Metal-Assisted Cleavage of a C–C Double Bond: Simple and Reversible

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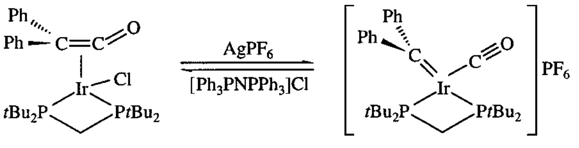
In the context of studies concerned with the mechanism of the Fischer–Tropsch synthesis, it has been speculated as to whether the generation of oxygen-containing products, formed in different amounts depending on the reaction conditions, is because of the initial coupling of a CH_2 and CO group.[1] It appeared plausible to assume that the ketene so formed, $CH_2{=}C{=}O$ is first transformed by hydrogenation to acetaldehyde and then to ethanol. The coupling of a carbene (or a precursor thereof) with CO in the coordination sphere of a transition metal had been demonstrated for the first time in 1960 by Rüchardt and Schrauzer who attempted to prepare a diphenylcarbenenickel complex from $[Ni(CO)_4]$ and Ph_2CN_2 but obtained diphenylketene.[2]

Considering the great importance of the Fischer–Tropsch synthesis, it is not surprising that also in the years after 1960 a host of efforts were made to find evidence for the metal-assisted formation of ketenes by a C–C coupling process. For this reason, mono- as well as dinuclear complexes which contain either a terminal or a bridging carbene ligand and which react with CO to give the corresponding ketene, were chosen as model systems.[3] However, in none of these studies had it been achieved to fragment a metal-bonded ketene into a CO and a carbene while both ligands remain coordinated to the metal center. All attempts which were undertaken in this direction led to the formation of di- or trinuclear complexes with bridging carbene units.[4]

Most recently, in a paper which immediately aroused considerable attention[5] Grotjahn et al. reported that diphenylketene linked to an iridium(I) center can be split into a CO and a diphenylcarbene ligand even at room temperature.[6] The starting material **1** [see Eq. (a)] was prepared from the dimer $[\{IrCl(C_8H_{14})_2\}_2]$, $t\mathrm{Bu_2PCH_2P}t\mathrm{Bu_2}$, and $Ph_2C{=}C{=}O$ in 61 % yield. The coordination of the ketene by the C=C instead of the C=O double bond was confirmed by an X-ray crystal structure analysis. Typical structural features of **1** are the nearly orthogonal position of the C=C bond of the ketene to the [P,Ir,P] plane and the relatively long C=C bond of 1.488(7) Å which is significantly longer than in other η^2-(C,C)-ketene complexes.[7, 8]



(a)

1 **2**

To initiate the desired cleavage of the C–C bond, the chloro ligand *cis* to the ketene of the 16-electron complex **1** was removed under mild conditions. Treatment of **1** with $AgPF_6$ in CH_2Cl_2 led to the elimination of chloride and the generation of a free coordination site, which allowed the C=O bond to "slide" into this position leading to the formation of the cationic carbene(carbonyl)iridium(I) complex **2**. The X-ray crystal structure analysis of **2** revealed a slightly distorted square-planar coordination geometry around the metal center, the distortion being caused both by the small bite angle of the bis(di-*tert*-butylphosphino)methane and the steric hinderance between the phenyl groups of the carbene ligand and the neighboring *tert*-butyl moieties. The Ir–C(carbene) bond of **2** is 1.996(8) Å and thus approximately 0.1 Å longer than in a recently described neutral diphenylcarbene iridium(I) complex.[9]

However, even more interesting than the cleavage of the C–C bond is the reversibility of the reaction. Upon addition of $[Ph_3P{=}N{=}PPh_3]Cl$ to a solution of **2** in CD_2Cl_2 at −50 °C and subsequent warming of the reaction mixture to room temperature, the ketene complex **2** is regenerated with 64 % yield. The carbonyl compound $[IrCl(CO)(\kappa^2\text{-}t\mathrm{Bu_2PCH_2P}t\mathrm{Bu_2})]$ was obtained as a byproduct in 31 % yield. The authors emphasize that the conditions for the back reaction are not yet optimized.[5] Theoretical studies by P. Hofmann and his group at Heidelberg lead to the conclusion that the activation energy for the carbene–CO coupling in the model system $[Ir(CH_2)(CO)(\kappa^2\text{-}H_2PCH_2PH_2)]^+$ amounts to about 105 kJ mol^{-1},[10] which seems reasonable with respect to the experimental data for the real compound **3**.

Moreover, the work by Grotjahn et al. with its highlight of the reversible C–C bond cleavage has drawn attention to the renaissance of the chemistry of ketene–metal complexes and the metal-assisted activation of these ketenes.[8, 11, 12] From the standpoint of the coordination chemist, two communications published most recently should be particularly mentioned. In both cases, rhodium plays a decisive role as the metal center. The first paper confirms with compounds **5** and **6** as an example (Scheme 1), that also in the case of ketene transition

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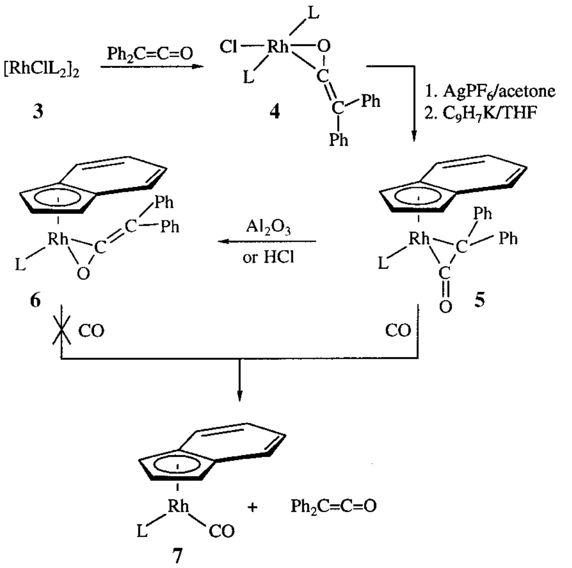
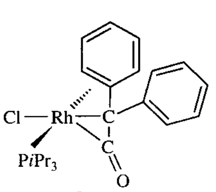


Scheme 1. Isomerization between C,C- and C,O-bound ketene–rhodium complexes; L = P*i*Pr$_3$

metal complexes an isomerization by an alternating shift of the C=C and the C=O bond (e.g., the formation of bond isomers) is possible.[13] The starting material for the preparation of **5** is compound **4**, which is obtained from **3**. As shown by an X-ray structure analysis **4** contains a C,O-bonded ketene ligand. Compound **4** is thermally remarkably stable and below its melting point of 110 °C does not rearrange into the C,C-bonded isomer. Compound **4** reacts in two steps with $AgPF_6$ and C_9H_7K to afford the indenyl complex **5** (86% yield), the spectroscopic data of which point to the unexpected isomerization. The X-ray crystal structure analysis confirmed this assumption. The C–C bond of the diphenylketene in **5** is longer and the C–O bond shorter than in **4**. In benzene under acidic conditions **5** rearranges quickly into the thermodynamically more stable isomer **6**. The η^2-(C,C)-bonded isomer **5** reacts spontaneously with CO to give the carbonyl complex **7** (and diphenylketene) while the η^2-(C,O)-bonded isomer **6** is completely inert toward CO. According to the HSAB concept the "soft" C=C bond and not the "hard" C=O bond should coordinate preferentially to the "soft" metal center, thus the enhanced stability of **6** compared to **5** is noteworthy indeed.

The main goal of the second paper, which—duplication of the events—appeared only 11 months after the first,[14] was also the synthesis and reactivity of the rhodium(I) compound **4** shown in Scheme 1. The authors prepared this compound in a one-pot procedure from $[\{RhCl(C_8H_{14})_2\}_2]$, P*i*Pr$_3$, and $Ph_2C{=}C{=}O$ with nearly quantitative yield. They were equally impressed by the high thermodynamic stability but in addition observed that, in the presence of $[\{RhCl(C_8H_{14})_2\}_2]$ or CuI, **4** reacts over a few days, by elimination of a phosphane ligand, to form complex **8**. The related compounds with coordinated PMe(tBu)$_2$ or PCy$_3$ instead of P*i*Pr$_3$ behave analogously. The X-ray crystal structure analysis of the PMe(tBu)$_2$ derivative confirms that in the course of the reaction the metal slips from the C–O to the C–C bond of the ketene and that in the isolated product two carbon atoms of one phenyl ring weakly interact with the rhodium center. The coordination of $Ph_2C{=}C{=}O$ can thus be described as that of a chelating vinylketene. Quite unexpectedly, compound **8** shows fluxional behavior in solution which, according to the authors, could be explained by a formal migration of the metal from one side of the phenyl ring to the other.[14]



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In conclusion, there is no doubt that the work by Grotjahn et al.[5] illustrated for the first time and in an impressive way a fundamentally important reaction for organometallic chemistry, namely the metal-assisted reversible cleavage of a C–C double bond. It is likely that this study will initiate new efforts to investigate once more the elementary steps of the Fischer-Tropsch synthesis with the aim of finding more appropriate catalysts for the selective generation of oxygen-containing products.

Received: July 31, 2000 [H1474]

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NMR Quantum Computing

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Nuclear magnetic resonance (NMR) is one of the most important methods for the identification of molecules and for the determination of their structure and dynamics. However, during the last few years, there has been a series of stimulating publications,[1, 2] in which the methods of NMR spectroscopy were applied to very simple and well known compounds. The goal of these projects was not to refine existing models of the structure or dynamics of these compounds but to realize experimentally the until then, purely theoretical concept of quantum computing. The idea to construct computers based on quantum-mechanical principles was first suggested in 1982 by the physicist Richard Feynman.[3]

In order to understand why quantum computers are of interest, it is helpful to compare the ways information is stored in classical and in quantum computers, respectively. In a classical computer, the smallest unit of information, a bit, can take values represented by either 0 or 1. In a quantum computer, the smallest unit of information is a quantum bit (qubit), which corresponds to a quantum-mechanical two-level system with basis states $|0\rangle$ and $|1\rangle$. For example, such a qubit can be represented by a ½-spin particle, in which the states $|0\rangle$ and $|1\rangle$ correspond to a parallel or an antiparallel alignment of the spins relative to an external magnetic field (Figure 1 a). However, in contrast to its classical analogue, a qubit can also exist in a quantum-mechanical superposition of $|0\rangle$ and $|1\rangle$ and is hence characterized by two complex numbers c_1 and c_2, the probability amplitudes of the two basis states. The state function is $|\psi\rangle = c_1|0\rangle + c_2|1\rangle$ with the normalization condition $|c_1|^2 + |c_2|^2 = 1$. For example, in NMR the superposition states $|\psi\rangle_x = 2^{-1/2}(|0\rangle + |1\rangle)$ and $|\psi\rangle_y = 2^{-1/2}(|0\rangle + \mathrm{i}|1\rangle)$ correspond to transverse x and y magnetization, respectively. With every additional qubit (such as a ½-spin particle), the number of base states of the quantum-mechanical system doubles (Figure 1 b). Hence, the complete characterization of a register consisting of N qubits (such as N coupled ½-spins) requires 2^N complex numbers (probability amplitudes), whereas a register of N classical bits is, by definition, completely characterized by N integers (0 or 1). The superposition principle and the exponential growth of the size of the quantum-mechanical state space makes it possible to perform a large number of quantum computations simultaneously, that is, in parallel. However, this requires the development of appropriate computational procedures (quantum algorithms) that make the best use of the laws of quantum mechanics.[4–6]

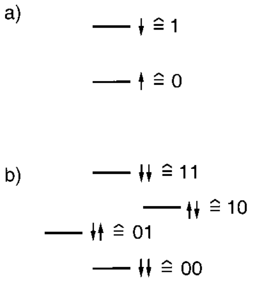

Figure 1. a) A ½-spin nuclei in an external magnetic field with basis states "spin up" and "spin down" is an example of a quantum-mechanical two-level system, which corresponds to a qubit with states 0 and 1, respectively. b) Two ½-spins in an external magnetic field form a four-level system. The basis states and the corresponding values of the two qubits are shown schematically. In contrast to classical bits, the quantum-mechanical system can also exist in a superposition of the basis states shown.

A quantum algorithm for prime factorization, developed by Peter Shor, is of particular interest.[5] One of the most important methods for cryptography is based on the difficulty of prime factorization (the RSA method)[7] because, for classical algorithms, the time required for the factorization of a given number increases exponentially with the number of digits. In contrast, the time required by Shor's quantum algorithm grows at a significantly slower rate (only as a polynomial function of the number of digits). Hence, this quantum algorithm could be a potential threat for encrypted messages if a sufficiently large quantum computer (with hundreds or thousands of qubits) could be realized. However, as stated 1998, "Many years will pass until a computer with the necessary number of qubits will crack private keys on this planet—a quantum computer with more than four qubits in this millennium would already be a sensation".[8]

Current experimental approaches for the realization of quantum computers are ion traps,[9] quantum dots,[10] Josephson contacts, [11] and NMR spectroscopy;[1] the latter is, so far, most advanced in the practical implementation of quantum algorithms. NMR spectroscopy provides elegant methods for the controlled manipulation of nuclear spins, which are particularly well suited to act as qubits because of their isolation from the environment. However, a liquid NMR sample contains an ensemble of many identical spin systems and it is not possible to manipulate or to detect individual spin systems. Hence, at the beginning of a computation, NMR quantum computers are commonly prepared in a "pseudo-pure" state rather than in a pure state and, furthermore, ensemble-averaged expectation values are detected rather than the observables of individual spin systems.[1] The basic computational steps of quantum algorithms can be realized with the help of radio-frequency pulses and can be broken down to spin-selective pulses and CNOT (conditional NOT) gates (Figure 2) between pairs of spins. The number of qubits is mainly restricted by the availability of compounds with suitable spin systems.

For the efficient implementation of an NMR quantum computer with N qubits, a molecule with N coupled ½-spins is

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