Carbon Dioxide Fixation

DOI: 10.1002/anie.200803953

Oxygen Atom "Cut and Paste" from Carbon Dioxide to a Fischer Carbene Complex**

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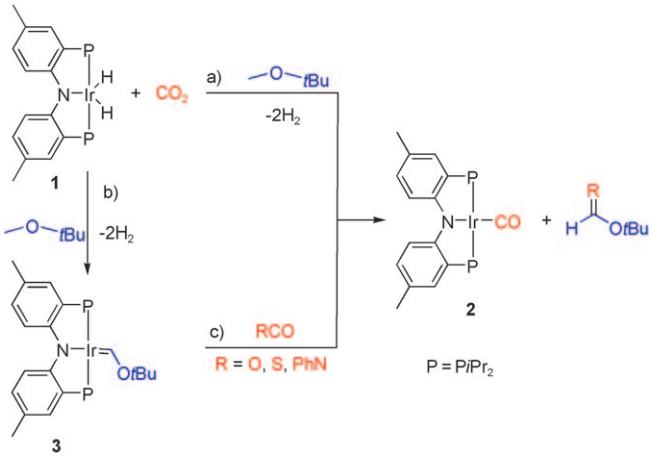
carbenes · carbon dioxide · iridium · metathesis · oxygen-atom transfer

Carbon dioxide could be a cheap and abundant feedstock for the large-scale formation of commodity chemicals and materials. Its chemistry has aroused much interest and has been extensively reviewed.[1–6] The inertness of carbon dioxide constitutes a serious drawback and makes it a difficult molecule to activate and functionalize. Nature has found ways to overcome the large carbon–oxygen double bond dissociation energy (BDE) of 127 kcal mol^{-1} [7] by utilizing late-first-row transition metals to reduce carbon dioxide.[4,8] A few metal-mediated processes involving cleavage of the strong carbon–oxygen double bond in solution under mild conditions in man-made systems have been reported.[9–13] However, activation and functionalization of this intriguing compound remain a great challenge.

Whited and Grubbs succeeded in transferring an oxygen atom from carbon dioxide to an organic substrate,[9] which can be considered a great stride forward and is the subject of this highlight article. The reaction is selective, occurs under mild homogeneous conditions, and can be carried out in a single reaction vessel. In particular, the previously reported iridium dihydride complex **1**[14] was used to reduce carbon dioxide, with concurrent oxygen atom transfer to a methyl ether and formation of an iridium–carbonyl complex (**2**). The methyl ether conveniently plays a double role as a solvent and oxygen acceptor. Interestingly, this new process involves the formation of a Fischer carbene complex (**3**; Scheme 1).[9] The unusual reactivity of complex **3** is not limited to carbon dioxide. It also reacts in a regioselective manner with carbonyl sulfide and phenyl isocyanate to afford *tert*-butyl thioformate and *tert*-butyl *N*-phenylformimidate, respectively, and, as before, complex **2**.

The reactivity and the stability of the iridium metal center is controlled by Ozerov's pincer ligand.[15] This system is a relatively poor σ donor but a good π donor and readily forms well-defined rhodium, iridium, and other metal complexes that exhibit interesting reactivity, coordination chemistry, and catalytic activity with a variety of substrates.[15–24] For example, complex **1** is also successful in activating various substrates by C–H and aryl–halide oxidative addition,[14,25,26] regioselective alkyne dimerization, and Heck olefin arylation.[15] Calimano and Tilley very recently used this popular complex (**1**) to generate an iridium–silylene complex that efficiently catalyzes the anti-Markovnikov hydrosilylation of alkenes by direct addition of the silicon–hydrogen bond of both aryl and alkyl-substituted primary silanes to carbon–carbon double bonds.[26]



Scheme 1. Single atom (O and S) and group (PhN) transfer chemistry.[9] a) Thermolysis of complex **1** under an atmosphere of carbon dioxide in MTBE results in the formation of a stoichiometric amount of *tert*-butyl formate and an iridium carbonyl complex **2**. b) Formation of a Fischer carbene complex **3** by α,α dehydrogenation of MTBE. c) O, S, and nitrene transfer to the carbene **3** generating complex **2** and an organic substrate.

The mechanism underlying the remarkable carbon dioxide reduction coupled with oxygen atom transfer to a Fischer carbene has been elucidated in much detail by Whited and Grubbs (Scheme 2).[9,27] The reaction pathway includes some interesting intermediates that were observed by NMR spectroscopy. The initial step is the release of dihydrogen from complex **1** and the formation of a MTBE adduct (**4**) or its reactive equivalent by coordination of the oxygen atom to the low-valent metal center (Scheme 2, **1**→**4**). Double C–H

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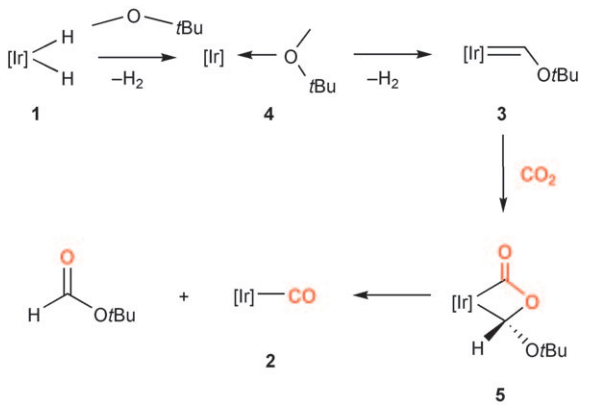
[**] M.E.vd.B. is supported by the G.M.J. Schmidt Minerva Center and the Helen and Martin Kimmel Center for Molecular Design. He is Head of the Minerva Junior Research Group on Molecular Materials and Interface Design.



Scheme 2. Reaction mechanism for the proposed "oxygen-atom metathesis" from carbon dioxide to a metal-bound Fischer carbene.[9]

bond activation at the α-carbon atom of the solvent, methyl *tert*-butyl ether (MTBE), with a further loss of dihydrogen results in the isolated metal-bound Fischer carbene complex (**4**→**3**). However, it is not entirely clear whether the formation of complex **4** is a necessary step in the reaction coordinate or a side equilibrium. Nevertheless, it is likely that the first C–H bond cleavage is facilitated by the coordination of the substrate to the unsaturated iridium center, whereas the second C–H bond activation probably proceeds by α-hydrogen migration. Norbornene can be added to act as a dihydrogen sink to prevent regeneration of complex **1** from intermediate **4**. The conversion of a methyl ether to a Fischer-type carbene has indeed been observed. The first such example was provided by Werner more than 15 years ago for an osmium complex.[28]

The structurally characterized complex **3** is a rare example of a (formally) iridium(I) carbene. The authors noted that this complex does not react with nucleophiles, which is not common for Fischer carbenes.[29] The subsequent reaction of complex **3** with carbon dioxide probably results in the four-membered metallalactone **5**, which might be formed by a nucleophilic attack of the d^8 metal center on the carbon dioxide molecule. The metallacycle of complex **5** is unstable and collapses with the elimination of an organic component, *tert*-butyl formate, and the concurrent formation of the robust iridium–carbonyl complex (**2**). Isotope labeling studies clearly revealed that carbon dioxide is the source of the carbonyl ligand of complex **2**. The formation of intermediate complex **5** was confirmed spectroscopically at −60 °C, which renders the collapse and ring opening of metallacycle **5** as the rate-determining step and not the activation of carbon dioxide by the Fischer carbene **3**. Kinetic experiments carried out at −20 °C indicate a reaction that is first order in both carbon dioxide and complex **3**, which suggests that carbon dioxide activation is the likely rate-limiting step at higher temperatures. In contrast to the carbon dioxide chemistry, no intermediates were observed with the two isoelectronic heterocumulenes. The formation of the unstable metallacyle **5** is especially intriguing since structurally related metallacyclobutane is a well-known key intermediate in olefin metathesis. This similarity suggests that much more important carbon dioxide and related chemistry awaits exploration with Fischer carbene complexes.

The transfer of an oxygen atom from carbon dioxide to an organic substrate to form a carbonyl ester group and a carbonyl ligand is a very remarkable aspect of Whited and Grubbs' work.[9] The reverse transfer of an oxygen atom from various substrates to metal–carbonyl complexes is known. There is an example reported by Gade et al. that shows the transfer of the oxygen atom of a cyclopropenone to a metal–carbonyl complex to form a metal-bound carbon dioxide unit.[30] This interesting process is thought to operate through a reverse pathway of the mechanism depicted in Scheme 2.

The next challenge is clear. Is it possible to achieve selective oxygen-atom transfer from carbon dioxide to a carbene in a catalytic fashion under mild homogeneous reaction conditions? Pincer-based complexes are known to catalyze various reactions,[26,31–37] including alkane dehydrogenation,[35] cross-coupling reactions,[38] and Milstein's direct coupling of alcohols with amines to form amides.[33] As pointed out by the authors, the system highlighted here has one drawback: the formation of the iridium–carbonyl moiety **2** makes the overall process thermodynamically favorable, but at the same time, unfortunately, it also destroys the catalytic process. Finding an escape route for the carbon dioxide will result in an elegant way to catalytically reduce carbon dioxide and functionalize Fischer carbenes by Whited and Grubbs' proposed "oxygen-atom metathesis" route.[9] This chemistry does not have to be limited to monoanionic pincer-based complexes. It is known that processes initially designed for such complexes have served as stepping stones for other systems.[39–41] Furthermore, the catalytic breakdown of carbon dioxide in homogenous systems is certainly not an impossible mission under ambient conditions, as beautifully demonstrated by Sadighi in 2005.[12]

Published online: December 3, 2008

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