

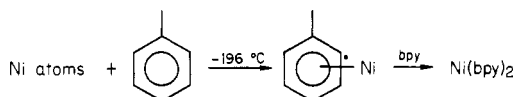
Metal-Vapor Synthesis and Electrochemistry of Bis(bipyridyl)nickel(0)

BRUCE J. HENNE and DUANE E. BARTAK*

Received April 20, 1983

The preparation of bis(2,2'-bipyridyl)nickel ($\text{Ni}(\text{bpy})_2$) has been accomplished by the use of metal-vapor methods. A nickel-toluene matrix technique in which "toluene-solvated" nickel atoms were present as intermediates was employed. Electrochemical data for $\text{Ni}(\text{bpy})_2$ and tris(2,2'-bipyridyl)nickel(II) perchlorate ($\text{Ni}(\text{bpy})_3(\text{ClO}_4)_2$) in acetonitrile was obtained with cyclic voltammetric, chronoamperometric, and coulometric techniques. A total of five stable formal oxidation states for these nickel-2,2'-bipyridine complexes were observed: +3, +2, 0, -1, -2. A comparison of the reduction potentials of these complexes indicates that a significant portion of the electron density of the lower valence complexes (e.g., -1 and -2 oxidation states) resides on the bipyridyl ligand. An overall scheme for the electron-transfer pathways for nickel-2,2'-bipyridine complexes is proposed.

The chemical syntheses of zerovalent nickel-bipyridine complexes have been previously reported in the literature.¹⁻³ However, with the recent development of metal-vapor techniques, it appears that the synthesis of many zerovalent bipyridine complexes of group 8 transition metals can be accomplished in a facile manner.^{4,5} With use of this technique, the production of relatively large quantities of $\text{Ni}(\text{bpy})_2$ can be obtained from a nickel atom-toluene matrix:



The "toluene-solvated" nickel atoms apparently exist in the form of very labile π -arene complexes with a relatively strongly bonded η^6 - π -toluene and a weaker π -toluene bond (e.g., η^2). This technique, which utilizes the formation of intermediate "toluene-solvated" nickel atoms, has shown promise in the synthesis of several catalysts of other group 8 transition metals.⁶

This report on the metal atom synthesis and electron-transfer chemistry of bipyridine complexes of nickel is of interest because of the ability of the bipyridyl ligand to stabilize several oxidation states of metals. This is due in part to the ability of the bipyridyl ligand to accumulate a significant amount of negative charge on itself.^{7,8} With the ability of nickel to exist in several stable formal oxidation states, the above property allows for a very rich electron-transfer chemistry of the nickel-bipyridine complexes. In addition, 2,2'-bipyridine is a flat bidentate ligand that could form square-planar stackings for a nickel complex in the solid state with the proper oxidation state (e.g., $\text{Ni}(+2)$ or $\text{Ni}(+3)$). This could be of interest to the field of organic metals. Finally, a comparison between the relative ease of reduction of the bis(bipyridyl) vs. the tris(bipyridyl) complexes of nickel is made.

Experimental Section

Apparatus. A metal atom vaporization apparatus, which was designed and previously described by Klabunde and co-workers, was employed in the synthesis of $\text{Ni}(\text{bpy})_2$.⁹ The manipulations of resultant materials were carried out in a drybox (Vacuum Atmospheres Dri

Lab with Model HE-493 Dri Train) employing prepurified nitrogen (99.99%). Crystallizations and solution-transfer reactions were carried out under purified nitrogen (passed over BASF R3-11 catalyst) in airless glassware and often in conjunction with degassing procedures on a conventional vacuum line.

The cyclic-voltammetric studies were performed on a previously described three-electrode potentiostat.¹⁰ A digital-controlled multipurpose function generator and a circuit for electronic compensation of ohmic potential drop between the working and reference electrodes were incorporated into the instrument. Large-scale, controlled-potential electrolysis was carried out on a second potentiostat (± 100 V, 0.1 A) with associated digital circuitry for coulometric measurements.¹¹ Readout for the cyclic-voltammetric experiments was accomplished with a Hewlett-Packard Model 1035 X-Y recorder or Tektronix Model 5103N storage oscilloscope.

Electrodes and Cells. All electrochemical experiments were carried out on an all-glass vacuum line, which has been previously described.¹² 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 R3-11 catalyst, 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 cm² or a glassy-carbon (Tokai) electrode (area 0.20 cm²), which was prepared by previously reported methods.¹³ Both electrodes were polished with 0.1- μm 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 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.

Solvents and Reagents. Acetonitrile (Burdick and Jackson, UV grade) was purified by the procedure of Walter and Ramaley (method B) and stored over activated alumina (Woelm W200, neutral, activity I) on a vacuum line.¹⁴ Pentane and toluene were purified by distillation from benzophenone ketyl under prepurified nitrogen and stored on a vacuum line. Tetraethylammonium perchlorate (TEAP) was

- (1) Herzog, S.; Taube, R. *Z. Chem.* 1962, 2, 208.
- (2) Behrens, H.; Muller, A. *Z. Anorg. Allg. Chem.* 1965, 341, 124.
- (3) Ittel, S. D. *Inorg. Synth.* 1977, 17, 117.
- (4) Groshens, T. G.; Henne, B.; Bartak, D. E.; Klabunde, K. *J. Inorg. Chem.* 1981, 20, 3629.
- (5) Radonovich, L. J.; Eyring, M. W.; Groshens, T. J.; Klabunde, K. *J. Am. Chem. Soc.* 1982, 104, 2816.
- (6) Klabunde, K. J.; Ralston, D.; Zoellner, R.; Hattori, H.; Tanaka, Y. *J. Catal.* 1978, 55, 213.
- (7) Christolm, M. H.; Huffman, J. C.; Rothwell, I. P.; Bradley, P. G.; Kress, N.; Woodruff, W. H. *J. Am. Chem. Soc.* 1981, 103, 4945.
- (8) Saito, Y.; Takemoto, J.; Hutchinson, B.; Nakamoto, K. *Inorg. Chem.* 1972, 11, 2003.
- (9) Klabunde, K. *J. Angew. Chem., Int. Ed. Engl.* 1975, 14, 287. Klabunde, K. J.; Timms, P. L.; Skell, P. S.; Ittel, S. *Inorg. Synth.* 1979, 19, 59.

- (10) Bartak, D. E.; Hundley, H. K.; Van Swaay, M.; Hawley, M. D. *Chem. Instrum. (N.Y.)* 1972, 4, 1.
- (11) Van Swaay, M. *J. Chem. Educ.* 1978, 55, A7.
- (12) Gores, G. J.; Koeppe, C. E.; Bartak, D. E. *J. Org. Chem.* 1979, 44, 380.
- (13) Phillips, J.; Gale, R. J.; Wier, R. G.; Osteryoung, R. A. *Anal. Chem.* 1976, 48, 1266.
- (14) Walter, M.; Ramaley, L. *Anal. Chem.* 1973, 45, 165.

prepared according to the method of Kolthoff and Coetzee.¹⁵ Ni(bpy)₃(ClO₄)₂ was prepared by the method of Nyholm and Burstall.¹⁶ All other reagents including 2,2'-bipyridine (Eastman) and nickel (Central Scientific) were commercially obtained and used without further purification.

Preparation of Ni(bpy)₂. A typical preparation, which utilized the metal-vaporization apparatus, required about 2 h, during which time 1.0 g (0.02 mol) of nickel was slowly vaporized. The vaporized nickel was codeposited with 200 mL (1.9 mol) of degassed toluene on the reactor walls, which were maintained at liquid-nitrogen temperatures. After vaporization of the metal, the contents of the evacuated reactor were allowed to slowly warm with stirring until a yellow-brown slurry of the "toluene-solvated" nickel atoms was formed. A solution of 3.0 g of 2,2'-bipyridine in degassed toluene (25 mL) was added to the cooled meltdown solution with stirring. After addition of the bipyridine the color of the reaction mixture turned black. After the mixture was allowed to reach ambient temperature, the black solution of Ni(bpy)₂ was siphoned out of the reactor vessel into an airless filtration-collection apparatus, which was transferred to the drybox. The solution was filtered a second time in the drybox through fine-porosity fritted glass; the resultant toluene solution was evaporated down to 20 mL under vacuum. Dark violet crystals of Ni(bpy)₂ were obtained by cooling to 0 °C for several days. The crystals were isolated in the drybox by removing the cool mother liquor by a syringe and finally vacuum-dried. A typical yield of Ni(bpy)₂, which had a melting point of 149 °C, was ca. 2.3 g, or 60% based upon bipyridine as the limiting reagent.

IR: 700 (s), 713 (s), 738 (vs), 757 (s), 845 (m), 855 (w), 935 (w), 968 (s), 980 (s), 1002 (vs), 1012 (w), 1030 (w), 1038 (w), 1091 (m), 1118 (m), 1145 (vs), 1243 (m), 1256 (m), 1272 (s), 1302 (s), 1320 (vs), 1400 (vs), 1425 (vs), 1450 (vs), 1458 (vs), 1523 (vs), 1575 (vs) cm⁻¹. ¹H NMR (C₆D₆): δ 7.1 (m, 4), 7.6 (m, 2), 10.2 (d, 2). Anal. Calcd for Ni(bpy)₂: C, 64.73; H, 4.35; N, 15.10; Ni, 15.82. Found: C, 64.50; H, 4.26; N, 14.92; Ni, 15.64.

Results and Discussions

Synthesis of Bis(bipyridyl)nickel(0) by Metal-Vapor Techniques. Klabunde and co-workers have shown that there are three metal-vapor approaches to the synthesis of M⁰(bpy)_n complexes: (1) cocondensation, (2) solution, and (3) toluene matrix. In cocondensation, the metal atoms are simultaneously codeposited with bipyridine vapor and toluene on a cold reactor wall (-196 °C) under vacuum. Although this procedure is the most commonly employed technique in metal atom chemistry, it requires that the ligand (bpy) be volatilized. The second approach utilizes a low-temperature solution of the ligand in a modified rotary-evaporator apparatus, which has the capability of metal vaporization. We have found the third approach, or toluene-matrix formation, to be the easiest to carry out. A bipyridine solution is simply syringed into a reactor, which contains the metal-toluene matrix that has been previously formed by codeposition of toluene and metal vapors. The resultant meltdown and mixing produce the metal-bipyridine complex. The dark violet crystals of Ni(bpy)₂ that were obtained after crystallization were used in the subsequent electrochemical studies.

Electrochemistry of Bis(bipyridyl)nickel(0). The cyclic-voltammetric (CV) behavior of bis(bipyridyl)nickel(0) in acetonitrile (AN) is shown in Figures 1-3. Figure 1 shows the equilibrium or rest potential of the Ni(bpy)₂ solution to be at -1.40 V vs. SCE. The scan was initiated in the anodic direction in this cyclic voltammogram, producing an oxidation wave with $E_{pa} = -1.23$ V. The corresponding reduction wave for this couple with $E_{pc} = -1.27$ V is observed on the cathodic cycle upon reversing the scan. The difference in peak potentials, $\Delta E_p = E_{pa} - E_{pc} = 40$ mV, is reasonably consistent with the theoretical ΔE_p for a reversible two-electron process ($\Delta E_p = 57/n$ mV). A chronoamperometric experiment (CA) was carried out in which the potential was stepped from the

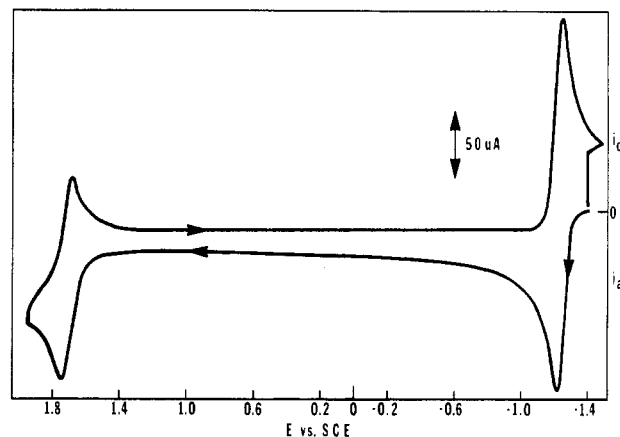


Figure 1. Cyclic voltammogram of 3.8×10^{-3} M bis(bipyridyl)nickel(0) in 0.2 M TEAP-acetonitrile at a scan rate of 0.1 V s^{-1} on a planar platinum electrode (0.25 cm^2) with the scan initiated in the positive direction from the rest potential at -1.40 V .

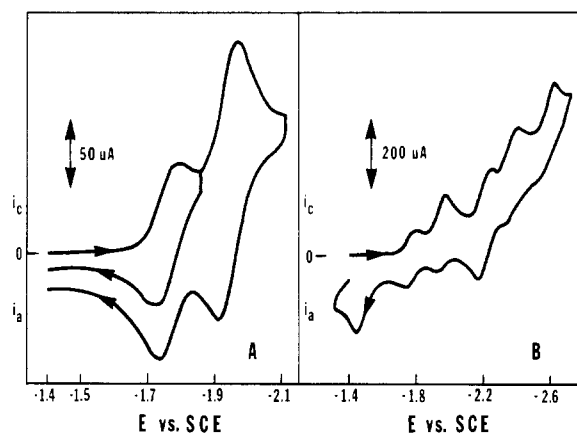


Figure 2. Cyclic voltammograms of 3.8×10^{-3} M bis(bipyridyl)nickel(0) in 0.2 M TEAP-acetonitrile at a scan rate of 0.1 V s^{-1} on a planar platinum electrode (0.25 cm^2) with the scan initiated in the negative direction from the rest potential at -1.40 V .

rest potential of -1.40 V to a potential of -0.60 V , which is well beyond the oxidation peak such that the concentration of the electroactive species at the electrode surface is virtually zero. The resultant current was diffusion controlled and produced an average $it^{1/2}C^{-1}$ value of $104 \pm 2 \text{ A s}^{1/2} \text{ mol}^{-1} \text{ cm}^3$. A convenient reference compound with size roughly similar to that of the nickel complex is ferrocene, which is known to be oxidized reversibly in a diffusion-controlled one-electron step. The $it^{1/2}C^{-1}$ value for the ferrocene one-electron oxidation process was found to be $64 \pm 3 \text{ A s}^{1/2} \text{ mol}^{-1} \text{ cm}^3$ under the same experimental conditions. Comparison of this value to the CA value of the -1.23 V oxidation wave of Ni(bpy)₂ indicates that Ni(bpy)₂ is oxidized by a two-electron oxidation process. The -1.23 V oxidation wave was examined further by using controlled-potential coulometry. Exhaustive oxidation of a Ni(bpy)₂ solution resulted in current, which upon integration yielded charge consistent with 2 faradays/mol. Thus, the -1.23-V oxidation wave can be described as in eq 1.

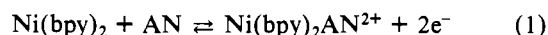
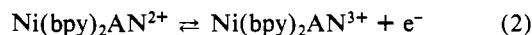


Figure 1 also reveals an additional oxidation wave at 1.75 V , which is consistent with a one-electron process by comparing the relative peak heights of the two oxidation waves (i.e., the -1.23-V wave is approximately 2.8 times higher than the 1.75-V wave). The electrode reaction for this oxidation wave can be described by eq 2.



(15) Kolthoff, I. M.; Coetzee, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 870.
 (16) Burstall, F. H.; Nyholm, R. S. *J. Chem. Soc.* **1952**, 3570.

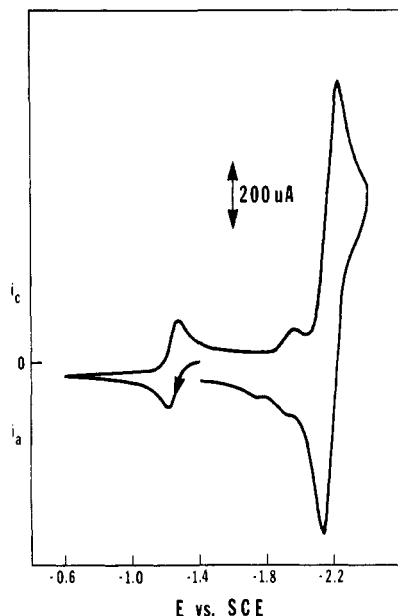
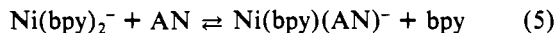
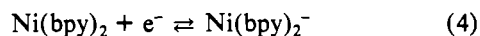


Figure 3. Cyclic voltammogram of the same solution under similar conditions as in Figure 1 except that a 10-fold excess of 2,2'-bipyridine was added.

The reductive electrochemistry of $\text{Ni}(\text{bpy})_2$ is shown in Figure 2. Reversible couples at $E_{\text{pc}} = -1.79, -1.97,$ and -2.23 V and two partially reversible waves at -2.40 and -2.62 V are observed upon scanning cathodically from the rest potential of -1.4 V. The reversible wave at -1.79 V is too small to be a one-electron wave though it is consistently seen in the reduction of freshly prepared solutions of zerovalent $\text{Ni}(\text{bpy})_2$. The magnitude of this wave decreases in solutions that have significantly decomposed (presumably to nickel metal and free bipyridine) and is virtually eliminated in fresh solutions with a large excess of bipyridine as seen in Figure 3. Because the waves can be suppressed by excess free bipyridine, these data are consistent with an electrochemically induced ligand-substitution reaction:



Reaction 3 can be considered to be two discrete steps:



The species undergoing electron transfer is the 18-electron $\text{Ni}(\text{bpy})_2$ complex with two bidentate bpy ligands. The effect of the homogeneous follow-up reaction (5) is to shift the reduction potential for $\text{Ni}(\text{bpy})_2$ in the positive direction. This is in fact observed by comparison of freshly prepared $\text{Ni}(\text{bpy})_2$ vs. the case where excess bipyridine is present. In the case where excess bipyridine is present, the equilibrium for reaction 5 is significantly shifted to the left and only the reduction of $\text{Ni}(\text{bpy})_2$ to $\text{Ni}(\text{bpy})_2^-$ is observed at -1.97 V. Acetonitrile would not normally be expected to substitute for a bidentate bipyridyl ligand. However, one of the bipyridyl ligands should be unidentate on the $\text{Ni}(\text{bpy})_2^-$ complex, since a 19-electron system would result if both bipyridyl ligands are considered as bidentate. Since acetonitrile (AN) is the solvent, effective substitution of the unidentate bipyridyl ligand could occur in the absence of free bipyridine.

The reversible reduction wave at -1.97 V in the presence of excess bipyridine is consistent with a one-electron wave since it is approximately one-third the size of the two-electron oxidation wave at -1.23 V. The $it^{1/2}C^{-1}$ values of 60 ± 1.5 and 63 ± 2 $\text{A s}^{1/2} \text{mol}^{-1} \text{cm}^3$ were obtained from CA's stepped from the rest potential to -2.05 and -2.08 V, respectively. Thus,

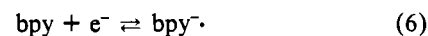
Table I. Cyclic-Voltammetric Data for the Nickel Complexes of 2,2'-Bipyridine^a

redox couple	substrate	
	$\text{Ni}(\text{bpy})_2$ $E_{\text{pc}}, E_{\text{pa}}$	$\text{Ni}(\text{bpy})_3(\text{ClO}_4)_2$ $E_{\text{pc}}, E_{\text{pa}}$
3+/2+	1.68, 1.75	1.66, 1.74
2+/0	-1.27, -1.23	-1.26, -1.22
0/1 ^{-b}	-1.79, -1.73	-1.75, -1.70
0/1 ^{-c}	-1.97, -1.91	-1.96, -1.90
1-/2-	-2.40, -2.32	-2.34, -2.28

^a The solutions contained 0.2 M tetraethylammonium perchlorate as supporting electrolyte in acetonitrile at 25 °C. The scan rate was 0.1 V s^{-1} on a planar platinum electrode. All potentials are in volts vs. a saturated calomel electrode. ^b This couple can be described by eq 3. ^c This couple can be described by eq 4.

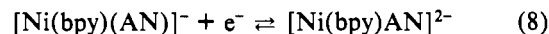
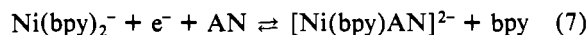
the reduction wave at -1.97 V can be described as a one-electron reaction in excess bipyridine and without ligand exchange (eq 4).

The reversible wave at -2.23 V vs. SCE is the reduction of bipyridine to its anion radical as described in eq 6. Evidence



to support this is that voltammetry on a solution of 2,2'-bipyridine produces a wave at this same potential, -2.23 V vs. SCE. In experiments where an excess of bpy was added (i.e., Figure 3) or where a $\text{Ni}(\text{bpy})_2$ solution has significantly decomposed, the wave at -2.23 V is increased. The height of this bpy wave can be used to monitor the decomposition of the zerovalent metal-bipyridine complexes. Thus, electrochemical techniques can be used to check freshly prepared complexes for the presence of excess bpy, which might not have been completely removed during the separation and isolation procedures (vide ante).

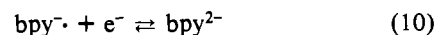
The wave at -2.40 V is partially reversible and is approximately of the same height as the one-electron wave at -1.97 V. These results are consistent with a further one-electron reduction of $\text{Ni}(\text{bpy})_2^-$ or $\text{Ni}(\text{bpy})\text{AN}^-$ to a somewhat unstable species in AN solution. The addition of excess bpy to a $\text{Ni}(\text{bpy})_2$ solution changes this partially chemically reversible couple into an irreversible system. Addition of excess bpy to the solution apparently shifts the equilibrium for reaction 5 to the left. However, in the absence of excess bpy, reaction 7 appears feasible with the reduction of $\text{Ni}(\text{bpy})_2^-$ to $\text{Ni}(\text{bpy})\text{AN}^{2-}$, an 18-electron species with the remaining bpy as a bidentate ligand. The further reduction of the product of the wave at -1.79 V, which is $\text{Ni}(\text{bpy})\text{AN}^-$, to $\text{Ni}(\text{bpy})\text{AN}^{2-}$ should also take place at approximately -2.40 V (eq 8). In



the presence of excess bpy, reaction 9 apparently is important with the irreversible formation of Ni^0 and bipyridine radical anions.



The partially reversible wave at -2.62 V is the one-electron reduction of bpy^- to its dianion, bpy^{2-} , as shown in eq 10. This assignment was substantiated by independent electrochemical studies on 2,2'-bipyridine.



The total of five formal oxidation states are therefore noted for nickel in the presence of bipyridine: +3, +2, 0, -1, and -2 (Table I). The stabilities of all the forms except -2 are such that the cyclic-voltammetric data show chemical rever-

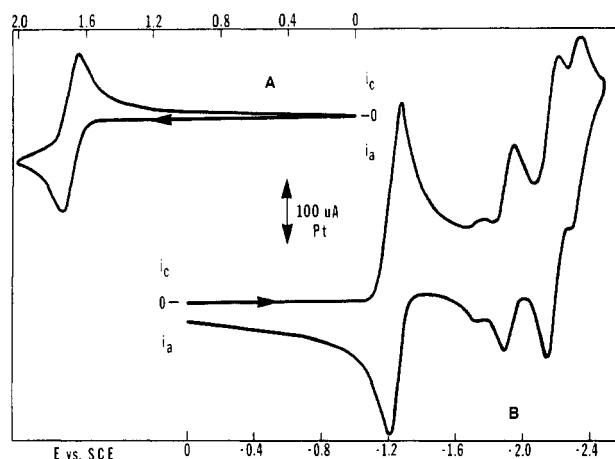


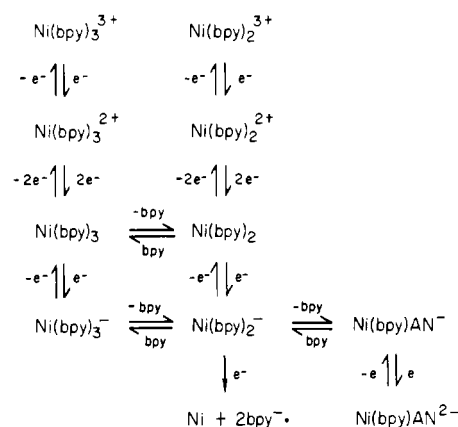
Figure 4. Cyclic voltammograms of 2.7×10^{-3} M tris(bipyridyl)-nickel(II) in 0.2 M TEAP-acetonitrile at a scan rate of 0.1 V s^{-1} on a planar platinum electrode (0.25 cm^2) with the scan initiated in the (A) positive direction and (B) negative direction from the rest potential of 0.0 V.

sibility down to a scan rate of 0.01 V s^{-1} . The -2 oxidation state as postulated in the form of $\text{Ni}(\text{bpy})\text{AN}^{2-}$ has a half-life of approximately 1 s as noted by cyclic voltammetry in the absence of excess bipyridine.

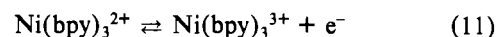
Electrochemistry of Tris(bipyridyl)nickel(II). Several polarographic investigations of the electrochemistry of $\text{Ni}(\text{bpy})_3(\text{ClO}_4)_2$ and other similar bipyridine-substituted complexes have been carried out. However, several of these studies employed techniques and solvent systems different from those employed in this study.¹⁷⁻²¹ Two of the above studies were concerned with the electrochemistry of $\text{Ni}(\text{bpy})_3^{2+}$ in acetonitrile.^{17,18} However, there appears to be some disagreement on the reduction electrochemistry of $\text{Ni}(\text{bpy})_3^{2+}$ in this solvent to lower valent complexes. Tanaka and Sato observed two polarographic reduction waves for $\text{Ni}(\text{bpy})_3^{2+}$ on mercury.¹⁷ Although the first reduction wave was complicated by a maximum, the ratio of the wave heights of the two waves was reported to be 2:1. In addition, comparisons of diffusion-current constants for known one-electron reduction processes vs. the above two waves suggested that $\text{Ni}(\text{bpy})_3^{2+}$ was reduced by a two-electron process to $\text{Ni}(\text{bpy})_3$ for the first wave. The second, more negative polarographic wave was assigned to the one-electron reduction of the resultant $\text{Ni}(\text{bpy})_3$ to $\text{Ni}(\text{bpy})_3^-$. In contrast, Prasad and Scaife reported that $\text{Ni}(\text{bpy})_3^{2+}$ was reduced in an initial one-electron wave to $\text{Ni}(\text{bpy})_3^+$ in acetonitrile.¹⁸ Furthermore, they reported the apparent synthesis of $[\text{Ni}(\text{bpy})_3]\text{ClO}_4$ by preparative electrolysis. Therefore, a study was initiated on the electrochemistry of $\text{Ni}(\text{bpy})_3(\text{ClO}_4)_2$ in acetonitrile, which utilized the same techniques employed in the examination of the zerovalent $\text{Ni}(\text{bpy})_2$.

The cyclic-voltammetric behavior of tris(2,2'-bipyridyl)-nickel(II) perchlorate, $\text{Ni}(\text{bpy})_3(\text{ClO}_4)_2$, in acetonitrile is shown in Figure 4. An oxidation wave is observed at $E_{pa} = 1.74 \text{ V}$ when the working electrode is scanned in the positive direction from the initial potential (Figure 4A). Upon reversal of the scan in the negative direction at $+2.0 \text{ V}$, the corresponding reduction wave with $E_{pc} = +1.66 \text{ V}$ is observed. The relative wave height and $\Delta E_p = 90 \text{ mV}$ indicated that this wave was a one-electron quasi-reversible oxidation process. Con-

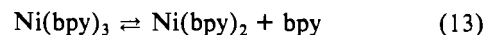
Scheme 1



trolled-potential coulometry yielded a n value of 1 for this oxidation process as was observed in the $\text{Ni}(\text{bpy})_2$ system. Thus, eq 11 describes this oxidation wave.



Reversible couples at $E_{pc} = -1.26, -1.75, -1.96,$ and -2.21 V , respectively, and a quasi-reversible wave at -2.34 V were observed upon scanning in the cathodic direction from the rest potential. Controlled-potential coulometry indicated the wave at -1.26 V to be a two-electron process as described in eq 12. Species such as $\text{Ni}(\text{bpy})_3$ (eq 12) might be expected to be unstable if the bpy ligands remained bidentate. However, this species and others apparently achieve stability either by the bipyridyl ligands becoming unidentate and/or by eliminating one of them as shown in eq 13.



The small wave at -1.75 V is too small to be a one-electron wave, and addition of excess bpy decreases and eventually eliminates this wave. This behavior is consistent with the polarographic results on mercury obtained by Tanaka and Sato and with the results obtained for the above $\text{Ni}(\text{bpy})_2$ system on platinum.¹⁷ The couples at $-1.96, -2.21,$ and -2.34 V are all one-electron waves. They directly correspond to the similar couples in the $\text{Ni}(\text{bpy})_2$ system and can be described by eq 4, 6, and 7, respectively. A summary of the electrochemical data for $\text{Ni}(\text{bpy})_3(\text{ClO}_4)_2$ in acetonitrile is presented in Table I.

The electrochemistry of $\text{Ni}(\text{bpy})_3(\text{ClO}_4)_2$ and $\text{Ni}(\text{bpy})_2$ can be summarized by Scheme I from the above results. Scheme I illustrates that both tris and bis complexes can exist at the electrode surface. The observed stability of the various species involved in this mechanism can be rationalized if 2,2'-bipyridine can act as both a uni- and bidentate ligand and the solvent, acetonitrile, can competitively act as a ligand with the unidentate form of bipyridine.

Conclusions. A comparison of the electrochemistry of $\text{Ni}(\text{bpy})_3(\text{ClO}_4)_2$ to that of $\text{Ni}(\text{bpy})_2$ reveals that the same general reaction scheme is operative in both systems. However, some differences in the peak-potential values between the bis and tris complexes are noted (Table I). In general, the peak potentials for the bis complexes are more negative than the corresponding peak potentials for the tris complexes. The shift in reduction potentials can be explained by an increase in the amount of back-bonding from the d orbitals of the metal into the π^* antibonding orbitals of three bpy ligands on the tris vs. two bpy ligands on the bis compounds. The increase in back-bonding effectively delocalizes electron density from the central metal atom to the ligands. The net effect is an increase in electron density on the ligands to the extent that the ligand accommodates negative charge and begins to resemble a

(17) Tanaka, N.; Sato, Y. *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 487.

(18) Prasad, R.; Scaife, D. B. *J. Electroanal. Chem.* **1977**, *84*, 373.

(19) Misono, A.; Uchida, Y.; Yamagishi, T.; Kageyama, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1438.

(20) Dhar, S. K.; Kurcz, W. E. *J. Electroanal. Chem.* **1974**, *53*, 325.

(21) Simic, M. G.; Hoffman, M. Z.; Cheney, R. P.; Mulazzani, Q. C. *J. Phys. Chem.* **1979**, *83*, 439.

radical anion of bpy. The overall effect is to lower the lowest unoccupied molecular orbital (LUMO) so as to allow the tris complex to be slightly easier to reduce than the bis complex.

Acknowledgment. The support of the University of North Dakota Research Committee is acknowledged with gratitude. We wish to especially thank Professor Kenneth J. Klabunde, who provided the metal-vaporization equipment and expertise

necessary for the metal atom synthesis of Ni(bpy)₂. We also wish to thank Tom Groshens for obtaining the spectral data on the characterization of Ni(bpy)₂.

Registry No. Ni(bpy)₂³⁺, 88130-85-2; Ni(bpy)₂²⁺, 31042-27-0; Ni(bpy)₂, 15186-68-2; Ni(bpy)₂⁻, 71592-66-0; Ni(bpy)₂²⁻, 88130-86-3; Ni(bpy)₃³⁺, 64592-13-8; Ni(bpy)₃(ClO₄)₂, 16166-37-3; Ni(bpy)₃, 88130-87-4; Ni(bpy)₃⁻, 88130-88-5; Ni(bpy)₃²⁻, 88130-89-6.

Contribution from the Department of Chemistry,
Northern Illinois University, DeKalb, Illinois 60115

Synthesis of Some Alkyl Phosphite Complexes of Platinum and Their Structural and Spectral Characterization

JOSÉ M. SOLAR, ROBIN D. ROGERS,* and W. ROY MASON*

Received June 1, 1983

In order to explain why Pt(II) products were frequently observed, the synthetic procedure for Pt(0) alkyl phosphite complexes has been reexamined. According to the procedure the Pt(0) complexes [Pt(P(OEt)₃)₄], [Pt(P(OMe)₃)₄], and [Pt(ETPB)₄] (ETPB = 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane) are formed initially by ligand reduction of PtCl₄²⁻ accompanied by Cl⁻ displacement. Subsequently, the Pt(0) complexes are found to undergo a reoxidation to Pt(II) if O₂ is not excluded from the reaction mixture. The oxidation is accelerated by H⁺, but the nature of the Pt(II) product depends on the counterion. When [Pt(P(OEt)₃)₄] in alcoholic solution is treated with HClO₄ and the solution saturated with air, [Pt(P(OEt)₃)₄](ClO₄)₂ can be isolated. In the presence of HCl, [Pt(P(OR)₃)₄] is converted to [Pt(P(OH)(OR)₂)(P(O)(OR)₂)₂] for R = Et or Me. These latter complexes contain four equivalent P atoms by ³¹P NMR and exhibit a low-field proton resonance (δ 16.5 (Me₄Si) for Me and δ 16.6 (Me₄Si) for Et) assigned to bridging hydrogens linking the (RO)₂POH and (RO)₂PO⁻ ligands together in the complex. The structure of [Pt(P(OH)(OMe)₂)(P(O)(OMe)₂)₂] has been determined by X-ray diffraction techniques. It crystallizes in the monoclinic space group *P*₂₁/*c* with unit cell parameters *a* = 7.147 (1) Å, *b* = 15.204 (2) Å, *c* = 10.680 (4) Å, β = 116.53 (2)°, and *D*_{calcd} = 2.02 g cm⁻³ for *Z* = 2. The Pt atom resides on a crystallographic center of inversion and is bonded in a square-planar geometry to the four P atoms. The two unique P ligands are equivalent, bridged by a symmetric O...H...O hydrogen bond.

Introduction

When a literature procedure^{1,2} for the preparation of [Pt(P(OEt)₃)₄] was followed, several times a white solid was isolated that gave an elemental analysis and ³¹P NMR spectrum that was quite different from that expected for the Pt(0) product. Similar difficulty with the synthetic procedure was reported by Pregosin and Sze,³ who obtained a white product with an analysis and ³¹P NMR spectrum nearly identical with that of ours. These workers formulated the product as the Pt(II) complex [Pt(P(OH)(OEt)₂)(P(O)(OEt)₂)₂], which is a known compound⁴ and which had been characterized by ³¹P NMR earlier.^{5,6} They also modified the synthesis of the Pt(0) complex slightly by changing the starting material from K₂PtCl₄ to the more soluble Na₂PtCl₄. In spite of this change, the procedure in our hands still frequently produced the Pt(II) product and similar results were obtained with the ligands P(OMe)₃ and P((OCH₂)₃CEt), 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (ETPB).

The synthetic procedure has been investigated carefully, and conditions that lead reproducibly to a Pt(0) product are de-

scribed herein. The relationship between the Pt(II) product and the Pt(0) complex has been formulated, and a method is described for the preparation of [Pt(P(OEt)₃)₄](ClO₄)₂ from Pt(P(OEt)₃)₄. Further, the interesting [Pt(P(OH)(OR)₂)(P(O)(OR)₂)₂], R = Me or Et, complexes are believed to contain bridging hydrogens linking the (RO)₂POH and (RO)₂PO⁻ ligands together.⁷⁻¹³ In order to characterize the bridge-hydrogen bonding in the Pt(II) complexes, we have determined the structure of [Pt(P(OH)(OMe)₂)(P(O)(OMe)₂)₂] by X-ray diffraction.

Experimental Section

Preparation of Compounds. The starting material for all of the Pt complexes was K₂PtCl₄. The ligands were used as purchased (Strem Chemicals, Inc.); their purity was checked by C-H analysis and IR and NMR spectroscopy.

Tetrakis(trimethyl phosphite)platinum(0), [Pt(P(OMe)₃)₄], **Tetrakis(triethyl phosphite)platinum(0)**, [Pt(P(OEt)₃)₄], and **Tetrakis(4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)platinum(0)**, [Pt(ETPB)₄]. The preparation of these compounds represents a modification of two previously reported syntheses.¹⁻³ Potassium

- (1) Meier, M.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1969**, *8*, 795.
- (2) Meier, M.; Basolo, F. *Inorg. Synth.* **1972**, *13*, 112.
- (3) Pregosin, P. S.; Sze, S. N. *Helv. Chim. Acta* **1977**, *60*, 1371.
- (4) Grinberg, A. A.; Troitskaya, A. D. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1944**, 178; *Chem. Abstr.* **1945**, *39*, 1604. See also (for the Me analogue): Troitskaya, A. D.; Itskovich, T. B. *Tr. Kazan. Khim.-Tekhnol. Inst.* **1953**, *18*, 59; *Chem. Abstr.* **1957**, *51*, 1148.
- (5) Pidcock, A.; Waterhouse, C. R. *J. Chem. Soc. A* **1970**, 2080.
- (6) Allen, F. H.; Pidcock, A.; Waterhouse, C. R. *J. Chem. Soc. A* **1970**, 2087.

- (7) Dixon, K. R.; Rattray, A. D. *Can. J. Chem.* **1971**, *49*, 3997.
- (8) Carty, A. J.; Jacobson, S. E.; Simpson, R. T.; Taylor, N. J. *J. Am. Chem. Soc.* **1975**, *97*, 7254.
- (9) Sperline, R. P.; Roundhill, D. M. *Inorg. Chem.* **1977**, *16*, 2612.
- (10) Sperline, R. P.; Roundhill, D. M. *Inorg. Synth.* **1979**, *19*, 98.
- (11) Naik, D. V.; Palenik, G. J.; Jacobsen, S.; Carty, A. J. *J. Am. Chem. Soc.* **1974**, *96*, 2286.
- (12) Cornock, M. C.; Gould, R. O.; Jones, C. L.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1307.
- (13) Southern, T. J.; Dixneuf, P. H.; LeMarouille, J.-Y.; Grandjean, D. *Inorg. Chem.* **1979**, *18*, 2987.