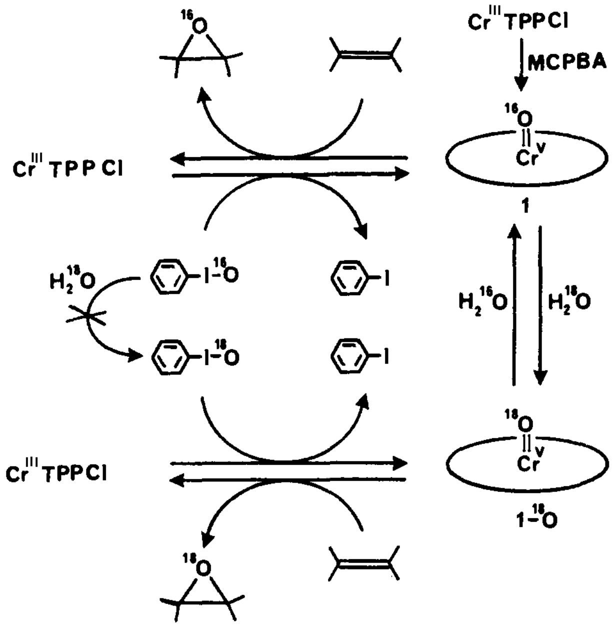
Scheme I



of methylene chloride caused by $Cr^{III}TPPCl$ (8 mg/mL) was found to be 7.4 Hz at 60 MHz. This shift corresponds to an experimental magnetic susceptibility of $3.8 \pm 0.2\ \mu_B$, in very good agreement with the theoretical spin-only value of $3.87\ \mu_B$ expected for chromium(III). The corresponding paramagnetic shift of **1** (6 mg/mL) was 0.95 Hz which corresponds to a magnetic susceptibility of $2.05 \pm 0.2\ \mu_B$. This low value is close to the spin-only magnetic susceptibility of $1.73\ \mu_B$ expected for a chromium(V) complex. Partial decomposition of the intermediate in the NMR probe (35 °C) was apparent during the measurement and would account for the small observed discrepancy.[13] Treatment of this solution of **1** with cyclohexanol caused the magnetic susceptibility to increase again to $3.8 \pm 0.2\ \mu_B$ consistent with the regeneration of $Cr^{III}TPPCl$.

Cytochrome P-450 is known to incorporate one oxygen atom from molecular oxygen into substrate molecules while the other appears as water.[2] It has been observed, however, that the oxidation of cyclohexane by cytochrome P-450 in the presence of $H_2{}^{18}O$ leads to a small but distinct amount (9%) of ^{18}O incorporation into the cyclohexanol.[14] A chemically reasonable explanation is that a transient intermediate in the oxidative cycle undergoes partial exchange of its oxo ligand before oxygen transfer takes place. An intermediate equivalent to FeO^{3+} is an attractive choice[15,16] since oxo-metal complexes are known to undergo oxygen exchange in water.[17]

We have found that treatment of **1** with excess $H_2{}^{18}O$ (95% ^{18}O) caused the disappearance of $\nu_{\mathrm{CR^{16}O}}$ at 1026 and appearance of $\nu_{\mathrm{Cr^{18}O}}$ at 982 cm^{-1}. The reaction of this exchanged material (**1**-^{18}*O*) with norbornylene afforded norbornylene oxide with 94% incorporation of the ^{18}O label. Controls indicated that iodosylbenzene did not undergo oxygen exchange under these conditions.[18] Clearly, the oxo ligand of **1** is labile toward aqueous exchange.

A mechanistic scheme consistent with these observations is presented in Scheme I. The generation of this stable oxochromium(V) complex and the observation that it reacts readily with hydrocarbons and exchanges its oxygen with water provide a significant new precedent for the intermediacy of an oxo-iron intermediate in the cytochrome P-450 cycle as well as in the simple iron-porphine system which we have recently described.[5]

Acknowledgments. Support of this work by the National Institutes of Health (GM25923), the National Science Foundation (CHE-77-21849), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. The National Science Foundation provided funds for the purchase of a GC-mass spectrometer.

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Remarkable Influence of Terminal Alkoxy Groups on Carbonyl Ligands as Seen in the New Compounds $Mo(OBu^t)_2(CO)_2(py)_2$ and $Mo_2(OPr^i)_8(CO)_2$

Sir:

Previously it was shown[1] that hydrocarbon solutions of $Mo_2(OBu^t)_6$ ($M{\equiv}M$) react with CO under very mild conditions (room temperature, ≤1 atmo of CO pressure) according to the stoichiometric reaction shown in eq 1.

$$2Mo_2(OBu^t)_6 + 6CO = Mo(CO)_6 + 3Mo(OBu^t)_4 \quad (1)$$

The first step in reaction 1 is rate determining, reversible, and involves the formation of $Mo_2(OBu^t)_6(\mu\text{-}CO)$ in which the CO ligand bridges a Mo=Mo of distance 2.498 (1) Å; ν(CO) is at 1670 cm^{-1} (Nujol mull) and the Mo-C and the C-O distances are 2.02 (1) and 1.21 (2) Å, respectively.[1]

Although analogous carbonylation of $Mo_2(OPr^i)_6$($M{\equiv}M$) also yields $Mo(CO)_6$, the stoichiometry of the reaction differs from that in eq 1. The Mo^{4+} isopropoxide is dinuclear, $Mo_2(OPr^i)_8$, and contains a M=M of 2.523 (1) Å[2] distance and reacts with CO to form a black, paramagnetic crystalline dicarbonyl compound, $Mo_2(OPr^i)_8(CO)_2$.[3] This compound is not thermally stable toward vacuum sublimation, but did

Table I. Pertinent Structural Data for the $Mo(OBu^t)_2(CO)_2(py)_2$ Molecule[a]

bond distances	Å	bond distances	Å	angles	degrees	angles	degrees
Mo-C(1)	1.94	Mo-O(3)	1.94	C(1)-Mo-C(2)	72	O(3)-Mo-O(4)	156
Mo-C(2)	1.95	Mo-O(4)	1.95	N(1)-Mo-N(2)	85	C(3)-O(3)-Mo	140
C(1)-O(1)	1.16	Mo-N(1)	2.34	C(1)-Mo-N(1)	101	C(4)-O(4)-Mo	141
C(2)-O(2)	1.17	Mo-N(2)	2.36	C(2)-Mo-N(2)	102	Mo-C(1)-O(1)	173
						Mo-C(2)-O(2)	174

[a] All distances and angles quoted are significant to ±1 in the last digit quoted.

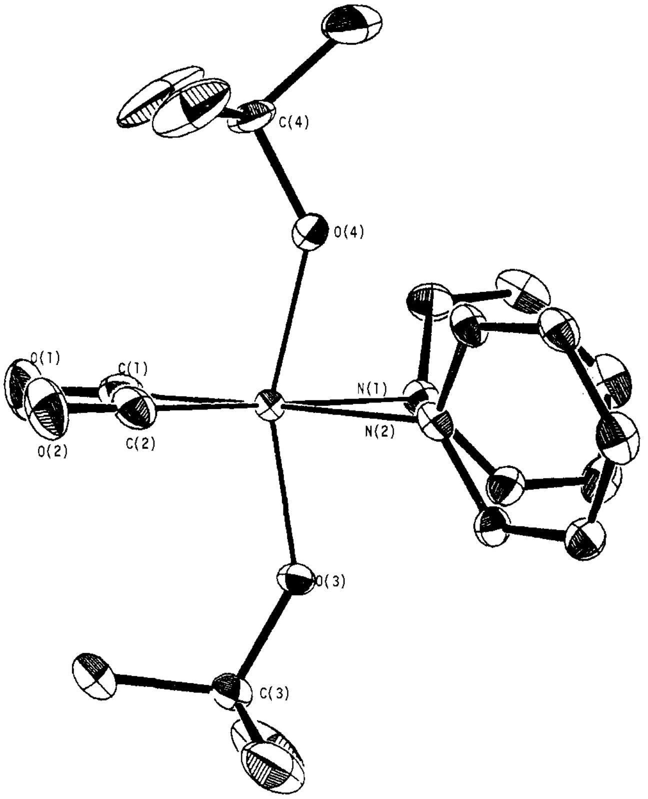


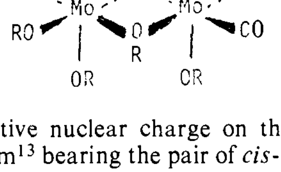
Figure 1. An ORTEP view of the $Mo(OBu^t)_2(CO)_2(py)_2$ molecule showing the atomic numbering scheme used in Table I. Thermal ellipsoids are drawn at the 50% probability level.

yield a strong molecular ion, $Mo_2(OPr^i)_8(CO)_2^+$, in the mass spectrometer.[4] In the infrared spectrum two sharp bands of approximately equal intensity were found at 1940 and 1820 cm^{-1}. This observation, taken together with the details of the mass fragmentation pattern found in the mass spectrum, was suggestive of a pair of cis terminally bonded carbonyl ligands. However, the low values of ν(CO) seemed inconsistent[5] with terminal CO ligands coordinated to a Mo_2^{8+} metal center.

In an attempt to trap alkoxide-carbonyl compounds of molybdenum in a reduced oxidation state in reaction 1, we carried out the mild carbonylation (room temperature, 1 atm of CO pressure) of $Mo_2(OBu^t)_6$ in hexane-pyridine solvent mixtures. In these reactions we obtained a green, air-sensitive, crystalline compound, $Mo(OBu^t)_2(py)_2(CO)_2$.[6] The structure of this new alkoxide-carbonyl compound of Mo^{2+} was solved by a detailed single-crystal X-ray study.[7] An ORTEP view of the molecule, together with the atomic numbering scheme, is shown in Figure 1. As can be seen from the view shown in Figure 1, the immediate coordination geometry about the molybdenum atom is that of a distorted octahedron with a pair of mutually *t*-OBu ligands; the molecule also has a virtual mirror plane containing C(4)-O(4)-Mo(1)-O(3)-C(3). Pertinent bond distances and bond angles are given in Table I.

There are a number of closely related Mo^{2+} compounds known to contain *cis*-CO ligands having the general formula $MoX_2(CO)_2L_2$, where X = halide, or $Mo(CO)_2(S_2X)_2$, where X may be CNR_2 or PR_2 or $P(OR)_2$, all of which contain six-coordinate molybdenum.[8] What is so remarkable about the $Mo(OBu^t)_2(py)_2(CO)_2$ molecule are the exceedingly low values of ν(CO) which are found at 1908 and 1768 cm^{-1} in the infrared spectrum (Nujol and Fluorlube mull). These may be compared, for example, with ν(CO) 1965 and 1895 cm^{-1} found for $MoCl_2(PPh_3)_2(CO)_2$.[8] The average ν(CO) value for $Mo(OBu^t)_2(py)_2(CO)_2$ is 1838 cm^{-1}, which is the lowest average value known (by a long way) for a pair of *cis*-carbonyl ligands coordinated to a Mo^{2+} center. The separation of the two carbonyl stretching frequencies, 140 cm^{-1}, is also the largest known—though, as Cotton[9] back in 1962 predicted, the stretch-stretch interaction constants of a pair of *cis*-carbonyl groups should increase as the π back bonding, Mo-d to CO-π^*, increases; i.e. ν(CO)(A) − ν(CO)(B) will increase as the average value of ν(CO)(A) and ν(CO)(B) decreases. The separation observed here of 140 cm^{-1} is thus unprecedented, but not surprising in view of the average low value of ν(CO) 1838 cm^{-1}. The values of ν(CO) 1908 and 1868 cm^{-1} differ little from the two ν(CO) values found in (dien)-$Mo(CO)_3$, 1898 and 1758 cm^{-1}, which have A and E symmetry, respectively.[10] Moreover, the distances of the Mo-C, and C-O (carbonyl) bonds in $Mo(OBu^t)_2(py)_2(CO)_2$ are, within experimental error, the same as those reported for *cis*-(diethylenetriamine)molybdenum tricarbonyl[11] for which the six electrons of the t_{2g} set in an octahedral environment are fully available for π back bonding to the CO π^* orbitals. Note also that the oxidation state of molybdenum is zero in (dien)-$Mo(CO)_3$.

We believe that the structure of the $Mo_2(OPr^i)_8(CO)_2$ molecule is closely related to that of the $Mo(OBu^t)_2(py)_2(CO)_2$ molecule: the pair of *cis*-pyridine ligands are replaced by a pair of bridging alkoxy ligands as shown.[12] The net



increase in effective nuclear charge on the six-coordinate molybdenum atom[13] bearing the pair of *cis*-carbonyl ligands shifts the values of ν(CO) from 1908 and 1768 cm^{-1} in $Mo(OBu^t)_2(py)_2(CO)_2$ to 1940 and 1820 cm^{-1} in $Mo_2(OPr^i)_8(CO)_2$. Note that the increase in the average values of ν(CO) (1838 cm^{-1} in $Mo(OBu^t)_2(py)_2(CO)_2$ to 1880 cm^{-1} in $Mo(OPr^i)_8(CO)_2$) produces a decrease in the separation of the two ν(CO) bands (140 cm^{-1} in $Mo(OBu^t)_2(py)_2(CO)_2$ to 120 cm^{-1} in $Mo_2(OPr^i)_8(CO)_2$) which is again in accord with the original prediction by Cotton.[9]

We attribute the anomalously low ν(CO) values found in these new compounds to the following effect. The terminal RO^- ligand is a good π donor, which has the effect of raising 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.

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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 $Mo(CO)_6$ 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 $R(F) = 0.0433$, $R_W(F) = 0.082$.

(8) See values quoted for compounds containing the *cis*-$Mo^{2+}(CO)_2$ moiety in G. J. J. Chen, R. O. Yelton, and J. W. McDonald, *Inorg. Chim. Acta*, **22,** 249 (1977), and references therein.

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(11) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4,** 314 (1965).

(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.

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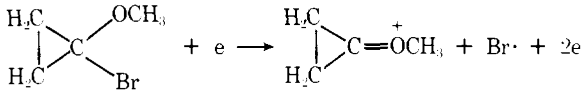
Independent Existence in the Gas Phase of the 1-Methoxycyclopropyl and 2-Methoxyallyl Cations, as Observed in an Ion Cyclotron Resonance Spectrometer[1]

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.

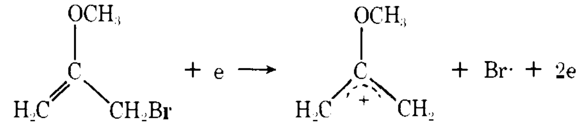
These observations are in line with ab initio molecular orbital calculations, which have suggested that the stabilization of the cyclopropyl cation by amino (and also hydroxy) substituents is so great that these species are not only more stable than the substituted perpendicular allyl cations but should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



(1)

1



(2)

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