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(4) The water-soluble metabolites of cannabinoids apparently are not all of the same chemical type. β-Glucuronidase type L-1 has been reported to release only ~30% of "conjugated" cannabinoids present in rat bile.[2a]

(5) D. J. Harvey, B. R. Martin, and W. D. M. Paton, *Biochem. Pharmacol.*, **25**, 2217 (1976). After this communication was submitted for publication, we were informed by Dr. D. J. Harvey that *O*-glucuronides of seven cannabinoids and some of their hydroxy and acid metabolites were identified by the Oxford group, as in vivo liver metabolites (D. J. Harvey, B. R. Martin, and W. D. M. Paton, *Res. Commun. Chem. Pathol. Pharmacol.*, **16**, 265 (1977)). It was pointed out, however, that these conjugates are not the only type of water-soluble metabolites present.

(6) The only *C*-glucuronide metabolites reported so far are of certain pyrazolidine-containing drugs which possess a strongly acidic hydrogen, but no hydroxyl or amino groups: W. J. Richter, K. O. Alt, W. Dieterle, J. W. Faigle, H. P. Kriemler, H. Mory, and T. Winkler, *Helv. Chim. Acta*, **58**, 2512 (1975).

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(10) Δ^6-THC-*C*-6′-glucuronide methyl ester triacetate (**5a**): NMR ($CDCl_3$) δ 0.85, 1.00, 1.32 (pyran ring and side-chain CH_3s), 1.61 (olefinic CH_3), 1.69 (C-2′ sugar $OCOCH_3$), 1.98, 2.00 (2 sugar $OCOCH_3$), 3.63 ($COOCH_3$), 3.83–4.30 (C-5′ sugar H), 4.50 (br d, J = 10 Hz, C-1′ sugar H), 5.00–5.60 (4 H, olefinic and C-2′, C-3′, C-4′ sugar H), 6.0 (arom H); mass spectrum (rel intensity) *m/e* 630 (46), 611 (5), 571 (7), 570 (7), 547 (19), 511 (10), 510 (8), 467 (8), 451 (100), 421 (13), 409 (66), 343 (27), 299 (15), 231 (20), 221 (27). Δ^6-THC-*C*-6′-glucuronide methyl ester tetraacetate (**5b**): nmr ($CDCl_3$) δ 0.9, 1.10, 1.35 (pyran ring and side-chain CH_3s), 1.68 (olefinic CH_3), 1.75 (C-2′ sugar $OCOCH_3$), 2.01, 2.03 (2, $OCOCH_3$), 2.25 (phenolic $OCOCH_3$), 3.70 ($COOCH_3$), 3.90–4.35 (C-5′ sugar H), 4.62 (br d, J = 10 Hz, C-1′ sugar H), 4.98–5.75 (4 H olefinic and C-2′, C-3′, C-4′ sugar H), 6.38 (arom H); mass spectrum (rel intensity) *m/e* 672 (50), 630 (27), 613 (13), 612 (9), 589 (16), 547 (11), 511 (14), 510 (11), 493 (68), 451 (100), 409 (27), 391 (25), 349 (43), 343 (18), 299 (17), 231 (14), 221 (25).

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(13) After this communication was submitted for publication we were informed by Professor C. Fenselau that in her laboratory *O*-glucuronides of cannabinol, cannabidiol, Δ^1- and Δ^6-THC (characterized by GLC–mass spectrometry) were obtained by an enzymatic synthesis closely related to the one used by us. However the partially purified UDPglucuronyltransferase used by the Baltimore group was immobilized on cyanogen bromide activated sepharose, while ours was a commercially available enzyme. This difference may perhaps explain the divergency of results (M. A. Lyle, S. Pallante, K. Head, and C. Fenselau, *Biomed. Mass Spectrom*, **4**, 190 (1977)).

B. Yagen,* S. Levy, R. Mechoulam*
Department of Natural Products
The Hebrew University—Pharmacy School
Jerusalem, Israel

Z. Ben-Zvi
Clinical Pharmacology Unit, Faculty of Health Science
Ben-Gurion University, Beer-Sheva, Israel

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Unusual Reactions of a Bridged Hydride Ligand in Aqueous Solution

Sir:

Bennett, Brencic, and Cotton[1,2] synthesised the salt $Cs_3Mo_2Cl_8H$ (compound I) and analogous salts $M^I_3Mo_2X_8H$ (M^I = Cs, Rb; X = Cl, Br). The complex ion $Mo_2Cl_8H^{3-}$ was shown to have two bridging chlorides and one bridging hydride between the two molybdenum(III) atoms.[2] The band at 1245 cm^{-1} in the IR spectrum of I was assigned to the anti-symmetric Mo–H–Mo stretching by Cotton and Kalbacher[2] and was shifted to 904 cm^{-1} in the deuterium-substituted salt[2] $Cs_3Mo_2Cl_8D$. These authors also observed that the decomposition of the ion $Mo_2X_8H^{3-}$ by water was accompanied by evolution of H_2 gas. Using the deuterium-substituted salt in H_2O they discovered that the main product of the reaction was HD, thereby proving that the bridging D^- was oxidized by an aqueous proton, $D^- + H^+ \rightarrow HD$.

The Mo species produced in the decomposition of I in water was examined in this laboratory. When the reaction is carried out in dilute aqueous acids (e.g., HCl 1 M or *p*-toluenesulfonic acid 1 M) the yellow solution of $Mo_2Cl_8H^{3-}$ quickly turns red, and then is slowly converted to a green end product. The second stage is accompanied by H_2 evolution. The green species was identified by ion-exchange chromatography and UV-vis spectrum, as the dichloromolybdenum(III) dimer[3] $Mo_2(OH)_2Cl_2^{2+}$. The net apparent oxidation number per molybdenum atom in compound I was 2½ as determined by permanganate titration in which molybdenum(III) is oxidized to 6+ and H^- to H^0 (H_2 is evolved during the titration). The same result is obtained with the intermediate red species which is probably a partially aquated product of I. During the conversion of the red species to the green molybdenum(III) dimer, the oxidation number increases until it reaches 3+ at the end of the reaction, as expected.

When fresh yellow solution of I reacts with acetic acid, a deep violet solution is formed. The oxidation number at this stage remains 2½+. The violet solution decomposes slowly, *without* any formation of gaseous H_2, to a yellow solution. The oxidation number *drops* during this stage from 2½+ to 2.0+. The spectrum of the yellow end product is identical with that of $Mo_2(OAc)_4$ and crystals of this compound are slowly precipitated from the solution. The reduction of the molybdenum atoms from 3+ to 2+ can only be explained by an accompanying oxidation of the H^- ligand to H^+.

$$2Mo^{III} + H^- \rightarrow 2Mo^{II} + H^+$$

This reaction is, in fact, the reversal of the reaction in which I is obtained from $Mo_2(OAc)_4$ by hot concentrated HCl.[1] Similar violet species are obtained from I with other carboxylic acids, amino acids, and other ligands containing a carboxylate group. All these violet species are slowly converted to the respective molybdenum(II) compounds. The violet species, obtained from I with glycine was absorbed on an ice-cooled cation-exchange column (Dowex 50X2) and eluted as a distinct band by 3 M acid (HCl or H_2SO_4). The eluted violet species did not contain any chloride. The visible absorption spectrum had maxima at 660 nm (ϵ 45), 538 (75), and 410 (sh) (58). The oxidation number was 2½+. H_2 was produced during the titration by permanganate as with I. The structural relation of the violet species to I was demonstrated by reversing the substitution reaction of Cl^- by glycine: addition of concentrated HCl to the violet species followed by CsCl precipitates the salt I. The retention of the μ-hydrido bridge in the violet species was further supported by the use of $Cs_3Mo_2Cl_8D$. This salt was prepared following the procedure of Cotton and Kalbacher.[2] It was reacted with glycine in H_2O and the violet species was separated chromatographically. Finally I was precipitated by

Table I. Infrared Absorptions (cm^{-1}) of $Mo_2(gly)_4Cl_4$. Compound II with H and II with D

$Mo_2(gly)_4Cl_4$	II with H	II with D
3390 (m, br)	3390 (m, br)	3390 (m, br)
3150 (m, vvbr)	3150 (m, vvbr)	3150 (m, vvbr)
	1635 (w, br)	
1600 (m, br)	1600 (m, br)	1600 (m, br)
1545 (m)	1545 (m)	1545 (m)
1460 (s)	1460 (s)	1460 (s)
1420 (s)	1420 (s)	1420 (s)
1345 (s)	1345 (s)	1345 (s)
1310 (m)	1310 (m)	1310 (m)
		1165 (w, br)
1110 (s)	1100 (s)	1100 (s)
1045 (m)	1040 (s)	1040 (s)
	965 (w)	965 (w)
900 (s)	890 (s)	890 (s)
	790 (w, br)	790 (w, br)
700 (m)	690 (m)	690 (m)
	660 (w)	
615 (s)	610 (s)	610 (s)
585 (m)	585 (m)	585 (m)
		472 (w)
425 (m)	435 (s)	435 (s)
340 (w)	345 (m)	345 (m)

addition of concentrated HCl and CsCl as above. The IR spectrum of I obtained in this way still possessed the Mo-D-Mo band[2] at 904 cm^{-1} and not the Mo-H-Mo band at 1245 cm^{-1}.

A crystalline gray-violet precipitate (compound II) separates slowly from an ice-cooled concentrated solution of the violet species in 3 M HCl. Single crystals suitable for x-ray crystallography were not obtained. The IR spectra of II, of deuterated II, and of $Mo_2(gly)_4Cl_4$, measured in Nujol mull and KBr pellets, are presented in Table I. Cotton and Webb[4] proved that the glycine ligands are coordinated to the two molybdenum(II) atoms in $Mo_2(gly)_4{}^{4+}$ by bridging carboxylates. The striking similarity between the spectrum of $Mo_2(gly)_4Cl_4$ and that of II columns 1 and 2, Table I) indicates that glycine is coordinated in II in the same way. The IR bands of II at 1635 and 660 cm^{-1} probably belong to the Mo-H-Mo vibrations (stretching and bending, respectively). In crystals of II obtained from $Cs_3Mo_2Cl_8D$ these bands are replaced by bands at 1165 and 472 cm^{-1} (Table I, column 3). These shifts are expected for an increase in the reduced mass by a factor of two. Analysis of II (found: Mo, 35.40; C, 9.2; N, 5.2; H, 2.7; Cl, 26.2) conforms to $[Mo_2(gly)_2H]Cl_4 \cdot 3H_2O$ (calcd: Mo, 35.68; C, 8.92; N, 5.20; H, 3.16; Cl, 26.39).

The chemical and spectroscopic evidence presented here indicates that two molybdenum(III) atoms are bridged by two carboxylic ligands, as in $[Mo_2(gly)_4]^{4+}$ [4] and by one hydride ligand as in I[2]. The charge 4+ of the complex ion, rather than 5+, may be due to the existence of an additional OH^- ligand (instead of one H_2O) in a bridging or terminal position. Alternatively, the charge 4+ may be due to the protonation of only one of the two amino groups of the complex ion. Efforts are made to obtain single crystals of II for x-ray analysis.

The difference between the oxidation reactions of the hydride ligand of I and II in aqueous solution may be due to a stronger and shorter metal to metal bond in the latter which enables its conversion to a quadruple bond and the accompanying oxidation of H^- to H^+. A shorter Mo-Mo bond in II is expected on steric grounds; bridging chlorides impede the approach of the Mo atoms to each other,[2] whereas bridging carboxylates fit in, and stabilize very short Mo-Mo bonds, as for example in $Mo_2(OAc)_4$ and $Mo_2(gly)_4(SO_4)_2 \cdot 4H_2O$.

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A. Bino and M. Ardon*
Department of Inorganic and Analytical Chemistry
The Hebrew University, Jerusalem, Israel

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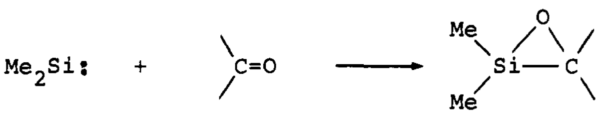
Evidence of the Formation of Oxasilacyclopropane from the Reaction of Silylene with Ketone

Sir:

Strained ring systems containing a silicon atom have long intrigued chemists, owing to their high reactivity resulting from the high strain energy.[1,2] Kumada,[3] Weber,[4] Skell,[5] and Seyferth[6] have provided the data for the evidence of silacyclopropane in the reaction of silylene and carbon-carbon double bond, and, in 1972, Lambert and Seyferth[7] were successful in preparing a stable silacyclopropane. More recently, Gaspar[8] has isolated tetramethyl-1-silacycloprop-2-ene at room temperature, as the addition product of dimethylsilylene to 2-butyne.

While many routes to silacyclopropanes and silacyclopropenes[9,10] have been investigated, there is no report on the synthesis of small ring compound containing silicon and oxygen. We previously reported evidence for a 1,2-silaoxetane intermediate from the intramolecular C-H insertion of siloxycarbene in the gas phase pyrolysis of silyl phenyl ketone.[11] No successful report of a three-membered-ring compound, with ring silicon and oxygen has appeared. We have strong evidence that it was synthesized as the addition product of dimethylsilylene to ketone.



Gas phase flow pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane (I, 3 mmol) in a nitrogen flow system (30 mL/min, at 700 °C) was employed to generate dimethylsilylene in the presence of fivefold excess of benzophenone with 40-fold excess benzene and the pyrolysate collected at −78 °C. Analysis of the pyrolysate by gas chromatography revealed three main components. Separation of these components by preparative gas chromatography afforded dimethyldimethoxysilane (II), 1,1-diphenylethylene (19%), and 1,1-dimethyl-1-sila-2-oxa-3-phenyl-4,5-benzocyclopentene (III, 17%). Pyrolysis of I with benzophenone and benzene at 500 °C gave II and III (24%) as main products (Scheme I). These products were identified by comparison of their GLC retention times and NMR and IR spectra with those of authentic samples.[11] It is possible that the silylene attacks on the π bond of carbonyl to produce the intermediate oxasilacyclopropane (IV) (Scheme II). Such a molecule could thermally cleave the silicon-carbon bond to give 1,5 diradical V followed by recombination to give product III. In this case, direct formation of 1,3 diradical is probably inconsistent with the demonstrated singlet nature of dimethylsilylene.[5,12] It is also known that in gas phase dimethylsilylene partially undergoes 1,2-hydrogen shift to methylsilene (VI).[13] Thus, the formation of 1,1-diphenylethylene may arise from the decomposition of 1,2-silaoxetane (VII) formed from the cycloaddition of the silene and carbonyl of benzophenone.[11,14]

Alkyl ketones (VIII) such as diethyl ketone, cyclohexanone, and acetophenone were found to react with dimethylsilylene generated from the gas phase flow pyrolysis of I with benzene