adduct formation reactions[1,18] of terminal CS groups in electron-rich complexes presumably also yield CSR carbyne complexes. These results suggest that similar adducts of terminal CO ligands could be reasonable intermediates in catalytic reactions[19] of carbon monoxide which lead to the cleavage of the C≡O bond.

Acknowledgment. We appreciate the support of this work by the National Science Foundation (Grant CHE75-15147) and the U.S. Department of Energy, Contract No. W-7405-Eng-82, Division of Materials Sciences Budget Code AK-01-02-03-1.

Supplementary Material Available: Fractional coordinates and thermal parameters (Table I), bond distances (Table II), important bond angles (Table III), and structure factors (13 pages). Ordering information is given on any current masthead page.

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Electronic Control of Stereoselectivity. 2. A Stereochemical Method for Qualitatively Assessing the Relative Electrophilicity of Various Electron-Deficient Species[1]

Sir:

Those trends observed in nucleophilic reactivity appear to be predetermined in large part by the intrinsic basicity and polarizability of the reagent as attested to by the quantitative equations developed by Swain and Scott[2] and by Edwards.[3] Striking for its absence is any comparable relative ordering of electrophilicity. This is due principally to the fact that the fundamental nature of S_N2 reactions permits the direct replacement of one nucleophile by another via transition states where both are intimately involved. No similar electrophilic process is available. Although a principal tenet of the selectivity relationship for electrophilic aromatic substitution[4,5] relates a lessening of electrophile reactivity to an increase in positional selectivity, the procedures involved in this type of data acquisition are less than direct.[5] As part of a systematic study of stereoelectronic control, we have uncovered a new, one-step technique capable of *qualitatively* ranking the electrophilicity of various electron-deficient species by means of a simple stereochemical citerion.

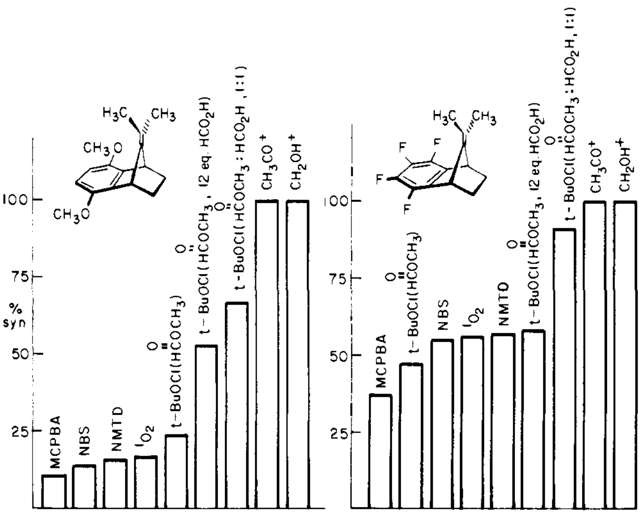
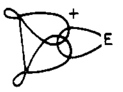
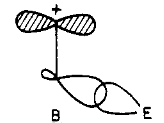


Figure 1. Percent syn epimer produced upon addition of various electrophiles to dimethoxy- (**3**) and tetrafluoro-7-isopropylidenebenzonorbornene (**4**).

Linear free-energy relationships such as the Hammett and Taft correlations, as well as more recent multiple parameter versions, are of limited use in establishing electrophilic transition state structures because a single set of substituent steric and polar parameters is inadequate for both open and bridged-ion pathways. One solution to this problem is the availability of a substrate, or group of substrates, which would give rise to stereochemically different products under these two sets of mechanistic circumstances. In this way, it should prove possible to establish if the rate-determining step for a particular electrophilic process involves substantial π bond distortion (A), as usually required by weak electrophiles, or more closely resembles the highly polarized open ion situation B commonly characteristic of more powerful electrophilic agents.



A



B

Recently, we disclosed that additions of such reagents as *m*-chloroperbenzoic acid (MCPBA), *N*-methyltriazolinedione (NMTD), singlet oxygen ($^1O_2$), and *N*-bromosuccinimide (NBS) in aqueous glyme to 7-isopropylidenebenzonorbornene (**1**) proceed with a strong contrasteric preference to provide high levels of anti products. Through manipulation of the electronic character of the aromatic ring in **1**, it was possible to show that the choice between the two bonding approaches to the exocyclic p orbital could be varied somewhat (Figure 1). Similar phenomena have been noted by Mukai in related systems[6] and Malpass in 7-aza analogues.[7]

We now report that the acetylations of **1**, **3**, and **4** with acetyl chloride and aluminum chloride in dichloromethane at −10 °C[8] or with zinc chloride in acetic anhydride at room temperature[9] lead in high yield to single products, e.g., **5**. The exclusivety of contrasting syn attack in these examples was established in the following illustrative manner. Of the two methyl peaks in the ^{1}H NMR spectrum of **5** (δ ($CDCl_3$) 1.97 (s), 1.75 (m, $\nu_{1/2}$ = 3 Hz)), only the upfield isopropenyl signal remained after suitable hydrogen-deuterium exchange provided **6**. Upon ozonolysis, both **5** and **6** were converted into

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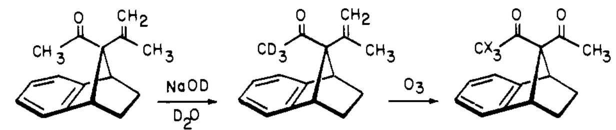
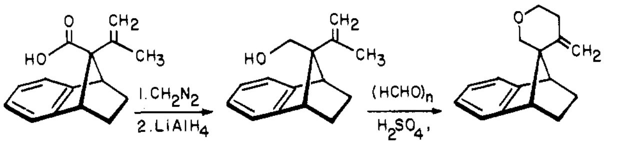


5 6 7a, X = H
b, X = D

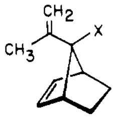
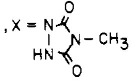
diacetyl derivative **7**. Whereas **7a** showed a pair of methyl singlets at δ 2.19 and 1.91 (in $CDCl_3$), the spectrum of **7b** was characterized by a lone absorption at 2.19. Since the more shielded methyl group in **7** resides above the benzene ring, structural assignment to **5** is secured.

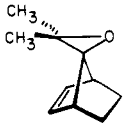
The response of **1**, **3**, and **4** to the Prins reaction (paraformaldehyde, 10 equiv of H_2SO_4, dioxane, 25 °C) proved entirely comparable. The stereochemical features of the only isolated products (e.g., **10**) were elucidated by independent synthesis. Thus, haloform degradation of **5** to give carboxylic acid **8**, esterification and hydride reduction of **8** to provide **9**, and independent submission of **9** to the Prins conditions delivered **10** exclusively.[10]



8 9 10

7-Isopropylidenenorbornene (**2**)[11] has proven equally responsive to changes in electrophilic demand. Urazole **11b** was spectroscopically correlated with the known **11a**[6] (as were the respective epimers with each other), while epoxide **12** was chemically transformed into this alcohol upon treatment with lithium diisopropylamide. Controlled diimide reduction of **13** permitted selective saturation of the norbornene double bond. This chemical change was accompanied by a downfield shift of the acetyl singlet (δ 2.03 → 2.13) while the isopropenyl methyl signal (1.75) remained unaltered. These findings are consistent with the indicated syn formulation. Ether **14** exhibits a methylene proton absorption (δ 4.82 (2 H)) differing little in chemical shift from that of **10** and its congeners (~ 4.94). This internal consistency comprises the reference point for this stereochemical assignment.


11 a, X = OH
b, X =
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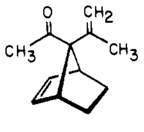
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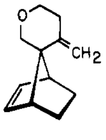
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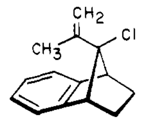
If it is conceded that the principal factor which governs the stereochemical response of these bridged systems is the electrophilicity of the attacking reagent, then, in principle, it should be possible to modify the characteristics of such species with attendant stereochemical consequences. To this end, the reaction of **1** with *tert*-butyl hypochlorite[12] was studied. In methyl formate solution, anti attack to give **15** prevailed to the extent of 85%. Admixture of 12 equiv of formic acid increased the amount of syn isomer **16** produced to 42%. Further adjustment of the solvent system to methyl formate-formic acid (1:1) led to additional enhancement in the level of **16** formed (80%). Entirely similar trends were encountered with **3** and **4** (Figure 1), although the overall ranges were somewhat narrower because of the aryl substitution.[1] While the effect of solvent change cannot be totally disregarded, these stereochemical crossovers can be reasonably attributed to increased levels of protonation of the reagent to give **17**, a species more electrophilic than the neutral molecule. That the levels of syn attack by **17** do not attain 100% is viewed to be a consequence of the fact that the positive charge is associated chiefly with the oxygen atom *adjacent to* the attacking center (Cl atom). This contrasts with the acetylium (**18**)[13] and hydroxymethyl cations (**19**) which carry a higher proportion of electron deficiency at their reaction sites.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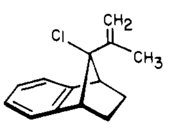
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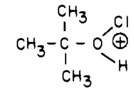
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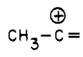
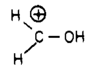

$CH_3-\overset{\oplus}{C}=O$

18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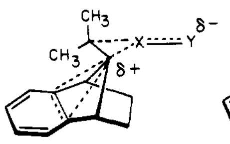
The present investigation is the first explicit example of a general stereochemical probe for the determination of electrophilicity. The significant determinants would appear to be whether or not the attacking electrophile requires considerable assistance from the π bond to become adequately polarized (uniparticulate cases,[14] **20**) or disengaged from its anionic component (biparticulate electrophiles, **21**). In such circumstances, the more sterically congested but electronically favorable anti transition states are kinetically preferred. A decisive factor would appear to be the ability of the flanking aromatic ring to enter into homoconjugative charge dispersal,[1] a phenomenon previously clarified through solvolysis studies.[15] When such π-bond assistance becomes unnecessary as the result of heightened electrophilicity, extended conjugation is less necessary, steric factors become dominant, and syn attack prevails (**22**). An additional contributing influence could be prior coordination of the stronger electrophiles to the benzo ring or norbornene double bond with ensuing intramolecular delivery to the syn surface of the double bond. At this moment, our knowledge of the kinetic relevance of transient complex formation, if operational at all, is very limited.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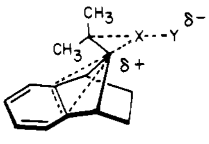
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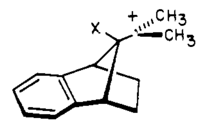
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In summary, the chemical properties of **1** and related molecules are seen to provide a new tool with which to study electrophilic additions.[16]

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Metal Core Binding Energy and Charge Delocalization in $[Os(NH_3)_4ClN_2Cl(NH_3)_4Os]Cl_3$, a Binuclear Mixed-Valence Osmium Complex: An ESCA Study

Sir:

Recently, there has been some disagreement[1-3] about the interpretation of core level photoelectron spectra[4] of transition metal mixed-valence class II and class III compounds.[5] Citrin[1] reported the presence of two sets of spectral lines from binuclear pyrazine-bridged ruthenium mixed-valence compounds and attributed his results to charge localization in the ground state of the mixed-valence complexes (class II). While it has generally been assumed that the observation of more than one set of lines with the expected intensity ratio and line shapes is proof of the presence of more than one oxidation state for a metal in a given substance, Hush has challenged the uniqueness of this interpretation. For ligand bridged binuclear mixed-valence compounds he has argued that final state relaxation would give rise to two sets of X-ray photoelectron lines with comparable intensities even if valence electron delocalization makes the two metal centers equivalent in the ground state (a class III compound). He thus concluded that the appearance of two metal binding energies was not in itself evidence for electronic ground-state asymmetry in a mixed-valence compounds.

Recently, some investigators[2] claimed to have observed two sets of Os 4f lines in the X-ray photoelectron spectrum of $\{[Os(NH_3)_4Cl]_2N_2\}Cl_3$, an Os(II)-Os(III) mixed-valence compound which is considered to be of the valence delocalized type. The two $4f_{7/2}$ lines, of approximately equal intensity, were reported to be separated by 1.2 eV. It was stated that the results support Hush's[3] treatment and provide evidence for the existence of two distinct localized ionized states of the compound.

We have repeated the measurement of the Os 4f spectrum of $\{[Os(NH_3)_4Cl]_2N_2\}Cl_3$. In contrast to the results just mentioned, we have seen only one set of Os 4f spin-orbit coupled peaks, with some relatively weak satellites (~13% of the main peak) on the high binding energy side of the spectrum (Table I). This, the first observation of only one set of lines in a well-characterized ligand bridged binuclear transition metal mixed-valence compound is clear confirmation of the fact that here one has a single delocalized initial state. For points of comparison we have also looked at the Os 4f spectra obtained from $[Os(NH_3)_5Cl]Cl_2$, an Os(III) compound, and $[Os(NH_3)_5N_2]Cl_2$, an Os(II) compound.

X-ray photoelectron spectra were obtained on a Varian IEE-15 spectrometer using the 1254-eV Mg ($K\alpha_{1,2}$) radiation. The pass energy of the spherical analyzer was set at 50.0 eV. Pressure in the spectrometer chamber was $\sim 10^{-6}$ Torr. For calibration the 4f lines emitted from a gold foil were employed.

Each sample was brushed onto one side of a double-backed adhesive tape that had been mounted on an aluminum cylinder. This was then attached to the probe and introduced into the spectrometer. The tape gave a flat photoelectron spectrum in the Os 4f region, and thus could not contribute in any way to the Os 4f spectra of the samples. No visible time dependent feature was observed in these spectra. No attempt was made to take account of sample charging. Os compounds were prepared according to literature methods[6,7] and gave satisfactory analysis.

All spectra were computer fitted to a set of combined Gaussian-Lorentzian spectral line functions plus a sloping linear background, using nonlinear least-squares techniques. The linear background was then subtracted both from the data and from the fitted curve before the net spectra (Figure 1) were plotted.

The Os $4f_{5/2,7/2}$ doublet obtained from $[Os(NH_3)_5Cl]Cl_2$ was fitted to two combined Gaussian-Lorentzian spectral functions, with the Gaussian fraction constrained to be equal for both peaks. When the Os 4f spectra obtained from $[Os(NH_3)_5N_2]Cl_2$ and $\{[Os(NH_3)_4Cl]_2N_2\}Cl_3$ were treated in the same manner, line widths and areas under the curves turned out to be considerably greater for the $4f_{5/2}$ lines than for the $4f_{7/2}$ lines. Under the assumption that this was the result of the presence of additional satellite peaks buried in the overall envelopes, each spectrum was fitted to four peaks under the following constraint: the separation between the spin-orbit $4f_{7/2}$ and $4f_{5/2}$ peaks was required to be the same as that between their satellites; the relative doublet intensity of the main peaks as well as that of the satellites was fixed at the theoretical value as observed in $[Os(NH_3)_5Cl]Cl_2$; the half-widths of all lines in a given spectrum were constrained to have the same value. The fitted parameters are given in Table I and the spectra are shown in Figure 1.

It is commonly recognized[4] that values of the experimental binding energies are not particularly useful for comparing electronic properties of different nonconducting solids. However, the presence of only one set of Os 4f main spectral lines for the mixed-valence Os compound with some weaker satellite structure is of great significance. An important point is that the resolved main Os 4f line width for the mixed-valence compound is not significantly different from that of the Os 4f of $[Os(NH_3)_5N_2]Cl_2$ or of $[Os(NH_3)_5Cl]Cl_2$. The sample, after having been kept in the refrigerator for 6 months, was rerun with a VG ADES 400 spectrometer at 200-eV pass energy. The Os 4f spectrum thus obtained looks the same as

Table I. XPS Parameter for Some Os Complexes

compd	Os $4f_{7/2}$, eV	S(7/2),[a] eV	I,[b] eV	Γ,[c] eV	λ,[d] eV
$\{[Os(NH_3)_4Cl]_2N_2\}Cl_3$	52.62 ± 0.01	55.5 ± 0.1	0.13 ± 0.01	2.25 ± 0.02	2.75 ± 0.02
$[Os(NH_3)_5Cl]Cl_2$	50.75 ± 0.05			2.26 ± 0.15	2.75 ± 0.10
$[Os(NH_3)_5N_2]Cl_2$	49.93 ± 0.05	51.4 ± 0.1	0.34 ± 0.06	1.97 ± 0.10	2.76 ± 0.03

[a] Position of Os $4f_{7/2}$ satellite. [b] Relative intensity of Os $4f_{7/2}$ satellite to the main peak. [c] Full width at half maximum. [d] λ = separation between Os $4f_{7/2}$ and $4f_{5/2}$ main peaks.

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