the relative energy of the metal filled d orbitals of the appropriate π symmetry from a position they would otherwise have. This closes the energy separation between the filled metal d orbitals and CO π^* orbitals, which in turn promotes extensive metal to carbonyl π bonding.[14] The values of ν(CO) and Mo-C and C-O distances are thus apparently inconsistent with what would be expected based solely on the formal oxidation state of the metal. A similar argument can and has been used to account for the exceedingly low values of ν(NO) found in the complexes $Mo_2(OPr^i)_6(NO)_2$ (1630 cm^{-1}) and $W(OBu^t)_3(py)(NO)$ (1560 cm^{-1}) which contain linear M-N-O groups.[15] Here terminal RO$^-$ groups may push up, by the presence of their filled π-type orbitals, the relative energies of the filled metal d_{xz},d_{yz} orbitals. This in turn promotes metal $(d_{xz},d_{yz})^4$ to NO π^* bonding.

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Supplementary Material Available: A table of observed and calculated structure factors (47 pages).[16] Ordering information is given on any current masthead page.

References and Notes

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(2) M. H. Chisholm, F. A. Cotton, M. W. Extine, and W. W. Reichert, *Inorg. Chem.*, 17, 2944 (1978).

(3) Satisfactory elemental analyses have been obtained for both of the new compounds reported herein.

(4) By the method of direct insertion using an AEI MS9 spectrometer at +6 °C (7 × 10^{-8} Torr). We thank Mr. Peter Cook and Professor D. C. Bradley for kindly obtaining this valuable spectral data for us.

(5) Or at least were totally surprising and had no precedent to our knowledge in metal carbonyl chemistry.

(6) This compound is insoluble in hexane and, though soluble in toluene, reacts rapidly to give $Mo(CO)_8$ and as yet unidentified oxidized molybdenum compounds. This has prevented any characterization of the solution properties of $Mo(OBu^t)_2(py)_2(CO)_2$. All reactions were carried out under a dried and O_2-free nitrogen atmosphere.

(7) Crystal data collected at −175 °C using a gaseous nitrogen cold stream and locally constructed goniostat system: monoclinic; space group $P2_1/c$ with unit cell dimensions a = 12.738 (2), b = 10.330 (5), c = 16.328 (11) Å; β = 93.86 (3)°; Z = 4. A total of 4919 unique data points were collected of which 4653 had $I > \sigma(I)$ and were used in the refinement $R(F)$ = 0.0433, $R_W(F)$ = 0.082.

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(12) Attempts to grow crystals suitable for detailed single X-ray crystallography are in progress.

(13) If the two μ-OR bridges are split symmetrically, the formal oxidation number of the carbonyl containing molybdenum atom is +3. However, one resonance form for the molecule could be written as $Mo^{6+}(\mu\text{-}OR)_2Mo^{2+}$.

(14) A more detailed argument based on the specific geometry observed for $Mo(OBu^t)_2(py)_2(CO)_2$ will be presented in a full paper.

(15) M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *Inorg. Chem.*, **18,** 116 (1979).

(16) The complete structural report, MSC Report 7950 is available upon request in microfiche from only the Indiana University Chemistry Library.

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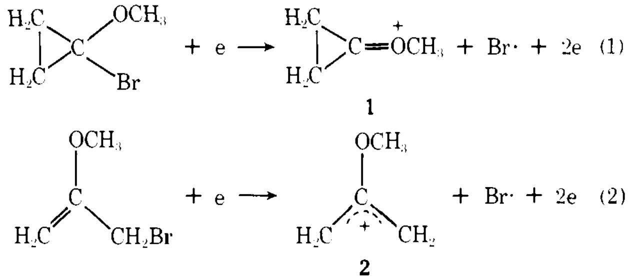
Independent Existence in the Gas Phase of the 1-Methoxycyclopropyl and 2-Methoxyallyl Cations, as Observed in an Ion Cyclotron Resonance Spectrometer[1]

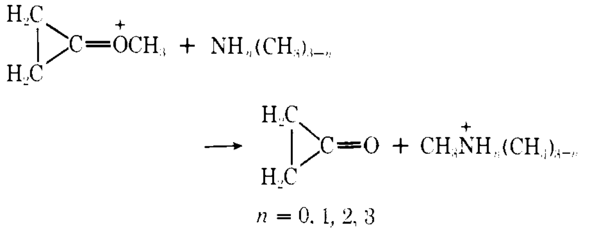
Sir:

Substitution reactions of cyclopropyl compounds which have a good leaving group X at C_1 occur in the condensed phase, often with a disrotatory cleavage of the C_2-C_3 bond.[2] However, this ring rupture can be suppressed or even prevented if an electron-donating group Y is present at C_1 since it can supply electron density to the cyclopropyl cation center at C_1 as the group X leaves. If this substituent effect predominates over the donation of electrons from the C_2-C_3 bond, then substitution of group X without ring cleavage can take place. This electronic stabilization of the intermediate cyclopropyl cation has been found for various electron-donating groups Y such as dialkylamino,[3,4] phenylthio,[5,6] *o*-hydroxyphenyl,[7] cyclopropyl,[8,9] vinyl,[10] methylthio,[11] *p*-methoxyphenyl,[12] *p*-tolyl,[13] methoxy,[13] arylethynyl,[14,15] and several aryl groups.[16,17] For Y = $N(CH_3)_2$[3,4] and $NHCH_3$[18] the intermediate cyclopropyl cations have been observed in NMR.

These observations are in line with ab initio molecular orbital calculations, which have suggested that the stabilization of the cyclopropyl cation by amino (and also hydroxy) substituents is so great that these species are not only more stable than the substituted perpendicular allyl cations but should be significantly more stable than the corresponding planar allyl cations.[19]

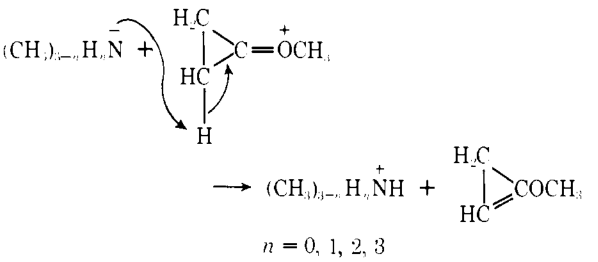
Evidence is now presented to show that 1-methoxycyclopropyl cations **1** are stable species in the gas phase and can be distinguished from the isomeric 2-methoxyallyl cations **2**. These ions have been generated independently in an ion cyclotron resonance drift cell[20] by electron impact ionization of 1-bromo-1-methoxycyclopropane[21] and 2-methoxyallyl bromide,[22] respectively, as shown in reactions 1 and 2. In the ions **1** the charge can be spread over the oxygen and adjacent cyclopropyl carbon atom, whereas in ions of structure **2** the charge is delocalized over the terminal carbon atoms. Ions **1** may be regarded as methyl cation bonded cyclopropanone species and, in contradistinction to ions **2**, they are therefore expected to be able to act as methyl cation donors to n-donor bases which have higher methyl cation affinities[23] (MCA) than cyclopropanone. Although the available MCA data are limited, amines are known to have higher MCA's than ketones: for example MCA(NH_3), 106; MCA(CH_3NH_2), 117, and MCA(CH_2O), 74 kcal/mol.[24] Possible reactions of ions **1** and **2** with ammonia, methylamine, dimethylamine, and trimethylamine have therefore been investigated by double resonance[20] experiments. They have all shown that ions **1**, but not ions **2**, do indeed transfer a methyl group as cation to these bases as summarized in eq 3. Variation of the electron energy used in the generation of the ions **1** and **2** over the range from 12 to 50 eV does not affect this observation. Furthermore, replacement of the methyl group in the ions **1** by a trideuteriomethyl group[25a] confirms the transfer of the original methyl group in reaction 3.





(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 $(\eta\text{-}C_5H_5)W(PPh_3)(CO)(CSPh)$: 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, $(\eta\text{-}C_5H_5)W(PPh_3)(CO)(CSPh)$, 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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