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Account

Shinji Murai: A Life in the Art of Catalysis

Tsumoru Morimoto,* Mamoru Tobisu, Fumitoshi Kakiuchi, and Naoto Chatani

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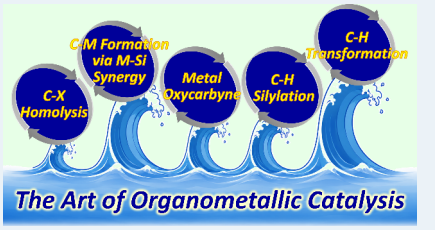
ABSTRACT: This memorial account traces the scientific legacy of Dr. Shinji Murai, a central figure in organometallic chemistry and homogeneous catalysis whose work influenced modern synthetic chemistry. From his early studies on organosilicon chemistry to his contributions to transition-metal-catalyzed bond activation and bond formation, Dr. Murai shaped research directions by recognizing possibilities in fundamental organometallic processes. A defining feature of his research was his ability to transform reactions that had been viewed as stoichiometric, isolated, or mechanistically specialized into general catalytic processes of broad synthetic significance. His studies involving organosilicon compounds, hydrosilanes, carbon monoxide, and unactivated C–H bonds identified reactivity patterns and expanded the conceptual foundation of catalysis. Equally characteristic of his work was independent thinking, careful observation, and persistent experimental exploration, qualities that enabled discoveries beyond the prevailing trends of the time. Dr. Murai's legacy extends far beyond the reactions associated with his name: through both his scientific achievements and his mentorship of generations of chemists, he helped shape the development of organometallic and catalytic chemistry in Japan and throughout the world. His career remains an enduring example of how creativity, rigor, and intellectual independence can transform the practice of chemical research.



KEYWORDS: *homogeneous catalysis, hydrosilanes, carbonylation, carbyne complexes, dehydrogenative silylation, C–H bond activation*

1. INTRODUCTION

On June 30, 2025, we received the deeply saddening news that Dr. Shinji Murai (Figure 1) had passed away at the age of 86. In reflecting on his life and achievements, we are reminded not only of his outstanding contributions to chemistry but also of the breadth of his intellect, creativity, and character.

Dr. Murai was born in Osaka in 1938. During his high school years, he served as president of the art club and devoted himself to painting. He was also known as a literary-minded youth who avidly read the works of Japanese writers such as Natsume Sōseki and Hideo Kobayashi. What ultimately shaped the course of his career was his encounter with the discovery of nylon, the world's first fully synthetic fiber. Deeply impressed by the ingenuity that made it possible to create "a thread finer than spider silk and stronger than iron" from such simple raw materials as water, air, and coal, he resolved to study chemistry and entered the Department of Applied Chemistry, Faculty of Engineering, Osaka University.

After graduation in 1961, he continued his studies at the Graduate School of Osaka University and completed his doctoral program in 1966 under the guidance of Professor Shigeru Tsutsumi, in a free and intellectually stimulating research environment that helped cultivate Dr. Murai's scientific insight and creativity. Immediately after receiving his doctorate, he was appointed Research Assistant in the same laboratory. Following a period of study with Professor Robert West at the University of Wisconsin, Madison, a leading authority in organosilicon chemistry, Dr. Murai joined Professor Noboru Sonoda's laboratory as Associate Professor, where he devoted himself to the development of organic synthetic reactions using transition-metal catalysts and organometallic species. In 1987, he was promoted to Professor in the Faculty of Engineering, Osaka University, and, until his retirement in 2002, he dedicated himself wholeheartedly to both research and education.

Throughout his career and after his retirement, Dr. Murai made extensive contributions to the broader scientific community through a range of leadership roles. In university administration, he served as Dean of the Faculty of Engineering at Osaka University and later helped guide institutional affairs at Nara Institute of Science and Technology as a Board Member and Vice President. His activities also extended to Japan's major chemical societies, where he held the presidencies of the Society of Synthetic Organic Chemistry, Japan, and the Chemical Society of Japan. In addition, he took part in national science administration through responsibilities associated with the Japan Science and Technology Agency (JST) and the Ministry of Education, Culture, Sports, Science and Technology (MEXT). In these capacities, he devoted himself to advancing

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Figure 1. Dr. Shinji Murai in his later career.

not only chemistry but also science in general and supporting the broader academic community in Japan.

Against this broad biographical background, it is, of course, Dr. Murai's scientific achievements that remain most vividly associated with his name. For many chemists, his name immediately evokes "C–H activation". His influence on synthetic organic chemistry, including organometallic chemistry and homogeneous catalysis, has been both profound and enduring. For researchers who followed his work from its early stages, the catalytic transformation of carbon monoxide using hydrosilanes remains a landmark achievement; for younger generations, his pioneering contributions to the catalytic activation of otherwise unreactive aromatic C–H bonds are equally emblematic of his scientific vision. Yet the accomplishments of Dr. Murai's extraordinary career extend far beyond these widely recognized breakthroughs. Although he discovered numerous groundbreaking reactions, only a few have come to be known by his name. This reflects not a lack of impact, but rather the exceptional breadth and continuity of his creativity. Throughout his career, he continued to uncover fundamentally new reactions, making it difficult for any single reaction to encapsulate the full scope of his contributions.

A defining feature of Dr. Murai's research was his persistent pursuit of chemistry founded on new concepts. Broadly speaking, his research strategies may be divided into two complementary approaches: a "*thinking-first*" approach and an "*experiment-first*" approach. In the former, an ingeniously conceived idea for a new reaction is first formulated, after which the strategy for its realization is meticulously designed. Experimental work is then carried out primarily to validate the underlying concept. In this sense, the "*thinking-first*" approach may be regarded as a true exercise in creativity. Two major achievements exemplify this style of research. One was the pioneering development of the chemistry of acyllithium species, which had long been considered too reactive for practical application in organic synthesis.[1−12] Another was his introduction of a novel concept for modulating the reactivity to π-allyl metal complexes, important intermediates in catalytic reactions. Based on this concept, he developed catalytic processes that include nucleophilic substitution on the central carbon atom of π-allyl palladium and platinum complexes.[13−18]

The "*experiment-first*" approach represents a research style in which extensive experimental exploration precedes conceptual understanding, allowing new reactions and ideas to emerge from unexpected observations. Rather than starting from a well-defined hypothesis, this approach relies on the careful examination of experimental outcomes and the insight to recognize the significance of unforeseen phenomena. Many of Dr. Murai's distinctive and innovative catalytic reactions also originated from this approach. Success in this mode of research depends not only on the ability to identify promising leads hidden within complex experimental results, but also, to a significant extent, on the fortuitous circumstances of encountering it. This Account, written in memory of Dr. Shinji Murai, focuses on his contributions to the development of new catalytic reactions that arose from such experimental explorations and reflects on how his persistent search for new phenomena shaped lasting advances in organic chemistry, organometallic chemistry, and catalysis.

2. EARLY CATALYTIC STUDIES AND THE CHEMISTRY OF SILYL ALKENYL ETHERS

Dr. Shinji Murai began his academic career in 1966 as an assistant professor in the Faculty of Engineering at Osaka University. Shortly thereafter, he published his first catalytic reaction, entitled "*Copper Salt Catalyzed Addition Reaction of Polychloroacetonitrile to Olefins*" (Scheme 1).[19] This reaction is initiated by the one-electron reduction of polychloroacetonitrile by a copper salt (CuX), followed by chloride elimination to generate chloroacetonitrile radical **1**, concomitant with the formation of Cl–CuX. This radical adds to an olefin, and the resulting carbon-centered radical abstracts a chlorine atom from Cl–CuX, regenerating CuX and completing the catalytic cycle. Notably, this catalytic system enabled the same overall transformation to proceed in high yield with only catalytic amounts of the copper salt, whereas the use of more than stoichiometric amounts of benzoyl peroxide as an oxidant afforded only moderate yields. Even at this early stage of his career, this work already foreshadowed a defining trait that would characterize many of Dr. Murai's later achievements: the ability to recognize the synthetic potential of fundamental chemical events and to translate that potential into useful catalytic reactions.

From 1967 to 1968, Dr. Murai conducted postdoctoral research in organosilicon chemistry in Professor Robert West's group at the University of Wisconsin, Madison. During this period, he encountered this field for the first time and became deeply fascinated by its breadth and depth.[20] Many of his subsequent discoveries of new catalytic reactions would involve silicon-containing molecules, reflecting the way in which organosilicon chemistry became deeply embedded in his later studies of catalysis. After returning to Japan, his first research project focused on the development of novel organic synthetic reactions that exploited the unique properties of silyl alkenyl ethers (now commonly referred to as silyl enol ethers or enol silyl ethers). Electron-deficient carbon radicals generated via one-electron transfer from copper salts to polyhaloalkanes were subsequently used in addition reactions with these substrates. He had already recognized that the highly electron-rich C=C

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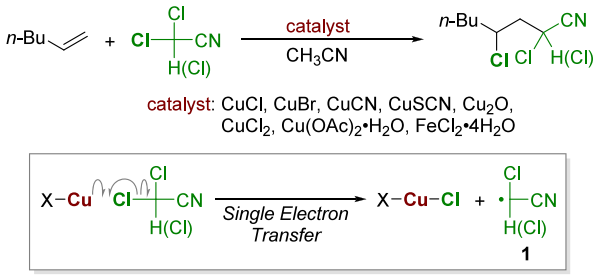
Scheme 1. First Catalytic Reaction Developed by Dr. Murai

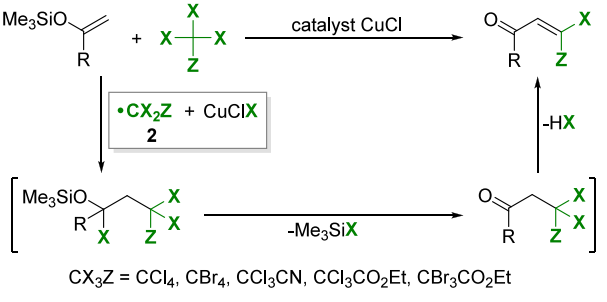


double bond of silyl alkenyl ethers could serve as a versatile platform in organic synthesis.

At that time, silyl alkenyl ethers had been actively investigated primarily as readily handled precursors of carbonyl enolates. Consequently, intensive efforts had been devoted to the in situ generation of metal enolates under neutral conditions through silicon–metal exchange reactions with metal salts. In contrast to this prevailing approach, Dr. Murai postulated that the extremely electron-rich C=C double bond of silyl alkenyl ethers could itself function as a nucleophile, without prior conversion to an enolate. On this basis, he set out to develop a method that would enable their direct reactions with electrophiles under neutral conditions. These efforts were soon rewarded. In 1972, he reported that silyl alkenyl ethers reacted with polyhalogenated compounds in the presence of catalytic amounts of copper chloride, resulting in C–C bond formation through a formal nucleophilic substitution at a polyhalogenated carbon atom (Scheme 2).[21] CuCl is believed to serve as a single-electron redox catalyst, generating a carbon radical **2** from the polyhalogenated compound. The resulting electrophilic carbon radical then adds to the electron-rich C=C double bond of the silyl alkenyl ether, followed by halogen abstraction from CuX_2 to form a formal C–X insertion intermediate. This intermediate subsequently undergoes sequential elimination of Me_3SiX and HX to furnish the conjugated enone product. This reaction represents not only the first example of a direct chemical transformation of silyl alkenyl ethers involving carbon–carbon bond formation, one of the most fundamental processes in organic synthesis, but also the first catalytic transformation of these compounds.[22−24]

Following this initial discovery, Dr. Murai developed a broad range of transformations employing silyl alkenyl ethers as substrates, thereby revealing their rich and versatile reactivity beyond their conventional role as masked enolates. In addition

Scheme 2. Direct Use of Silyl Alkenyl Ethers for Catalytic C–C Bond Formation



to the catalytic reactions described above, both the S–Cl bond of phenylsulfenyl chloride and the carbon–halogen bonds of acyl chlorides, such as polychloroacetyl chlorides and oxalyl chloride, were found to react with the C=C double bond of silyl alkenyl ethers via electrophilic addition, without the need for activators such as metal salts.[25,26] Simmons–Smith cyclopropanation using $ZnEt_2/CH_2I_2$ was also achieved by taking advantage of the high electron density of the C=C double bond in silyl alkenyl ethers.[27−29] It was further demonstrated that photoexcited silyl alkenyl ethers can serve as synthetic equivalents of enols, reacting with Michael acceptors such as acrylates, acrylonitrile, and methyl vinyl ketone to afford cyclobutyl silyl ether with high regioselectivity.[30] Finally, he developed a method for the oxidation of silyl alkenyl ethers to α,β-unsaturated ketones using oxidizing reagents such as 2,3-dichloro-5,6-dicyanoquinone (DDQ)).[31] This transformation further underscores the synthetic versatility of silyl alkenyl ethers as key intermediates in organic synthesis. Taken together, these studies provided important contributions to organosilicon chemistry and organic synthesis and foreshadowed several qualities that would later become hallmarks of Dr. Murai's research: a willingness to look beyond conventional reactivity patterns, a keen eye for hidden synthetic potential, and a persistent effort to transform mechanistic insight into useful catalysis. Thus, the first half-page publication[21] can be regarded as a remarkably fruitful "catalyst" for uncovering the diverse synthetic potential of silyl alkenyl ethers.

3. CATALYTIC REACTIONS USING HYDROSILANES AND CARBON MONOXIDE

One of Dr. Murai's notable contributions is a series of catalytic transformations using hydrosilanes and carbon monoxide as reagents. This line of research, initiated around 1976, was inspired by the well-recognized analogy between the reactivity of H_2 and that of $HSiR_3$ toward transition-metal complexes. Scheme 3 illustrates one of the clearest examples of this analogy, as reported by Haszeldine.[32] In addition to the stoichiometric reactions shown in Scheme 3a, similar relationships can also be found in catalytic hydrogenation and hydrosilylation reactions of various substrates, as summarized in Scheme 3b.

This analogy led Dr. Murai to ask what reaction might occur if hydrosilanes were used in place of hydrogen in hydroformylation. When he discussed this idea with a professor at another university in Japan, he learned that a different research group had already explored the same concept. Although no discernible reaction had been identified in that study, the professor offered to share the experimental data. He, however, declined the offer and instead embarked on an independent and systematic investigation of a wide range of catalysts, focusing primarily on those commonly employed in olefin hydroformylation.

After accumulating many minor or inconclusive results, a familiar stage in exploratory research, Dr. Murai eventually succeeded in identifying the reaction shown in Scheme 4.[33] In a subsequent literature survey, however, he was disappointed to learn that Colleuille had already filed a patent describing essentially the same reaction.[34] At that time, electronic databases such as SciFinder were not yet available, and researchers had to rely on the printed volumes of Chemical Abstracts, making literature searches extremely time-consuming and labor-intensive. Had this patent come to his attention before the study began, or had he decided to discontinue the project after learning of the earlier unsuccessful attempts at the other

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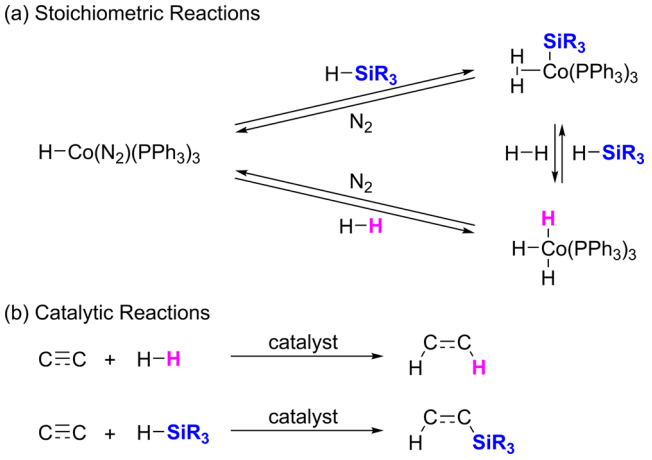
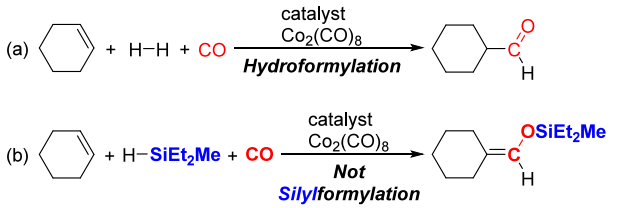
Scheme 3. Analogous Reactivity of H_2 and $HSiR_3$ in Stoichiometric (a) and Catalytic (b) Transformations



Scheme 4. (a) Hydroformylation with H_2 and CO; (b) Nonanalogous Reaction with HSi and CO

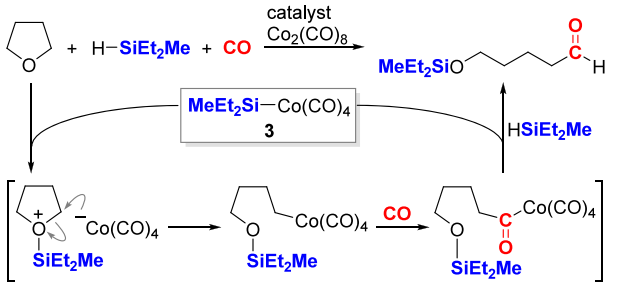


university, this reaction, together with the subsequent discoveries that developed from it, might never have been realized.

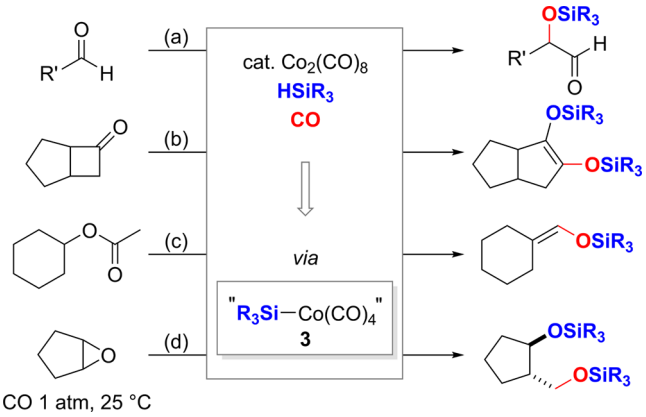
Further unexpected observation emerged during the optimization of the reaction conditions. Dr. Murai found that, when THF was used as the solvent, the solvent itself underwent an unanticipated transformation. The resulting product incorporated two carbon monoxide molecules and three silyl groups, yielding a compound with a substantially higher boiling point than the products originally expected. As a result, the product was detected only because the GC analysis had inadvertently run for an extended period while a student had stepped away to play baseball. This serendipitous observation prompted a more detailed investigation of the reaction conditions and ultimately led to the identification of the ring-opening silylformylation of cyclic ethers (Scheme 5).[35,36] These studies established that the $R_3Si–Co(CO)_4$ species **3**, generated from $Co_2(CO)_8$ and hydrosilanes, serves as the catalytically active species in this reaction. The transformation is driven by the strong affinity of the silicon atom for oxygen, together with the high nucleophilicity of the anionic $Co(CO)_4$ fragment.

This finding subsequently led to the development of a variety of reactions between Si–Co species and oxygen-containing substrates (Scheme 6), including aldehydes (Scheme 6a),[37] cyclobutanones (Scheme 6b),[38] and esters (Scheme 6c).[39,40] Moreover, highly reactive oxygenated substrates such as epoxides (Scheme 6d),[41] oxetanes,[42] acetals,[43] and orthoesters[44] were found to undergo related transformations under relatively mild conditions, without the need for elevated temperatures or high pressures. Taken together, these studies illustrate how Dr. Murai transformed the simple analogy between hydrogen and

Scheme 5. Expansion of the $Co_2(CO)_8$/Hydrosilane/CO System to Oxygen-Containing Compounds



Scheme 6. Catalytic Reactions of Oxygen-Containing Compounds Mediated by $R_3Si–Co(CO)_4$ 3 as the Key Catalytic Species



hydrosilanes into a broader class of carbonylative transformations involving Si–Co species and oxygen-containing substrates.

4. CATALYSIS VIA CONVERSION OF A CO LIGAND TO A CARBYNE LIGAND: A THIRD MODE OF CO INCORPORATION

During the studies aimed at developing new catalytic reactions mediated by silylmetal species generated from hydrosilanes and carbon monoxide, Dr. Murai discovered a novel catalytic process that revealed a third elementary mode for incorporating carbon monoxide into organic compounds. Until then, catalytic carbonylation reactions had generally been understood to proceed through one of two elementary pathways: (1) migration of an organic group from a metal center to a coordinated CO ligand, or (2) nucleophilic attack by an external nucleophile on a coordinated CO ligand. His work uncovered a third mode of CO incorporation, in which bond formation occurs through an oxycarbyne complex **4** (Scheme 7).

The reaction of 1-hexene with $HSiEt_2Me$ and carbon monoxide in the presence of $[IrCl(CO)_3]_n$ afforded a silyl alkenyl ether (Scheme 8a).[45] This sequence, consisting of an iridium-catalyzed transformation followed by acidic workup, provides a new synthetic route to acylsilanes from readily available terminal olefins. At the time of its discovery, the reaction mechanism remained entirely unknown. Only later, after the diyne reactions described below (Scheme 8b) had been shown to proceed

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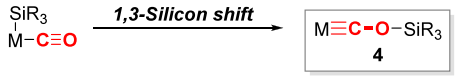
Scheme 7. Third Catalytic Mode of CO Incorporation via a Metal Carbyne Complex



through an oxycarbyne ruthenium complex **6**, did it become clear that this reaction also involved a carbyne intermediate **5**.

The following year, Dr. Murai reported a novel ruthenium-catalyzed reaction of 1,6-diynes with hydrosilanes and carbon monoxide that affords *O*-monosilylated catechol derivatives (Scheme 8b).[46] The catalytic cycle was proposed to involve this third mode of carbon monoxide incorporation through oxycarbyne complex **6**. This transformation is particularly remarkable because it represents both a rare example of catalytic CO incorporation into a diyne and the first example of the successive incorporation of two molecules of carbon monoxide. In the proposed mechanism, a hydrosilane undergoes oxidative addition to the catalytically active Ru(0)–CO species to generate a Ru(II) intermediate, which undergoes a 1,3-silyl shift to form the siloxycarbyne ruthenium complex **6**, a rare but crucial intermediate. Subsequent coupling of the carbyne ligand with a second molecule of carbon monoxide on the ruthenium center generates complex **7**, bearing a dioxyethyne unit, which finally undergoes [2 + 2 + 2] cocyclization with the diyne to afford the catechol derivative, while regenerating the Ru–CO species.

This reaction represents the first catalytic process involving an oxycarbyne complex as the key catalytic intermediate, as well as the first example of the successive incorporation of two molecules of carbon monoxide into diynes. The third mode of carbon monoxide incorporation and bond formation demonstrated in this work opened a new perspective in carbonylation chemistry. The study was highlighted in the "Science and Technology" section of *C&EN* on December 6, 1993.[47] Remarkably, another of Dr. Murai's studies was highlighted in *C&EN* the following week (vide infra),[48] underscoring the exceptional visibility and impact of his research during this period.

Building on this insight, Dr. Murai further demonstrated that the same conceptual framework could be extended beyond hydrosilane-based reactions. By exploiting the water–gas shift reaction, they developed a ruthenium-catalyzed synthesis of catechols from diynes.[49] The proposed catalytic cycle involves the reaction of a ruthenium carbonyl species with water to generate oxycarbyne-type ruthenium intermediate **8**, which subsequently incorporates a second molecule of carbon monoxide to furnish 1,2-dioxyethyne equivalent **9** (Scheme 8c). This reaction emphasized that the significance of this chemistry lies not merely in a particular hydrosilane-mediated process, but rather in the ability of a transition-metal center to reorganize coordinated carbon monoxide into a reactive unit capable of C–C bond formation.

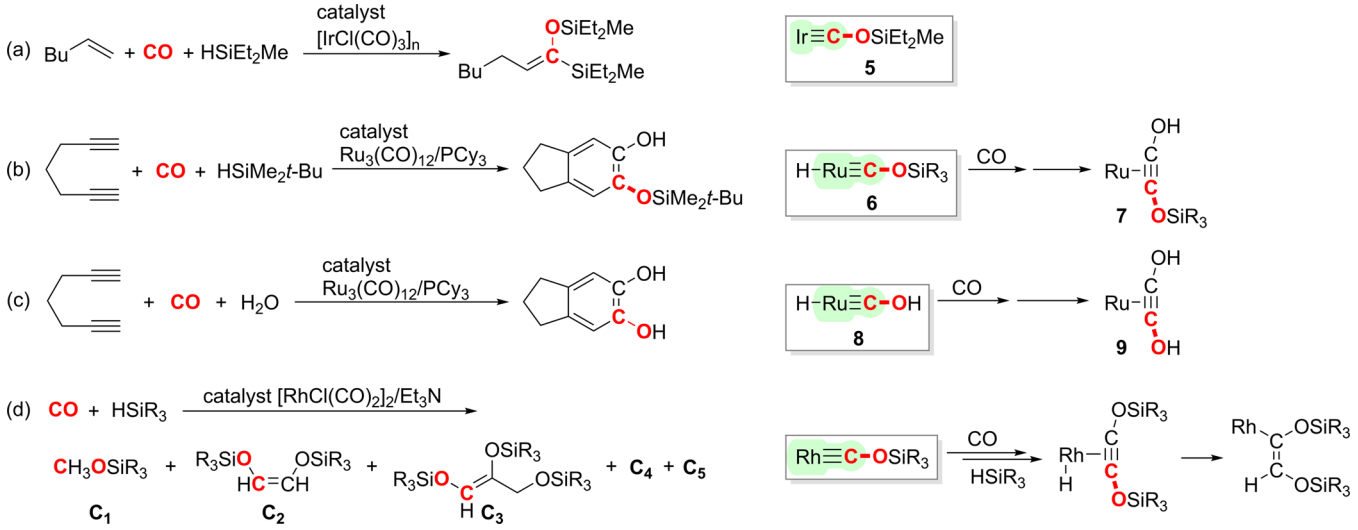
Dr. Murai also extended this concept to the Rh(I)-catalyzed reductive oligomerization of carbon monoxide with hydrosilanes (Scheme 8d).[50] Under relatively harsh conditions, carbon monoxide was converted into a series of silyl-protected C1–C5 oxygenated products. Although the detailed product distribution and proposed intermediates provide valuable mechanistic insight, the broader importance of this reaction lies in its role as a molecular model for CO homologation, in which multiple CO molecules are assembled on a metal center through oxycarbyne- and dioxycarbon-type intermediates.

This series of studies exemplifies Dr. Murai's distinctive approach to catalysis. Rather than treating carbon monoxide merely as a one-carbon feedstock, he revealed that it could be reorganized on transition-metal centers into highly unusual reactive intermediates, including oxycarbyne and dioxycarbon species. These findings broadened the mechanistic landscape of CO activation and opened new possibilities for the catalytic transformation and homologation of carbon monoxide. In doing so, these studies on silylmetal species set the stage for an even more unusual mode of CO activation, in which a coordinated CO ligand itself is transformed into a carbyne-type ligand.

5. FROM HYDROSILANES TO VINYLSILANES: DEHYDROGENATIVE SILYLATION

In the early 1980s, considerable research effort was directed toward the development of new synthetic reactions using organosilicon compounds. Among the important advances of this period was the recognition of vinylsilanes as versatile synthetic

Scheme 8. Catalytic Transformation via Oxycarbyne Complexes as a Key Species



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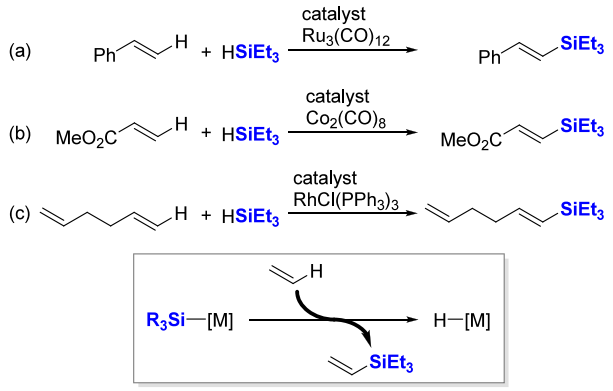
intermediates. Owing to the electron-rich character imparted by the silyl group, vinylsilanes react readily with electrophiles to give substitution products. In many cases, electrophiles are introduced stereoselectively at the carbon atom originally bearing the silyl group, thereby enabling the synthesis of a wide range of substituted olefins. In addition, epoxidized vinylsilanes can be readily converted into carbonyl compounds and may therefore be regarded as synthetic equivalents of carbonyl functional groups.

By the time Dr. Murai began developing dehydrogenative silylation reactions of olefins, numerous hydrosilylation reactions of alkynes with hydrosilanes had already been reported as representative methods for the synthesis of vinylsilanes. A major drawback of these methods, however, was the formation of alkylsilanes as byproducts. These byproducts arise from both simple hydrosilylation and subsequent reactions of the initially formed vinylsilanes with hydrogen derived from the hydrosilanes and the olefin. Even when such overreduction is suppressed, the range of applicable olefins remained largely limited to styrene derivatives.

In 1980, Dr. Murai and co-workers developed a reaction of olefins with hydrosilanes using $Ru_3(CO)_{12}$ as a catalyst to produce vinylsilanes (Scheme 9a).[51] This reaction exhibited excellent product selectivity (>99%) and high stereoselectivity for *E*-vinylsilanes, while accommodating a wide range of olefin substrates. In addition, vinylsilanes were obtained with essentially quantitative selectivity when $Fe_3(CO)_{12}$ was used as the catalyst.[52] The selectivity of the reaction, however, depended strongly on both the structure of the olefin and the nature of the catalyst employed. For example, in the reaction of 1-hexene, even $Ru_3(CO)_{12}$ afforded a mixture of vinylsilanes and allylsilanes, the latter arising from double-bond isomerization of the initially formed vinylsilane. $Co_2(CO)_8$ proved effective for the reaction of acrylic esters (Scheme 9b),[53,54] whereas 1,5-dienes selectively afforded vinylsilanes when $RhCl(PPh_3)_3$ was used as the catalyst (Scheme 9c).[55]

The dehydrogenative silylation studies described above also constitute an important prelude to the landmark discovery of catalytic C–H bond functionalization discussed later. They are related to that discovery in two significant ways. First, dehydrogenative silylation can be viewed as a transformation in which an olefinic C–H bond is replaced by a C–Si bond via silylmetalation followed by β-hydride elimination; in this sense, a reaction concept now described as C–H bond functionalization was already embodied in these studies. Second, a subsequent investigation involving vinylsilanes unexpectedly led to the discovery of catalytic directed C–H bond functionalization itself. Thus, this body of work occupies a distinctive position in Dr. Murai's research: it represented both a significant advance in organosilicon synthesis and an intellectual stepping stone toward one of his most influential contributions to catalysis.

Scheme 9. Dehydrogenative Silylation of Olefins (Direct C–H Bond Silylation)



6. CATALYTIC REACTIONS INVOLVING THE C–H BOND CLEAVAGE: THE DAWN OF C–H BOND ACTIVATION CATALYSIS

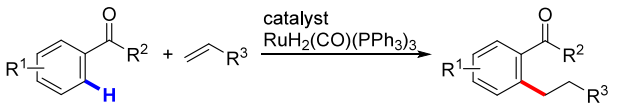
Among Dr. Murai's most influential contributions to chemistry was the discovery of a catalytic reaction that directly converts C–H bonds into C–C bonds. This reaction, catalyzed by a ruthenium phosphine complex, $RuH_2(CO)(PPh_3)_3$, enables the regioselective coupling of substrates such as acetophenones with olefins through the cleavage of an aromatic C–H bond directed by a coordinating functional group. The reaction proceeds with remarkable efficiency and selectivity across a broad range of substrates, establishing it as a powerful transformation in catalytic organic synthesis (Scheme 10).[56−58]

At the time of this discovery, efforts to develop catalytic C–H bond functionalization in Dr. Murai's group remained exploratory and were being pursued primarily by a single graduate student rather than as a full-scale team project. Transition-metal complexes known to undergo oxidative addition of C–H bonds to low-valent metals were examined as potential catalysts. For nearly two years, however, these efforts yielded no promising results.

A decisive breakthrough finally emerged in April 1992. The pivotal observation arose from the reaction of acetophenone with trimethylvinylsilane in the presence of $RuHCl(CO)(PPh_3)_3$, purchased from a chemical supplier, as the catalyst. This experiment had originally been examined in connection with an entirely different research project. GC and GC/MS analyses indicated the formation of new products, and subsequent ^1H NMR analysis revealed that the *ortho*-C–H bond of acetophenone had added across the C=C double bond of the vinylsilane, affording an *ortho*-monoalkylated and an *ortho*-dialkylated products. This transformation embodied precisely the type of catalytic C–H bond functionalization that Dr. Murai had long sought to realize. The discovery marked a watershed moment in organic synthesis and initiated a major stream of research that has continued to flourish worldwide for more than three decades.

At first glance, this finding might appear to have been the result of extraordinary fortune. In reality, it was far more than that. As Louis Pasteur famously stated, "*Le hasard ne favorise que les esprits préparés*" (chance favors only the prepared mind). Dr. Murai himself later remarked, "*It's not just serendipity.*" Detailed NMR analysis revealed that the commercially

Scheme 10. Ruthenium-Catalyzed Coupling of Aromatic Ketones with Olefins



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purchased $RuHCl(CO)(PPh_3)_3$, obtained for a different research purpose, contained a substantial amount of another complex, $RuH_2(CO)(PPh_3)_3$, which is formed through a closely related synthetic route (Figure 2). This ruthenium dihydride complex exhibited high catalytic activity, ultimately leading to the recognition of $RuH_2(CO)(PPh_3)_3$ as the actual catalyst precursor responsible for the C–H alkylation of acetophenone with the vinylsilane (Figure 3).

The catalytic transformation of C–H bonds did not begin with Dr. Murai. Stoichiometric C–H activation reactions had already been reported, and catalytic reactions employing large excesses of substrate or conducted under photoirradiation conditions were also known. However, their efficiency and regioselectivity were far from sufficient for practical use as synthetic methods. The development of highly efficient and regioselective catalytic functionalization of inert C–H bonds therefore remained an elegant but long-standing goal in organic synthesis. In textbooks and specialized monographs on organometallic and coordination chemistry, C–H activation was mentioned only briefly, typically as a few stoichiometric examples in chapters devoted to oxidative addition.

Against this background, the significance of the Murai reaction was not simply that it cleaved an aromatic C–H bond, but that it incorporated such cleavage into a highly efficient catalytic C–C bond-forming process. When Dr. Murai's group initiated its C–H functionalization project, several mechanisms for C–H bond cleavage by transition-metal complexes had already been recognized, including oxidative addition to low-valent metal centers, electrophilic cleavage at high-valent metal centers, and ligand-assisted cleavage. The ruthenium-catalyzed reaction, however, revealed a distinctive oxidative addition pathway. The proposed reaction pathway, later supported by DFT studies, is shown in Scheme 11.[59,60] As the ruthenium center approaches the C–H bond, it interacts simultaneously with the C–H bond and the ortho carbon atom of the aromatic ring, generating an intermediate in which the metal–carbon bond is largely formed while the hydrogen atom remains partially associated with the carbon atom. Subsequent hydrogen migration to the metal center completes C–H bond cleavage. This σ-interaction-driven pathway represents one of the truly innovative aspects of his discovery and is fundamentally distinct from Michael-type addition to a conjugated π-system.

Since Dr. Murai's seminal report, a wide variety of strategies for C–H bond functionalization have been developed,

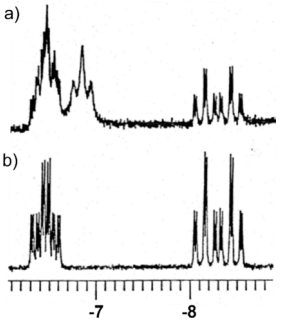

Figure 2. (a) ^1H NMR spectrum of the hydride region of the purchased $RuHCl(CO)(PPh_3)_3$. (b) ^1H NMR spectrum of the hydride region of the prepared $RuH_2(CO)(PPh_3)_3$.

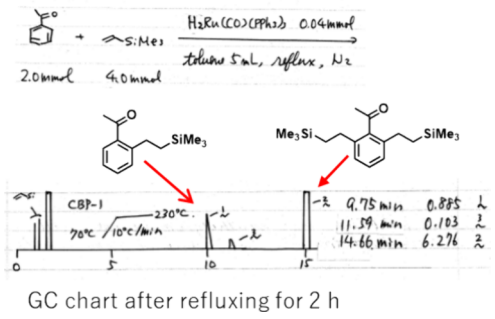

Figure 3. A page from the experiment notebook documenting the first coupling reaction of acetophenone with trimethylvinylsilane using $RuH_2(CO)(PPh_3)_3$ as a catalyst.

stimulating extensive research worldwide. Among transition-metal complexes employed in catalytic C–H functionalization via oxidative addition, $RuH_2(CO)(PPh_3)_3$ proved effective for a broad range of substrates beyond aromatic ketones. It exhibits wide-ranging catalytic activity in C–H alkylation,[61−63] alkenylation,[64,65] arylation,[66,67] and silylation[68,69] of diverse substrates, including carbonyl compounds, imines, nitriles, heteroaromatic compounds, and conjugated systems. Although this complex was not initially recognized as a general catalyst for such transformations, it ultimately became clear that, in terms of catalytic performance, "the first choice had turned out to be the best choice."

It is noteworthy that the term "C–H activation" does not appear in the titles of Dr. Murai's papers on these reactions. He strongly disliked the use of such terminology merely as a fashionable label and avoided emphasizing nomenclature for its own sake. In his view, "true C–H activation" referred specifically to oxidative addition of a C–H bond to the metal center of a transition-metal complex. Once this elementary process had been incorporated into a catalytic reaction, however, C–H activation itself was no longer the central message. In his subsequent publications, he consistently emphasized the novelty and synthetic significance of the chemical transformations themselves, often drawing attention to the availability and simplicity of the substrates rather than to the terminology used to describe the underlying mechanism.

This attitude reflected Dr. Murai's broader philosophy of organic synthesis. One essential objective of synthetic chemistry is to develop reactions that use readily available organic compounds, while another is to minimize the number of reaction steps and the overall energy required to construct target molecules. Through catalytic C–H bond functionalization, he established a synthetic strategy that addressed both objectives. This perspective illustrates how deeply his work was rooted in the logic and spirit of organic synthesis.

One of the hallmarks of his regioselective catalytic C–H functionalization was the utilization of a coordinating functional group, now commonly referred to as a directing group. By bringing the metal center into close proximity to a specific C–H bond and stabilizing the resulting C–M–H intermediate through formation of a metallacycle, the directing group enables highly regioselective C–H bond cleavage. In the $RuH_2(CO)(PPh_3)_3$-catalyzed C–H alkylation of aromatic ketones with olefins, the ketone carbonyl group functions as this directing group. Coordination of the carbonyl oxygen atom

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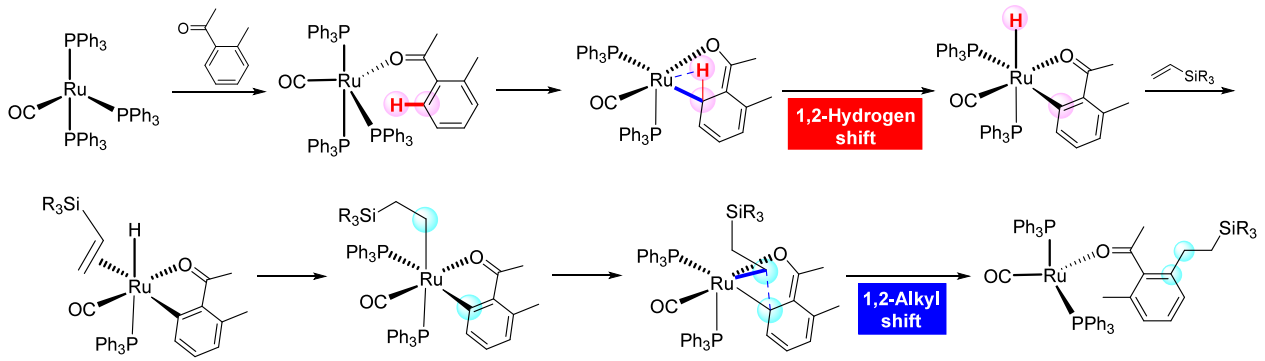
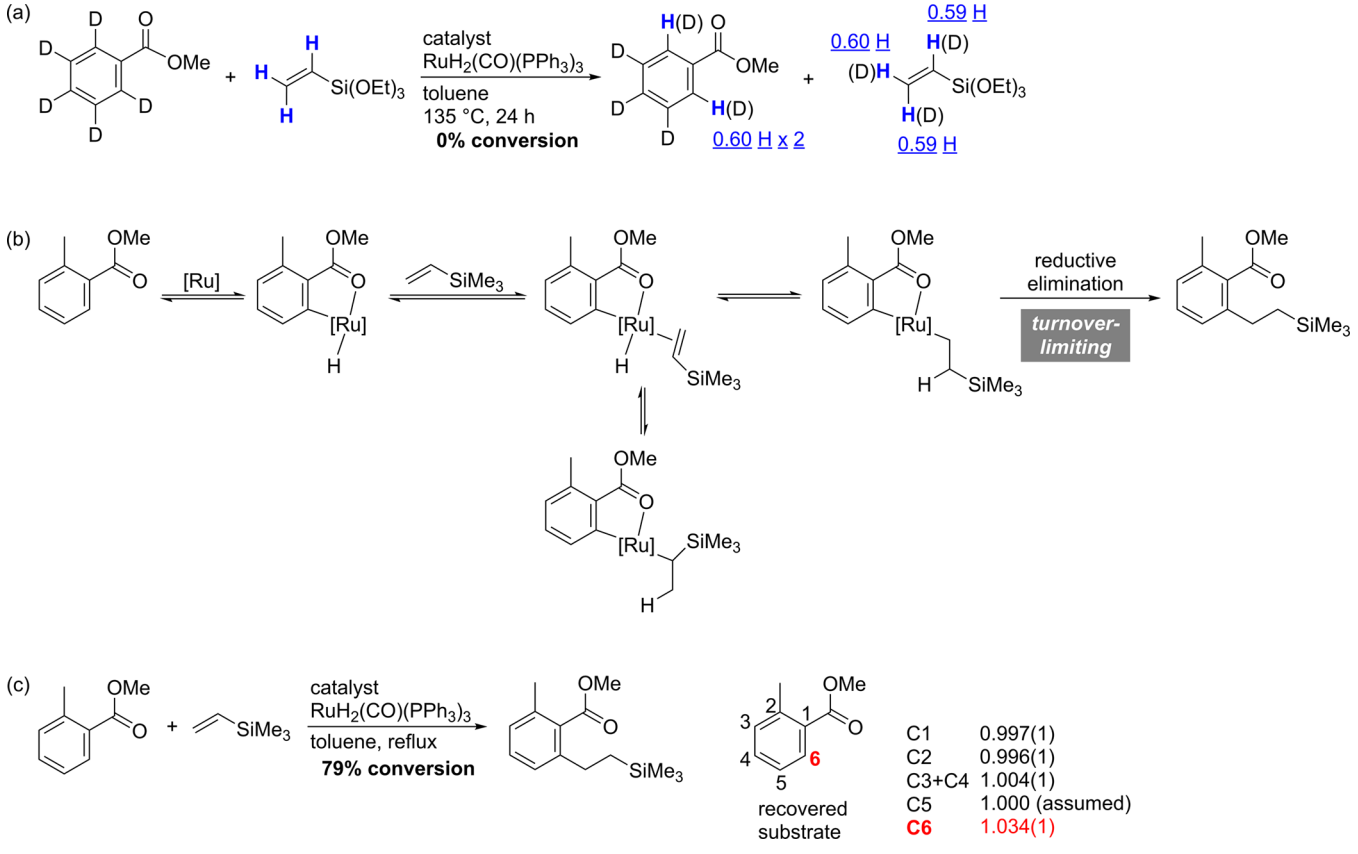
Scheme 11. Plausible Reaction Pathway via 1,2-Hydrogen and 1,2-Alkyl Shifts



to ruthenium enables selective ortho C–H bond cleavage, leading to a stable five-membered ruthenacycle intermediate (Scheme 11). The Ru–H bond of this intermediate then adds to the olefin double bond in an anti-Markovnikov manner, and subsequent reductive elimination releases the C–C bond-forming product while regenerating the catalytically active species.

Another unexpected yet highly informative finding was that C–H bond cleavage is not the turnover-limiting step. Because of the large bond dissociation energy of C–H bonds, typically around 100 kcal/mol, their cleavage had often been intuitively assumed to be the highest-energy process in catalytic C–H functionalization reactions. In the Murai reaction, however, deuterium-labeling experiments revealed that the ruthenium intermediates formed prior to reductive elimination are in equilibrium,[62,63] and theoretical studies by Morokuma's group demonstrated that C–H bond cleavage proceeds with a remarkably low activation barrier (Scheme 12).[59,60] Together, these findings indicated that the key kinetic bottleneck lies after C–H bond cleavage. Although Dr. Murai was not a coauthor of Morokuma's papers,[59,60] the two groups remained in close communication throughout the computational studies. Dr. Murai himself requested that the work be published independently as a theoretical chemistry paper, a gesture that reflected both his modesty and his scientific integrity.

Scheme 12. (a) Deuterium-Labeling Experiments Using Methyl Benzoate-d_5, (b) Equilibria Prior to the Reductive Elimination. (c) ^{13}C KIE Experiment



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To place this mechanistic picture on firmer experimental footing, Dr. Murai employed an innovative method: the measurement of the natural-abundance ^{13}C kinetic isotope effect in the $RuH_2(CO)(PPh_3)_3$-catalyzed reaction of methyl 2-methylbenzoate with trimethylvinylsilane.[70] Deuterium-labeling experiments had shown that the steps prior to reductive elimination are reversible and remain in equilibrium (Scheme 12a,b). If reductive elimination, namely the C–C bond-forming step, was turnover-limiting, a ^{13}C kinetic isotope effect would be expected at C6 of the ester substrate. Indeed, the recovered starting material showed a slightly higher ^{13}C abundance at C6 than the natural isotopic ratio. This independent experimental evidence confirmed the mechanistic picture suggested by the deuterium labeling and theoretical studies: the turnover-limiting event is reductive elimination, not C–H bond cleavage (Scheme 12c).

The Murai reaction transformed the way chemists viewed C–H bonds in organic molecules. It showed that a C–H bond, long regarded primarily as an inert structural element, could be transformed directly and selectively into a C–C bond under catalytic conditions. Equally important, it demonstrated that the central challenge was not merely to cleave a strong C–H bond, but to design an entire catalytic sequence in which C–H activation, substrate coordination, migratory insertion, and reductive elimination are orchestrated in a productive manner. In this sense, the Murai reaction helped shift C–H activation from a specialized topic discussed largely in the context of stoichiometric organometallic processes to the foundation of a broad field now recognized as catalytic C–H bond functionalization. This conceptual advance helped launch one of the major movements in modern catalytic chemistry and remains one of the most enduring legacies of Dr. Murai's work.

7. CONCLUSIONS

In this Account, we have reflected on the outstanding achievements and lasting legacy of Dr. Shinji Murai, whose work had a profound impact on organic chemistry, organometallic chemistry, and catalysis. What distinguished his science was not a tendency to follow prevailing trends, but a firm resolve to open new directions in chemistry. Throughout his career, he never entered a field simply because it was fashionable. Instead, he consistently looked beyond established paradigms, framed his own questions, and created new paths through original discoveries. Many of his contributions continue to influence subsequent generations of researchers. The numerous honors bestowed upon him, including the Chemical Society of Japan Award for Academic Achievement in Chemistry (1985), the Chemical Society of Japan Award (1998), the Special Award of the Society of Synthetic Organic Chemistry, Japan (2005), the Fujiwara Prize (2006), the Japan Academy Prize (2010), the Asahi Prize (2015), and his designation as a Person of Cultural Merit (2017), testify to the depth and breadth of his impact on chemistry.

At the heart of this approach was Dr. Murai's unwavering belief that science advances through discovery, and that discovery is the source of the fascination and joy not only of chemistry, but of science as a whole. For him, research was not merely the accumulation of knowledge or the production of results; it was a creative endeavor that required sustained thought and engagement with the unknown. Having served as the president of the art club during his high school years, he may also have sensed in scientific work a creative dimension akin to art. This did not mean embellishing research achievements, but rather identifying a meaningful question on one's own and refining it until one could be fully satisfied with the answer. Because of his deep love of chemistry, he sought to convey to his students that research was not only a demanding pursuit of results, but also an endeavor in which the very act of thinking could be enjoyed.

This philosophy was vividly reflected in the words he repeatedly shared with Dr. Murai's students. He often urged them to "*Always think about chemistry*," emphasizing that chemistry should not be confined to the laboratory but should be cultivated in everyday thought. He also encouraged rigorous intellectual engagement through his memorable expressions, such as "*Sleep with the Aldrich chemical catalog as your pillow*" and "*Think until your brain sweats*." These words remain clearly etched in the memories of those who learned from him, not merely as humorous remarks, but as expressions of the kind of scientist he was: one who loved chemistry wholeheartedly and found genuine joy in thinking. Those who worked closely with Dr. Murai witnessed this passion firsthand. His spirit has naturally taken root in his students and colleagues and continues to guide researchers in academia as well as those engaged in industrial development.

At the same time, for Dr. Murai, enjoying research never meant taking an easy or superficial approach. Rather, he valued above all the willingness to face problems directly and continue thinking until reaching genuine conviction. His maxim, "*Conduct many experiments and write few papers*," aptly expressed this attitude. It conveyed the importance of resisting the temptation to rush toward publication and instead continuing to experiment and reflect patiently until the essence of the chemical reaction became clear. He understood more deeply than anyone that such sincerity is what ultimately advances and enriches chemical research.

This rigor was equally evident in the way Dr. Murai mentored his students. Even when experiments did not proceed as hoped, he would often say, "*Accept setbacks*," reminding them that difficulties themselves can provide opportunities for deeper understanding. Even when the problems assigned to students were extremely challenging and progress came slowly, he stood alongside them and seemed to enjoy the process of overcoming such hurdles together. As was the case for the authors of this Account, many students were drawn to Dr. Murai's laboratory not only by the originality of his science, but also by his open-mindedness, generosity, and warmth. In an environment where such rigor and kindness coexisted, his students learned not only the difficulties inherent in research, but also the joy of exploring the unknown.

It is deeply saddening that we can no longer discuss chemistry with Dr. Murai or enjoy his warm sense of humor. Nevertheless, the scientific frontiers he opened, the attitude toward research that he embodied, and the profound love of chemistry that he imparted will continue to live on in many researchers he inspired. With deep respect and gratitude, we dedicate this Account to the memory of Dr. Shinji Murai.

AUTHOR INFORMATION

Corresponding Author

Tsumoru Morimoto – *Division of Materials Science, Graduate School of Science and Technology, Nara Institute of Science*

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and Technology (NAIST), Nara 630-0192, Japan; orcid.org/0000-0002-1956-8777;
Email: tsumoru.morimoto@naist.ac.jp

Authors

Mamoru Tobisu – *Department of Applied Chemistry, Graduate School of Engineering, The University of Osaka, Osaka 565-0871, Japan;* orcid.org/0000-0002-8415-2225

Fumitoshi Kakiuchi – *Department of Chemistry, Faculty of Science and Technology, Keio University, Kanagawa 223-8522, Japan;* orcid.org/0000-0003-2605-4675

Naoto Chatani – *Department of Applied Chemistry, Faculty of Engineering, The University of Osaka, Suita Osaka 565-0871, Japan; Institute of Scientific and Industrial Research, The University of Osaka, Ibaraki, Osaka 567-0047, Japan;* orcid.org/0000-0001-8330-7478

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Author Contributions

This account originated from a manuscript that Dr. Shinji Murai and his former PhD student, Dr. T.M., had begun preparing before Dr. Murai's passing. Following his passing, the manuscript was revised and further developed as a memorial account with contributions from Drs. M.T., F.K., and N.C., all of whom were former PhD students of Dr. Murai.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Murai, S.; Ryu, I.; Iriguchi, J.; Sonoda, N. Acyllithium to Lithium Enolate Conversion by a 1,2-Silicon Shift. A Shortcut to Acylsilane Enolates. *J. Am. Chem. Soc.* **1984**, *106* (8), 2440–2442.

(2) Ryu, I.; Hayama, Y.; Hirai, A.; Sonoda, N.; Orita, A.; Ohe, K.; Murai, S. Intramolecular Conversions of Acyllithium. Cyclization in the Reaction of Carbon Monoxide with [1-(Silyl)vinyl]lithium. *J. Am. Chem. Soc.* **1990**, *112* (19), 7061–7063.

(3) Orita, A.; Fukudome, M.; Ohe, K.; Murai, S. Reactions via Carbonyl Anions. [4+1] Cyclocoupling of the Azadienyllithium with Carbon Monoxide. *J. Org. Chem.* **1994**, *59* (2), 477–481.

(4) Orita, A.; Ohe, K.; Murai, S. Reaction of Lithium Silylamides with Carbon Monoxide Leading to Carbamoylsilanes. *Organometallics* **1994**, *13* (4), 1533–1536.

(5) Orita, A.; Ohe, K.; Murai, S. The Reaction of Carbamoylcopper with a Silyl Chloride to Give a Carbamoylsilane. *J. Organomet. Chem.* **1994**, *474* (1-2), 23–25.

(6) Ryu, I.; Yamamoto, H.; Sonoda, N.; Murai, S. Lithium Dienolate Generation by α-Regioselective Reaction of (1-Silylallyl)lithiums with Carbon Monoxide. *Organometallics* **1996**, *15* (26), 5459–5461.

(7) Kai, H.; Iwamoto, K.; Chatani, N.; Murai, S. Ynolates from the Reaction of Lithiosilyldiazomethane with Carbon Monoxide. New Ketenylation Reactions. *J. Am. Chem. Soc.* **1996**, *118* (32), 7634–7635.

(8) Kai, H.; Yamauchi, M.; Murai, S. Reaction of Carbon Monoxide with *N*-Lithioketimines Derived by the Addition of Alkyllithium to *ortho*-Substituted Benzonitriles. Diverse Courses of Cyclization via Carbonyl Anions. *Tetrahedron Lett.* **1997**, *38* (52), 9027–9030.

(9) Kai, H.; Orita, A.; Murai, S. Incorporation of two Molecules of Carbon Monoxide into *N*-Lithioketimine Leading to Azetidine-2,3-diones. *Synth. Commun.* **1998**, *28* (11), 1989–2000.

(10) Iwamoto, K.; Chatani, N.; Murai, S. Carbonyllithium Chemistry. Intramolecular Conversion of an Acyllithium via the Utilization of an Anionic 1,2-Stannyl Rearrangement. *J. Organomet. Chem.* **1999**, *574* (1), 171–175.

(11) Iwamoto, K.; Chatani, N.; Murai, S. Reaction of *o*-Oxazolinylphenyllithium with Carbon Monoxide. Carbonylative Cyclization via an Aroyllithium Intermediate. *J. Org. Chem.* **2000**, *65* (23), 7944–7948.

(12) Iwamoto, K.; Kojima, M.; Chatani, N.; Murai, S. Ynolate Chemistry. Reaction of a Silylynolate with Aziridines Leading to γ-Lactams. *J. Org. Chem.* **2001**, *66* (1), 169–174.

(13) Ohe, K.; Ishihara, T.; Chatani, N.; Murai, S. Palladium-Catalyzed Reaction of Methyleneoxazolidinones. Intervention of a Palladium Complex of a Y-Shaped $CH_2(NTs)CH_2$ Molecule as an Isostructure of Trimethylenemethane. *J. Am. Chem. Soc.* **1990**, *112* (26), 9646–9647.

(14) Ohe, K.; Matsuda, H.; Ishihara, T.; Ogoshi, S.; Chatani, N.; Murai, S. Palladium-Catalyzed Reaction of 5-Methylene-1,3-dioxolan-2-ones. A New Access to and Reactivity of Oxatrimethylenemethane Palladium. *J. Org. Chem.* **1993**, *58* (5), 1173–1177.

(15) Ohe, K.; Matsuda, H.; Morimoto, T.; Ogoshi, S.; Chatani, N.; Murai, S. Nucleophilic Substitution at the Central Allyl Carbon Atom of a (π-Allyl)platinum Complex. *J. Am. Chem. Soc.* **1994**, *116* (9), 4125–4126.

(16) Kadota, J.; Komori, S.; Fukumoto, Y.; Murai, S. A New Platinum Complex Catalyzed Reaction Involving Nucleophilic Substitution at the Central Carbon Atom of the π-Allyl Ligand. *J. Org. Chem.* **1999**, *64* (20), 7523–7527.

(17) Kadota, J.; Katsuragi, H.; Fukumoto, Y. Murai, S. Platinum and Palladium Complex-Catalyzed Regioselective Nucleophilic Substitutions with Two Different Nucleophiles at the Central and Terminal Carbon Atoms of the π-Allyl Ligand. *Organometallics* **2000**, *19* (6), 979–983.

(18) Kadota, J.; Chatani, N.; Murai, S. A Platinum Complex-Catalyzed Reaction of 3-Chloro-1,3-diene Monoepoxides with Carbon Nucleophiles Involving Nucleophilic Substitution at the Central Carbon Atom of the π-Allyl Ligand in the Intermediate Complex. Dependency of Regioselectivity upon the Added Lewis Acids. *Tetrahedron* **2000**, *56* (15), 2231–2237.

(19) Murai, S.; Tsutsumi, S. Copper Salts Catalyzed Addition of Trichloro- and Dichloroactonitriles to Olefins. *J. Org. Chem.* **1966**, *31* (9), 3000–3003.

(20) West, R.; Ishikawa, M.; Murai, S. New Anionic Rearrangements. VIII. 1,4-Anionic Rearrangement of Silylethylenediamines. *J. Am. Chem. Soc.* **1968**, *90* (3), 727–731.

(21) Murai, S.; Kuroki, Y.; Aya, T.; Sonoda, N.; Tsutsumi, S. Silyl Alkenyl Ethers as the Synthetic Equivalent of Enols. A New Synthesis of α,β-Unsaturated Ketones. *J. Chem. Soc., Chem. Commun.* **1972**, (*12*), 741.

(22) Mukaiyama, T.; Narasaka, K.; Banno, K. New Aldol Type Reaction. *Chem. Lett.* **1973**, *2* (9), 1011–1014.

(23) Matsuo, J.-I.; Murakami, M. The Mukaiyama Aldol Reaction: 40 Years of Continuous Development. *Angew. Chem. Int. Ed.* **2013**, *52* (35), 9109–9118.

(24) Murakami, M. Achievements of the Late Professor Teruaki Mukaiyama. *Chem. Rec.* **2021**, *21* (1), 2–16.

(25) Murai, S.; Kuroki, Y.; Hasegawa, K.; Tsutsumi, S. Silyl Alkenyl Ethers as the Synthetic Equivalent of Enols. New Syntheses of β-Keto-sulphides and 1,3-Diketones. *J. Chem. Soc., Chem. Commun.* **1972**, (*16*), 946–947.

(26) Murai, S.; Hasegawa, K.; Sonoda, N. Synthesis and Thermal Decarbonylation of 2,3-Furandiones. *Angew. Chem., Int. Ed. Engl.* **1975**, *14* (9), 636–637.

(27) Murai, S.; Aya, T.; Sonoda, N. Synthesis via Silyl Alkenyl Ethers. IV. Synthesis of 1-Hydroxybicyclo[n.1.0]alkanes from Silyl Alkenyl Ethers. A Novel Class of Cyclopropanols. *J. Org. Chem.* **1973**, *38* (25), 4354–4356.

(28) Ryu, I.; Murai, S.; Otani, S.; Sonoda, N. Synthesis of Cyclopropyl Ethers from Silyl Enol Ethers. *Chem. Lett.* **1976**, *5* (1), 93–94.
(29) Ryu, I.; Murai, S.; Sonoda, N. One-Pot-Conversion of 1-Siloxycycloalkenes to 4-Siloxy Spiro[n,2]alkanes by Diethylzinc-Methylene Iodide. *Tetrahedron Lett.* **1977**, *18* (52), 4611–4614.
(30) Mizuno, K.; Okamoto, H.; Pac, C.; Sakurai, H.; Murai, S.; Sonoda, N. Photoreaction of Silyl Enol Ethers of α-Tetralone and α-Indanone with Electron Deficient Olefins; The Photo-Michael Reaction. *Chem. Lett.* **1975**, *4* (3), 237–238.
(31) Ryu, I.; Murai, S.; Hatayama, Y.; Sonoda, N. A Ketone-Enone Conversion via the Reaction of Enol Silyl Ethers with DDQ. *Tetrahedron Lett.* **1978**, *19* (37), 3455–3458.
(32) Archer, N. J.; Haszeldine, R. N.; Parish, P. V. Complexes Containing Cobalt-silicon Metal-metal bonds. *J. Chem. Soc., Chem. Commun.* **1971**, (*11*), 524.
(33) Seki, Y.; Hidaka, A.; Murai, S.; Sonoda, N. The Reaction of Olefins with Silane and Carbon Monoxide Catalyzed by $Co_2(CO)_8$. *Angew. Chem., Int. Ed. Engl.* **1977**, *16* (3), 174–175.
(34) [a] Colleuille, Y.; Rhone-Poulenc, S. A. Preparation of Organosilicon Compounds. DDR Patent 55, 012, **1967**. [b] Colleuille, Y.; Rhone-Poulenc, S. A. Preparation of Alkenyloxysilanes. U.S. Patent 3, 450, 737, **1969**.
(35) Seki, Y.; Murai, S.; Yamamoto, I.; Sonoda, N. $Co_2(CO)_8$ Catalyzed Reactions of Cyclic Ethers with Hydrosilanes and Carbon Monoxide. *Angew. Chem., Int. Ed. Engl.* **1977**, *16* (11), 789.
(36) Murai, T.; Yasui, E.; Kato, S.; Hatayama, Y.; Suzuki, S.; Yamasaki, Y.; Sonoda, N.; Kurosawa, H.; Kawasaki, Y.; Murai, S. Cobalt Carbonyl-Catalyzed Reactions of Cyclic Ether with a Hydrosilane and Carbon Monoxide. A New Synthetic Reaction Equivalent to Nucleophilic Oxymethylation. *J. Am. Chem. Soc.* **1989**, *111* (20), 7938–7946.
(37) Murai, S.; Kato, T.; Sonoda, N.; Seki, Y.; Kawamoto, K. Catalytic Conversion of Aldehydes into Higher α-Siloxy Aldehydes by Hydrosilane and Carbon Monoxide, *Angew. Chem. Int. Ed. Engl.* **1979**, *18* (5), 393–394.
(38) Chatani, N.; Furukawa, H.; Kato, T.; Murai, S.; Sonoda, N. Catalytic Incorporation of Carbon Monoxide into a Ketonic Carbon. Conversion of Cyclobutanones to Disiloxycyclopentenes with Hydrosilane and Carbon Monoxide in the Presence of Cobalt Carbonyl, *J. Am. Chem. Soc.* **1984**, *106* (2), 430–431.
(39) Chatani, N.; Murai, S.; Sonoda, N. Conversion of Alkyl Acetates to (Siloxymethylene)alkanes by Dicobalt Octacarbonyl-Catalyzed Reaction with a Hydrosilane and Carbon Monoxide. *J. Am. Chem. Soc.* **1983**, *105* (5), 1370–1372.
(40) Chatani, N.; Fujii, S.; Yamasaki, Y.; Murai, S.; Sonoda, N. Cobalt Carbonyl Catalyzed Reactions of Esters and Lactones with Hydrosilane and Carbon Monoxide. A Novel Synthetic Method for the Introduction of the Siloxymethylidene Group. *J. Am. Chem. Soc.* **1986**, *108* (23), 7361–7373.
(41) Murai, T.; Kato, S.; Murai, S.; Toki, T.; Suzuki, S.; Sonoda, N. Oxymethylative Opening of Oxiranes Leading to 1,3-Diol Derivatives by Cobalt Carbonyl Catalyzed Reaction with a Hydrosilane and Carbon Monoxide. *J. Am. Chem. Soc.* **1984**, *106* (20), 6093–6095.
(42) Fukumoto, Y.; Yamaguchi, S.; Chatani, N.; Murai, S. Ring-Opening Silylformylation of Oxetanes Catalyzed by $[RhCl(CO)_2]_2$-Amine. *J. Organomet. Chem.* **1995**, *489* (1-2), 215–219.
(43) Ikeda, S. I.; Chatani, N.; Murai, S. Rhodium-Catalyzed Reaction of *N,N*-Acetals with a Hydrosilane and Carbon Monoxide. *Organometallics* **1992**, *11* (11), 3494–3495.
(44) Chatani, N.; Kajikawa, Y.; Nishimura, H.; Murai, S. $Co_2(CO)_8$-Catalyzed Reaction of Cyclic Ortho Esters with a Hydrosilane and Carbon Monoxide. A Novel Method for Homologation of 1,2-, 1,3-, and 1,4-Diols. *Organometallics* **1991**, *10* (1), 21–23.
(45) Chatani, N.; Ikeda, S.-i.; Ohe, K.; Murai, S. Conversion of Alkenes to Enol Silyl Ethers of Acylsilanes by Iridium-Catalyzed Reaction with a Hydrosilane and Carbon Monoxide. *J. Am. Chem. Soc.* **1992**, *114* (24), 9710–9711.
(46) Chatani, N.; Fukumoto, Y.; Ida, T.; Murai, S. Ruthenium-Catalyzed Reaction of 1,6-Diynes with Hydrosilanes and Carbon Monoxide: A Third Way of Incorporating CO. *J. Am. Chem. Soc.* **1993**, *115* (24), 11614–11615.
(47) Stinson, S. Carbonylation Proceeds via Oxacarbyne Complex. *Chem. Eng. News* **1993**, *71* (49), 40–41.
(48) Zurer, P. Organometallic Synthesis – Aromatics Added to Alkenes in One Step. *Chem. Eng. News* **1993**, *71* (50), 6–7.
(49) Crudden, C. M.; Maekawa, Y.; Clarke, J. J.; Ida, T.; Fukumoto, Y.; Chatani, N.; Murai, S. $Ru_3(CO)_{12}$-Catalyzed Reaction of 1,6-Diynes, Carbon Monoxide, and Water via the Reductive Coupling of Carbon Monoxide. *Org. Lett.* **2020**, *22* (22), 8747–8751.
(50) Chatani, N.; Shinohara, M.; Ikeda, S.-i.; Murai, S. Reductive Oligomerization of Carbon Monoxide by Rhodium-Catalyzed Reaction with Hydrosilanes. *J. Am. Chem. Soc.* **1997**, *119* (18), 4303–4304.
(51) Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, N. $Ru_3(CO)_{12}$-Catalyzed Synthesis of Vinylsilanes from Olefins and Hydrosilanes. *Angew. Chem., Int. Ed. Engl.* **1980**, *19* (11), 928.
(52) Kakiuchi, F.; Tanaka, Y.; Chatani, N.; Murai, S. Completely Selective Synthesis of (*E*)-β-(Triethylsilyl)styrenes by $Fe_3(CO)_{12}$-Catalyzed Reaction of Styrenes with Triethylsilane. *J. Organomet. Chem.* **1993**, *456* (1), 45–47.
(53) Takeshita, K.; Seki, Y.; Kawamoto, K.; Murai, S.; Sonoda, N. Synthesis of 3-Silylacrylates by $Co_2(CO)_8$-Catalyzed Reaction of Methyl Acrylate with Hydrosilanes. *J. Chem. Soc. Chem. Commun.* **1983**, (*21*), 1193.
(54) Takeshita, K.; Seki, Y.; Kawamoto, K.; Murai, S.; Sonoda, N. The Catalyzed Reaction of α,β-Unsaturated Esters with Various Hydrosilanes. *J. Org. Chem.* **1987**, *52* (22), 4864–4868.
(55) Kakiuchi, F.; Nogami, K.; Chatani, N.; Murai, S. Dehydrogenative Silylation of 1,5-Dienes with Hydrosilanes Catalyzed by $RhCl(PPh_3)_3$. *Organometallics* **1993**, *12* (12), 4748–4750.
(56) Murai, S.; Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. Efficient Catalytic Addition of Aromatic Carbon-Hydrogen Bonds to Olefins. *Nature* **1993**, *366* (6455), 529–531.
(57) Kakiuchi, F.; Murai, S. Catalytic C-H/Olefin Coupling. *Acc. Chem. Res.* **2002**, *35* (10), 826–834.
(58) Kakiuchi, F.; Kochi, T.; Murai, S. Chelation-Assisted Regioselective Catalytic Functionalization of C-H, C-O, C-N and C-F Bonds. *Synlett* **2014**, *25* (17), 2390–2414.
(59) Matsubara, T.; Koga, N.; Musaev, D. G.; Morokuma, K. Density Functional Study on Activation of *Ortho*-CH Bond in Aromatic Ketone by Ru Complex. Role of Unusual Five-Coordinated d^6 Metallacycle Intermediate with Agostic Interaction. *J. Am. Chem. Soc.* **1998**, *120* (48), 12692–12693.
(60) Matsubara, T.; Koga, N.; Musaev, D. G.; Morokuma, K. Density Functional Study on Highly *ortho*-Selective Addition of an Aromatic CH Bond to Olefins Catalyzed by a $Ru(H)_2(CO)(PR_3)_3$ Complex. *Organometallics* **2000**, *19* (12), 2318–2329.
(61) Murai, S.; Chatani, N.; Kakiuchi, F. Catalytic Addition of C-H Bonds to Multiple Bonds. *Pure Appl. Chem.* **1997**, *69* (3), 589–594.
(62) Kakiuchi, F.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N.; Murai, S. Catalytic Addition of Aromatic Carbon-Hydrogen Bonds to Olefins with the Aid of Ruthenium Complexes. *Bull. Chem. Soc. Jpn.* **1995**, *68* (1), 62–83.
(63) Kakiuchi, F.; Kochi, T.; Mizushima, E.; Murai, S. Room-Temperature Regioselective C-H/Olefin Coupling of Aromatic Ketones Using an Activated Ruthenium Catalyst with a Carbonyl Ligand and Structural Elucidation of Key Intermediates *J. Am. Chem. Soc.* **2010**, *132* (50), 17741–17750.
(64) Kakiuchi, F.; Yamamoto, Y.; Chatani, N.; Murai, S. Catalytic Addition of Aromatic C-H Bonds to Acetylenes. *Chem. Lett.* **1995**, *24* (8), 681–682.
(65) Kakiuchi, F.; Uetsuhara, T.; Tanaka, Y.; Chatani, N.; Murai, S. Ruthenium-Catalyzed Addition of Olefinic C-H Bonds in Conjugate Enones to Acetylenes to Give Conjugate Dienones. *J. Mol. Catal. A: Chem.* **2002**, *182-183*, 511–514.

https://doi.org/10.1021/acscatal.6c04752
ACS Catal. XXXX, XXX, XXX–XXX

(66) Kakiuchi, F.; Kan, S.; Chatani, N.; Murai, S. A Ruthenium-Catalyzed Reaction of Aromatic Ketones with Arylboronates: A New Method for the Arylation of Aromatic Compounds via C-H Bond Cleavage. *J. Am. Chem. Soc.* **2003**, *125* (7), 1698–1699.
(67) Kakiuchi, F.; Matsuura, Y.; Kan, S.; Chatani, N. A $RuH_2(CO)(PPh_3)_3$-Catalyzed Regioselective Arylation of Aromatic Ketones with Arylboronates via Carbon-Hydrogen Bond Cleavage. *J. Am. Chem. Soc.* **2005**, *127* (16), 5936–5945.
(68) Kakiuchi, F.; Matsumoto, M.; Tsuchiya, K.; Igi, K.; Hayamizu, T.; Chatani, N.; Murai, S. The Ruthenium-Catalyzed Silylation of Aromatic C-H Bonds with Triethylsilane. *J. Organomet. Chem.* **2003**, *686* (1-2), 133–144.
(69) Kakiuchi, F.; Tsuchiya, K.; Matsumoto, M.; Mizushima, E.; Chatani, N. $Ru_3(CO)_{12}$-Catalyzed Silylation of Benzylic C-H Bonds in Arylpyridines and Arylpyrazoles with Hydrosilanes via Bond Cleavage. *J. Am. Chem. Soc.* **2004**, *126* (40), 12792–12793.
(70) Kakiuchi, F.; Ohtaki, H.; Sonoda, M.; Chatani, N.; Murai, S. Mechanistic Study of the $Ru(H)_2(CO)(PPh_3)_3$-Catalyzed Addition of C-H Bonds in Aromatic Esters to Olefins. *Chem. Lett.* **2001**, *30* (9), 918–919.

https://doi.org/10.1021/acscatal.6c04752
ACS Catal. XXXX, XXX, XXX–XXX