

melting point analysis: mp 81–82 °C (lit.⁹ mp 81 °C).

Dicyclopentadieny[bis(trimethylsilyl)amido]zirconium(IV). Lithium bis(trimethylsilyl)amide–bis(diethyl ether) (100 mL) was added to dicyclopentadieny[zirconium dichloride]⁷ (2.4 g, 0.0082 mol) suspended in diethyl ether (100 mL). The pale yellow suspension was stirred at room temperature for 24 h. Diethyl ether was removed under reduced pressure, and the residue was heated (60 °C) under vacuum (6 h). Trituration with pentane (2 × 100 mL) followed by filtration yielded a pale yellow solution, which was then concentrated under reduced pressure to ca. 20 mL. Cooling (–70 °C) afforded white blocks, which were identified as $\text{LiN}(\text{SiMe}_3)_2 \cdot 0.5\text{OEt}_2$ (1.3 g) by ¹H NMR spectroscopy. The mother liquor was further concentrated under reduced pressure to ca. 5 mL. Cooling (–70 °C) yielded the zirconium amide, which was collected and dried under vacuum. The amide was dissolved in cold (0 °C) pentane (10 mL). Concentration to ca. 3 mL and cooling (–70 °C) afforded the pure compound in 18% yield (0.8 g). Anal. Calcd for $\text{C}_{22}\text{H}_{46}\text{N}_2\text{Si}_4\text{Zr}$: C, 48.8; H, 8.50; N, 5.18. Found: C, 48.5; H, 8.77; N, 5.02. The ¹H NMR spectrum consisted of singlets at δ 6.11, 0.53, and 0.30 due to Cp_2Zr and $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Zr}$, in area ratio 10:18:18, respectively. The ¹³C NMR spectrum consisted of a doublet centered at δ 115.2 ($J_{\text{CH}} = 174$ Hz) due to Cp_2Zr and a pair of quartets centered at δ 7.3 ($J_{\text{CH}} = 117$ Hz) and 6.7 ($J_{\text{CH}} = 117$ Hz) due to $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Zr}$.

Preparation of $\text{Cp}_2\text{ZrCH}_2\text{SiMe}_2\text{NSiMe}_3$. Lithium bis(trimethylsilyl)amide–bis(diethyl ether) (2.3 g, 0.0075 mol) in diethyl ether (100 mL) was added to a suspension of dicyclopentadieny[zirconium hydrochloride]¹⁰ (1.9 g, 0.0074 mol) in diethyl ether (50 mL). The

mixture was stirred at room temperature (24 h) in the dark and then filtered. Diethyl ether was evaporated from the filtrate, and the yellow powder was extracted with pentane (2 × 50 mL). The extract was filtered, and the filtrate was concentrated under reduced pressure to ca. 10 mL and cooled (–70 °C). The white blocks were collected and shown to be $\text{LiN}(\text{SiMe}_3)_2 \cdot 0.5\text{OEt}_2$ by ¹H NMR spectroscopy (0.70 g). The mother liquor was concentrated to ca. 3 mL and cooled (–70 °C) to yield the waxy, pale yellow metallocycle. The metallocycle sublimed [70–80 °C (10^{-3} mm)] as pale yellow sheets (0.5 g, 18%). Anal. Calcd for $\text{C}_{16}\text{H}_{27}\text{NSi}_2\text{Zr}$: C, 49.2; H, 6.92; N, 3.59. Found: C, 48.5; H, 6.88; N, 3.60. The ¹H NMR spectrum consisted of singlets at δ 5.93, 1.88, 0.27, and 0.17 due to Cp_2Zr , ZrCH_2 , $\text{ZrCH}_2\text{SiMe}_2$, and $\text{ZrCH}_2\text{SiMe}_2\text{NSiMe}_3$ in area ratio of 10:2:6:9, respectively. The ¹³C NMR spectrum consisted of a doublet centered at δ 111.6 ($J_{\text{CH}} = 171$ Hz), a triplet centered at δ 42.0 ($J_{\text{CH}} = 128$ Hz), and a pair of quartets centered at δ 3.50 ($J_{\text{CH}} = 119$ Hz) and 4.60 ($J_{\text{CH}} = 117$ Hz) due to Cp_2Zr , ZrCH_2 , $\text{ZrCH}_2\text{SiMe}_2$, and $\text{ZrCH}_2\text{Si}(\text{Me})_2\text{NSiMe}_3$, respectively.

Neither metallocycle reacts with deuterium (20 atm) at room temperature in pentane.

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Registry No. $\text{Cp}_2\text{TiCH}_2\text{SiMe}_2\text{NSiMe}_3$, 52326-35-9; $\text{Cp}_2\text{ZrCH}_2\text{SiMe}_2\text{NSiMe}_3$, 78804-37-2; Cp_2TiCl_2 , 1271-19-8; Cp_2ZrCl_2 , 1291-32-3; $\text{Cp}_2\text{Zn}(\text{H})(\text{Cl})$, 37342-97-5; $\text{LiN}(\text{SiMe}_3)_2$, 4039-32-1; $\text{LiN}(\text{SiMe}_3)_2 \cdot 0.5\text{OEt}_2$, 78804-38-3.

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Metal Vapor Synthesis, Chemical Oxidation, and Electrochemistry of Bis(bipyridyl)cobalt(0). Preparation of Bromide, Tetracyanoethylene, and Tetracyanoquinodimethane Salts

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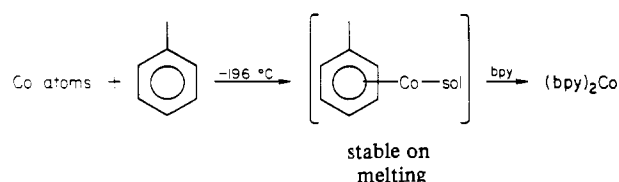
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The first preparation of bis(2,2'-bipyridyl)cobalt [$\text{Co}(\text{bpy})_2$] has been carried out by metal vapor methods. Three techniques have been employed: (a) solution, (b) cocondensation, and (c) the use of toluene-solvated Co atoms. Method c was preferred. Spectral analysis of $\text{Co}(\text{bpy})_2$ suggests that substantial $\text{Co} \rightarrow \text{bpy}$ charge transfer has taken place. Chemical oxidations with Br_2 , tetracyanoquinodimethane (TCNQ), and tetracyanoethylene (TCNE) have yielded $(\text{bpy})_2\text{CoBr}$ with the bpy ligands highly negative, $(\text{bpy})_2\text{Co}(\text{TCNQ})_2$ with the bpy ligands neutral and the TCNQ ligands highly negative, and $(\text{bpy})\text{Co}(\text{TCNE})$ with one bpy displaced and the other neutral. It appears that the TCNE ligand bears high negative charge. Cyclic voltammetric behavior of $\text{Co}(\text{bpy})_2$ suggests that in acetonitrile a disproportionation reaction to produce $\text{Co}(\text{bpy})_2^-$ and $\text{Co}(\text{bpy})_2^+ \cdot \text{sol}$ takes place. The electrochemical redox behavior then shows similarities to that of $\text{Co}(\text{bpy})_3^{2+}$; that is, a series of facile, reversible electron-transfer processes are observed. Overall, $(\text{bpy})_2\text{Co}$ appears to be a useful new Co(0) intermediate.

Introduction

When the organic chemistry of nickel vs. that elucidated for cobalt is compared, a very noticeable feature is the relative abundance of Ni(0) starting complexes but the scarcity of corresponding Co(0) complexes. We have had an interest in the chemistry of Ni(0) and Co(0) complexes as compared with that of Ni and Co atoms. Recently we have developed procedures for the facile synthesis of zerovalent bipyridyl (bpy) complexes of the group 8 transition metals. Of particular

interest has been the production of usable amounts of $(\text{bpy})_2\text{Co}^0$ from a Co atom–toluene matrix. In this reaction sequence



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“toluene-solvated Co atoms” probably exist as highly labile

π -arene complexes possessing at least one strongly bound η^6 - π -toluene and at least one weakly bound solvating toluene molecule (sol; η^6 , η^4 , or η^2 bound). Complexes of this type have recently proven valuable for carrying out organometallic synthesis and/or preparing highly dispersed catalysts of Fe, Co, Ni, Pd, Cu, and Ag metals.^{2,3}

Our interest in obtaining the $\text{Co}(\text{bpy})_2$ complex stems from several considerations: (1) the need for a useful and readily available $\text{Co}(0)$ organometallic; (2) the ability of bpy to stabilize a variety of oxidation states of metals as well as take on negative charge itself;⁴⁻⁸ (3) the ability of Co metal to exist in stable complexes in a variety of oxidation states; (4) the fact that bpy is a flat bidentate ligand that may allow square-planar stacking⁹ in the solid phase and still be capable of oxidation-state changes (this kind of stacking structure would be most likely in a +2 or +3 oxidation state for Co). This general property is of interest in the molecular metals field;¹⁰ (5) the possibility that $\text{Co}(\text{bpy})_2$ may serve as a useful model compound for oxygen carrier studies (related to metal porphyrins).

Results

Preparation of $\text{Co}(\text{bpy})_2$. We have successfully employed three synthetic methods all using metal atoms¹¹ to prepare $(\text{bpy})_n\text{M}^0$ complexes:

(1) M atoms were codeposited with bpy vapor and toluene vapor (matrix diluent) simultaneously on a cold wall (-196°C) under vacuum. This matrix was allowed to warm, the resultant solution was filtered, and the bpy-M complex was crystallized from toluene. This procedure represents the most common method used in metal atom chemistry—that of co-deposition. However, it is inconvenient in this instance since bpy is not very volatile and it is difficult to bring into the metal atom reactor as a vapor. Unwieldy inlet-heating methods must be employed.

(2) Co metal was evaporated, and the atoms were impinged into a low-temperature solution of (bpy) in toluene. This procedure was carried out in a modified rotary evaporator apparatus,¹² and the atoms were directed toward the top of the apparatus where there is always a film of cold bpy-toluene solution present because of the rotary motion of the reactor flask. This method works well if such an apparatus is available but has some drawbacks because of problems in solvent choice and the necessity for a fairly large low-temperature bath of organic material, which arouses some safety concerns.

(3) A Co-toluene matrix was prepared as described in the Introduction by simultaneous deposition, followed by syringing in a bpy-toluene solution and then matrix meltdown and mixing. The resulting bpy-M complex can then be filtered and crystallized from the toluene solution. We have found this method to be the quickest and most convenient.

Properties and Spectra of $\text{Co}(\text{bpy})_2$. There are previous reports describing the preparation of $(\text{bpy})_3\text{Co}^0$ ¹³ and the infrared spectrum of $(\text{bpy})_3\text{Co}^0$.⁴ Notice the tris formulation, which was supported by analytical data. Our analytical data

support a bis formulation, a stoichiometry that seems reasonable from electronic considerations and by comparison with the known $(\text{bpy})_2\text{Ni}^0$ ¹⁴ and $(\text{bpy})_2\text{Rh}^0$.¹⁵

The earlier transition metals do form $(\text{bpy})_3\text{M}^0$ complexes,^{5,6,16} and it appears that even the group 8 metal Fe will do so.^{7,17} It is possible that for Co both bis and tris formulations exist depending on reaction conditions and realizing that bpy can be mono- or bidentate. In support of this idea we have found that the presence of a slight excess of bpy during the reaction allows the isolation of a complex for which analytical data supports a mixture of $(\text{bpy})_2\text{Co}$ and $(\text{bpy})_3\text{Co}$. However, by avoiding excess bpy, we obtain the bis formulation in pure form, and it is this complex with which this report is concerned.

(a) Magnetic Resonance Spectra. Paramagnetism would be predicted for the 17-electron $(\text{bpy})_2\text{Co}^0$ formulation. The complete absence of NMR signals is supportive of that notion. Unfortunately, however, we have also been unable to obtain an EPR signal for this complex in the solid state or dissolved in toluene in the temperature range 77–300 K. This absence of an EPR signal is not typical for a d^9 complex.¹⁸ It may indicate that the complex has unusually fast magnetic relaxation times.

EPR studies of an analogous $\text{Rh}(0)$ complex prepared electrochemically did exhibit a spectrum at low temperatures but not at ambient temperatures.¹⁵

(b) Infrared Spectra. Nakamoto and co-workers have masterfully shown that IR data can elucidate the charge-transfer interactions (M-bpy or M^+bpy^-) and the strength of the M-N interaction for bpy-metal complexes. In general, our IR data are similar but not identical with those obtained by Nakamoto and co-workers (note that they worked with tris complexes).

According to Nakamoto,⁴ for a neutral Co complex (formally $\text{Co}(0)$) strong far IR bands at 280 and 257 cm^{-1} should be observed for $\nu_{\text{Co-N}}$. We observe strong bands at 281 and 257 cm^{-1} . This weak Co-N interaction is indicative of partially filled e_g antibonding orbitals, which is in turn indicative of charge transfer from Co to bpy. Furthermore, comparisons in the 1625–1475- and 1000–900- cm^{-1} regions suggest that Nakamoto's complex, our complex, and Li^+bpy^- are similar. That is, a very strong band in the 900–1000- cm^{-1} region and several medium-intensity bands in the 1585–1490- cm^{-1} region support the M^+bpy^- bonding mode. Nakamoto observes bands at 1575, 1506, and 975, and we observe bands at 1582, 1527, and 978 cm^{-1} .

No bands in the 1600–1610 cm^{-1} region, indicative of M-bpy bonding without charge transfer, were observed. Thus, IR data supports a M^+bpy^- charge-transfer type of Co-bpy interaction.

(c) UV-Visible Spectra. Reynolds and co-workers^{7,17} and Koenig and Herzog^{5,6} have studied a series of $(\text{bpy})_3\text{M}$ complexes by UV-visible spectroscopy. A variety of oxidation states for M were investigated. In general for the Ti, V, and Cr 3+, 2+, 1+, and 0 valent tris complexes, UV-visible spectra support limited charge transfer to bpy for M^{3+} and M^{2+} , whereas for M^+ and M^0 it is believed that a great deal of charge transfer takes place.^{5,6} Furthermore, comparisons of Na^+bpy^- with $\text{Fe}(\text{bpy})_3$ showed similarities: Na^+bpy^- showed bands at 560 and 530 nm, and $(\text{bpy})_3\text{Fe}$ showed bands at 525, 502, and 357 nm, and so an Fe^+bpy^- formulation would seem most likely from the UV-visible data.^{7,17} Solutions of $\text{Fe}(\text{bpy})_3$ showed very low conductance, however,¹⁷ and initial EPR evidence was not very supportive with regard to charge

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transfer.¹⁷ Further work by Mahon and Reynolds served to clarify some of the contradictory evidence and showed that UV-visible and EPR spectroscopy supported a charge-transfer (to bpy) formulation for $\text{NaFe}(\text{bpy})_3$.⁷

According to these previous studies, it appears that a band or bands in the 550-nm region of the UV-visible spectrum is characteristic of a bpy^- ligand. Our $\text{Co}(\text{bpy})_2$ complex exhibits bands at 560, 351, 284, and 243 nm, again supporting a Co^+bpy^- bonding mode.

(d) Magnetic Susceptibility. Measurements on a Faraday balance yield a consistent $\mu_{\text{eff}} = 2.02 \mu_{\text{B}}$ for $(\text{bpy})_2\text{Co}$, which supports an electron configuration with one unpaired electron.

Chemical Oxidation of $(\text{bpy})_2\text{Co}$ with Bromine (Br_2), Tetracyanoquinodimethane (TCNQ), and Tetracyanoethylene (TCNE). **(a) Bromine (Br_2).** Slow titration of the Co complex in benzene with Br_2 (0.5 mol/mol of Co) yielded a blue precipitate that was insoluble in toluene and moderately soluble in acetonitrile. The bromide complex is very air sensitive and analyzed as $(\text{bpy})_2\text{CoBr}$. UV-visible spectral analysis showed bands at 554, 357, 294, and 244 nm, the 554-nm band characteristic of charge transfer to bpy ($\rightarrow\text{bpy}^-$). Far-IR showed weak Co-N interactions, as was found for the unbrominated complex and which also supports the charge-transfer formulation (far-IR, cm^{-1} , 240 (s), 247 (s), 355 (m), and 357 (m)). Likewise, in the IR a strong band at 970 cm^{-1} and medium to weak bands at 1562, 1580, and 1599 cm^{-1} with no bands in the $1600\text{--}1610\text{-cm}^{-1}$ region also support the charge-transfer formulation and agree very well with Nakamoto's findings for $\text{Co}^+\text{-bpy}$ complexes (970 (s), 1565 (w), and 1590 (m)).⁴ Again, no magnetic spectra were observed (NMR or EPR). However, the magnetic susceptibility of the compound is $3.53 \mu_{\text{B}}$, which would support a configuration with two unpaired electrons.

(b) Tetracyanoquinodimethane (TCNQ). Slow addition of a toluene solution of TCNQ to $\text{Co}(\text{bpy})_2$ in toluene yielded a green precipitate after a 2:1 TCNQ:Co ratio was reached. Analysis indicated a formulation of $(\text{bpy})_2\text{Co}(\text{TCNQ})_2$. This compound is moderately air sensitive and very easy to prepare and isolate in large amounts.

UV-visible spectral analysis revealed a complex absorption system. However, no bands near 550 nm were observed. According to far-IR the Co-N interaction had become stronger with bands observed at 243, 284, and 325 cm^{-1} . And, very significantly, the $900\text{--}1000\text{-cm}^{-1}$ region only exhibited one *very weak* band at 975 cm^{-1} . Also, only a very weak band at 1580 cm^{-1} was found as well as a medium band at 1600 cm^{-1} (Nakamoto and co-workers show 1575 (w) and 1600 (m) cm^{-1} for their $\text{Co}^{2+}\text{-bpy}$ complexes).⁴ These spectral data support a picture of greatly lessened charge transfer to bpy . Furthermore, the IR bands due to TCNQ are of interest in that the $\nu_{\text{C}\equiv\text{N}}$ stretch moves from 2230 (m) , 2110 (m) to 2187 (vs) . This weakening of $\text{C}\equiv\text{N}$ indicates that TCNQ has taken on substantial negative charge.¹⁹

No magnetic resonance spectra (NMR or ESR) were exhibited by this compound. Magnetic susceptibility measurements yielded a value of $6.05 \mu_{\text{B}}$.

(c) Tetracyanoethylene (TCNE). Addition of a toluene solution of TCNE to $\text{Co}(\text{bpy})_2$ caused the displacement of a bpy molecule and the formation of a π -TCNE complex analyzed as $(\text{bpy})\text{Co}(\text{TCNE})$. An IR study showed a very weak band at 976 cm^{-1} and two strong bands at 1602 and 1604 cm^{-1} , indicative of neutral bpy. The TCNE $\nu_{\text{C}\equiv\text{N}}$ values moved from 2260 , 2220 to 2180 , 2163 , 2100 upon complexation, indicative of high electron density and/or π^* back-bonding. In view of the stoichiometry of the reaction and the fact that a great

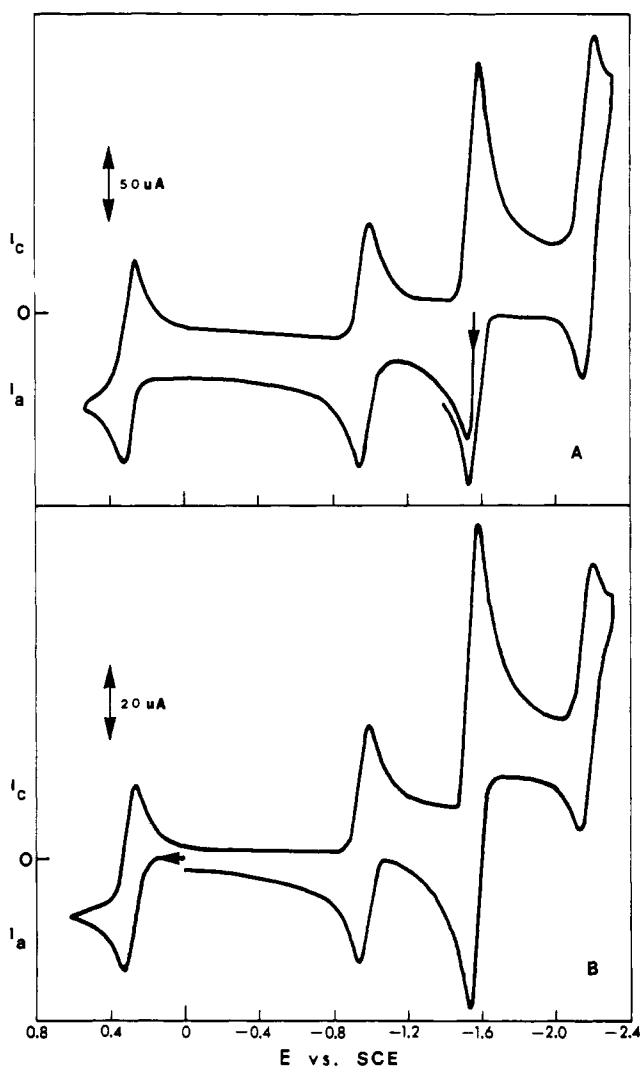
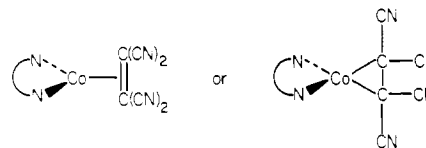


Figure 1. Cyclic voltammograms in acetonitrile with 0.2 M TEAP at a scan rate of 0.1 V s^{-1} : (A) $2.7 \times 10^{-3} \text{ M}$ bis(bipyridine)cobalt(0), $\text{Co}(\text{bpy})_2$, with the scan initiated at the rest potential of -1.56 V ; (B) $1.7 \times 10^{-3} \text{ M}$ tris(bipyridine)cobalt(II) with the scan initiated at the rest potential of 0.0 V . The working electrode used was planar platinum with an area of 0.25 cm^2 .

number of metal- π complexes of TCNE are known, it is tempting to assign that type of formation:



$\nu_{\text{C}\equiv\text{N}}$ values for these types of complexes are generally in the $2220\text{--}2240\text{-cm}^{-1}$ range,²⁰⁻²² considerably higher than the $2100\text{--}2180\text{-cm}^{-1}$ range we observe. It appears that in our $(\text{bpy})\text{Co}(\text{TCNE})$ complex substantially more negative charge resides on TCNE than for normal metal-TCNE π complexes. Searching the literature, we find that IR bands at 2190 and 1360 cm^{-1} are characteristic of TCNE^- .^{23,24} Thus, the $(\text{bpy})\text{Co}(\text{TCNE})$ absorptions at 2163 , 2180 , 2100 , and 1375

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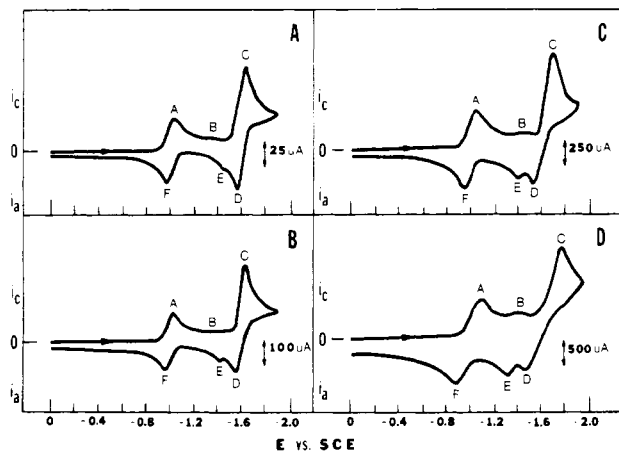


Figure 2. Cyclic voltammograms of 8.5×10^{-4} M $\text{Co}(\text{bpy})_2(\text{ClO}_4)_2$ in 0.2 M TEAP-acetonitrile at a planar platinum electrode (0.25 cm^2) using the following scan rates: (A) 0.1 V s^{-1} , (B) 1.0 V s^{-1} , (C) 10 V s^{-1} , and (D) 50 V s^{-1} .

cm^{-1} indicate more similarity to TCNE^- than π -complexed TCNE.

Electrochemistry and Conductivity of $(\text{bpy})_2\text{Co}^0$. The cyclic voltammetric behavior for $\text{Co}(\text{bpy})_2$ in acetonitrile is shown in Figure 1A. The most significant observation is that the rest or equilibrium potential is -1.56 V vs. SCE for the zerovalent complex; this value is within experimental error of the $E_{1/2}$ value for the $\text{Co}(\text{bpy})_3^+/\text{Co}(\text{bpy})_2^-$ wave (vide ante). Upon sweeping in the positive direction from the rest potential, we observe three oxidation waves at -1.54 , -0.94 , and 0.33 V , respectively. Upon reversal of the direction of potential sweep at 0.60 V , reduction waves are observed at 0.27 , -1.00 , and -1.57 V , all of which correspond to the reversible reduction of the products formed at the oxidation waves stated above. Continuing the sweep in the negative direction produces a reduction wave at -2.20 V . Upon reversal at -2.35 V , an oxidation wave is seen at -2.14 V . Thus all of the redox couples in the range observed were chemically reversible as well as quasi- or electrochemically reversible.

Comparison of the cyclic voltammetric behavior of $\text{Co}(\text{bpy})_2$ to that of $\text{Co}(\text{bpy})_3(\text{ClO}_4)_2$ is illustrated in Figure 1B. The electrochemistry of $\text{Co}(\text{bpy})_3^{2+}$ has been the subject of several recent publications.^{25,26} The couple at $+0.30 \text{ V}$ has been reported as the $\text{Co}(\text{bpy})_3^{3+}/\text{Co}(\text{bpy})_3^{2+}$ couple and that at -0.97 V assigned to the $\text{Co}(\text{bpy})_3^{2+}/\text{Co}(\text{bpy})_3^+$ couple. The significantly larger wave at -1.56 V has been assigned to the reduction of $\text{Co}(\text{bpy})_3^+$ to $\text{Co}(\text{bpy})_2^-$. The wave at -2.20 V can be shown to be due to the reduction of free bipyridine to a stable radical anion, which can be reoxidized on the cyclic voltammetric time scale. Thus, the electrochemical data for $\text{Co}(\text{bpy})_2$ is consistent with previously reported data for $\text{Co}(\text{bpy})_3^{2+}$ electrochemistry.

The bis(bipyridine) form of $\text{Co}(\text{II})$ was examined in an effort to further understand the $\text{Co}(\text{bpy})_2$ electrochemistry. $\text{Co}(\text{bpy})_2(\text{ClO}_4)_2$ was produced in situ by the addition of a stoichiometric amount of bpy to $\text{Co}(\text{ClO}_4)_2$ in acetonitrile. The electrochemistry of $\text{Co}(\text{bpy})_2(\text{ClO}_4)_2$ is similar to $\text{Co}(\text{bpy})_3(\text{ClO}_4)_2$ with the exception that the $\text{Co}^{3+}/\text{Co}^{2+}$ wave is diminished in height and more irreversible and a small oxidation wave is observed at approximately -1.4 V (wave E, Figure 2). Since the relative height of wave E is dependent upon scan rate (compare the relative height of wave E to wave D as a function of scan rate from 0.1 V s^{-1} to 50 V s^{-1}), the concentration of the species responsible for wave E is kinetically

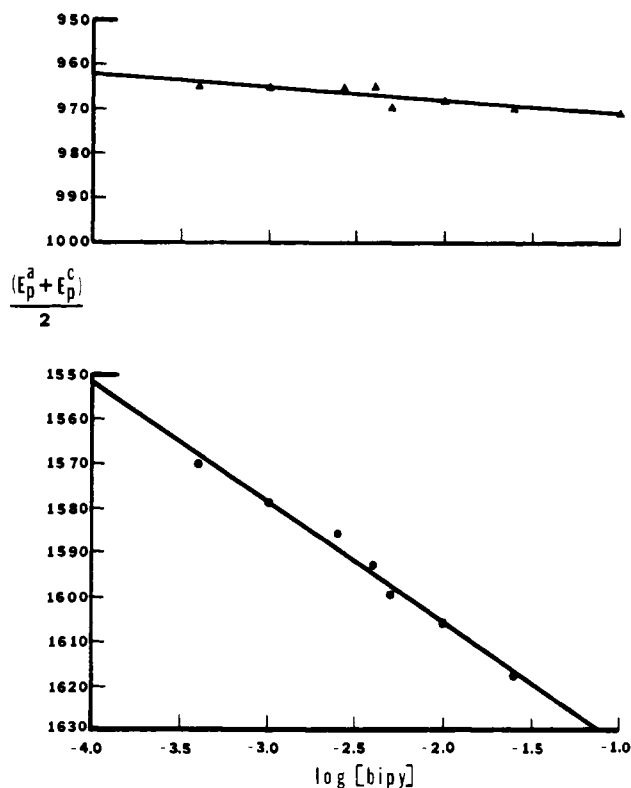
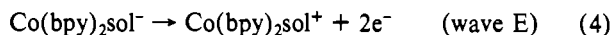
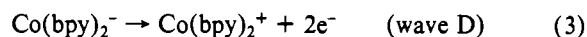
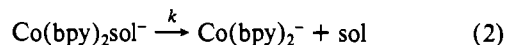
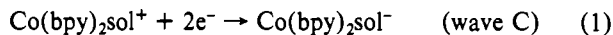
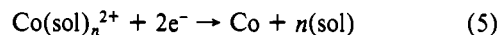


Figure 3. Cyclic voltammetric data for a 2.0×10^{-3} M bis(bipyridine)cobalt(0) in 0.2 M TEAP-acetonitrile in the presence of added bipyridine. The average of cathodic and anodic peak potentials for the (\blacktriangle) $\text{Co}(2+)/\text{Co}(1+)$ couple and (\bullet) $\text{Co}(1+)/\text{Co}(1-)$ couple with a scan rate of 0.1 V s^{-1} on platinum is shown.

controlled. In addition the wave disappears when a slight excess of bipyridine is added. A scheme consistent with these results is summarized in eq 1-4. A reduction wave (wave B)



is also noted at approximately -1.4 V , but it is not kinetically controlled in the same manner or directly related (i.e., the other half of a redox couple) to wave E. The reduction wave (B) is more difficult to explain. It apparently is the result of insufficient bpy ligands, as it also disappears when a slight excess of bpy is added. A possible reaction for wave B is shown by (5).



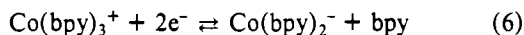
It should be noted that the anodic wave at -1.4 V was present in some of the metal vapor preparations of $\text{Co}(\text{bpy})_2$. The absence of the wave in Figure 1A is probably due to a slight excess of bpy, which was not completely separated out during the purification of $\text{Co}(\text{bpy})_2$ (see Experimental Section). Note that the relative height of the bpy/bpy^- wave vs. the $\text{Co}(1+)/\text{Co}(1-)$ wave for $\text{Co}(\text{bpy})_2$ (Figure 1A) is greater than that for $\text{Co}(\text{bpy})_3(\text{ClO}_4)_2$ (Figure 1B), which indicates the presence of a slight excess of bpy in the $\text{Co}(\text{bpy})_2$ preparation.

The effect of excess bipyridine on the electrochemistry of $\text{Co}(\text{bpy})_2$ was examined. Figure 3 shows the results of a study of the average of the anodic and cathodic peak potentials for $\text{Co}(\text{bpy})_2$ as a function of added bipyridine concentration. The slope for the $\text{Co}(1+)/\text{Co}(1-)$ wave is 27 mV/decade change in bipyridine concentration, while the slope for the Co -

(25) N. Tanaka and Y. Sato, *Bull. Chem. Soc. Jpn.*, **41**, 2059 (1968).

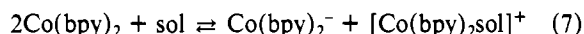
(26) S. Margel, W. Smith, and F. C. Anson, *J. Electrochem. Soc.*, **125**, 241 (1978).

(2+)/Co(1+) wave is 3 mV/decade change. These data are consistent with a reversible two-electron transfer accompanying the involvement of one molecule of bipyridine in the Co(1+)/Co(1-) wave (eq 6). These data indicate that Co(1+)

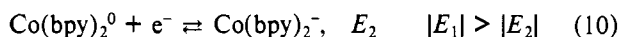
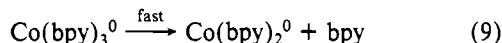
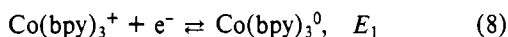


will go to the tris form in the presence of excess bpy, while Co(1-) remains in the bis form. This behavior has been previously observed for Co(1+) with use of $\text{Co}(\text{bpy})_3^{3+}$ as a precursor.²⁶ The slope of 3 mV/decade change in bipyridine concentration for the Co(2+)/Co(1+) wave indicates that both Co(2+) and Co(1+) exist in the tris formation.

The cyclic voltammetric data and, in particular, the redox potential for $\text{Co}(\text{bpy})_2$ at the $E_{1/2}$ of the $\text{Co}(\text{bpy})_3^+/\text{Co}(\text{bpy})_2^-$ wave indicate two possibilities for $\text{Co}(\text{bpy})_2$ in solution: (1) In acetonitrile (sol), $\text{Co}(\text{bpy})_2$ undergoes a disproportionation reaction to a significant extent to produce $\text{Co}(\text{bpy})_2^-$ and $[\text{Co}(\text{bpy})_2\text{sol}]^+$ (reaction 7). (2) The $\text{Co}(\text{bpy})_2$ species exists as a dimer in solution.



The first possibility is consistent with the observation that the reduction of $\text{Co}(\text{bpy})_3^+$ is a two-electron process to form $\text{Co}(\text{bpy})_2^-$.²⁶ The two-electron wave for $\text{Co}(\text{bpy})_3^+$ suggests that the reduction potential for $\text{Co}(\text{bpy})_2^0$ (E_2) is less negative than the reduction potential for $\text{Co}(\text{bpy})_3^+$ (see eq 8-10).

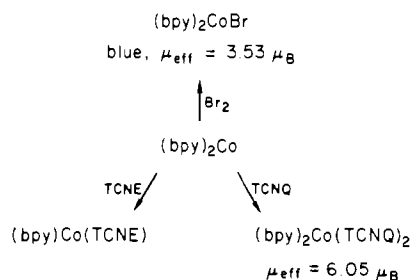


Thus, the equilibrium constant (K) for the disproportionation reaction (reaction 7) should be greater than unity. In addition, our results for the $\text{Co}(\text{bpy})_3^+/\text{Co}(\text{bpy})_2^-$ couple indicate two-electron quasi-reversibility with $E_{pa} - E_{pc} = 40$ mV.

Conductivity measurements were also made on $\text{Co}(\text{bpy})_2$ solutions to indicate whether or not disproportionation (reaction 7) occurs upon dissolution of $\text{Co}(\text{bpy})_2$ in acetonitrile. A solution of 5×10^{-3} M $\text{Co}(\text{bpy})_2$ in acetonitrile gave a specific conductance of $5 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$. This can be compared to a 5×10^{-3} M tetrabutylammonium perchlorate solution, which had a specific conductance of $6 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$. In contrast, a 5×10^{-3} M 2,2'-bipyridine solution in acetonitrile has a specific conductance of less than $3 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$. Thus, the conductivity data indicates appreciable ion formation upon dissolution of $\text{Co}(\text{bpy})_2$ in acetonitrile.

The second possibility of a dimeric $\text{Co}_2(\text{bpy})_4$ species in solution was considered. Literature reports on binuclear complexes have shown that when metal-metal bond cleavage accompanies electron transfer, the electrochemistry observed is irreversible.^{27,28} We have briefly investigated the electrochemistry of $\text{Co}_2(\text{CO})_8$ in acetonitrile and have observed that the electrochemistry is irreversible. DeArmond and co-workers have investigated the $\text{Rh}(\text{bpy})_2$ zerovalent complex and have found that it is a monomeric species in acetonitrile; a series of facile electron-transfer processes were observed for the $\text{Rh}(3+)/\text{Rh}(2+)$, $\text{Rh}(2+)/\text{Rh}(1+)$, $\text{Rh}(1+)/\text{Rh}(0)$, and $\text{Rh}(0)/\text{Rh}(1-)$ couples.²⁹ Thus, since the electrochemistry of $\text{Co}(\text{bpy})_2$ is seen as a series of facile, reversible electron-transfer processes, it appears that the possibility of a dimeric cobalt species in acetonitrile is somewhat remote. Furthermore, the conductivity experiments and equilibrium potential (i.e., at $E_{1/2}$ for the Co(1+)/Co(1-) wave) suggest that $\text{Co}(\text{bpy})_2$ disproportionates to Co(1+) and Co(1-) in acetonitrile.

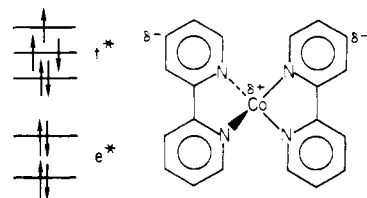
Scheme I



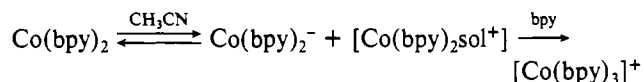
Discussion

We have shown that pure $(\text{bpy})_2\text{Co}^0$ can be readily prepared. However, during the preparation excess bpy must be avoided; otherwise some $(\text{bpy})_3\text{Co}^{3+}$ also forms.

$(\text{bpy})_2\text{Co}^0$ exists in toluene solution and in the solid state as highly charge transferred with the bpy ligands taking on a great deal of negative charge. Overall, the complex possesses one unpaired electron, and on the assumption of a tetrahedral geometry, this would correspond to a low-spin $(e^*)^4(t^*)^5$ electronic configuration. Magnetic resonance spectra for this paramagnetic complex were not obtained apparently because of extremely fast magnetic relaxation.

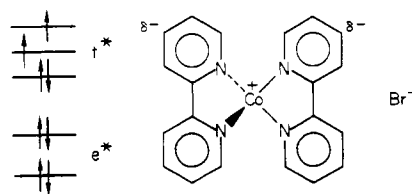


Electrochemical and conductivity studies of $(\text{bpy})_2\text{Co}^0$ in acetonitrile show that an unusual disproportionation takes place yielding ions such as $\text{Co}(\text{bpy})_2^-$ and $[\text{Co}(\text{bpy})_2\text{sol}]^+$. In the presence of excess bpy the cation takes on another bpy molecule (probably with solvent loss), while $\text{Co}(\text{bpy})_2^-$ does not:



Overall, the electrochemistry of $(\text{bpy})_2\text{Co}^0$ is seen as a series of facile, reversible electron-transfer processes.

$(\text{bpy})_2\text{Co}^0$ exhibits some very interesting oxidation chemistry, as illustrated in Scheme I. The bromide salt is formally a Co(I) species. Its magnetic susceptibility indicates two unpaired electrons, and this would be in accord with a tetrahedral d^8 complex of $(e^*)^4(t^*)^4$ electronic configuration.



Furthermore, the IR and UV-visible data indicate a great deal of electron density is present in the bpy ligands. Therefore, even a Co(I) species still prefers to strongly donate charge to the bpy acceptors.

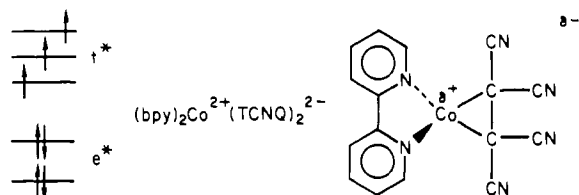
TCNQ addition yields a complex salt possessing two TCNQ ligands that both take on negative charge, leaving the bpy ligands more neutral. It is apparent that in this case $(\text{bpy})_2\text{Co}$ is oxidized to a +2 state and the Co(II) complex does not allow negative charge buildup on the bpy ligands. A high magnetic susceptibility of $\mu_{\text{eff}} = 6.05 \mu_B$ suggests three to five unpaired electrons. With two TCNQ radical anions plus the three

(27) C. J. Pickett and D. Pletcher, *J. Chem. Soc., Dalton Trans.*, 879 (1975).

(28) R. E. Dessy, P. M. Weissmann, and R. L. Pohl, *J. Am. Chem. Soc.*, **88**, 5117 (1966).

(29) G. Kew, K. DeArmond, and K. Hanck, *J. Phys. Chem.*, **78**, 727 (1974).

unpaired electrons predicted for a $(e^*)^4(t^*)^3$ configuration, the high μ_{eff} is reasonable. However, square-planar Co(II) is also a possibility, but we cannot differentiate between tetrahedral or square planar on the basis of the data we have at present. Structure information by X-ray crystallography will hopefully be forthcoming.



A ligand displacement reaction takes place with TCNE and so the oxidation state of Co remains formally zero. However, the spectra data support high electron density on TCNE and lessened charge density on bpy. Therefore, the complex may exist in a highly polar form.

Further oxidation-reduction chemistry, conductivities, and structural information would be quite useful with $(\text{bpy})_2\text{Co}$ and its derivatives. Indeed, $(\text{bpy})_2\text{Co}$ appears to be a very useful and versatile source of Co(0).

Experimental Section

Reagents and Solvents. Manipulations of solids were carried out in a drybox (Vacuum Atmospheres Dri Lab with Model HE-493 Dri Train) employing prepurified nitrogen (99.99%). Crystallizations and solution-phase reactions were carried out under purified nitrogen (passed over BASF Chem. Dynamics Corp. R3-11 deoxygenation catalyst just prior to use) in airless glassware, often in conjunction with degassing procedures on a conventional vacuum line. Pentane and toluene were continuously refluxed over benzophenone ketyl under purified nitrogen, and acetonitrile was purified by the procedure of Walter and Ramaley (method B)³⁰ and stored over activated alumina (Woelm W200, neutral, activity 1) on a vacuum line. Deuteriosolvents CDCl_3 , CD_2Cl_2 , and $\text{C}_6\text{D}_5\text{CD}_3$ were obtained from Merck and used as received after degassing. TCNQ was recrystallized twice from hot purified acetonitrile. TCNE was sublimed at 90 °C and 10^{-3} torr onto a cold water probe.

Physical Measurements. IR spectra were recorded on a Beckman IR-12 in Nujol mulls prepared in the drybox with NaCl plates. Far-IR (200–400 cm^{-1}) spectra were obtained in Nujol mulls between polyethylene plates. Attempts at obtaining magnetic resonance spectra were carried out on a Varian EM-390 or JEOL FX-60 for NMR and a Bruker 420-e for EPR. Elemental analyses were performed by Schwarzkopf, Woodside, N.Y. under inert atmosphere. Melting points are uncorrected. Magnetic susceptibilities were obtained on a Faraday balance built in this laboratory. UV-visible spectra were obtained on a Cary 14 spectrometer.

Metal Atom (Vapor) Apparatus and Techniques. (a) **Cocondensation.** Our apparatus has been described before³¹ and recently in great detail.¹¹ For the heating of the ligand inlet system, heating tape was wrapped around the glassware leading to the metal atom reactor and heated electrically to 60–80 °C. For the heating of the ligand inlet section inside the reactor, 1-mm nichrome wire was wrapped 35 times about the tube, and the ends of the wire were attached to the two electrodes. In this way some of the power used to vaporize the metal was diverted to heat the inlet tube.

(b) **Solution.** A Buchi Rotovap was modified after the design of Mackenzie and Timms.¹²

Preparation of $\text{Co}(\text{bpy})_2$ (Preferred Method). During a $1\frac{1}{2}$ -h period 0.8288 g of Co metal (14.06 g-atom) was codeposited at –196 °C with 200 mL (1.9 mol) of dry, degassed toluene, yielding a yellow-brown matrix. Then a solution of 3.02 g of 2,2'-bipyridine (bpy) (19.3 mmol) in 25 mL of toluene was syringed in under a flow of N_2 . The contents of the reactor were allowed to warm with stirring. During this time, the matrix formed a yellow-brown solution on meltdown (cobalt-toluene). After addition of the bpy-toluene, the color changed to black.

The green-black solution was syringed out and filtered through medium-porosity fritted glass, and toluene was removed under vacuum to a volume of 20 mL. Crystals were obtained by cooling at 0 °C. The crystals were isolated by decanting the mother liquor and were then dried under vacuum; yield 2.228 g (62% based on bpy added as limiting reagent). No NMR or EPR signals could be detected.

IR (cm^{-1}): 692 (w), 730 (vs), 758 (m), 840 (vw), 855 (vw), 930 (sh, w), 978 (sh, s), 1000 (vs), 1010 (sh, s), 1030 (vw), 1098 (w), 1152 (s), 1230 (m), 1240 (m), 1265 (m), 1280 (m), 1320 (s), 1340 (vs), 1390 (sh, s), 1420 (vs), 1435 (vs), 1455 (s), 1527 (w), 1580 (sh, m), 1582 (m). Far-IR (cm^{-1}): 220 (vw), 237 (m), 257 (s), 281 (s), 343 (w), 370 (w). UV-visible (in acetonitrile; λ_{max} , nm (molar ϵ): 560 (289), 351 (7884), 284 (11 594), 243 (5565). Anal. Calcd: C, 64.69; H, 4.35; N, 15.09. Found: C, 64.62; H, 4.25; N, 14.98.

Preparation of $(\text{bpy})_2\text{CoBr}$. A 50-mL benzene solution of $(\text{bpy})_2\text{Co}$ (0.245 g, 0.66 mmol) was placed in a 125-mL flask in the drybox. Bromine (0.10 g, 1.95 mmol) was dissolved in 25 mL of benzene in the drybox, and this solution was placed in a 10-mL buret. Then 3.37 mL of (0.3 mmol Br_2) of the Br_2 solution was slowly added to the $(\text{bpy})_2\text{Co}$ solution. The $(\text{bpy})_2\text{Co}$ solution changed from dark green-black to very light yellow, and a blue precipitate was formed (further Br_2 addition caused the precipitate to turn brown). The blue precipitate was isolated by filtration with a medium-porosity filter frit and washed three times with 10 mL of toluene. No magnetic resonance signals could be detected.

IR (cm^{-1}): 735 (m), 758 (m), 970 (s), 1152 (m), 1252 (m), 1302 (m), 1378 (s), 1430 (m), 1443 (sh), 1462 (vs), 1540 (w), 1562 (w), 1580 (w), 1599 (m). Far-IR (cm^{-1}): 240 (s), 247 (s), 355 (m), 357 (m). UV-visible (in acetonitrile; λ_{max} , nm (molar ϵ): 554 (1845), 357 (3895), 294 (31 660), 244 (27 015). Anal. Calcd: C, 53.24; H, 3.57; N, 12.42; Br, 17.71. Found: C, 53.18; H, 3.79; N, 11.74; Br, 17.00.

Preparation of $(\text{bpy})_2\text{Co}(\text{TCNQ})_2$, Reaction of $\text{Co}(\text{bpy})_2$ and TCNQ (1:1). A solution of 0.1030 g of TCNQ (0.504 mmol) dissolved in 50 mL of toluene in the drybox was slowly added to a solution of 0.1873 g of $\text{Co}(\text{bpy})_2$ (0.504 mmol) with stirring. There was no color change in the green-black solution, but a green precipitate was formed. The precipitate was separated by filtration. The IR of the dried toluene soluble portion showed it to be unreacted starting material.

Reaction of $\text{Co}(\text{bpy})_2$ and TCNQ (1:2). A solution of 0.770 g of TCNQ (3.482 mmol) in 50 mL of toluene was slowly added to a solution of 0.6464 g of $\text{Co}(\text{bpy})_2$ (1.74 mmol) with stirring in the drybox. Within 15 min, the toluene solution was clear with a green precipitate. The product was filtered and washed three times with 10 mL of toluene and dried under vacuum.

IR (cm^{-1}): 738 (m), 765 (s), 810 (w), 830 (w), 864 (s), 975 (vw), 1020 (w), 1155 (w), 1252 (w), 1315 (w), 1360 (w), 1380 (m), 1445 (vs), 1508 (s), 1548 (w), 1580 (vw), 1600 (m), 2118 (m), 2130 (m), 2160 (m), 2180 (vs), 2230 (m). Far-IR (cm^{-1}): 224 (s), 243 (s), 255 (m), 284 (s), 325 (m), 360 (m). UV-visible (in acetonitrile; λ_{max} , nm (molar ϵ): 845 (71 760), 814 (73 320), 759 (78 780), 745 (95 940), 695 (29 640), 682 (31 200), 667 (26 520), 627 (9360), 613 (7020), 600 (4680), 432 (73 320), 422 (104 520), 409 (99 840), 395 (87 360), 304 (62 400), 297 (63 960), 245 (60 840), 236 (68 640), 219 (74 880). Anal. Calcd: C, 67.78; H, 3.10; N, 21.56. Found: C, 67.85; H, 3.11; N, 21.35.

Preparation of $(\text{bpy})\text{Co}(\text{TCNE})$. A solution of 50 mL of toluene and 0.091 g of TCNE (0.71 mmol) was slowly added to a solution of 50 mL of toluene and 0.264 g of $\text{Co}(\text{bpy})_2$ (0.712 mmol) in the drybox with stirring. After 1 h the toluene solution was clear with a brown precipitate. The precipitate was recovered by filtration, washed three times with 20 mL of toluene, and dried in vacuo to a red-brown powder.

IR (cm^{-1}): 739 (s), 760 (vs), 810 (m), 902 (w), 976 (vw), 1020 (s), 1045 (w), 1060 (w), 1102 (w), 1157 (m), 1178 (w), 1215 (w), 1252 (w), 1315 (s), 1375 (vs), 1447 (vs), 1470 (vs), 1495 (m), 1572 (m), 1579 (m), 1602 (vs), 1604 (s), 2100 (vs), 2163 (vs), 2180 (vs), 2190 (vs), 2220 (s). Anal. Calcd: C, 55.99; H, 2.35; N, 24.49. Found: C, 55.90; H, 2.66; N, 24.54.

Cyclic Voltammetric Studies of $(\text{bpy})_2\text{Co}^0$. Electrochemical Measurements and Instrumentation. The cyclic voltammetric studies were performed on a previously described three-electrode potentiostat.³² A digital-controlled multipurpose-functional generator and a circuit

(30) M. Walter and L. Ramaley, *Anal. Chem.*, **45**, 165 (1973).

(31) K. J. Klabunde, *Angew. Chem., Int. Ed. Engl.*, **14**, 287 (1975).

(32) D. E. Bartak, H. K. Hundley, M. van Swaay, and M. D. Hawley, *Chem. Intrum. (N.Y.)*, **4**, 1 (1972).

for electronic compensation of ohmic potential loss were incorporated into the instrument. Large-scale, controlled-potential electrolysis was carried out on a second potentiostat, which used a Harrison Model 6824A amplifier (± 50 V, 1 A) in the control circuit. Readout for cyclic voltammetric experiments was accomplished by a Hewlett-Packard Model 7035B X-Y recorder or Tektronix Model 5103N storage oscilloscope.

Chemicals. The zerovalent $\text{Co}(\text{bpy})_2$ used in electrochemical studies was prepared as described above. The $\text{Co}(\text{bpy})_3(\text{ClO}_4)_2$ was prepared by standard methods.³³ Tetraethylammonium perchlorate was prepared according to the method of Kolthoff and Coetzee.³⁴

Electrodes and Cells. All electrochemical experiments were carried out on an all-glass vacuum line, which has been previously described.³⁵ Acetonitrile solvent was distilled from flask to flask until totally degassed. Finally, the solvent was distilled into the cell on the vacuum line, and the contents in the cell were freeze-pump-thawed at least twice. After the cell and its contents were brought to ambient temperature, helium, which was passed over BASF catalyst R3-11, was introduced until normal atmospheric pressure was obtained. A conventional three-electrode three-compartment cell was used on the vacuum line; in addition, a large platinum basket electrode was placed in the working electrode chamber to carry out coulometric and voltammetric experiments as desired. The working electrode for microscale experiments was a modified Beckman platinum button

electrode (No. 39273) with a geometric area of 0.24 cm^2 or a glassy carbon (Tokai) electrode (area, 0.20 cm^2), which was prepared by previously reported methods.³⁶ Both electrodes were polished with $0.1\text{-}\mu\text{m}$ alumina prior to use. A silver wire, which was used as a quasi-reference electrode in several experiments, was also polished with alumina immediately before use. An aqueous saturated calomel electrode was used as a reference electrode; the reference electrode was isolated by means of a glass frit and a bridge containing a 0.2 M solution of tetraethylammonium perchlorate in acetonitrile. No attempt was made to position the reference electrode to minimize IR loss; however, electronic compensation as stated above was used in all voltammetric experiments. The auxiliary electrode for microscale experiments was a platinum foil, which was positioned within 1 cm of and parallel to the working electrode surface. The auxiliary electrode for coulometric studies was a large coil of platinum wire, which was isolated by a glass frit from the working-electrode compartment.

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Registry No. $\text{Co}(\text{bpy})_2$, 71534-63-9; $(\text{bpy})_2\text{CoBr}$, 78683-94-0; $(\text{bpy})_2\text{Co}(\text{TCNQ})_2$, 78624-84-7; $(\text{bpy})\text{Co}(\text{TCNE})$, 78624-85-8; $(\text{bpy})_3\text{Co}(\text{ClO}_4)_2$, 21349-81-5; $\text{Co}(\text{bpy})_2(\text{ClO}_4)_2$, 78624-86-9.

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Solvated Nickel Atoms and Nickel Slurries: Nickel Atom-Toluene Microsolution and Matrix Optical Spectroscopy

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The "solvated" nickel atoms and nickel slurries initially described by Klabunde and co-workers have been probed by nickel atom-toluene microsolution and matrix optical spectroscopy in methylcyclohexane and argon, over the extended temperature range 12–290 K. In Klabunde's terminology "solvated" nickel atoms are interpreted in terms of a highly thermally unstable bis(arene)nickel complex. The stages I to IV described by Klabunde in his procedure for preparing nickel cluster catalysts from nickel atom-toluene condensates appear to be best ascribed as follows: bis(arene)nickel coexisting with Ni_2 and Ni_3 , stage I; nickel clusters of colloidal dimensions or less, stage II; bulk nickel microcrystallites, stages III and IV. Stages I and II appear also to be formed on depositing nickel atoms into 150 K toluene/methylcyclohexane solutions and 210 K poly(methylphenyl)siloxane (DC510) liquid films. An appreciation of the nickel atom and cluster species existing at the various stages of a Klabunde-type preparation should greatly enhance the value of the method as a viable synthetic route to finely dispersed, narrow-size-distribution metal cluster catalysts.

Introduction

One of the most significant recent developments in the field of metal vapor synthesis is the discovery by Klabunde and co-workers of "solvated" metal atoms and their application for the production of highly reactive metal slurries and supported metal catalysts.¹ The method consists of cocondensing metal vapors with various organic solvents (toluene, tetrahydrofuran, alkanes, etc.), usually at liquid-nitrogen temperature, to create lightly stabilized or "solvated" metal atoms. These condensates are often highly colored and, when subjected to controlled meltdown, solvent evaporation, and pyrolysis procedures in either the absence or the presence of an oxide

support, can lead to finely dispersed, narrow-size-distribution metal cluster compositions whose catalytic efficacy can rival that of some of the best known catalyst systems. The morphological, magnetic, and chemical properties of these materials continue to be of considerable interest² even though the nature of the species formed at various stages of the preparation remains uncertain. In this paper we wish to report the results of an optical spectroscopic study, using both matrix and microsolution techniques,³ which sheds considerable light on

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