

In comparison with **3a**, which has no effect on the esterase's activity (Table I), **4a** is an efficient suicide-type inhibitor^{8,10} of the enzyme (Table II). This result is attributed to the direct hydrolysis of **4a** to highly reactive **2a** within, and subsequent binding to, the enzyme's active site.⁸ The irreversible inhibition of esterase activity effected by **4a** is markedly diminished by preincubation with a reversible inhibitor (**5d**), demonstrating involvement of the active site in the inhibition process (Table II). Incubation of ethyl *N*-allylnitrosocarbamate (**4b**) and ethyl *N*-ethylnitrosocarbamate (**4c**) with esterase under identical conditions afforded 51 and 28% irreversible inhibition, respectively. The lower levels of inhibition observed for **4b** and **4c** (Table II) are attributed to an increase in the partitioning of their hydrolysis intermediates, **2b** and **2c**, to stable diazoalkanes.^{11,12} The benzyl analogue (**4d**) gives 100% inhibition as anticipated, because of the predominant diversion of its hydrolysis product **2d** to a "carbonium-ion"-type intermediate. We interpret these results to mean that the enzymatically formed α -hydroxynitrosamine is sufficiently stable to diffuse away from the site of its formation before further decomposition and, therefore, may be considered a "transportable" metabolite. Further elaboration of the concept of transportable metabolites using *in vitro* experiments is ongoing.

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- A reviewer has raised the possibility that **1** decomposes to the corresponding anti diazotate, whereas it has been demonstrated that nitrosocarbamates afford the syn isomer.⁶ The significance of the possible formation of the anti isomer is that it is less reactive than the syn isomer (Thiele, *J. Chem. Ber.* **1908**, *41*, 2806–2811; *Justus Liebigs Ann. Chem.* **1910**, *376*, 239–268) and could account for the failure of **3** to inhibit the enzyme. Although, this possibility cannot be unambiguously discounted, there is evidence that indicates that the syn diazotate arises from the hydrolysis of **3**. First, we have decomposed acetoxymethylmethylnitrosamine in diethyl ether using KO-*t*-Bu and the CH₃N₂O⁻K⁺ isolated shows the syn geometry according to ¹H NMR (Sühr, *H. Chem. Ber.* **1963**, *96*, 1720–1725). Secondly, Moss has shown that *syn*- and *anti*-1-phenylethane diazotate do not give the same percent net retention upon ethylation. In fact the results show almost a 10-fold increase in percent net retention of the ether produced with the syn isomer compared with the anti isomer (Moss, R. A.; Powell, C. E. *J. Am. Chem. Soc.* **1976**, *98*, 283–285).
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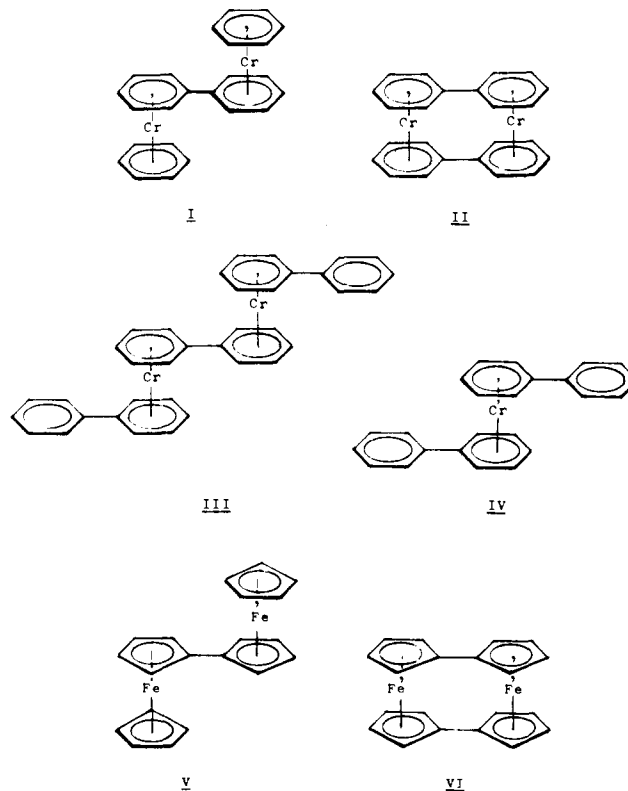
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μ -(η^6 : η^6 -Biphenyl)-bis[(η^6 -benzene)chromium] and Bis[μ -(η^6 : η^6 -biphenyl)]-dichromium. Novel Species to Explore Mixed-Valence Sandwich Complex Chemistry¹

Sir:

At present there exists a profound interest in mixed-valence species in general^{2,3} as well as in binuclear mixed-valence metallocenes in particular.^{4–9} Although a multitude of spectroscopic techniques have been applied in the study of the latter systems, certain controversial points concerning intervalence transfer in the monocations and the nature of spin-spin interaction in the dications remain.⁸ Since we have recently investigated the kinetics of electron exchange in solutions containing bis(η -arene)chromium(0) and the corresponding bis(η -arene)chromium(I⁺) radical cations,¹ favoring a head-on disposition of the exchange partners in the transition state, we attempted the synthesis of bis[μ -(η^6 : η^6 -biphenyl)]-dichromium monocation (II⁺), where the two-sandwich complex moieties would be fixed in a rigid side-on arrangement. In this communication we report on the preparation of II and of μ -(η^6 : η^6 -biphenyl)-bis[(η^6 -biphenyl)chromium]



- (11).¹⁰ Since bis(η -arene)chromium (d⁵) complexes possess a nondegenerate ²A_{1g} ground state,¹¹ yielding well-resolved ESR spectra in solution as well as in glassy media, it was expected that proton hyperfine structure would supply information pertaining to spin distribution in the monocations I⁺ and II⁺ and to spin-spin interaction in the dications I²⁺ and II²⁺.

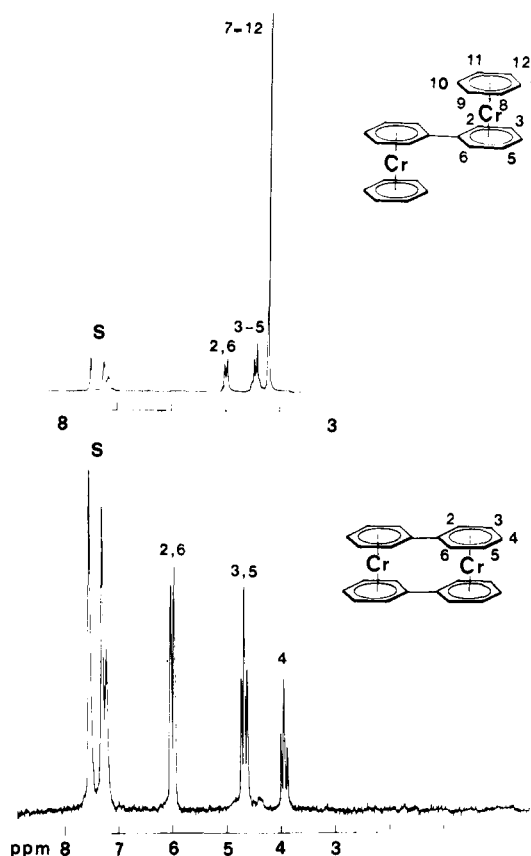
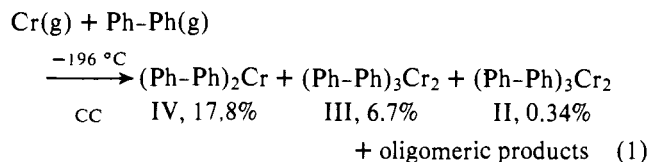


Figure 1. ^1H NMR spectra (100 MHz) of I and II (solvent, biphenyl- d_{10} ; temperature, $+175^\circ\text{C}$).

II is formed, albeit in minute yield, together with bis(η^6 -biphenyl)chromium (IV), the binuclear complex III, and oligomeric products upon cocondensation (CC) of chromium atoms with biphenyl (Ph-Ph):



Via a succession of extraction and fractional crystallization steps, II may be obtained in pure form.¹² Like its metallocene analogue biferrocenylene (VI), complex II is exceedingly insoluble in all common solvents. Therefore, ^1H NMR spectra could only be obtained from solutions of II in molten biphenyl- d_{10} (Figure 1). Owing to the large spread of the resonance lines over a range of 2 ppm, II exhibits a simple quasi-first-order ^1H NMR spectrum which can be easily assigned: II in biphenyl- d_{10} , $+160^\circ\text{C}$, δ 3.98 (t, $J = 5.5$ Hz, H_4), 4.71 (t, $J = 5.5$ Hz, $\text{H}_{3,5}$), 6.04 (d, $J = 5.5$ Hz, $\text{H}_{2,6}$). This contrasts with the NMR spectra for I and IV which display a narrowly spaced area of resonances for the η -arene protons; I in tolu-

ene- d_8 , 30°C , δ 4.10 (s, H_{7-12}), 4.32 (m, $\text{H}_{3,4,5}$), 4.83 (m, $\text{H}_{2,6}$); IV in benzene- d_6 , 55°C , δ 4.79 (dd, $J_{o,p} = 0.9$, $J_{o,m} = 5.6$ Hz, $\text{H}_{2,6}$), 4.26 (m, $\text{H}_{3,4,5}$), 7.13 (m, $\text{H}_{9,10,11}$), 7.4 (m, $\text{H}_{8,12}$). To rationalize the conspicuously different spread of chemical shifts of η -arene ring protons on I and II, we assume that the usual upfield coordination shift¹³⁻¹⁵ is counteracted by the diamagnetic anisotropy of a neighboring bis(η -arene)-chromium moiety. This downfield shift should be particularly pronounced in the ortho positions of II where, owing to the rigid, parallel disposition of the two sandwich complex units, the deshielding influences of two benzene rings reinforce each other.^{16,17}

On exposure to air, I and II are oxidized to the respective dications I^{2+} and II^{2+} which may be isolated as hexafluorophosphates I (PF_6)₂ and II (PF_6)₂. Generation of the monocations I^+ and II^+ from the dications I^{2+} and II^{2+} is achieved by electrochemical means which also proved to be the most convenient method for ESR spectroscopic study.¹⁸ In Figures 2 and 3 ESR spectra for I^+ , II^+ , I^{2+} , and II^{2+} , recorded in fluid solution as well as in glassy media, are shown. The spectroscopic parameters are collected in Table I. In solution, ESR absorptions are observed only for the monocations I^+ and II^+ .¹⁹ The hyperfine pattern in the spectrum of I^+ is analyzed in terms of the coupling constant $a(22\ ^1\text{H}) = 1.75$ G. Compared with characteristic ESR data for singly substituted mononuclear bis(η -arene)chromium⁺ radical cations,¹¹ for I^+ the number of interacting protons is doubled whereas the magnitude of the coupling constant is halved. This signalizes, that for I^+ in fluid solution, the unpaired electron is delocalized over both moieties. For reasons which remain to be clarified, the doubly bridged monocation II^+ in solution only yields one broad ESR absorption void of hyperfine structure.²⁰ In glassy media, for I^+ as well as II^+ , spectra are obtained, which are analyzed in terms of tetragonal g tensors and hyperfine coupling constants $A_{\parallel}(\ ^1\text{H})$ and $A_{\perp}(\ ^1\text{H})$ typical for an interaction of the unpaired electron with the protons of one bis(η -arene)-chromium unit only. Conceivably, the change from spin delocalization (fluid solution) to spin localization in one moiety of the radical cations (rigid solution) is due to immobilization of the counterion.

The dications I^{2+} and II^{2+} in rigid solution display ESR spectra, which are typical for randomly oriented triplet-state species. In the case of the doubly bridged dication II^{2+} , a calculation of the mean distance R between the two electrons using the zero-field splitting parameter $D(\text{II}^{2+}) = 0.032\ \text{cm}^{-1}$ and the expression $R = (0.650\ \text{g}^2/D)^{1/3} [\text{\AA}]$ ²¹ yields the value $R_{\text{ESR}} = 4.31\ \text{\AA}$, which is in good agreement with $R(\text{Cr-Cr}) \approx 4.36\ \text{\AA}$, obtained from a molecular model. No reliable estimate is possible in the case of the singly bridged dication I^{2+} , since a range of conformations about the C-C bond linking the two bis(η -arene) units, is tolerated.²² However, in any of these conformations for I^{2+} , $R(\text{Cr-Cr})$ is larger than $R(\text{Cr-Cr})$ in the rigid species II^{2+} and this is born out in the magnitudes of D for the two dications. The differing mean separation between the two unpaired electrons in I^{2+} and II^{2+} is also reflected in the different relative intensity of the half-field line ($\Delta(M_s) = 2$) compared with the intensity of the $\Delta(M_s) = 1$ spectrum. If

Table I. ESR Parameters for the Cations I^+ , II^+ , I^{2+} , and II^{2+}

| cat- ion | solu- tion ^a | g values | hyperfine coupling constants, G | zero-field splitting, cm^{-1} |
|------------------|----------------------------|---|--|--|
| I^+ | fluid | $\langle g \rangle = 1.9868^b$ | $a(\ ^1\text{H}) = 1.75^c$ | |
| | rigid | $g_{\parallel} = 2.0030$, $g_{\perp} = 1.9792^b$ | $A_{\parallel}(\ ^1\text{H}) = 3.2$, ^d $A_{\perp}(\ ^1\text{H}) = 3.7$, ^d $A_{\perp}(\ ^{53}\text{Cr}) = 26^e$ | |
| II^+ | fluid | $\langle g \rangle = 1.9856^b$ | nr ^f | |
| | rigid | $g_{\parallel} = 2.0025$, $g_{\perp} = 1.9792^b$ | $A_{\parallel}(\ ^1\text{H}) = 3.2$, ^d $A_{\perp}(\ ^1\text{H}) = 3.7$, ^d $A_{\perp}(\ ^{53}\text{Cr}) = 26^e$ | |
| I^{2+} | rigid | $g_x = 1.982$, $g_y = 1.995$, $g_z = 1.988^g$ | nr ^f | $ D' = 0.0257$ $E' = 0.0038$ |
| II^{2+} | rigid | $g_x = 2.001$, $g_y = 1.983$, $g_z = 1.975^g$ | nr ^f | $ D' = 0.0321$ $E' = 0.0079$ |

^a Temperature and solvent; see Figure 2-4. ^b ± 0.0005 . ^c ± 0.03 . ^d ± 0.1 . ^e ± 1 . ^f Not resolved. ^g ± 0.005 .

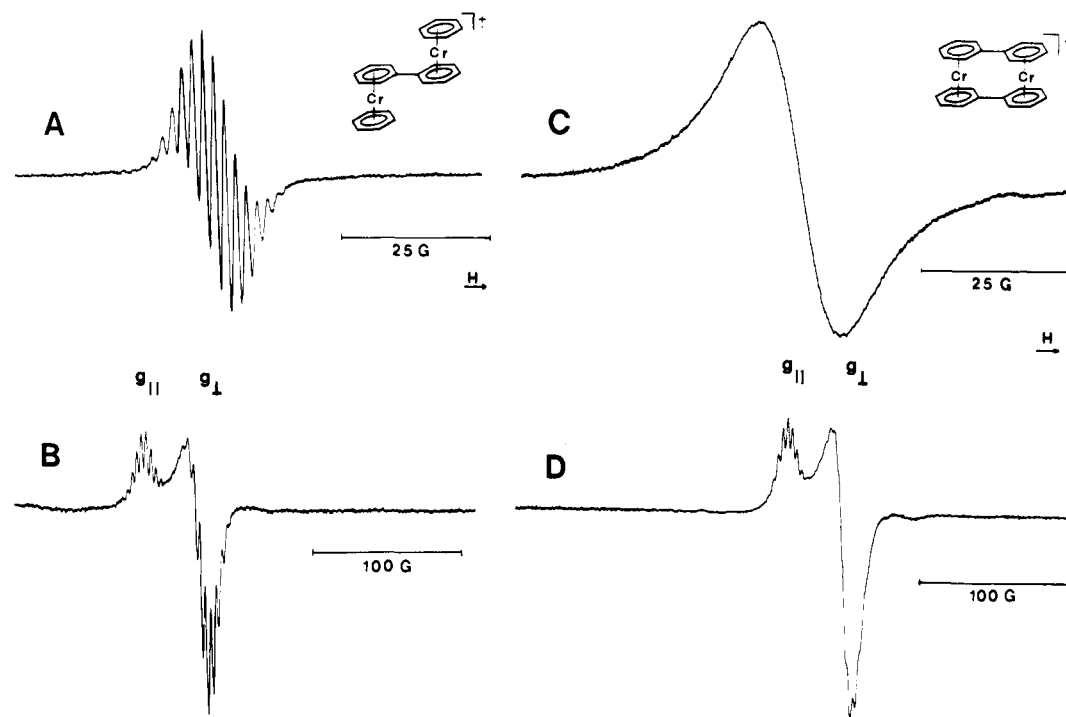


Figure 2. ESR spectra of dinuclear monocations I^+ and II^+ (solvent, DMF- $CHCl_3$ (1:1), $(C_2H_5)_4NBF_4$, 5×10^{-5} M): A, I^+ , $-35^\circ C$ (fluid solution); B, I^+ , $-130^\circ C$ (glassy solution); C, II^+ , $-70^\circ C$ (fluid solution); D, II^+ , $-120^\circ C$ (glassy solution).

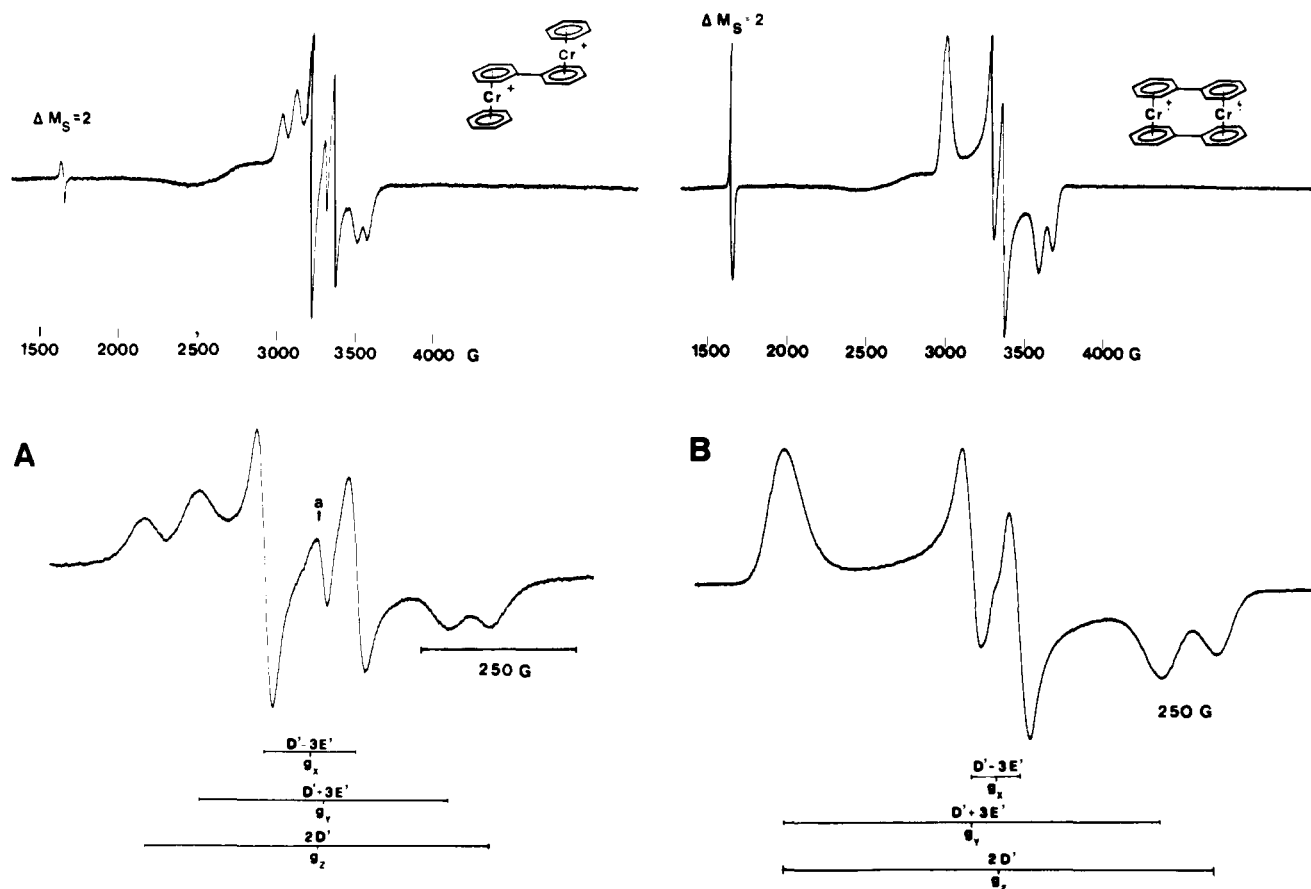


Figure 3. ESR spectra (X band) of dinuclear dications I^{2+} and II^{2+} in glassy solution (solvent, DMF- $CHCl_3$ (1:1)): A, I^{2+} , $-85^\circ C$; B, II^{2+} , $-155^\circ C$; a, residual doublet species.

the dinuclear bis(η -arene)chromium species I and II are compared to their ferrocene analogues V and VI, the paramagnetism of II^{2+} contrasting with the diamagnetism of VI^{2+} ⁵ emerges as the most significant difference between these prototype sandwich complexes. This difference can be ra-

tionalized in terms of the particular nature of the singly occupied orbital in the respective mononuclear radical cation and the different metal-metal distances (Figure 4). Spin pairing and concomitant diamagnetism is favored for VI^{2+} because the two metal atoms are in closer proximity in the metallocene

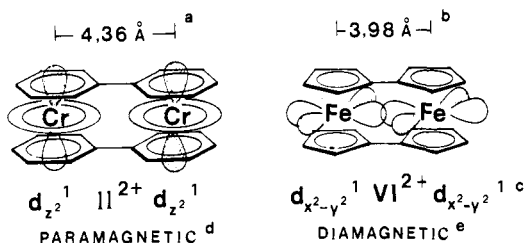


Figure 4. Comparison of the dinuclear species II^{2+} and VI^{2+} . Only the metal contributions to the singly occupied molecular orbitals are shown. ^a Estimate from a molecular model. ^b Reference 23. ^c Reference 24. ^d This work. ^e Reference 5.

as compared with the bis(arene) complex. Furthermore, metal orbital overlap should be more effective in VI^{2+} (equivalent to 50% σ , 50% π^{24}) than in II^{2+} (equivalent to 25% σ , 75% δ ; see Figure 4).

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- (12) Chromium vapor (1.88 g, 36 mmol) was cocondensed at -196°C , 10^{-4} Torr with biphenyl (95 g, 615 mmol). The resulting product was dissolved in 300 mL of O_2 -free toluene and unreacted chromium was removed by filtration. The solvent was distilled off and the residue extracted with low boiling petroleum ether, methylcyclohexane, and toluene, each during an 8-h period at reflux temperature. From the toluene fraction, dark brown needles together with amorphous red-brown material precipitated after a few days. The two components can be separated by virtue of their different rates of sedimentation. Analytically pure samples were obtained after repeated recrystallization from toluene (2×200 mL); 23 mg of II, yield 0.34% referred to chromium evaporated. Anal. Calcd for $C_{24}H_{20}Cr$: C, 69.90; H 4.89. Found: C, 70.06; H, 4.94. Mass spectrum (field ionization): m/e 412 (M^+ , 100%). III is contained in the methylcyclohexane fraction and can be isolated via sublimation (180°C ($<10^{-4}$ Torr)). Mass spectrum (field ionization): m/e 572 (M^+ , 100%). Complete separation from II has not yet been achieved, however.
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- (19) Fluid solutions of the dications I^{2+} and II^{2+} do not display ESR signals if freshly prepared. However, I^{2+} and II^{2+} gradually cleave off one-half sandwich unit (η -arene) Cr^+ yielding mononuclear radical cations. Unaware

- of this fact, in a previous paper¹⁰ we erroneously attributed biradical character to the species I^{2+} .
- (20) The appearance of the spectrum is unaffected by changes in solvent and by dilution down to 10^{-5} M.
 - (21) N. D. Chasteen and R. L. Belford, *Inorg. Chem.*, **9**, 169 (1970).
 - (22) Conformation of η -biphenyl in I: fully eclipsed, $R(\text{Cr}-\text{Cr}) = 5.40$ Å; fully staggered, $R(\text{Cr}-\text{Cr}) = 4.90$ Å; $R_{\text{ESR}} = 4.68$ Å.
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 - (24) The degeneracy of the HOMO of ferrocene (e_{2g} , metal AO contributions $\text{Fe } d_{xy}, d_{x^2-y^2}$) is raised upon formation of the dinuclear complex VI.

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Homonuclear and Heteronuclear Coupling in 5'-AMP as Probed by Two-Dimensional Proton Nuclear Magnetic Resonance Spectroscopy

Sir:

We have obtained the two-dimensional, homonuclear, J -resolved, ^1H NMR spectrum¹⁻³ of 5'-adenosine monophosphate (5'-AMP).⁴

The normal ^1H NMR spectrum of 5'-AMP⁵ (Figure 1a) is complicated by strong homonuclear coupling combined with heteronuclear coupling to ^{31}P , which are normally difficult to unravel. Two-dimensional NMR spectroscopy has allowed us to distinguish between homo- and heteronuclear coupling by inspection.

The pulse sequence used ($90^\circ-\tau-180^\circ-\tau$ -echo) causes transitions which are connected by homonuclear, scalar coupling to be "stretched out" across the second dimension (F_1),³ whereas heteronuclear coupling causes transitions to appear side by side in the first dimension (F_2), since the heteroatom is unaffected by the pulses.

Figure 2 shows the two-dimensional spectrum of the ribose 3', 4', 5', and 5'' protons. The 3' proton shows two homonuclear couplings: one to the 2' proton and one to the 4' proton. Thus, to first order, the 3' proton resonates as a doublet of doublets stretched out over F_1 . By contrast in the 4' region we see two pairs of side-by-side transitions. The splitting within a pair is caused by long-range, heteronuclear coupling to ^{31}P and the

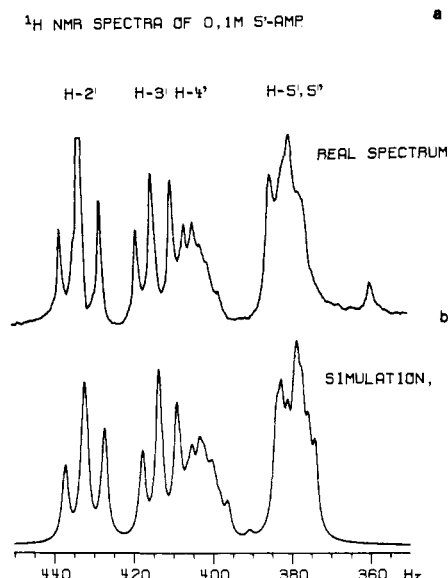


Figure 1. (a) The 90-MHz ^1H NMR spectrum of the higher field ribose protons in 5'-AMP. The central part of the H-2' multiplet is overlapped by a peak due to HDO. (b) Simulation of the spectrum in Figure 1a using δ and J values obtained from the 2D spectrum.