries about a transition metal.[19]

The severe steric crowding predicted by the hypothetical structures in Figure 4 can be used to rationalize the formation of a 17-electron distorted tetrahedral biquinolyl complex, $Co(biq)_2$, and an 18-electron distorted trigonal-pyramidal *dimeric* 2,2'-bipyridyl complex, bis[bis(2,2'-bipyridyl)cobalt].[8] The geometries about the metal centers in the two molecules are distinctly different and the difference is attributed to steric effects. The complex adopts a tetrahedral geometry to relieve the steric crowding invoked by the coorination of two 2,2'-biquinolyl ligands, and the observed 17-electron system results. Steric hindrance accommodates minimal distortion from a tetrahedral geometry and prevents the dimerization of two cobalt centers to form a more electronically stable 18-electron system analogous to bis[bis(2,2'-bipyridyl)cobalt]. The interligand C–C contact distances pictured in the hypothetical square-planar biquinolyl complex of Figure 4 become 4.429 (2), 4.410 (2), 4.748 (2), and 6.247 (2) Å in the actual tetrahedral complex [normal C---C contact ≥ 3.54 Å].[18] In contrast, a distorted square-planar geometry involving two bipyridyl ligands leaves open coordination sites at the metal center. Two 17-electron bis(2,2'-bipyridyl)cobalt monomers can then adequately approach, forming the observed dimeric 18-electron complex. Thus, steric effects are believed to be the dominating force in the formation of different molecular geometries for 2,2'-bipyridyl and 2,2'-biquinolyl complexes of Co(0).

Previous reports suggest that extensive π back-bonding from iron[20] and cobalt[8] to the 2,2'-bipyridyl ligand involved extremely short metal to nitrogen distances and a significant shortening of the bond bridging the two pyridyl fragments in 2,2'-bipyridyl. The X-ray structure of $Co(biq)_2$ also reveals the same trend. A comparison of the observed bond distances to those in the free molecule 2,2'-biquinoline[21] and those observed in several 2,2'-biquinolyl complexes[4a,b] is given in Table IV. The C_2–$C_{2'}$ inter-quinoline bridging distance is 1.49 Å in free biquinoline and normally remains within 0.03 Å of this value in typical complexes. In $Co(biq)_2$, however, this distance is considerably shorter at 1.429 (6) Å. The average C–N distance appears slightly longer while the average C–C distance is similar to typical free 2,2'-biquinoline bond parameters although there is a trend toward an alternating pattern of long and short bonds. In addition, the Co–N distance in $Co(biq)_2$ is the shortest reported for a 2,2'-biquinolyl complex and is significantly shorter than the expected distance predicted for Co(0)–N(sp^2). This short Co–N distance and the observed parameters for the 2,2'-biquinolyl ligand suggest multiple-bond character to cobalt and are consistent with extensive π back-bonding from cobalt to the π^* orbitals of 2,2'-biquinolyl.

Although valence-bond terminology cannot adequately represent π back-bonding, a resonance form can be drawn to account for the acceptance of charge on the 2,2'-biquinolyl ligand that is consistent with the bond parameters observed in the complex.



A synergistic bonding mode similar to the metal carbonyls is proposed in which donation through the σ framework is reinforced by π acceptance.[20,23]

In summary, the results from this X-ray study provide some insight for potential applications of the 2,2'-biquinolyl ligand. Upon coordination, this ligand not only invokes a large steric effect but the results of this investigation indicate there is also the capacity for a high degree of electronic stabilization through substantial π back-bonding to metals in low oxidation states.

Acknowledgment. Support of this work from the National Science Foundation (RII8610675) is acknowledged with gratitude as well as support from 3M Corp.

Registry No. $Co(biq)_2$, 120120-08-3; hydridobis[1,2-bis(diphenylphosphino)ethane]cobalt, 18433-72-2; bis(bis(2,2'-bipyridyl)cobalt), 120172-56-7; cobaltocene, 1277-43-6; methylcobaltocene, 12146-91-7.

Supplementary Material Available: Table of anisotropic thermal parameters (4 pages); observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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