relative contributions of trinuclear vs. tetranuclear ruthenium carbonylates in the catalysis of the water–gas shift reaction. Our results are described below.

Reactions with H_2 and CO were carried out on 3-mL quantities of 0.01 M THF or ethoxyethanol solutions of potassium salts at 0.9 atm (5.7 mmol of CO or H_2). Solutions were analyzed by ^1H NMR and IR spectroscopy and mass spectrometry of initial and final gas mixtures. Chemical reactions were established through isolation of products and a determination of mass balances as well as spectroscopic identification. Although inert to H_2, $[H_3Ru_4(CO)_{12}]^-$ reacts with CO according to equation 7. Forward and reverse steps have been independently established by using either $[H_3Ru_4(CO)_{12}]^-$ or a 3:1 ratio of $[HRu_3(CO)_{11}]^-$ to $Ru_3(CO)_{12}$ as the starting point. Studies conducted under varying CO/H_2 ratios at a total gas pressure of 1 atm indicate an equilibrium constant of 2×10^{-2} at 60 °C in glyme.

$$3[H_3Ru_4(CO)_{12}]^- + 9CO \rightleftharpoons 3[HRu_3(CO)_{11}]^- + Ru_3(CO)_{12} + 3H_2 \quad (7)$$

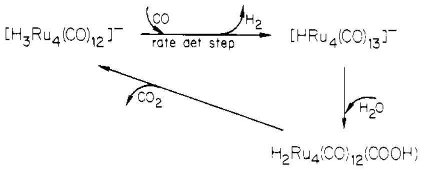
The forward reaction of equation 7 was examined under 1 atm of CO as a function of time at 60 and 80 °C in glyme. At 60 °C no intermediate species could be detected. However, at 80 °C this reaction proceeds through the intermediate $[HRu_4(CO)_{13}]^-$, the concentration of which never exceeds 12% of all ruthenium species since it is rapidly consumed by CO to give $[HRu_3(CO)_{11}]^-$ and $Ru_3(CO)_{12}$. Reaction 7 probably proceeds through the following sequence.

$$[H_3Ru_4(CO)_{12}]^- + CO \rightleftharpoons [HRu_4(CO)_{13}]^- + H_2 \quad (8)$$

$$[HRu_4(CO)_{13}]^- + 2CO \rightleftharpoons [HRu_3(CO)_{11}]^- + {}^1/_3Ru_3(CO)_{12} \quad (9)$$

Forward and reverse steps of eq 8 and 9 were observed at 80 °C in separate reactions.

A current view[9] that tetranuclear ruthenium clusters catalyze the water–gas shift reaction assumes the equivalent of reaction 8 as the rate determining step in the catalytic cycle (see eq 10).



(10)

This cycle is presumed to be operative whether the starting point is $H_4Ru_4(CO)_{12}$[12] or $Ru_3(CO)_{12}$ in basic solution since the "mature" catalytic system in each case has the same activity, and the same tetranuclear ionic species, $[H_3Ru_4(CO)_{12}]^-$, is observed in solution.[9] No $[HRu_4(CO)_{13}]^-$, a component of the cycle in eq 10, is observed. This is not unexpected since we see a rapid reaction of $[HRu_4(CO)_{13}]^-$ with base to give mixtures of $[H_3Ru_4(CO)_{12}]^-$ and $[H_2Ru_4(CO)_{12}]^{2-}$.[13] However, since we also observe reaction 9, in which $[HRu_4(CO)_{13}]^-$ is converted to $Ru_3(CO)_{12}$ and $[HRu_3(CO)_{11}]^-$ by CO, it is possible that over a period of time the effectiveness of the above cycle would be diminished and catalytic activity would be due primarily to trinuclear species.

If H_2 could be removed as it is formed in the water–gas shift reaction, then according to equilibrium 7 the concentration and subsequent contribution of $[H_3Ru_4(CO)_{12}]^-$ to the catalysis could be minimized. This point was tested by setting up a water–gas shift experiment in which H_2 was continuously removed from the apparatus by diffusion through a palladium thimble while CO remained behind. As expected, only $[HRu_3(CO)_{11}]^-$ was observed in solution even though $H_4Ru_4(CO)_{12}$ was the starting cluster. In this effectively H_2-free environment the turnover was approximately 4 times that observed in an earlier report[9] in which H_2 was allowed to accumulate in the catalytic system. The presence of H_2 shifts equilibrium 7 toward $[H_3Ru_4(CO)_{12}]^-$, but the presence of H_2 also inhibits the reductive elimination step according to equilibrium 8.

Thus it is clear that the trinuclear combination $[HRu_3(CO)_{11}]^-$–$Ru_3(CO)_{12}$ plays the major role in catalysis of the water–gas shift reaction in basic media, irrespective of whether the reaction is initiated by tetranuclear or trinuclear ruthenium carbonylates.

Furthermore, it seems reasonable that participation of trinuclear species in the catalysis of the water–gas shift reaction proceeds through a mechanism that involves a hydridic character of $[HRu_3(CO)_{11}]^-$ in the presence of CO.

Acknowledgment. We thank the National Science Foundation for support for this work through Grant CHE 79-18148.

Registry No. CO, 630-08-0; $K[HRu_3(CO)_{11}]$, 80662-65-3; $Ru_3(CO)_{12}$, 15243-33-1; $[HRu_3(CO)_{11}]^-$, 60496-59-5; $[Ph_3C][BF_4]$, 341-02-6; $[H_3Ru_4(CO)_{12}]^-$, 70073-18-6; $[HRu_4(CO)_{13}]^-$, 76917-52-7; $K[H_3Ru_4(CO)_{12}]$, 80662-68-6; $K[HRu_4(CO)_{13}]$, 76917-54-9.

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[12] $H_4Ru_4(CO)_{12}$ is rapidly deprotonated (ref 10) under these basic catalytic conditions to yield $[H_3Ru_4(CO)_{12}]^-$, which has been presumed to be one of the active species in the water–gas shift catalysis.

[13] In an earlier report (ref 9) the isolation of $H_2Ru_4(CO)_{13}$ from neutralized basic solutions that catalyze the water–gas shift was taken as evidence for the presence of $[HRu_4(CO)_{13}]^-$ in the active solutions. However, our results indicate that $[HRu_4(CO)_{13}]^-$ will not exist in basic solutions.

Dienophilic Thioaldehydes

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Thioaldehydes have been virtually ignored in synthesis, probably due to their reported tendency to polymerize. Isolated reports mention carbon bond-forming reactions of transient thioaldehydes with 1,3-dienes[1] or with butyllithium,[2] but other publications that postulate thioaldehyde formation include little systematic information on their potential for intermolecular reactions other than polymerization.[3-5]

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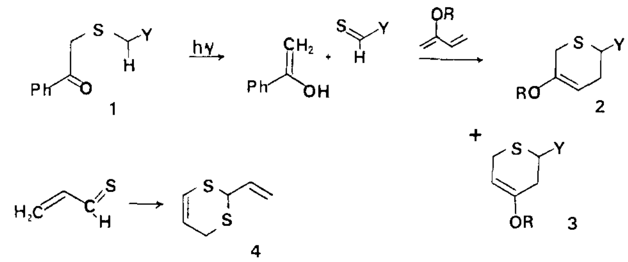
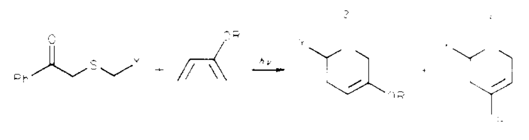
Scheme I



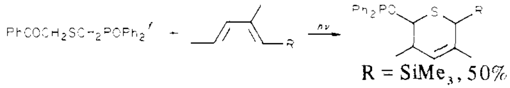
In earlier work, we had found that transient S=CHCN (from Br_2CHCN + $EtOCS_2^-K^+$) could be trapped by 2-ethoxybutadiene to give the Diels–Alder adduct in 15% yield.[1c] A report that a thioaldehyde generated by Norrish Cleavage of a phenacyl sulfide $C_6H_5COCH_2SCH_2Y$, **1** (Y = a penicillin-derived fragment) can be trapped in more respectable yield (55% thiirane using a diphenyldiazomethane trap)[4] encouraged us to reexamine the Diels–Alder experiment using the photochemical method.[5] Our new results show that thioaldehydes S=CHY (Y = unsaturated electron-withdrawing group) generated photochemically are excellent dienophiles. In the presence of 2-alkoxybutadienes, enol ethers **2** of synthetically versatile thian-3-ones are formed in useful yield.

The precursors **1** for generation of S=CHY are available by reaction of phenacyl chloride with mercaptans $HSCH_2Y$ (Y = CO_2R, CN, $POPh_2$, Ph, $CH_2CH{=}CH_2$, etc., method A) or reaction of $C_6H_5COCH_2SH$[4,6] and appropriate halides such as $ClCH_2COCH_3$ (method B). Upon photolysis of **1** in CH_2Cl_2, toluene, or THF (275-W sunlamp through Pyrex, N_2 purge, cooling to maintain ≤28 °C) in the presence of ca. 1.5 equiv of 1,3-diene (0.15 M), fragmentation to acetophenone can be demonstrated in all cases studied. In those examples where the thioaldehyde bears an activating substituent Y = acyl, CN, $POPh_2$, etc., Diels–Alder adducts are isolated in good yields (Table I).[7a,8] With Y = COC_6H_5, careful monitoring of product yield over the irradiation period is necessary because the adduct **2** has essentially the same chromophore as **1** and is destroyed by prolonged irradiation. In other examples, this problem is less severe and the reactions can be carried through to complete consumption of **1** without serious harm.

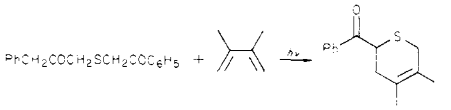
Table I



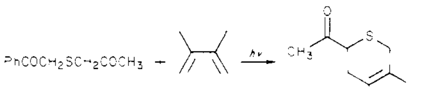
	Y	R	yield (isol), %	product ratio **2**:**3**
a.	CN[e]	C_2H_5	76	13:1
b.	CN[e]	t-BuMe$_2$Si	74	18:1
c.	COC_6H_5[c]	Et	54	*d*
d.	COC_6H_5[c]	t-BuMe$_2$Si	64	12:1
e.	$CO_2CH(CH_3)_2$[a]	t-BuMe$_2$Si	62	6:1
f.	CO_2CH_3[a]	t-BuMe$_2$Si	58	d
g.	$COCH_3$[b]	t-BuMe$_2$Si	55	3.5:1
h.	$COCH_3$[b]	C_2H_5	38	7:1



R = $SiMe_3$, 50%
R = $CH_3CH(OAc)$, 51%



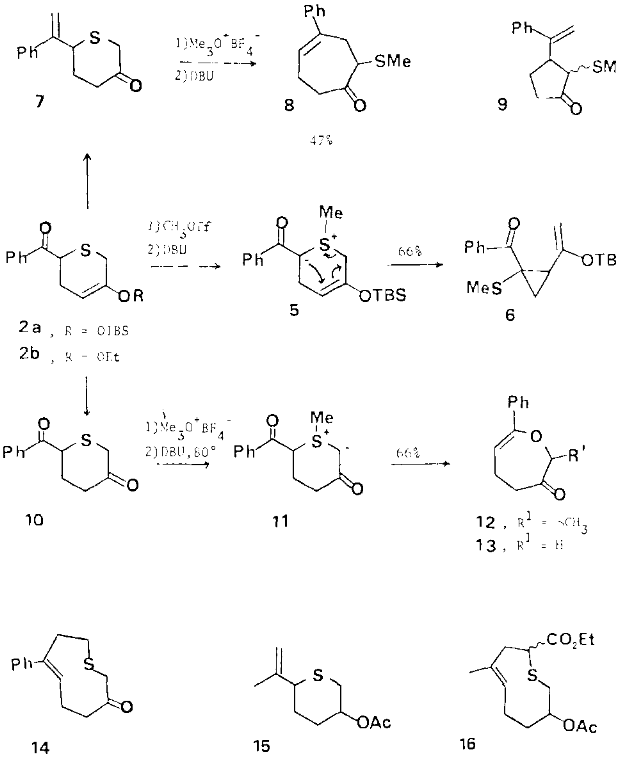
61%



50%

[a] Prepared by method A. [b] Prepared by method B. [c] Tafel, J.; Mauritz, A. *Chem. Ber.* 1897, *23*, 3474. [d] Product ratio not determined. [e] Method A, $HSCH_2CN$ generated in situ from CH_3COSCH_2CN (Boehme, H.; Dick, A.; Arch. Pharm. *Ber. Dtsch. Pharm.* 1961, *294*, 475), with K_2CO_3/CH_3OH. [f] Method A; experiment performed by J. M. Dolphin.

Scheme II



When Y = C_6H_5, 2-ethoxybutadiene fails to trap the presumed thiobenzaldehyde,[3a] and no sulfur-containing products of low

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(7) (a) Representative adducts (refer to Table I). Entry a **2**, identical with authentic material.[1c] **3**: mp 48–49 °C; NMR (270 MHz, $CDCl_3$) δ 4.90 (1 H, dt, J = 5.7, 2.9 Hz), 3.84 (1 H, t, J = 4 Hz) 3.8 (1 H, partly obscured dd, J = 16.9, 5.7 Hz), 3.73 (2 H, q, J = 7.3 Hz), 3.21 (1 H, dd, J = 16.9, 5.7 Hz), 2.62 (2 H, J_{AB} = 18 Hz), 1.30 (3 H, t, J = 7.3 Hz); IR ($CHCl_3$, cm^{-1}) 2230, 1670. Entry c **2a**: mp 43–5 °C; NMR (100 MHz, $CDCl_3$) δ 7.89 (2 H, m), 7.38 (3 H, m), 4.68 (1 H, t, J = 4 Hz), 4.38 (1 H, t, J = 6 Hz), 3.64 (2 H, q, J = 7 Hz), 3.04 (2 H, m), 2.60 (2 H, m), 1.20 (3 H, t, J = 7 Hz); IR (CCl_4, cm^{-1}) 1685. (b) **4** (oil), NMR (270 MHz, $CDCl_3$) δ 6.31 (1 H, dt, J = 10.8, 1.6 Hz), 5.9–6.05 (2 H, m), 5.4 (1 H, br d, J = 16.6), 5.31 (1 H, br d, J = 10.1 Hz), 4.73 (1 H, d, J = 6.8 Hz) 3.32 (2 H, ABXY, J_{AB} = 17.5 Hz, J_{AY} = J_{BY} = 1.8 Hz, J_{AX} = 5.0 Hz, J_{BX} = 4.5 Hz). (c) **6** (oil), NMR (270 MHz, $CDCl_3$) δ 8.13 (2 H, m), 7.53 (1 H, m), 7.42 (2 H, m), 4.37 (1 H, d, J = 1.3 Hz), 4.3 (1 H, d, J = 1.3 Hz), 2.26 (1 H, dd, J = 8.8, 7.0 Hz), 2.02 (3 H, s), 1.85 (1 H, dd, J = 8.8, 5.3 Hz), 1.34 (1 H, dd, J = 7.0, 5.3 Hz), 1.00 (9 H, s), 0.28 (3 H, s), 0.26 (3 H, s); IR ($CDCl_3$, cm^{-1}) 1670 (s), 1630 (m), 1600 (m). (d) **8** (oil); NMR (270 MHz, $CDCl_3$) δ 7.3 (5 H, m), 6.00 (1 H, t, J = 5.5 Hz), 3.41 (1 H, t, J = 7.3 Hz), 3.29 (1 H, ddd, J = 10.7, 10.0, 6.8 Hz), 2.96 (2 H, d, J = 7.3 Hz), 2.67 (1 H, m), 2.41–2.58 (2 H, m), 2.11 (3 H, s); IR ($CHCl_3$, cm^{-1}) 1700. (e) **13** (mp 154–155 °C); NMR (270 MHz, $CDCl_3$) δ 7.53 (2 H, m), 7.34 (3 H, m), 5.59 (1 H, t, J = 4.8 Hz), 4.57 (2 H, s), 3.02 (2 H, m), 2.56 (2 H, m); IR ($CDCl_3$, cm^{-1}) 1720 (s), 1655 (m). (f) **16**, two diastereomers, equilibrated by DBU to a 3:2 mixture; major component (oil), NMR (270 MHz, $CDCl_3$) δ 5.73 (1 H, dd, J = 11.8, 4.1 Hz), 4.63 (1 H, m), 4.19 (2 H, q, J = 7.1 Hz), 3.15 (1 H, dd, J = 12.1, 3.1 Hz), 2.68 (2 H, d, J = 6.1 Hz), 2.51 (1 H, dd, J = 12.4, 3.1 Hz), 2.26 (1 H, dd, J = 12.4, 12.1 Hz), 2.1–2.4 (2 H, m), 2.02 (3 H, s), 1.87 (2 H, m), 1.75 (3 H, s), 1.29 (3 H, t, J = 7.1 Hz); IR (CCl_4, cm^{-1}) 1735.

(8) Satisfactory elemental composition for all sulfur heterocycles was determined by high-resolution mass spectroscopy.

molecular weight can be found. Similarly, no adducts of structure **2** can be detected for Y = $CH{=}CH_2$ (thioacrolein). However, in this case we do find a thioacrolein self-condensation product, **4** (24%).[7b,8] An earlier claim of thioacrolein generation by pyrolysis of diallyl sulfide does not mention the formation of any specific sulfur-containing products.[3a,k]

The regioselectivity of activated thioaldehyde Diels–Alder additions favors **2** over **3**, the same general pattern as observed with other thiocarbonyl dienophiles.[1c,9] By comparison with the analogous cyano or α-oxo dithioesters,[1c] the thioaldehydes are somewhat less selective as might be expected from their enhaced reactivity. Minor adducts **3** have been detected in all cases where a thorough search has been made.

Thianes of general structure **2** are of interest as synthetic precursors to a variety of ring systems. Ramberg–Backlund sulfur extrusion to form cyclopentane derivatives is already known.[10] A brief survey of other possibilities appears in Scheme II, with adducts of phenylthioglyoxal ($C_6H_5COCH{=}S$) or thiopyruvaldehyde ($CH_3COCH{=}S$) in representative examples. From the adduct **2a**, a simple sequence of alkylation ($CH_3OSO_2CF_3$, CH_3CN) and treatment with DBU afford the alkenyl cyclopropyl ketone **6**, 66%.[7c,8] The mechanism is presumed to involve the 2,3-sigmatropic shift of the ylide intermediate **5**.[11]

Treatment of **2b** with salt-free $CH_2{=}PPh_3$ followed by dilute acid affords ketone **7**. After methylation ($Me_3O^+BF_4^-$) and deprotonation (DBU, 0 °C) **7** is converted into a stabilized ylide which rearranges to cycloheptenone **8**[7d,8] (47% yield; 2,3-shift) together with a trace of **9** (Stevens rearrangement).[12] At higher temperatures, better mass balance is observed but the reaction produces significant amounts of dimeric products and more of **9** as might be expected from literature precedent.[13]

Similar alkylation–deprotonation of the diketone **10** apparrently generates the ylide intermediate **11**, which rearranges to the cyclic enol ether **12** (66%).[8] The structure is established by NMR spectroscopy and by desulfurization to **13**[7e,8] with nickel boride.[14] The rearrangement from **11** to **12** can be viewed as a 2,3-shift involving benzoyl C=O in the migrating three-atom component. Formation of **12** is closely analogous to the rearrangement leading to **8** and also has precedent in reactions of other keto ylides.[15]

Of particular concern in our laboratory is the possibility of converting Diels–Alder adducts **2** into large ring sulfides by 2,3-sigmatropic ring expansion.[16] This reaction can be surprisingly facile. For example, treatment of **7** with $(CH_3)_3O^+BF_4^-$ followed by KO-*t*-Bu (instead of DBU as in preparation of **8**) produces the thiacyclononene **14** as the major product (32%) via the kinetically favored methylide and **8** (11%) derived from the carbonyl-stabilized ylide. Under conditions more carefully selected to promote ring expansion to a thiacyclononene, excellent yields can be achieved. Thus, **15** (available from thiopyruvaldehyde, Table I, entry g)[17] can be treated with EtO_2CCH_2OTf followed by DBU to give **16**,[7f,8] 87%.

Thioaldehydes are promising intermediates for carbon bond formation under extremely mild conditions. We will describe specialized applications of thioaldehyde chemistry to more complex synthetic problems in future publications.

Acknowledgment. This work was supported by a grant (CA 17918) from the National Institute of Health.

Registry No. 1a, 80737-85-5; **1c**, 2461-80-5; **1e**, 80737-86-6; **1f**, 36615-92-6; **1g**, 6581-69-7; **2a**, 73496-60-3; **2b**, 80737-87-7; **2c**, 80737-88-8; **2d**, 80737-89-9; **2e**, 80737-90-2; **2f**, 80737-91-3; **2g**, 80737-92-4; **2h**, 80737-93-5; **4**, 80028-57-5; **6**, 80737-94-6; **7**, 80737-95-7; **8**, 80737-96-8; **9**, 80737-97-9; **10**, 80737-98-0; **12**, 80737-99-1; **13**, 80738-00-7; **14**, 80738-01-8; **15**, 80738-02-9; **16**, 80738-03-0; $PhCOCH_2SCH_2POPh_2$, 80738-04-1; 2-ethoxy-1,3-butadiene, 4747-05-1; 2-*tert*-butyldimethylsilyloxy-1,3-butadiene, 80738-05-2; 2-methyl-1-trimethylsilyl-1,3-pentadiene, 80738-06-3; 6-acetoxy-4-6-dimethyl-2,4-heptadiene, 80738-07-4; 2,3-dimethyl-1,3-butadiene, 513-81-5; 3,5-dimethyl-6-diphenylphosphinyl-2-trimethylsilyl-2,5,6-trihydrothiopyran, 80738-08-5; 2-(1-acetoxyethyl)-3,5-dimethyl-6-diphenylphosphinyl-2,5,6-trihydrothiopyran, 80738-09-6; 3,4-dimethyl-6-phenylcarbonyl-2,5,6-trihydrothiopyran, 80738-10-9; 6-acetyl-3,4-dimethyl-2,5,6-trihydrothiopyran, 80738-11-0.

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[12] A related case of seven-membered ring formation by 2,3-shift has been reported: Vedejs, E.; Arnost, M. J.; Hagen, J. P. *J. Org. Chem.* **1979**, *44*, 3236.

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[16] Vedejs, E.; Arco, M. J.; Powell, D. W.; Renga, J. M.; Singer, S. P. *J. Org. Chem.* **1978**, *43*, 4831. Cere, V.; Paolucci, C.; Pollicino, S.; Sandri, E.; Fava, A.; Lunazzi, L. *Ibid.* **1980**, *45*, 3613 and referneces therein.

[17] The adduct of 2-*tert*-butyldimethylsiloxy)butadiene and thiopyruvaldehyde was treated with salt-free $CH_2{=}PPh_3$, dilute acid, $Et_3BH^-K^+$, and acetic anhydride to prepare **15**.

Ionization Energies of *p*-Quinodimethane and 2,5-Dimethyl-*p*-quinodimethane

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Some years ago Koenig et al.[1,2] reported ultraviolet photoelectron spectra (UV-PES) for *p*-quinodimethane (**1**) and its 2,5-dimethyl derivative (**2**), these being formed in situ by flash vacuum thermolysis of their dimers (e.g., **3**). Each spectrum showed three π-type bands (B_{1-3}) with comparable areas in the region below 11.5 eV, which would normally be assigned to the first three π ionizations. The fourth π ionization and the σ ionizations are expected to appear at higher energies. The spectrum of **2** also showed a broad, weak band (B_x) with much structure centered at 9.8 eV, while B_2 in **2** had a somewhat larger area than B_1 (ratio 1.2:1[3]), due to a tail at the high-energy side. Features such as this would usually be attributed to byproducts formed during the pyrolyses, particularly for **2**, which contains labile methyl groups.

Koenig et al.,[1,2] however, claimed that B_2 in **1** corresponds to superimposed π ionizations, I_2 and I_3, on the basis of SR[4] and INDO[5] calculations. They inferred that B_x in **2** then corresponds to I_3, shifted out of coincidence with I_2 by the methyl substituents. The low intensities of these extra bands would normally rule out any such assignment. However, Koenig et al. suggested that this might be due to configurational mixing between the ion corresponding to I_3 and an ion formed by loss of one electron from the HOMO of **2** combined with excitation of the other to the LUMO.[6] It is well-known[7] that similar mixing of the second and third $\pi \rightarrow \pi^*$ excited configurations of an alternant hydrocarbon (AH) results

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[6] This process leads to a state with the correct symmetry to interact with that formed by removal of an electron from the third MO.

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