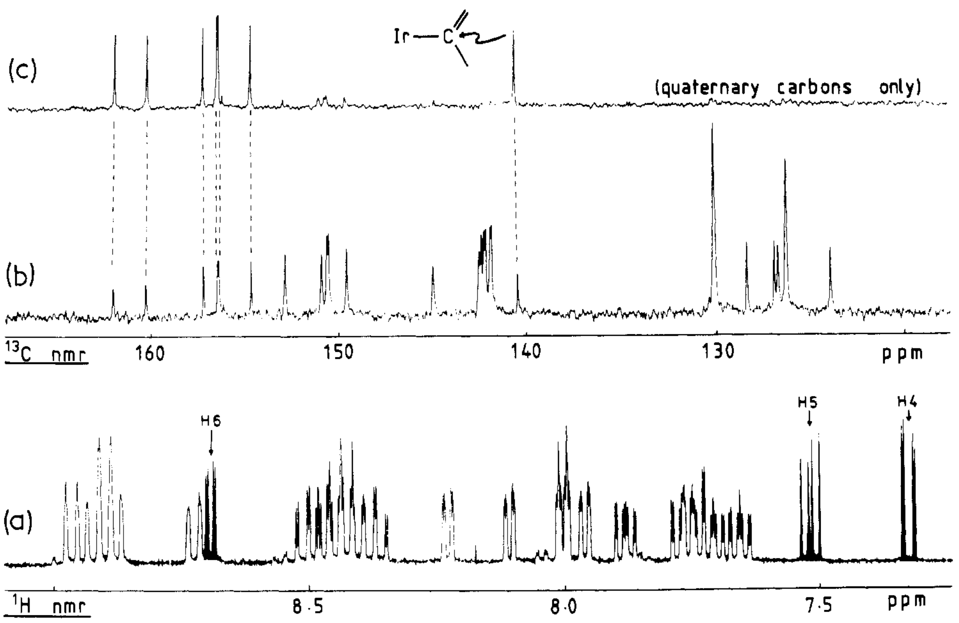

Figure 1. NMR spectra of I^{2+} in MeOH-d_4: (a) ^{1}H spectrum (360.13 MHz; line sharpened); (b) proton-decoupled ^{13}C spectrum (90.56 MHz); (c) proton-decoupled ^{13}C spectrum (90.56 MHz) for quaternary carbons only.

reversible reduction waves at −1.03 and −1.23 vs. SCE and two further waves, reversible and quasireversible, at −1.86 and −2.21 V, respectively. These reductions, also reported by Kahl et al.,[7] are characteristic of two and only two ordinary bipyridine ligands chelated to Ir(III). Moreover, the measured electrode potentials imply[8] the simultaneous presence of an effectively monoanionic neighboring ligand, represented by the chelated bipyridinyl group. Thus we note the first reduction potential is intermediate between that of $[Ir(bpy)_3]^{3+}$ (−0.82 V) and $[Ir(bpy)_2Cl_2]^+$ (−1.20 V), and the system is elegantly modeled by the further reductions of $[Ir(bpy)_2(bpy^-)]^{2+}$ at −1.00 and −1.20 V. I^{2+} also shows a new irreversible two-electron oxidation wave ($E_p = +0.95$ V), which we associate with the C-metalated ligand. It should be noted that the voltammetric behavior of I^{2+} is in marked contrast with Kahl's $[Ir(phen)_2(phen')(OH)]^{2+}$ (where phen represents bidentate and phen′ monodentate *o*-phenanthroline), for which three early reductions are reported.[4]

The electronic spectra of I^{2+}, I^+, and I^0 have been compared by using an optically transparent thin-layer electrolysis cell. I^{2+} and I^+ (but not I^0) both show the well-known[9] $\pi(6) \rightarrow \pi(7)$ transition of coordinated bpy around 33 000 cm^{-1}, with appropriately reduced intensity compared to $[Ir(bpy)_3]^{3+}$.[10] Equally, I^+ and I^0 (but not I^{2+}) show the characteristic absorptions of coordinated bpy^- near 11 000, 20 000, and 26 000 cm^{-1} in accordance with the now familar pattern of localized reductions in $(d\pi)^6$ bpy complexes.[10,11] In addition, I^+ (but not I^0 or I^{2+}) shows a band at 5000 cm^{-1} ($\epsilon = 220$ mol^{-1} dm^3 cm^{-1}) characteristic of ligand–ligand ($bpy^- \rightarrow bpy$) intervalence charge transfer.[12]

I^{2+} has been resolved into its optical isomers and shows an exciton couplet around 33 000 cm^{-1} readily assigned to a *cis*-$M(bipy)_2$ moiety.[9] Reduction to I^0, followed by reoxidation to I^{2+}, does not cause any loss of optical activity. These observations are, of course, consistent with successive ligand-based reductions at a kinetically inert Ir(III) center.

Collectively, these data demonstrate clearly that "pseudo-$[Ir(bpy)_3(OH)(BF_4)_2]$" contains a deprotonated N,C-bound ligand that is indeed physically and electronically unique and remains distinct from the accompanying normal bipyridine ligands in nonaqueous solution.[13]

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Registry No. $I^{2+}(BF_4^-)_2$, 91467-35-5; I^+, 91467-36-6; I, 91467-37-7.

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Molecular Orbital Study of the Substituent Effect on the Redox Properties of Disubstituted Bipyridines and Their Ruthenium(II) Complexes

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In the electrochemical reduction of $[Ru(bpy)_3]^{2+}$ (**1**) (bpy = 2,2′-bipyridine) and its analogues with substituted 2,2′-bipyridines, six reduction waves can be observed.[1] Within the framework of simple molecular orbital (MO) theory, this is due to the fact that each bpy or its substituted analogue accepts up to two electrons in its lowest unoccupied MO level.[2] The six reduction waves found for **1** and [Ru(5,5′-

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Table I. Half-Wave Potentials ($E_{1/2}^{r}$) of bpy, 4,4′-(CO_2Et)$_2$bpy, 5,5′-(CO_2Et)$_2$bpy, and Their Ru(II) Complexes[a,b]

compd	$-E_{1/2}^{r}$/V		
bpy	2.54	3.05[c]	
4,4′-(CO_2Et)$_2$bpy	2.05	2.40	3.06
5,5′-(CO_2Et)$_2$bpy	1.77	2.10	
[Ru(bpy)$_3$]$^{2+}$	1.76	1.92	2.14
	2.78	3.00	3.30[c]
[Ru(4,4′-(CO_2Et)$_2$bpy)$_3$]$^{2+}$	1.34	1.46	1.62
	2.02	2.19	2.45
	2.88	2.97	3.19
	3.34		
[Ru(5,5′-(CO_2Et)$_2$bpy)$_3$]$^{2+}$	1.14	1.21	1.33
	1.75	1.89	2.04

[a] In DMF containing 0.1 M NEt_4PF_6 at −54 °C. [b] Vs. ferrocenium/ferrocene. [c] Distorted wave.

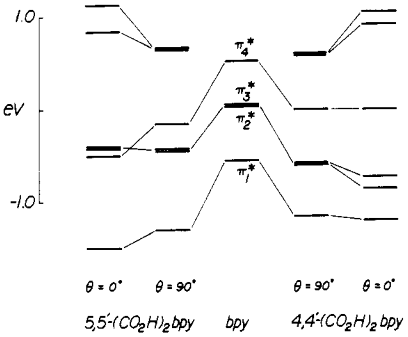
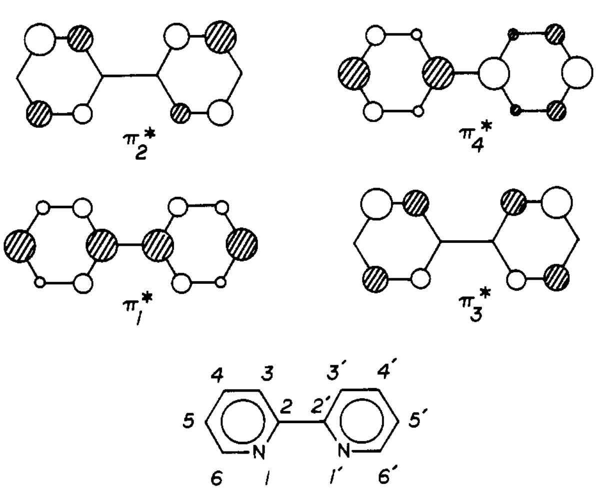


Figure 1. Low-lying unoccupied π* levels of bpy, 4,4′-(CO_2H)$_2$bpy, and 5,5′-(CO_2H)$_2$bpy obtained from MNDO calculations, where θ refers to the dihedral angle between CO_2H and bpy units. θ is defined such that CO_2H and bpy units are coplanar at θ = 0°.

(CO_2Et)$_2$bpy)$_3$]$^{2+}$ (**2**) in 0.1 M $NEt_4{\cdot}PF_6$ solution of *N*,*N*-dimethylformamide at −54 °C are summarized in Table I. Under the same conditions, however, [Ru(4,4′-(CO_2Et)$_2$bpy)$_3$]$^{2+}$ (**3**) gives rise to 10 reduction waves.[3] If reduction of 4,4′-(CO_2Et)$_2$bpy is primarily responsible for the four extra reduction waves (beyond the first six) of **3**, the electrons associated with the extra waves will be accommodated by the second lowest unoccupied MO level of 4,4′-(CO_2Et)$_2$bpy. In general, the more negative reduction potential is related to the higher lying unoccupied level associated with the reduction process. Since the extra waves are not observed for **1** and **2**, the second lowest unoccupied MO levels of bpy and 5,5′-(CO_2Et)$_2$bpy must lie higher in energy than that of 4,4′-(CO_2Et)$_2$bpy. This expectation is consistent with the fact that two reduction waves are observed for bpy and 5,5′-(CO_2Et)$_2$bpy but three for 4,4′-(CO_2Et)$_2$bpy (see Table I).[3] On the other hand, the reduction potentials of Table I suggest that the lowest unoccupied levels increase in the order 5,5′-(CO_2Et)$_2$bpy < 4,4′-(CO_2Et)$_2$bpy < bpy. Therefore, to understand the different redox behaviors of **2** and **3**, it is crucial to examine how the low-lying unoccupied orbitals of bpy are affected by CO_2Et substituents. In the present work, this question was probed by performing MNDO molecular orbital calculations[4] on bpy, 4,4′-(CO_2H)$_2$bpy, and 5,5′-(CO_2H)$_2$bpy.

The first four π* levels of bpy are schematically shown in **4**, and Figure 1 summarizes how these π* levels are modified by the position of CO_2H substituents and by the twist angle θ between bpy and CO_2H groups. For 4,4′-(CO_2H)$_2$bpy and 5,5′-(CO_2H)$_2$bpy, Figure 1 also shows two additional levels derived mainly from the π* orbitals of CO_2H groups. In the absence of the π-conjugation effect of CO_2H substituents (i.e., at θ = 90°), the π_1^*–π_4^* levels of 4,4′-(CO_2H)$_2$bpy and 5,5′-(CO_2H)$_2$bpy are low in energy with respect to those of bpy. This may be considered as due to the inductive effect of CO_2H substituents. The π-conjugation effect of CO_2H substituents is found to preferentially lower the π_1^* and π_4^* levels in 5,5′-(CO_2H)$_2$bpy but the π_2^* and π_3^* levels in 4,4′-(CO_2H)$_2$bpy.[5] Thus, at θ = 0°, the second lowest unoccupied levels of 4,4′-(CO_2H)$_2$bpy and 5,5′-(CO_2H)$_2$bpy are derived upon lowering the π_2^* and π_4^* levels of bpy, respectively. Therefore, the second lowest unoccupied level of 4,4′-(CO_2H)$_2$bpy is significantly lower in energy than that of 5,5′-(CO_2H)$_2$bpy. Regardless of the value of θ, Figure 1 shows that the second lowest unoccupied levels increase in order 4,4′-(CO_2H)$_2$bpy < 5,5′-(CO_2H)$_2$bpy < bpy, while the lowest unoccupied levels increase in the order 5,5′-(CO_2H)$_2$bpy < 4,4′-(CO_2H)$_2$bpy < bpy. These results are consistent not only with the aforementioned redox properties of the free ligands bpy, 4,4′-(CO_2Et)$_2$bpy, and 5,5′-(CO_2Et)$_2$bpy but also with those of their Ru(II) complexes.



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Needless to say, MNDO calculations are parameterized primarily for ground-state properties so that caution needs to be exercised in using the unoccupied levels obtained from such calculations. Nevertheless, the electron densities on the carbon atoms of bpy$^-$ calculated from the coefficients of π_1^* are in excellent agreement with those predicted from the proton hyperfine coupling constants of bpy$^-$ (i.e., $a_5 \gg a_3 > a_4 \gg a_6$).[6] The present calculations show that the lowest unoccupied level of bpy is lowered by 0.58 and 0.88 eV upon introduction of two CO_2H substituents at the 4,4′ and 5,5′ positions, respectively (for θ = 0°). This is again in excellent agreement with the corresponding values of 0.49 and 0.77 eV estimated from the first half-wave potentials of bpy, 4,4′-(CO_2Et)$_2$bpy, and 5,5′-(CO_2Et)$_2$bpy. Thus, it seems quite reasonable to employ MNDO calculations in describing the redox properties of bpy and its substituted analogues.

In summary, the second lowest unoccupied level of a disubstituted bpy lies low in energy with two π-acceptor substituents on the 4 and 4′ positions, while this is not the case with those on the 5 and 5′ positions. This explains why a third reduction wave (associated with an electron occupation of the second lowest unoccupied level) is observed in 4,4′-

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$(CO_2Et)_2$bpy but not in 5,5′-$(CO_2Et)_2$bpy.[3] In addition, the Ru(II) complex of 4,4′-$(CO_2Et)_2$bpy (i.e., **3**) exhibits four extra reduction waves beyond the six observed from the Ru(II) complex of 5,5′-$(CO_2Et)_2$bpy (i.e., **2**). This can be easily understood if the reduction of the 4,4′-$(CO_2Et)_2$bpy and 5,5′-$(CO_2Et)_2$bpy ligands is primarily responsible for the reduction process of complexes **2** and **3**, respectively.

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Registry No. **1**, 15158-62-0; **2**, 74093-18-8; **3**, 75324-93-5; bpy, 366-18-7; 4,4′-$(CO_2Et)_2$bpy, 1762-42-1; 5,5′-$(CO_2Et)_2$bpy, 1762-46-5; 4,4′-$(CO_2H)_2$bpy, 6813-38-3; 5,5′-$(CO_2H)_2$bpy, 1802-30-8.

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Mechanisms of Alkylation of Mercuric Ions by Alkylcobalamins

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The reactions of alkylcobalamins with electrophiles such as Hg(II) ions have been considered as direct electrophilic attacks at the α-carbons.[1] However, our recent work on the methylation of Pt(II)/Pt(IV) couples,[2] diaquocobinamide,[3] and tetracyanoethylene[4] provides results that are not consistent with the S_E2 mechanism. Consequently, these results are interpreted in terms of a mechanism that involves a "complexation" between the reactants and an electron-transfer process to generate a radical pair. The radical pair collapses to products. In these studies, the "complexation" was observed both kinetically and spectroscopically but the electron-transfer process was proposed mainly on the basis of kinetic observations. Nevertheless, these studies raised the question of an alternative route, i.e. the single-electron-transfer (SET) mechanism. Thus, the reactions of CH_3-B_{12} with the electrophiles might be similar to the electron-transfer reactions of alkylcobaloximes (or other B_{12} model compounds)[5] and macrocyclic dimethylcobalt(III) complexes[6] and to the reactions of TCNE on organometallic compounds of Pb and Sn.[7]

The experiences of the reactions between CH_3-B_{12} and the above electrophiles inevitably led us to suspect that a reexamination of the mechanisms of reactions between alkylcobalamins and mercuric ions is warranted. A survey in the literature indicates that although previous reports on the CH_3-B_{12} methylation of mercuric ions provided some valuable information on the "medium" effects, the kinetic and mechanistic data are not sufficiently quantitative to make a case for an S_E2 mechanism.[8] In particular, the validity of the very great difference between the dealkylation rates of $Hg(OAc)_2$ with methylaquocobinamide and $Hg(OAc)_2$ with ethylaquocobinamide[8b] is not totally unquestionable. Since this difference is essential for the S_E2 mechanism, we decided to investigate the Hg(II) dealkylation of CH_3-B_{12} and C_2H_5-B_{12} in hydrochloric acid solutions.

This note presents the results of our reexamination.

Experimental Section

All the corrinoids used in this report were generous gifts from H. P. C. Hogenkamp.[9] The mercuric chloride and the other chemicals were reagent grade and were used as received. The information with regard to the chloride complex formation of Hg^{2+} has been reported by Sillen,[10] whose results showed $HgCl_3^-$ and $HgCl_4^{2-}$ to be the dominant species for a mercuric chloride solution at 0.10 M KCl. Since the present report concerns the reactions in 1.0 M chloride solutions, the Hg(II) ions are referred to as $HgCl_n^{2-n}$ hereafter.

Pulse Fourier transformed ^{13}C (75.5 MHz) NMR spectra of the methyl-transfer products of the reactions between $^{13}CH_3$-B_{12} (90% enriched) and $HgCl_n^{2-n}$ were obtained at 25 °C with a Nicolet 300 spectrometer locked to the resonance of internal D_2O. The spectra were obtained under conditions of simultaneous proton noise decoupling. Chemical shifts were measured with respect to external TSP.

The reaction rates were monitored at 350 nm (γ-bands of the aquocorrinoids) with a Cary 14 spectrophotometer at 25 ± 0.3 °C under a dim light. All the rate measurements were performed under pseudo-first-order conditions in alkylcorrinoid at 1.0 M ionic strength (maintained with NaCl). The pH values were controlled in a range 0–1 with HCl. The equilibrium constant for the "complex" formation between the base-off CH_3-B_{12} and $HgCl_n^{2-n}$ was measured spectrophotometrically at 25 ± 0.3 °C.

Results and Discussion

Addition of 10 mg of mercuric chloride to 2.5 mL of HCl solution (0.10 M) containing 2.4 mM $^{13}CH_3$-B_{12} (90% enriched) resulted in a downfield shift from 0.039 ppm (base-off $^{13}CH_3$-Co) to 6.378 ppm. The ^{13}C resonances of the methyl-transfer products are a pseudotriplet with a spin–spin coupling constant from the outer peaks of 1576 Hz. The peak ratio is 1:10:1, corresponding to the 16.84% natural-abundance ^{199}Hg nuclei. This ^{13}C NMR study clearly demonstrates the methyl transfer between Co and Hg atoms and is in agreement with the ^1H NMR study of ref 8b. In the ^1H NMR spectrum, however, the satellites of CH_3-Hg are buried under the corrin proton resonances. The corrinoid products were identified as H_2O-B_{12}^+ spectrophotometrically. Addition of 1 equiv of $HgCl_n^{2-n}$ to an unbuffered $^{13}CH_3$-B_{12} solution (2.4 mM, pH

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