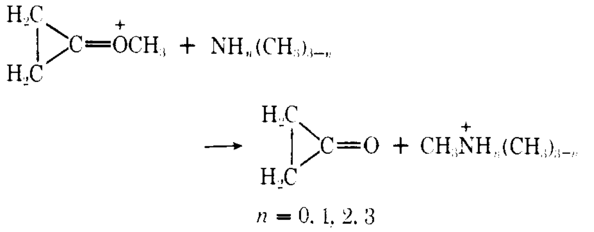
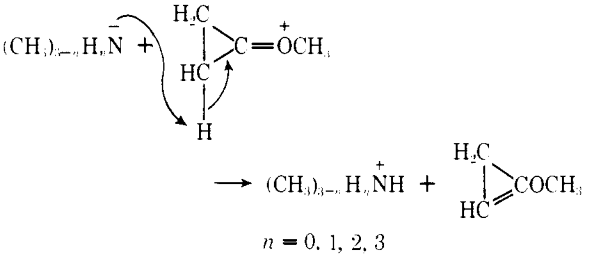


(3)

The double resonance experiments have also shown that ions **1**, but not ions **2**, are able to transfer a proton to ammonia, methylamine, dimethylamine, and trimethylamine. Deuterium-labeling experiments show that it is one of the ring methylene protons which is transferred in this process, as indicated in reaction 4. Substitution of one of the methylene groups in the ions **1** by a dideuteriomethylene group[25b] reveals the existence of a kinetic isotope effect in reaction 4; using dimethylamine as the base this isotope effect is 1.7 at an electron energy of 12 eV decreasing to 1.6 at 14 eV and 1.3 at 16 eV.[26]



(4)

The ions **1** and **2** are studied under ICR conditions on a time scale of ~10^{-3} s, but they might have differing internal energies, which could also lead to different reactivities. However, we feel confident that the experimental results obtained strongly support the view that at least part of the ions **1** have a structure different from that of ions **2**. This is reinforced by the observation of a composite metastable peak for the loss of the bromine atom from the molecular ions of 1-bromo-1-methoxycyclopropane, whereas a noncomposite metastable peak is observed for loss of the bromine atom from the molecular ions of 2-methoxyallyl bromide.[27] This observation of the composite metastable peak indicates[28] that the molecular ions of 1-bromo-1-methoxycyclopropane which decompose within 10^{-6} s do so to form two different $(M - Br)^+$ ions, presumably with and without rupture of the ring to give ions **2** and **1**, respectively.

Acknowledgment. The authors thank the Netherlands Organisation for Pure Research (SON/ZWO) for the purchase of the basic ICR mass spectrometer.

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(26) A referee has suggested that ions with the structure $CH_3CH{=}C{=}OCH_3^+$ might also transfer a methyl cation or a proton to the bases studied. However, the formation of such ions from ions **1** requires cleavage of the C_1–C_2 or C_1–C_3 bond of the cyclopropane ring. This would only be possible after the migration of a hydrogen atom from C_2 or C_3 to C_1. The heat of formation of the intermediate 2-methoxycyclopropyl cations is expected to be 30–50 kcal/mol higher than that of ions **1**; see R. D. Bowen, J. R. Kalman, and D. H. Williams, *J. Am. Chem. Soc.*, **99**, 5481 (1977); R. D. Bowen, D. H. Williams, G. Hvistendahl, and J. R. Kalman, *Org. Mass Spectrom.*, **13**, 721 (1978). This value is similar to or higher than the activation energy of ~32 kcal/mol, which we have measured for the loss of formaldehyde from ions **1**. Therefore, it is very unlikely that those ions **1** which do not lose formaldehyde have rearranged to structure $CH_3CH{=}C{=}OCH_3^+$.
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Synthesis and Structure of (η-C_5H_5)W(PPh_3)(CO)(CSPh): Transformation of a Thiocarbonyl Ligand into a Carbyne Ligand

Sir:

It was previously established in this laboratory[1] that the thiocarbonyl ligand in certain thiocarbonyl complexes can be alkylated with $MeOSO_2F$ or R_3O^+ to give the CSR ligand, e.g.,

$$(Ph_2PCH_2CH_2PPh_2)_2W(CO)(CS) + MeOSO_2F \rightarrow (Ph_2PCH_2CH_2PPh_2)_2W(CO)(CSMe)^+SO_3F^- \quad (1)$$

For this reaction to occur, it is necessary for the starting complex to be sufficiently electron rich to exhibit a ν(CS) value of ~1200 cm^{-1} or below. We now report a new and unexpected route to CSR complexes together with the first X-ray diffraction study of this type of ligand.

The title compound, (η-C_5H_5)W(PPh_3)(CO)(CSPh), A, was prepared by the following sequence of reactions:

$$W(CO)_4(CS)I^- + C_5H_5^- \rightarrow (\eta\text{-}C_5H_5)W(CO)_2(CS)^- + I^- + 2CO \quad (2)$$

$$(\eta\text{-}C_5H_5)W(CO)_2(CS)^- + I_2 \rightarrow (\eta\text{-}C_5H_5)W(CO)_2(CS)I + I^- \quad (3)$$

$$(\eta\text{-}C_5H_5)W(CO)_2(CS)I + PPh_3 \rightarrow (\eta\text{-}C_5H_5)W(PPh_3)(CO)(CS)I + CO \quad (4)$$

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$$(\eta\text{-}C_5H_5)W(PPh_3)(CO)(CS)I + LiPh \rightarrow (\eta\text{-}C_5H_5)W(PPh_3)(CO)(CSPh) + LiI \quad (5)$$

Anhydrous $Bu_4N[W(CO)_4(CS)I]$[2] and NaC_5H_5 (eq 2) were stirred at 60 °C in tetrahydrofuran (THF) for 1.5 h, and the resulting anion, $(\eta\text{-}C_5H_5)W(CO)_2(CS)^-$, was treated in situ with an equivalent amount of I_2 at 0 °C. Elution of the dried reaction mixture on Florisil with CH_2Cl_2 gave *trans*-$(\eta\text{-}C_5H_5)W(CO)_2(CS)I$ (77% yield), which was characterized by its C and H elemental analyses, IR spectrum (ν(CO) 2025 (m) and 1972 (s) cm^{-1} and ν(CS) at 1267 (s) cm^{-1} in CS_2), and ^{13}C NMR spectrum (CO, −195.01 downfield from Me_4Si in $CDCl_3$; CS, −310.52 ppm). In reaction 4, equimolar amounts of $(\eta\text{-}C_5H_5)W(CO)_2(CS)I$ and triphenylphosphine were refluxed in toluene for 2.5 h. The solution was evaporated to dryness under vacuum; elution of the residue on silica gel with CS_2, followed by CH_2Cl_2, gave $(\eta\text{-}C_5H_5)W(PPh_3)(CO)(CS)I$ in 78% yield. The product was identified by its C and H analyses, IR spectrum (ν(CO) at 1964 (s) cm^{-1} and ν(CS) at 1225 (s) cm^{-1} in CS_2), and ^{13}C NMR spectrum (CO, −224.52 (J_{PCO} = 10.0 Hz in $CDCl_3$); CS, −353.10 (J_{PCS} = 23.8)).

Compound A was prepared according to eq 5 using equimolar $(\eta\text{-}C_5H_5)W(PPh_3)(CO)(CS)I$ and LiPh in THF at 0 °C. After the solvent was evaporated under vacuum, the residue was eluted on grade II alumina with benzene. The yellow fraction was recrystallized from 4:1 pentane–CS_2 at 20 °C to give orange needles of $(\eta\text{-}C_5H_5)W(PPh_3)(CO)(CS\text{-}Ph)$ in 43% yield. The *S*-phenyl complex was characterized by its C and H analyses, IR spectrum (ν(CO) at 1886 cm^{-1} in CS_2), and ^{13}C NMR spectrum (CO, −237.70 (J_{PCO} = 7 Hz in $CDCl_3$); CS, −254.90 (J_{PCS} = 12 Hz)).

Considering the well-known reaction of alkyl- and aryllithium derivatives with transition metal halo complexes to yield the corresponding σ-alkyl and σ-aryl complexes, the addition of Ph^- to the CS sulfur atom in reaction 5 is especially surprising. It seems unlikely that this reaction proceeds by direct nucleophilic attack of Ph^- on the sulfur. While initial attack at the W or CS carbon atom is possible, there is no evidence for such intermediates. Organic thioketones, $R_2C{=}S$, are known to react with LiPh to give the *S*-phenyl products, R_2CHSPh.[3] A charge-transfer–radical mechanism has been postulated for this latter reaction. If reaction 5 followed such a mechanism, initial electron transfer to $(\eta\text{-}C_5H_5)W(PPh_3)(CO)(CS)I$ would be followed by recombination of the resulting radicals. That electron transfer is possible in these systems is suggested by the reaction of $(\eta\text{-}C_5H_5)Mo(CO)_3I$ with PhMgBr to give $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$ and biphenyl[4] and the reactions of $(\eta\text{-}C_5H_5)M(CO)_4^+$, where M = Mo or W, with LiPh to yield $[(\eta\text{-}C_5H_5)M(CO)_3]_2$ and biphenyl.[5]

A single crystal of $(\eta\text{-}C_5H_5)W(PPh_3)(CO)(CSPh)$ ~0.2 × 0.15 × 0.4 mm was chosen for the X-ray diffraction study. The observed Laue symmetry and extinctions indicated the monoclinic space group $P2_1/c$ with a = 14.581 (3), b = 10.106 (2), c = 18.838 (3) Å; β = 105.38 (2)°; Z = 4; ρ_c = 1.592 g cm^{-3}. Two octants of data were collected on a four-circle diffractometer designed and built at Ames Laboratory[6] using graphite-monochromated Mo Kα X-rays (λ = 0.70954 Å) to a 2θ limit of 50°. Of the 5041 measured intensities, 3972 were considered observed ($I > 3.0\sigma_I$). The data were corrected for Lorentz-polarization effects and absorption; equivalent data were then averaged yielding 3694 independent reflections. The heavy atom was located on a sharpened Patterson map and the remaining atoms on subsequent electron density maps.[7] A combination of block and full-matrix refinement[8] of the structure with anisotropic thermal parameters and fixed hydrogen positions yielded a conventional residual R = 0.054 and a weighted residual R_w = 0.074. A computer-generated view of the molecule is shown in Figure 1.

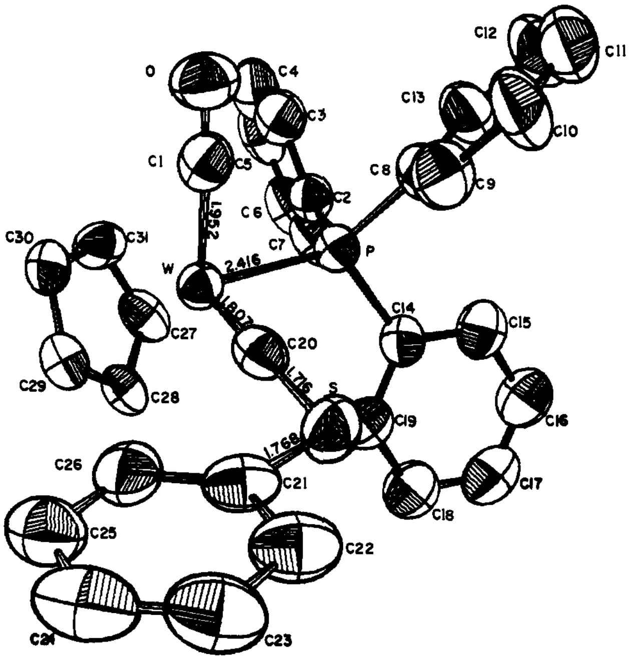
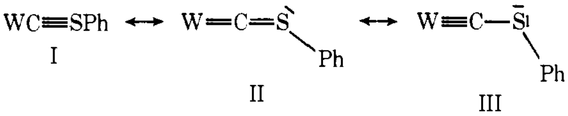


Figure 1. Computer drawing of $(\eta\text{-}C_5H_5)W(PPh_3)(CO)(CSPh)$ showing thermal ellipsoids at the 50% probability level.

The average distance from the tungsten to the cyclopentadienyl carbon atoms is 2.366 Å.[9] The other three ligands lie at nearly right angles to each other as indicated by the following values: OC-W-P, 88.7 (3); SC-W-P, 92.8 (5); SC-W-CO, 92.9 (4)°. The W-P bond distance is 2.416 (3) Å. The W-CO and C-O distances are 1.952 (11) and 1.151 (12) Å, respectively, and the W-C-O angle is 177.2 (9)°.

There are several resonance forms which might be considered as representing the bonding in the CSPh ligand (eq 6).



$$\underset{\text{I}}{\mathrm{WC{\equiv}SPh}} \longleftrightarrow \underset{\text{II}}{\mathrm{W{=}C{=}\ddot{S}{-}Ph}} \longleftrightarrow \underset{\text{III}}{\mathrm{W{\equiv}C{-}\bar{S}{-}Ph}} \qquad (6)$$

Form III, commonly called a carbyne ligand,[10] appears to best describe the CSPh ligand present in A. Support for this view comes from a comparison of the W-C(carbyne) bond distance in A with those in the carbyne complexes, $(\eta\text{-}C_5H_5)W(CO)_2(CC_6H_4CH_3)$[11] and $(\eta\text{-}C_5H_5)W(CO)_2(CSiPh_3)$.[12] The W-C(carbyne) distances in these latter two complexes are 1.82 (2)and 1.81 (2) Å, respectively, and are nearly identical with the 1.807 (10) Å observed in complex A. Also like the W-C-R angles in the compounds prepared by Fischer and his co-workers,[11,12] the W-C-S angle is nearly linear, 174.2 (6)°. The C-S-C angle is less than tetrahedral, 106.2 (5)°, but comparable with those found in organic sulfides, R_2S,[13,14] and the S-C(Ph) distance is 1.768 (12) Å, which is normal for S-C(sp^2) single bond distances such as those found in $C(SPh)_4$.[13]

The S-C(carbyne) distance in A, 1.716 (10) Å, is very close to the value expected for an S-C(sp) single-bond distance if the C(sp) radius is assumed to be 0.05 Å smaller than the C(sp^2) radius.[15] In addition, the S-C(carbyne) bond length is substantially longer than the longest known C-S distance in thiocarbonyl complexes, 1.57 Å.[16] It is also longer than the C-S distance in the bridging "carbyne" group of $[(\eta\text{-}C_5H_5)_2Fe_2(CO)_3(CSEt)]BF_4$, 1.666 (11) Å.[17]

In conclusion, the arylation reaction (eq 5) reduces the multiple bonding in the terminal CS ligand of $(\eta\text{-}C_5H_5)W(PPh_3)(CO)(CS)I$ to a C-S single bond in the carbyne product. The previously reported alkylation (eq 1) and Lewis 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.

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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.

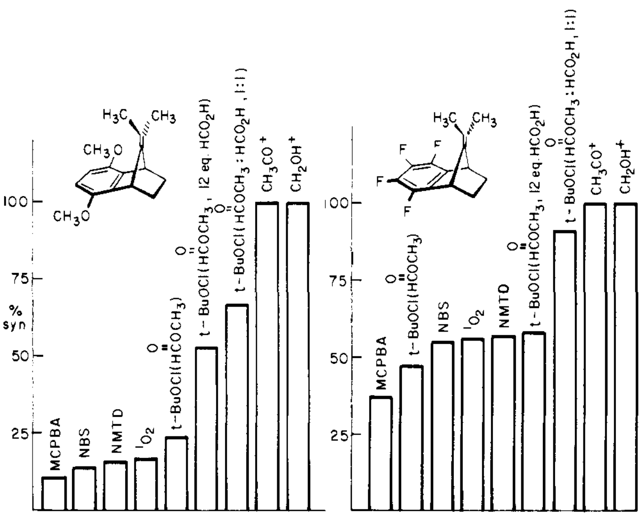
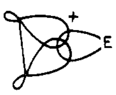
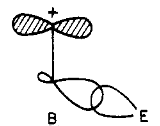


Figure 1. Percent syn epimer produced upon addition of various electrophiles to dimethoxy- (**3**) and tetrafluoro-7-isopropylidenebenzonorbornene (**4**).

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 ^1H 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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