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DISCOVERY OF METHYLCHLOROSILYLENE (CH_3SiCl:) AS A KEY INTERMEDIATE IN THE DIRECT SYNTHESIS OF DIMETHYLDICHLOROSILANE, $(CH_3)_2SiCl_2$

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Preambulo

En uno de los números recientes de la revista Organometallics (2021, 40, 459-462) en la que se incluye una sección dedicada a personalidades pioneras en la química organometálica y cuyas investigaciones han tenido gran influencia en el campo industrial, se hace referencia al Dr. Kenrick M. Lewis, cuyos trabajos son reconocidos al impactar en aspectos fundamentales de la química de organosilanos, entre ellos, la famosa reacción directa de producción de diclorodimetilsilano (Me_2SiCl_2), compuesto químico esencial para la industria moderna de los polímeros de silicio. En este número de la revista Naturaleza y Tecnología, el Dr. Lewis generosamente comparte los detalles que condujeron al descubrimiento de una especie química intermediaria clave en el proceso de síntesis del referido compuesto y que en años recientes publicó, luego de qué durante un buen tiempo al ser parte de un secreto industrial, la información estuvo reservada.

Con el propósito de obtener una mejor comprensión de la descripción que el Dr. Lewis presenta en este artículo de divulgación, conviene hacer referencia a la reacción química involucrada, llamada Síntesis Directa o Proceso Directo, y que se clasifica como una adición oxidante sólido-gas catalizada por cobre. El Me_2SiCl_2 era conocido con anterioridad desde antes de la Segunda Guerra Mundial, sin embargo, su síntesis, se basaba en una reacción de metátesis entre tetracloruro de silicio ($SiCl_4$) y un reactivo de Grignard, por ejemplo, MeMgBr. Se conocía que su hidrólisis permitía obtener el poli(dimetilsiloxano), por lo que resultaba muy conveniente y atractiva su síntesis debido a su estabilidad térmica y a muchas aplicaciones que potencialmente se podrían desarrollar en aislantes para motores eléctricos, radios de vuelo y muchas más, motivado a la vez por la necesidad de materiales con aplicaciones militares. Sin embargo, la reacción no era factible de ser escalada o trasladada a una producción industrial, lo que llevó a que el profesor Eugene Rochow en General Electric, y durante la Segunda Guerra, descubriera que la reacción directa entre silicio y cloruro de metilo en fase gas, catalizada por cobre, generaba principalmente el compuesto deseado.

$$2CH_3Cl(g) + Si(s) \rightarrow (CH_3)_2SiCl_2(l) \qquad (1)$$

La referencia que se hace en el número de Organometallics arriba citado, menciona que el resultado de la reacción fue publicado por Rochow en un artículo de 3 páginas (The Direct Synthesis of Organosilicon Compounds, J. Am. Chem. Soc. 1945, 67, 963−965), que no

importando lo breve, se considera como uno de los artículos más importantes en la química orgánica de silicio por el impacto que a lo largo de los años ha tenido en la industria química. Años después se conoció y se reconoció, que por los mismos años (1945) Richard Müller en Alemania, había trabajado de igual manera en la misma reacción, por lo que el proceso es llamado también la Síntesis Directa Rochow-Müller (Müller publicó su experiencia en One hundred years of organosilicon chemistry. J. Chem. Educ. 1965, 42, 41). El primer experimento exitoso de Rochow generó 5 mL de Me_2SiCl_2, cantidad obviamente difícil de considerar viable como un producto para dar lugar a tantas aplicaciones. Sin embargo, luego de investigaciones y desarrollos tecnológicos en los que se involucraron diseño de reactores de lecho fluidizado, de haber optimizado el empleo del catalizador de cobre, se sabe que en la actualidad se producen algo así como 1.4 millones de toneladas métricas anualmente de esta molécula que ha sido pieza clave en la industria química moderna de los polímeros de silicio.

Abstract

My intention, in this memoir, is to document the events leading to discovery of methylchlorosilylene (silylenoid) as a key intermediate in the Rochow-Müller Direct Synthesis of dimethyldichlorosilane. In particular, I want to discuss the influence of various factors and individuals and pay tribute to mentors and contributors.

Key words: methylchlorosilylene, Direct Synthesis, Rochow-Müller, dimethyldichlorosilane

Resumen

El propósito en esta memoria es dar a conocer, las etapas y eventos que dieron lugar al descubrimiento de la especie metilclorosilileno (sililenoid) como un intermediario clave en la Síntesis Directa Rochow-Müller. De manera particular, deseo discutir la influencia de distintos factores y situaciones específicas que dieron lugar al descubrimiento, y a la vez pagar tributo a mis guías, a mis consejeros y a mis colaboradores.

Palabras clave: metilclorosilileno, Síntesis Directa Rochow-Múller, diclorodimetilsilano

When, in January 1979, I transferred from the Linde Research Department of Union Carbide to the Exploratory and Basic Group of Silicones R&D, one of my first assignments was to identify and develop exploitable concepts and phenomena to improve the performance of the Rochow-Müller Direct Synthesis of methylchlorosilanes. Dr. Bernie Kanner, my Group Manager, had told me that there was much that was still unknown about the reaction, despite almost forty years of commercial practice at that point. I was excited by the fact the Direct Synthesis is a copper-catalyzed reaction. My fascination with copper chemistry had started during my senior year at the University of Alberta (Edmonton) with a lecture by Prof. Robert Jordan on the physiological role of copper enzymes and copper proteins. It continued through graduate school at the University of Massachusetts (Amherst), where I had studied the corrosion chemistry of the copper intrauterine device (IUD) during my doctoral research. In the Linde Research Department, use of chelation technology to recover copper and other metals from industrial wastes and hydrometallurgical solutions was one of my projects. Now, in Silicones R&D, I was going to study the catalysis of the Direct Synthesis with emphasis on the role of copper.

My review of the published literature had revealed that the role of copper in the catalysis had not been elucidated. Prevailing ideas about the mechanism of the Rochow-Müller Direct Synthesis of dimethyldichlorosilane had originated from the research of Voorhoeve and coworkers, and van den Berg and coworkers in The Netherlands, Bazant and coworkers in Czechoslovakia and from Golubtsov, Lobusevich and coworkers in the USSR. Voorhoeve's monograph, ***Organohalosilanes: Precursors to Silicones***, was the primary authoritative source of published information. The tenets of the prevailing hypothesis were:

1. Cu_3Si (η phase) is the active catalyst leading to selective formation of $(CH_3)_2SiCl_2$.

2. The polarity of the metal – silicon bond in metal silicides determines or influences product selectivity.

3. The Cu – Si bond energy (46 kcal/mole) is greater than the Si – Si bond energy (42 kcal/mole).

4. Promoters, particularly zinc, cadmium and antimony, enhance catalytic activity and selectivity when used in small (< 1 weight percent) amounts.

5. Neither methyl chloride adsorption nor copper diffusion is the rate-limiting step of the reaction.

6. Methyl chloride is dissociatively chemisorbed on the catalytic surface.

7. The reaction follows Langmuir-Hinshelwood kinetics.

8. $(CH_3)_2SiCl_2$ is formed from a surface intermediate with dimethylsilyl groups.

At the conclusion of his Plenary Lecture at the International Symposium on Organosilicon Chemistry in 1969, Bazant acknowledged the difficulty of mechanistic research on a reaction as complex as the Rochow-Müller Direct Synthesis of methylchlorosilanes (see ***Pure & Applied Chem., 19(1969) 473 – 488***). This is a copper-catalyzed, gas – solid reaction, not the familiar reaction of gaseous reactants over a heterogeneous catalyst. Bazant's remarks inspired the surface-chemical investigations, which we initiated in 1980. Our objectives were:

- To understand the significance of bonding, thermochemical and morphological changes accompanying alloy formation in the Cu-Si binary and Cu-Si-Zn ternary systems.

- To determine surface compositions in these systems in the temperature range (280° – 350°C) in which selectivity to dimethyldichlorosilane is high.

- To characterize the valence states of Cu, Zn and Si in these systems *in vacuo* and following methyl chloride chemisorption.

- To elucidate structure and composition of the surface intermediates and active sites following chemisorption.

- To assess state-of-the-art mechanistic proposals and make new ones consistent with the surface analytical results.

- To exploit findings that will improve the performance of our commercial reactors.

Although our research was begun independently, it soon became a joint effort with that of Prof. John Falconer's group at the University of Colorado (Boulder). John's group used Auger Electron Spectroscopy (AES) and Temperature Programmed Desorption/ Mass Spectrometry (TPD/MS) and we, at Tarrytown, employed X-Ray Photoelectron Spectroscopy (XPS) and Mass Spectrometry. Early on, John and his collaborators (Timothy Frank and Keith Kester) and Don McLeod and I both discovered the surface enrichment of silicon which occurs on copper - silicon alloys and solid solutions and the enhancement of this enrichment by zinc, a known promoter of selectivity to dimethyldichlorosilane. Lead, a well-known poison of the reaction, inhibited the surface enrichment of silicon. High tin concentrations also suppress silicon surface enrichment. Tin-induced zinc surface enrichment provided evidence of interactive effects of zinc and tin on the catalytic surface. Whereas both zinc and tin were evaporated from the surface above about 450 K at 10^{-10} torr, lead was retained. The Boulder team showed that silicon surface enrichment was predicted by the empirical rule of Burton and Machlin. Their results were published in ***Applied Surface Science, 14(1982 – 83) 359***. We showed that the thermodynamics of silicon enrichment was in agreement with the comprehensive model of Wynblatt and Ku, but it was 1987 before we were permitted to publish our results (***Catalysis 1987, J. W. Ward, Editor, pp 415 – 434***).

In the meantime, we had calculated the Cu-Si bond energy to be 30.6 ± 2.4 kcal/mole, that is, less than the Si-Si bond energy of 53 kcal/mole. An independent quantum mechanical calculation by Chou, et al. (***J. Amer. Chem. Soc., 109(1987) 1880***)) found 30.7 kcal/mole as the Cu-Si bond energy. The reduced energy of Cu-Si bonds compared to Si-Si bonds is consistent with copper catalysis and the fact that it is the alloyed silicon, which is reactive. The composition of the catalyst surface at reaction temperatures is 40 - 55 atom % Si and not the 25 atom % expected from the formula, Cu_3Si. In fact, it emerged that Voorhoeve and other researchers had associated Cu_3Si with high catalytic effectiveness because of the accident of its faster nucleation when reacted copper-silicon masses had been cooled to room temperature for x-ray diffraction measurements. Calculation of Auger Parameters and application of various electronegativity scales allowed Don McLeod and me to conclude that, while both copper and silicon are formally zerovalent in Cu_3Si prior to exposure to methyl chloride, the $Cu^{\delta+}$ - $Si^{\delta-}$ bond is polarized with a partial positive charge on copper and a partial negative charge on silicon. These results had challenged and vanquished some of the key tenets of the prevailing hypothesis.

Chemisorption studies with methyl chloride disclosed that there was a desorbable intermediate leaving the catalytic surface above 160°C at 10^{-9} torr. Based on the simultaneous decrease of silicon, carbon and chlorine intensities in the XPS spectra, I concluded that this intermediate contained these three elements. Moreover, with a Si 2p binding energy of 102.8 eV, this species had a silicon valence between those of elemental silicon (Si 2p = 99.3 eV) and tetravalent silicon (Si 2p = 103.4 eV) and was most probably divalent. We did not yet have a mass spectrometer attached to our high vacuum reaction chamber. So, we had no data on the masses of the desorbates. We acquired one later.

At that time, there were only two literature references to the silylene, CH_3SiCl, even though the early eighties was the era in which silylene chemistry was one of the hot organosilicon chemistry topics. Tom Barton's group (***J. Amer. Chem. Soc., 99(1977) 5199 - 5200***), Morey Ring's group, (***Inorg. Chem., 12(1973) 2968 - 2972***) and much later, G. Maier's group (***Chem. Ber., 117(1984) 2369 – 2381; J. Organomet. Chem., 366(1989) 25 - 38***) and Heinecke, et al. (***J. Anal. Appl. Pyrol., 28(1994) 93 - 105***) demonstrated the intermediacy of CH_3SiCl in gas phase trapping experiments. Others before me, for example Rochow, et al., (***J. Amer. Chem. Soc., 74(1952) 5545 – 5546),*** Hertwig (***Z. Naturforsch., 6B(1951) 337 – 338***) and Schenk, et al., (***Z. Anorg. Allg. Chem., 334(1964) 57 – 65***), had suggested that silylenes might be intermediates in the Direct Synthesis, but no experimental verification of these suggestions had been undertaken under Direct Synthesis conditions. I wanted more proof before I proclaimed so revolutionary an idea as an unknown (or unpublished) silylene as a key intermediate in a mechanism, which had been so rife with controversy. At the 1966 International Symposium on Organosilicon Chemistry, Prof. Bazant responded to critical comments on his proposed mechanism by asking the questioners, " were you there and did you see what the active sites and activated complexes looked like?" I wanted to avoid that type of contention.

So it was that in the summer of 1982 that I journeyed to Boulder to share results with Prof. Falconer and review the status of his research. In our first conversation, he said that a desorbate of mass 78 was consistently observed following methyl chloride chemisorption on the silicon-enriched surfaces of copper - silicon catalysts. This species was more abundant than could be accounted for by the mass spectral fragmentation of dimethyldichlorosilane and other methylchlorosilanes. He could not explain its formation. You can well imagine my joy at having independent confirmation of the intermediacy of CH_3SiCl (methylchlorosilylene, mass 78) in the Direct Synthesis as I wrote down, for John's benefit, the silylene insertion reactions that made up my proposed mechanism. We had just successfully challenged another of the basic tenets of Voorhoeve's monograph on the Direct

Synthesis. The Klebansky-Vikhtengol'ts-Voorhoeve mechanism proposed a dimethylsilyl ($(CH_3)_2Si$) intermediate as the surface species leading to $(CH_3)_2SiCl_2$. Later, Timothy Frank showed that the intensity ratio of mass 78/mass 80 ($CH_3Si^{35}Cl/CH_3Si^{37}Cl$) was 0.3 and temperature independent as required by the natural isotopic distribution of chlorine.

As often happens in research, serendipity was to intervene, not once but three times. First, Keith Kester, who had done his doctoral research on the Direct Synthesis of dimethyldichlorogermane with Prof. Rochow at Harvard, was one of John's colleagues and collaborators. He made us aware of results, published only in his dissertation, that $(CH_3)_2GeCl_2$ adsorbed on germanium can decompose to CH_3GeCl, (methylchloro-germylene) and CH_3Cl (methyl chloride) under the influence of radio-frequency fields. This information became significant when we sought to obtain reference XPS and AES/TPD spectra for $(CH_3)_2SiCl_2$ on copper – silicon alloys. The data were indistinguishable from those of methyl chloride on the alloys. In addition, mass 78 and mass 50 (CH_3Cl), both of which are weak in the mass spectrum of $(CH_3)_2SiCl_2$, were quite prominent. Thus, both the Boulder and Tarrytown groups demonstrated that CH_3SiCl and CH_3Cl are formed when $(CH_3)_2SiCl_2$ is chemisorbed on copper-silicon surfaces.

John visited Tarrytown in November 1982 and we both presented seminars on the discoveries and status of the research to the R&D staff. Later, there was a brainstorming session in Bernie's office on what additional confirmatory experiments on the intermediacy of CH_3SiCl in $(CH_3)_2SiCl_2$ formation could be undertaken, how CH_3SiCl might be trapped in laboratory reactors and how this new knowledge might be exploited commercially. Ethylene, acetylene and 1,3-butadiene were suggested as trapping agents, but I was concerned about extensive carbon formation in my fluidized bed reactor. My preferred trapping agents were H_2 and an Si-H monomer like $(CH_3)_3SiH$. A 6 – 15 fold increase in the intensity of the mass 78 peak had been observed in XPS/MS experiments when CH_3Cl – H_2 mixtures had been used for chemisorption. It had been reported in the literature that the insertion of silylenes into H_2 and into Si-H bonds proceeded with near zero activation energy. Furthermore, based on the findings of DeCooker, et al., (***J. Organomet. Chem., 99(1975) 371 – 377***), I was already studying the effects of H_2 on product selectivity, especially in the absence of zinc and other promoters.

Our fluidized bed reactions confirmed that selectivity to CH_3SiHCl_2 and $(CH_3)_2SiHCl$ is increased by the use of CH_3Cl – H_2 in the absence of promoters like zinc, antimony and tin. There was no evidence of CH_3SiH_2Cl until one day in May 1984, when the methyl chloride supply from the cylinder was insufficient to fluidize the bed. Thereafter, CH_3SiCl trapping with H_2 was done with the fluid bed reactor operated as a fixed bed. GC/MS, GC/FTIR and ^{29}Si NMR data and comparison of these results with those of an authentic sample confirmed the presence of CH_3SiH_2Cl in the reaction product. Gas circulation in the fluidized bed had increased the probability of the redistribution reactions, which consume CH_3SiH_2Cl. This was a good illustration that batch or plug-flow reactors provide better selectivity to early intermediates in reaction pathways. However, the serendipitous decrease of the methyl chloride flow had allowed Rudy Cameron and me to trap CH_3SiCl in a large laboratory reactor as well as accomplish the Direct Synthesis of CH_3SiH_2Cl.

Jeff Larnerd and I performed fluidized bed experiments with $CH_3Cl – H_2$ and periodic injections of methylchlorosilanes, particularly CH_3SiCl_3. The objective was to trap CH_3SiCl as the disilane ($CH_3Cl_2SiSiCl_2CH_3$). The disilane was not detected. Instead, the rate of formation of the methylchlorohydrosilanes increased 2 - 5 fold. We had earlier expended a great deal of effort to find promoters for this Direct Synthesis (***see US 4,973,725***). Serendipity had intervened for a third time. We pursued its lead and never got back to investigating the effect of injecting methylchlorosilanes or Si-H monomers into the fixed bed Direct Reaction with $CH_3Cl – H_2$. Based on our results and those of Michael Clarke and Ian Davidson, the Ono group and Gerhard Roewer’s group with 1,3-butadiene, I am confident that the silylene (silylenoid) intermediates will someday be trapped as disilanes.

The surface-chemical studies, silylene trapping experiments and other studies conducted by various groups from 1980 to the present permit an updated understanding of the course of the Rochow – Müller Direct Synthesis:

- The active catalytic surface is a solid solution containing 40 – 55 atom percent Si along with Cu, Zn and Sn.
- Zn is a structural promoter (affecting energy of activation) and Sn and P are textural promoters (affecting number of active sites)
- M – Si bond polarities do not correlate with product selectivity
- Cu – Si bond energy (~ 31 kcal/mole) < Si – Si bond energy (~ 53 kcal/mole)
- Surface precursor of $(CH_3)_2SiCl_2$ is CH_3SiCl. Other silanes (except $Si(CH_3)_4$ and $SiCl_4$) and the disilanes also originate from silylene intermediates
- The divalent silicon intermediate mechanism is also applicable to other Direct Syntheses of silanes.

Experimental evidence in support of these ideas has been published in ***Catalyzed Direct Reactions of Silicon (K. M. Lewis and D. G. Rethwisch, Editors), Elsevier, 1993***. Nonetheless, very many questions about the atomic and molecular events of the reaction still remain unanswered. Some of these are:

- What is the structure of the active site leading to selective formation of $(CH_3)_2SiCl_2$?
- Why is the reaction so much more sensitive to Sb, Sn and P than to Zn?
- Do silylenes (for example, RSiX, R = H, CH_3, X = Cl, Br, OCH_3, $N(CH3)_2$) disproportionate ($2RSiX \leftrightarrow R_2Si + SiX_2$) under Direct Synthesis conditions, and how significant is this reaction in product selectivity?

- Why are the Direct Reactions with HCl, ROH and $(CH_3)_2NH$, which are selective for the trifunctional silanes, inhibited by promoters of $(CH_3)_2SiCl_2$ formation?

Throughout the telling of this story, I have mentioned the names of my assistants, collaborators and mentors. I want to acknowledge their contributions to the successes we have had and to thank them for their support, their assistance and their inspiration. Others I want to recognize include the members of the analytical group and the Library staff at Tarrytown, Cynthia Vail, my secretary, and my wife for putting up with my work habits. Bernie Kanner stands out as an influential mentor. One day in 1983, following the methylchlorosilylene and silicon, zinc and tin surface-enrichment discoveries, I reminded him of my question to him during our initial meeting in January 1979. The question was whether there were enough challenging problems in silicon chemistry yet to be solved to keep researchers interested and productive. At that time, silicon's position in the periodic table and the existence of inorganic polymers called silicones were about the limits of my knowledge of silicon chemistry. Bernie had replied that he and others like Don Bailey and Bela Prokai, had had very productive careers up to that point and that he was looking forward to making many more contributions before his retirement. He also said that there was still much that was not known about the Direct Synthesis of methylchlorosilanes, a copper-catalyzed reaction.

Now, in 1983, in response to my reminder, Bernie said that when H. C. Brown, (Bernie's Ph.D. adviser at Purdue University and later a Nobel Laureate), began to realize the potential of hydroboration he remarked that he felt like a guy who had fallen into a pit full of gold nuggets. He was too busy filling his pockets to stop to query how they got there, or how he was going to climb out so fully laden. Bernie was saying that organosilicon chemistry had provided a similar gold mine for us. I shall add that for me copper also glitters.

About the author:

Ken Lewis is currently a Corporate Research Fellow at Momentive, the highest distinction for a scientist in the company. While Ken's interest in silicon and silicone chemistry has persisted since this time, the names of his employers have not. Over the years, Union Carbide's silicones business became OSi Specialties, which was then sold to the Witco Corporation but kept the name. Eventually OSi Specialties became part of GE Advanced Materials, and when GE sold this business to Apollo Management, the company was named Momentive Performance Materials.

Ken ha sido profesor visitante del Cuerpo Académico de Química y tecnología de Silicio del Departamento de Química de la DCNE y permanente apoyo en discusiones sobre proyectos relacionados con los temas de investigación de este cuerpo académico.