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THE ISOLATION AND CHARACTERIZATION OF COPPER METHYLENE VIA MATRIX ISOLATION SPECTROSCOPY

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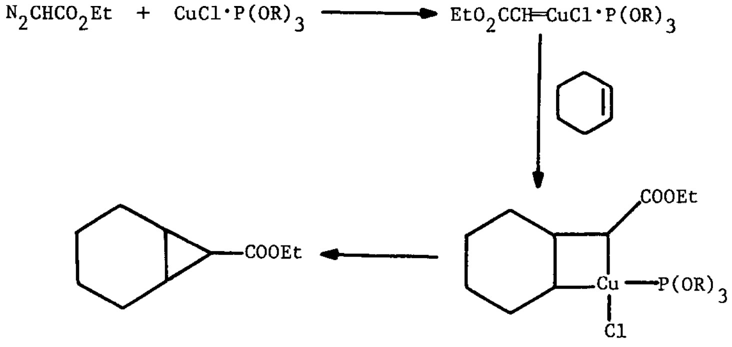
Summary: The reactions of copper atoms with diazomethane have been investigated via FTIR matrix isolation spectroscopy. In argon matrices $CuCH_2$ and N_2CuCH_2 have been characterized whereas only N_2CuCH_2 is observed in nitrogen matrices.

The copper-catalyzed decomposition of diazo compounds is an old reaction[1] which continues to be used extensively in synthesis (cyclopropanation). Several studies[2] support a copper-methylene complex as proposed originally by Yates.[3] More recently, a metallacycle mechanism has been invoked by Negishi[4] to account for the cyclopropanation reaction as exemplified by the following scheme:



To the best of our knowledge, no spectroscopic evidence for copper-methylene complexes has been reported.[5] In this communication we report the isolation and characterization of $CuCH_2$ by FTIR matrix isolation spectroscopy.

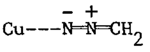
Copper atoms were codeposited with a mixture of argon and diazomethane[6] onto a rhodium-plated copper mirror at 11 K using the apparatus described previously.[7] The infrared spectrum, measured with an IBM IR98 Fourier Transform Spectrometer, showed peaks at 3034.7, 2960.7, 1344.9, 614.0, and 526.0 cm^{-1} which can be assigned to the unligated species $CuCH_2$. The assignments of these bands along with those of the isotopically labeled species are verified and confirmed with a normal coordinate analysis and presented in Table I. A doublet splitting with a 2:1 ratio for the 614.0 cm^{-1} band indicates that this absorption is due to a CuC stretching mode where only one copper atom is involved (natural abundance of Cu^{65} = 69.1%, Cu^{63} = 30.8%).

Table I. Measured and Calculated Infrared Frequencies (cm^{-1}) for $CuCH_2$, $Cu^{13}CH_2$, CuCHD, and $CuCD_2$ in Solid Argon.

	$CuCH_2$		$Cu^{13}CH_2$		CuCHD		$CuCD_2$	
Vibration Mode	obs	cal	obs	cal	obs	cal	obs	cal
CH_2 s-stretch	2960.7	2961.6	2955.6	2954.8	2219.0	2218.5	------	2160.4
CH_2 scissor	1344.9	1346.0	1338.6	1339.7	1196.0	1191.8	1013.7	1015.2
CuC stretch	614.0	615.6	597.6	599.4	610.9	609.6	570.4	567.2
CH_2 a-stretch	3034.7	3035.9	3024.1	3022.9	2996.6	2996.7	------	2263.4
CH_2 rock	------	573.2	------	569.9	------	474.1	------	433.2
CH_2 wag	526.0	524.8	521.7	520.0	471.0	472.3	409.1	413.0

Two additional species were also characterized. One exhibited a spectrum analogous to CH_2N_2 and was assigned to a $Cu(CH_2N_2)$ complex. The other showed absorption peaks at 2957.3, 2279.9, 600.3, and 573.5 cm^{-1}. The strong absorption at 2279.9 cm^{-1} assigned to a N≡N stretching mode and the similarity of the remaining bands to those of $CuCH_2$ led to the assignment of this species as a $CuCH_2(N_2)$ complex.

Photolysis of the matrix at $\lambda \geq$ 500 nm led to the disappearance of bands assigned to the $Cu(CH_2N_2)$ adduct with a simultaneous 2:1 enhancement of bands assigned to $CuCH_2$ and N_2CuCH_2, respectively, as compared to a 4:1 ratio for the spontaneous reaction observed upon deposition. Possible structures for the $Cu(CH_2N_2)$ adducts are:



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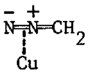
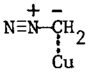


2



3

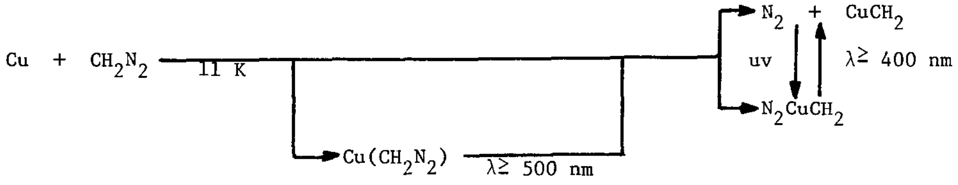
Structures **1** and **2** would probably be trapped, whereas **3** might proceed directly to product.

Additional photolysis studies showed that the two sets of bands assigned to $CuCH_2$ and N_2CuCH_2 are photoreversible. Thus the set assigned to N_2CuCH_2 decreases in intensity due to photodissociation of N_2 after $\lambda \geq$ 400 nm photolysis, whereas uv photolysis leads to the reverse process.

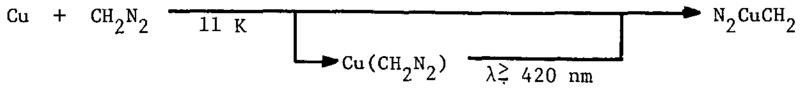
Both spontaneous and photo-assisted reactions via $Cu(CH_2N_2)$ adducts are also observed in nitrogen matrices. The vibrational absorptions of the insertion products in the nitrogen matrices are generally similar to N_2CuCH_2 in argon matrices. Thus it seems likely that only one N_2 molecule is interacting significantly with $CuCH_2$ in the nitrogen matrix. The coordinated N_2 cannot be photodissociated.

The overall reaction pattern of copper atoms in cryogenic matrices can then be summarized as follows:

In Argon Matrices



In Nitrogen Matrices



Acknowledgment

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