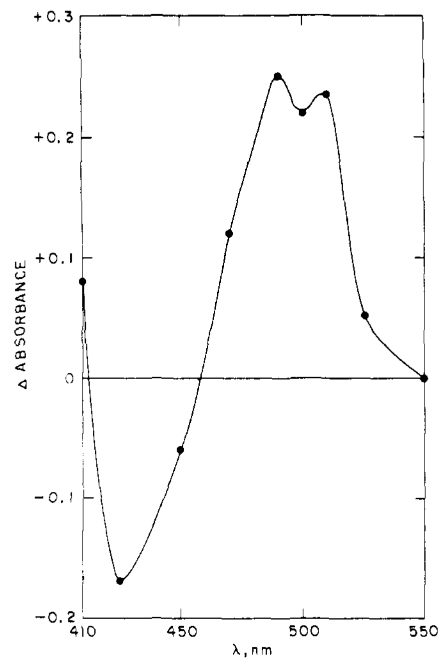

Figure 2. Difference spectrum for $Ru(bpy)_3^+$-$Ru(bpy)_3^{2+}$: 0.08 M Eu(II), 1.4×10^{-4} M $Ru(bpy)_3^{2+}$, 0.5 M Cl^-, 0.05 M H^+, 25 °C, 10 nm band pass for probe beam.

solution absorbance (eq 7, Figure 1c). At 25 °C, $k_q = 2.8 \times 10^7\ M^{-1}\ s^{-1}$ [11] and $k_7 = 2.7 \times 10^7\ M^{-1}\ s^{-1}$.

$$Ru(bpy)_3^{2+} \underset{1/\tau_0}{\overset{\lambda\ 530\ nm}{\rightleftharpoons}} {}^*Ru(bpy)_3^{2+} \qquad (5)$$

$$^*Ru(bpy)_3^{2+} + Eu(II) \xrightarrow{k_q} Ru(bpy)_3^{+} + Eu(III) \qquad (6)$$

$$Ru(bpy)_3^{+} + Eu(III) \xrightarrow{k_7} Ru(bpy)_3^{2+} + Eu(II) \qquad (7)$$

The difference spectrum obtained for the transient is presented in Figure 2. The spectrum was the same at 0.05 M H^+ (shown), 0.4 M H^+, and pH 3. The same transient is produced in smaller yields from reaction of $^*Ru(bpy)_3^{2+}$ with $Ru(NH_3)_6^{2+}$ and $Fe(CN)_6^{4-}$. In addition, 500-nm-absorbing transients are produced when solutions containing Eu(II) and RuL_3^{2+} (L = 1,10-phenanthroline, 4,4′-dimethyl-2,2′-bipyridine, 4,7-dimethyl-1,10-phenanthroline, and 5-chloro-1,10-phenanthroline) are flash photolyzed. Detailed observations for the latter systems will be reported elsewhere. Figure 2 is similar to, but not identical with, the spectrum reported by Baxendale and Fiti.[10] The reduced species which they generated by reaction of $Ru(bpy)_3^{2+}$ with e_{aq}^- or Zn^+ has λ_{max} 510 nm (ϵ $1.2 \times 10^4\ M^{-1}\ cm^{-1}$), 530 nm (here 490, 510 nm) with a second, less intense, maximum at ~610 nm which we do not observe. Using the reaction of $^*Ru(bpy)_3^{2+}$ with Fe^{3+} (yield of $Ru(bpy)_3^{3+} + Fe^{2+}$, 0.8 ± 0.2[7]) to estimate the initial post-flash concentration of $^*Ru(bpy)_3^{2+}$, allowing for the fraction of excited state quenched, and assuming a yield of 1.0 for reaction 6, the molar absorptivity of $Ru(bpy)_3^+$ at 490 nm is calculated to be $(1.4 \pm 0.3) \times 10^4\ M^{-1}\ cm^{-1}$. Thus in intensity and band shape the visible spectrum of $Ru(bpy)_3^+$ strongly resembles that of $Ru(bpy)_3^{2+}$,[1a] and it is possible that the 490–510-nm band in the spectrum of $Ru(bpy)_3^+$ (like the 450-nm band for $Ru(bpy)_3^{2+}$) is associated with a metal-to-ligand charge-transfer ($d^6(\pi^*)^1 \rightarrow d^5(\pi^*)^2$) transition.[14]

There is now ample evidence that the charge-transfer excited state of $Ru(bpy)_3^{2+}$ readily undergoes both oxidation and reduction, as is predicted from thermodynamic and spectroscopic considerations.[2,11] One additional implication of such considerations can be seen by subtracting eq 1 from eq 3 to give eq 8. Disproportionation of the excited state (eq 8) is thus estimated to be favored by ~1.7 V. Evidence for the occurrence of reaction 8 is presently being sought at high $Ru(bpy)_3^{2+}$ concentrations and high light intensities.

$$2^*Ru(bpy)_3^{2+} \rightleftharpoons Ru(bpy)_3^{3+} + Ru(bpy)_3^{+} \qquad (8)$$

The flash-photolysis technique described here thus offers a convenient means of probing the chemistry of both the excited state $^*Ru(bpy)_3^{2+}$ and the unstable oxidation state $Ru(bpy)_3^+$. Fundamental studies of this kind may also be of considerable practical import in solar energy conversion as complexes like $Ru(bpy)_3^{2+}$ have properties which make them useful mediators in the photodissociation of water.[15,16]

Acknowledgment. This work was performed under the auspices of the U.S. Energy Research and Development Administration.

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(13) Even in the absence of added Eu(III) the decay of the transient remained exponential ($\tau \leqslant 50\ \mu s$) rather than displaying second-order kinetics as expected from eq 7. A second-order decay is expected on other grounds, as well, since Baxendale and Fiti report that $Ru(bpy)_3^+$ undergoes reaction with itself with a rate constant of $3.5 \times 10^8\ M^{-1}\ s^{-1}$.[10] The absence of second-order behavior is attributed to the fact that the small amounts (10^{-4}–10^{-3} M) of Eu(III) unavoidable as an impurity in Eu(II) solutions raise the Eu(III) concentration to well above the post-flash $Ru(bpy)_3^+$ concentration ($\leqslant 10^{-5}$ M). Consequently k_7[Eu(III)] is always $> 3.5 \times 10^8$ [$Ru(bpy)_3^+$] so that reaction 7 predominates and follows pseudo-first-order kinetics under all conditions.

(14) By contrast, the lowest energy absorption maximum for $^*Ru(bpy)_3^{2+}$, which like $Ru(bpy)_3^+$ has one electron in the ligand π^* system but only five metal d electrons, occurs at ~360 nm (C. Creutz, unpublished observations, 1975). A referee has suggested that the assignment $d^6(\pi^*)^1 \rightarrow d^7$ for the 490–510-nm band of $Ru(bpy)_3^+$ may more readily account for the positions of the band maxima in $Ru(bpy)_3^+$ and $^*Ru(bpy)_3^{2+}$. Although this assignment is not unreasonable on energetic grounds, the band seems remarkably intense ($\epsilon > 10^4\ M^{-1}\ cm^{-1}$) for this kind of transition.

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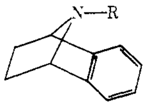
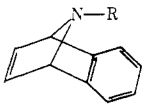
Homoallylic[1] Interaction Involving Nitrogen Lone Pairs, a Reexamination

Sir:

Recently published work has examined the significance of homoallylic interaction between a nitrogen lone pair and a remote π bond in bicyclic amines.[2-5] Comparison with data from well-established model systems led us to reassign the photoelectron spectra (PES) of the bicyclic amines **5–8** of ref 2a and hence challenge the reported conclusions regarding the importance of homoallylic interaction in such systems. The recent report[5] of the NMR data for **5–8** confirmed our skep-

Table I[a]

	R = H (5, 7) IP	M	G	R = CH_3 (6, 8) IP	M	G
 5,6	8.44	n	π_S	8.33	n	π_S
	9.10	π	π_A	8.96	π	n, π_A
	9.4[b]		n			
 7,8	8.25	n	π_S	8.18	n	π_S
	9.05	π	n, π_A	8.78	π	n
	9.97	π	π_O	9.06	π	π_A
				9.66	π	π_O

[a] Ionization potential (eV), M, G are the Morishima and Grutzner assignments, respectively. [b] See ref 13.

ticism concerning both the importance of homoallylic interaction and the PES assignment. The observation that **5** and **6** exist as isomeric mixtures in solution clearly demonstrates that n–π interaction in these systems is of minor energetic consequence. A 94:6 ratio for **6** was the greatest deviation from equal populations. Protonation of the nitrogen lone pair of **6** had minimal effect on the isomer ratio. The only change in conditions which substantially altered the ratio was a solvent change from $CHCl_3$ to Me_2SO.

Direct experimental proof for a reassignment of the PES is not possible because peak broadening prevents the analysis of vibrational fine structure. The original (M) and our proposed (G) assignments are shown in Table I. While our assignment may still need revision, the key point to note is that in each case Morishima has assigned the lowest ionization potential (IP) to a nitrogen lone pair. The reasons for reassigning this as a benzene band are as follows.

(1) Benzene π_S band. The benzene π_S band in 1,2-dialkyl substituted benzenes occurs in the 8.40 ± 0.2 region and is almost independent of possible strain effects.[2a,6] The M assignment places these bands in the 8.78–9.10 region. This strikingly high value could only arise through strong interaction with an orbital whose unperturbed vertical IP was lower than the 8.42 eV value of benzonorbornene. See for example ref 25. The G assignment places this band within its normal range of 8.18–8.44 eV.

(2) N lone pair band. The IP of the nitrogen lone pair is sensitive to ring size and substitution.[2a,4,7-9] The nitrogen IP in monocycles increases with decrease in ring size and has been correlated with carbon–hydrogen coupling constants.[7] In bicyclic diaza compounds a similar increase of IP with decreasing ring size has been observed.[4,9] The range of possible IP for **5** in the absence of interaction can be estimated. A low value of 8.5 can be deduced from the value for 2-azabicyclo[2.2.2]octane[1] (8.22) and the increased IP due to contraction of the CNC angle. A high value of 9.0 can be derived from the C–H coupling constant of benzonorbornadiene[10] and the correlation of ref 7. While there is a wide discrepancy between these predicted values,[11] the significant feature is that none lie below the benzene π_S value.

Methyl substitution at nitrogen causes a lowering of the lone pair IP.[2a,4,7,8] The observed range is 0.1–0.6 eV with a most common value[12] of 0.35 ± 0.05 eV. In the M assignment methyl substitution gives shifts of only 0.11 and 0.07 eV. The G assignment gives shifts of ~0.4[13] and 0.27.

(3) Homoallylic interaction. Homoallylic interaction in olefinic hydrocarbons has been extensively studied by Heilbronner.[14] The results for 7-methylenenorbornene and its derivatives[14,15,25] show negligible shifts relative to the corresponding monoenes. Similarly the low IP region of the spectrum of 7-oxanorbornene shows little evidence of oxygen lone pair–olefin interaction.[16] Comparison of the results for benzonorbornadiene[2a] and norbornadiene[14] shows that a benzo group interacts more weakly than an equivalent double bond. (Haselbach[25] has concluded that benzo group and double bond interactions are almost equal.) A large nitrogen perturbation in **5** is thus quite inconsistent with the analogous carbon and oxygen compounds.

The question of the conformational preference of the lone pair is also pertinent to the discussion. Morishima has claimed that **5** and 2-azabicyclo[2.2.2]oct-5-ene (**17**) exist as an approximately equal mixture of lone pair conformers on the basis of chemical shift differences.[2b,5] Each conformer should produce an independent PES.[17] Heilbronner[14,18] has shown that PE spectra depend significantly on the stereochemistry of groups which interact homoallylically. In fact the PES of both **5** and **17** show no evidence of the presence of two components. If the solution data can be transferred to the gas phase, one can conclude that the interaction between nitrogen lone pair and the unsaturated center is less than instrumental resolution. Furthermore, the claim of approximately equal population of the lone pair conformers in **17** and the substantial change in population in the methyl derivative **18** argues against significant stabilization in the ground state. By contrast stabilizing homoallylic interactions are well known to dominate stereochemistry.[19] Alternatively one could argue that **5** and **17** exist substantially as single isomers. Underwood[3] has reached this conclusion for **5**. Chemical shifts may be predicted for the protons at position 3 in **17** with an anti lone pair by correcting the observed shifts for **18** for the effects of an eclipsing methyl group.[20] The calculated δ values are 2.49 and 2.97 ppm to be compared with the observed values of 2.46 and 2.92 ppm. Thus a conclusion that **17** also exists as the anti isomer is plausible. The lack of additional bands in the PES of **5** and **17** is thus consistent with either the presence of one major isomer or a small homoallylic interaction.

The diene systems **7** and **8** now permit consideration of homoallylic interaction when spatial overlap cannot be avoided. There are three limiting conformational possibilities for the PE spectra: (a) both isomers present for both compounds; (b) a single isomer with the same lone pair orientation for both, and (c) a single isomer but different lone pair conformations for each. If case (a) applies and nitrogen interaction is large, two olefin and three benzene bands should have been observable unless syn and anti interactions were fortuitously the same. Underwood[3] has shown that the vinyl hydrogens in **7** and **8** are shifted in opposite senses by contact interaction between the lone pair and nickel. Thus the mechanism of syn and anti interaction is different. It stretches credulity to expect the same magnitude interaction and band shifts from different mechanisms for both compounds. If case (c) applies the methylation induced band shifts are inconsistent with large nitrogen interaction. The unsaturated centers should move in opposite senses as the lone pair orientation is changed. Experimentally the change from **7** to **8** causes a decrease in IP for all bands which move. Note that these conclusions for (a) and (c) are independent of the choice of M or G assignment. For case (b), the M assignment would again require fortuitous equivalence of syn and anti interaction as both unsaturated bands move equally on conversion from **7** to **8**. Thus the spectra are most consistent with either a small nitrogen splitting, or a predominant conformer and the G assignment. Either possibility supports our basic contention that homoallylic interaction in **5** and **6** is small.

We thus conclude that the effect of homoallylic interaction between the nitrogen lone pair and π bond in the ground state is small (though detectable[2b,3]). These conclusions are also in agreement with both the small energy difference between the isoelectronic syn and anti 7-norbornenyl carbanions,[20,21] and the often stated idea[14,22-24] that a formally antihomoaromatic system will minimize the destabilizing interaction by minor conformational variation to diminish overlap between the filled orbitals. The contrast between stabilizing and destabilizing homoallylic interaction is emphasized.

Since this work was submitted, Haselbach[25] has published a PES study of 9-isopropylidenebenzonorbornadienes and related systems. His work lends additional support for our conclusions. It also reemphasizes the conformational idea that interaction between a lone pair in a bicyclic system and the other unsaturated bridges should have little influence on lone pair orientation. If the interaction is between a lone pair and a single unsaturated bridge, the molecule will distort so that both the unfavorable interaction and its stereochemical impact will be minimized. If the interaction is between a lone pair and two unsaturated bridges, the lone pair orientation will reflect the delicate balance of all π- and σ-type interactions.

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(13) This value differs from the tabulated value of ref 2a and was derived from the actual spectrum of **5**. The band at 9 eV of Figure 2 is measurably broader and exhibits a shoulder at 9.4 eV which indicates that it is composed of two bands.
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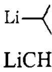
η^5-Cyclohexadienyltricarbonylchromium(0) Intermediates in the Reaction of Carbanions with η^6-Arenetricarbonylchromium(0)

Sir:

The electron withdrawing effects of a chromium tricarbonyl unit π-bonded to an aromatic ring are reflected clearly in the reactivity patterns of the arene and its substituents.[1] We[2] and others[3] have observed coupling of carbanions with π-arene ligands, in processes which promise to be valuable in organic synthesis. The reaction of a carbanion derived from a carbon acid of pK_a = 25 or higher converts complex **1**, η-benzenetricarbonylchromium(0), into an intermediate within minutes at 0 °C or below in tetrahydrofuran.

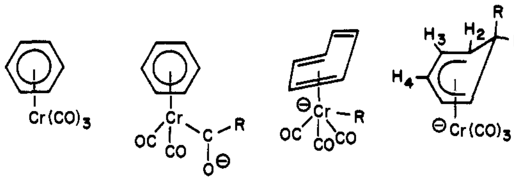
Table I.[a] ^{1}H NMR Data for Complex 4

Carbanion, R	H_4	H_3	H_2	H_1	H in R
1. $LiC(CH_3)_2CN$	4.87	4.61	2.7	2.6	1.00 (s, $-CH_3$)
2. $LiCH_2CN$	4.92	4.22	2.6	2.6	1.48 (d, $J \simeq 6$ Hz, $-CH_2$)
3. Li	4.82	4.35	[——— 3.1–1.4 (~10 H) ———]		
4. $LiCH(SPh)_2$	4.92	4.41	2.80	2.40	3.40 (d, $J \simeq 10$ Hz, $-CH$) 7.20 (m, $-C_6H_5$)

[a] All spectra were measured in THF-d_8 at −30 to −60 °C. The pattern of absorption for H_4 and H_3 was essentially the same for all four entries. Peak positions are in parts per million downfield from Me_4Si.

At least three structural types are reasonable for the intermediate: structure **2** results from attack of the carbanion, R^-, at a carbonyl ligand, as observed for **1** and phenyllithium;[4] structure **3** shows the carbanion attached to chromium with concomitant loss of one coordination site on the arene (or loss of one carbon monoxide, not shown);[5] and structure **4** results from addition of the carbanion to the arene ligand, a transition-metal analogue of the Meisenheimer complex.

Scheme I



1 **2** **3** **4**

The reactivity of this intermediate has been probed by exposing it to oxidizing agents, proton sources, and organic electrophiles. We wish to report preliminary results of these studies along with ^{1}H NMR spectral data which point to the structural type represented by **4** for the key intermediates, the first examples of η^5-cyclohexadienyltricarbonylchromium(0) complexes.

Monitoring of the reaction of lithiocyanomethane[6] with **1** at −40 °C in THF-d_8 under argon shows complete conversion of **1** within minutes (absence of singlet at δ 5.45). New absorptions appear at δ 4.92 (broad, triplet, 1 H, H_4 in **4**), 4.22 (m, 2 H, H_3), 2.6 (m, 3 H, H_2 and H_1), and 1.48 (d, J = 6 Hz, 2 H, $-CH_2CN$ as R in **4**). The peak assignments are parallel with those for closely related manganese,[7] iron,[8] and iridium[9] η^5-cyclohexadienyl complexes, and are supported by the following double irradiation experiments. Irradiation at δ 2.6 (H_2 and H_1) provides a triplet at δ 4.92 ($J_{4,3}$ = 6 Hz), a broad doublet at 4.22 ($J_{4,3}$ = 6 Hz), and a singlet at 1.48. Irradiation at 4.92 converted the absorption at δ 4.22 to a broad singlet, with small unresolved couplings (apparently $J_{4,2}$ or $J_{4,1}$ is >0 but <2 Hz), and left the other absorptions essentially unchanged. Irradiation at δ 4.22 provides a broad singlet at δ 4.92 with no other significant changes. Irradiation at δ 1.48 had no significant effect on the spectrum. These decoupling experiments generally support the chemical shift assignments and provide strong evidence that the carbanion unit is attached to one carbon of the arene ring.

The intermediate is stable for long periods below 0 °C but decomposes rapidly in the presence of oxidizing agents (air) or electrophilic species (see below). No fluxional behavior was observed up to 37 °C. Similar data have been obtained for a series of carbanions, as displayed in Table I. Generally, H_1 and H_2 overlap significantly, but entry 4 (Table I) shows an example where they appear separately. The stereochemistry of