Communication

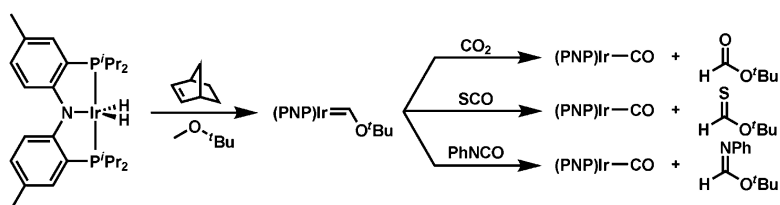# Oxygen-Atom Transfer from Carbon Dioxide to a Fischer Carbene at (PNP)Ir

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Oxygen-Atom Transfer from Carbon Dioxide to a Fischer Carbene at (PNP)Ir

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Though there is significant interest in reductive transformations of carbon dioxide,[1,2] direct scission of the C=O bond is seldom realized due to the thermodynamic stability of the highly oxidized carbon and the bond strength (127 kcal/mol).[3] Highly reducing early transition metal and uranium complexes have been reported to effect the cleavage of CO_2,[4] but it is rarely accomplished at late transition metal centers.[5,6] Peters and co-workers have recently described a low valent iron complex that breaks the C=O bond, yielding a bimetallic dimer with a structurally unique μ-carbonyl/μ-oxo core.[5a] Additionally, Sadighi and co-workers have reported the copper-catalyzed deoxygenation of CO_2 via net oxygen-atom transfer to diborane reagents.[5c]

Herein we describe the preparation of an iridium-supported Fischer carbene complex via double C–H activation of methyl t-butyl ether and the quantitative transfer of oxygen from CO_2 to the metal carbene to yield t-butyl formate and an iridium carbonyl. The carbene has also been found to effect sulfur-atom and nitrene-group transfer from carbonyl sulfide and phenyl isocyanate, respectively. Although transition metal carbene complexes are fundamentally important in a number of transformations, both catalytic and stoichiometric, to our knowledge the only reports of reactivity between metal-bound carbenes and CO_2 involve nucleophilic attack by the carbene.[7] Thus, the decarbonylative pathways described in this contribution represent a unique mode of reactivity for metal carbenes.

Our studies began with the observation that, while metal–carbon multiple bonds are known for group 9 metals, the reactivity of these moieties has not been extensively investigated. In light of the well-known dehydrogenative ability of iridium(I),[8] we were interested in the reaction between pincer-supported iridium and methyl ethers. In these cases, a directed C–H activation could be followed by α-hydrogen migration to yield the Fischer carbene since β-elimination would be inaccessible.[9] If Ir=C bonds could be formed spontaneously, we reasoned, a catalytic cycle for C–C bond formation could be envisioned.[10]

Indeed, α,α-dehydrogenation was realized upon exposure of the previously reported dihydride $(PNP)IrH_2$ (**1**)[11] to 2 equiv of norbornylene in methyl t-butyl ether (MTBE). Rapid formation of the MTBE adduct is observed by ^{31}P NMR (δ 45 ppm), followed by double C–H activation and loss of H_2 over a period of 16 h to afford the Fischer carbene of iridium(I), $(PNP)Ir=C(H)O^tBu$ (**2**) (Scheme 1). Two equivalents of norbornylene is required to ensure complete reaction since regeneration of **1** occurs readily upon exposure of the Ir(I) ether adduct to H_2. The identity of **2** has been confirmed by NMR, combustion analysis, and X-ray diffraction. The crystal structure of **2** is provided in the Supporting Information and is discussed in greater detail elsewhere.[10] However, we note that the Ir=C bond length (1.88 Å) is consistent with those previously reported for iridium alkoxycarbenes.[9a,12]

Scheme 1
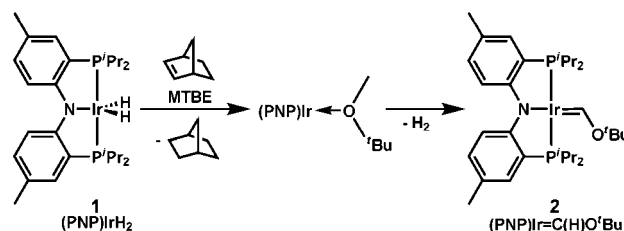
An initial survey of the reactivity of **2** revealed a strong propensity to decarbonylate the carbene upon thermolysis, releasing isobutylene and forming the *trans*-dihydrido iridium carbonyl complex (v_{CO} = 1991 cm^{-1}),[10] precluding the possibility of a bimolecular reaction between two carbenes to form a carbon–carbon bond. Also, unlike numerous reported Fischer carbenes,[13] **2** does not react with nucleophiles such as amines, alkoxides, or alkyllithium reagents, indicating the low electrophilicity of the carbene bound to low valent iridium.

In light of these findings, we anticipated that distinct reactivity might be realized. Since simple molecular orbital considerations indicate that the square planar Ir(I) should have a HOMO of d_{z^2} origin oriented out of the plane of the complex, we were intrigued by the possible reactivity of **2** with electrophiles.[13d] Exposure of a solution of **2** in C_6D_6 to an atmosphere of CO_2 resulted in the quantitative formation of (PNP)Ir–CO (**3**, v_{CO} = 1930 cm^{-1}) over a period of 30 min with concomitant expulsion of t-butyl formate (eq 1 in Figure 1). Reaction of **2** with [13]CO_2 afforded (PNP)Ir–[13]CO (v_{CO} = 1883 cm^{-1}), confirming that the carbonyl ligand is derived from carbon dioxide. Although oxygen-atom transfer from CO_2 to free carbenes has been reported and studied theoretically,[14] this reaction represents an unusual instance of oxygen extrusion from carbon dioxide by a metal-bound carbene.

We propose a mechanism wherein initial nucleophilic attack at CO_2 by iridium is followed by cyclization to form a four-membered metallalactone analogous to the metallacyclobutane demonstrated as an intermediate in olefin metathesis.[15] Subsequent elimination of t-butyl formate results in an effective "oxygen-atom metathesis" from CO_2 to the metal-bound Fischer carbene (Scheme 2).[16] When the reaction is monitored by ^{1}H NMR at −60 °C, small amounts of an intermediate species are observed. Consistent with the assignment of this species as the metallacycle is the appearance of a triplet (δ 6.5 ppm, $^3J_{PH}$ = 9 Hz) formulated as the metallalactone proton. Also consistent with the proposed mechanism are kinetic studies confirming that the reaction is first order in both **2** and CO_2 (−20 °C, pseudo-first-order conditions).

In light of this finding and previous results from Mayer's laboratory,[4b] it seemed likely that **2** would effect the decarbo-
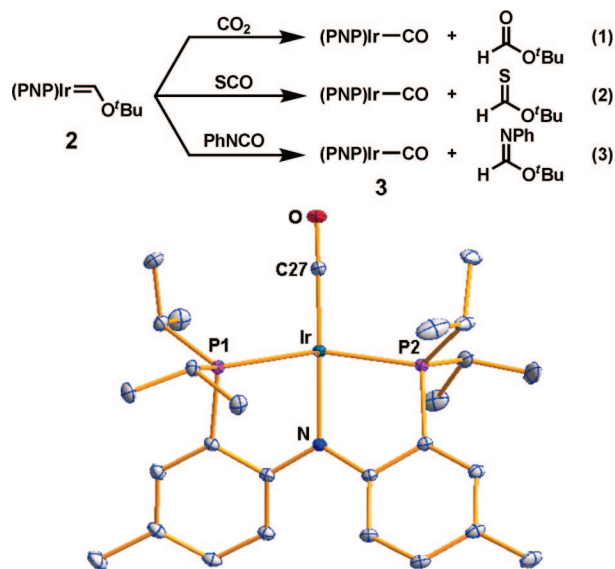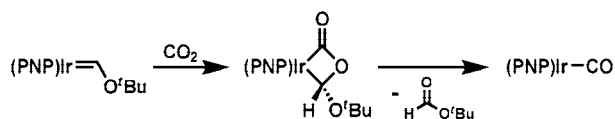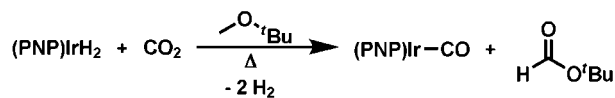
Figure 1. Reactions of **2** with carbon dioxide, carbonyl sulfide, and phenyl isocyanate, and a displacement ellipsoid (35%) representation of (PNP)Ir—CO (**3**). Selected bond lengths (Å) and angles (°): Ir—N 2.073(1), Ir—C27 1.826(1), Ir—P1 2.2865(4), Ir—P2 2.2886(4), P1—Ir—P2 161.20(1), N—Ir—C27 176.68(7).

Scheme 2

Scheme 3

nylation of other oxygen-containing heterocumulenes. Exposure of **2** to carbonyl sulfide (1 atm) results in immediate and quantitative formation of **3** and *t*-butyl thioformate (eq 2 in Figure 1). Similarly, addition of phenyl isocyanate to a solution of **2** in C_6D_6 effects nitrene transfer to the Fischer carbene to generate **3** and *N*-phenyl *t*-butylformimidate (eq 3 in Figure 1). To our knowledge, the closest precedent for this type of reaction comes from Ibers' report of sulfur-atom transfer from SCO to triphenylphosphine at low valent iron and ruthenium centers.[17] The formation of isocyanates by the interaction of nitrenes and CO at transition metals has also been reported.[18] The facility with which the SCO and PhNCO reactions proceed at low temperatures precludes the observation of reactive intermediates or thorough kinetic analysis, but four-membered metallacyclic intermediates are proposed since carbonyl sulfide and phenyl isocyanate are isoelectronic to carbon dioxide.

The acceptorless oxidation of methyl *t*-butyl ether to *t*-butyl formate can be accomplished in one pot by thermolysis of **1** in MTBE under an atmosphere of CO_2, generating **3** and 1 equiv of *t*-butyl formate (Scheme 3). At this time, it seems that the unusually high driving force for all of the transformations described can be attributed to the stability of (PNP)Ir—CO (**3**). Thus, development of catalytic reactions is likely to be hampered by the large energy input required to regenerate **1**.

In summary, we have described the synthesis of a pincer-type iridium carbene which interacts with CO_2 in an unusual

way, abstracting oxygen to produce a formate ester and an iridium carbonyl. The complex reacts in analogous fashion with carbonyl sulfide and phenyl isocyanate to generate the same iridium carbonyl and the corresponding thioformate or formimidate. Current efforts are underway to examine the scope of these reactions and better clarify the mechanism by which they occur.

Supporting Information Available: Complete ref 2a, detailed experimental procedures and characterization data for compounds **2** and **3** as well as kinetic data for the reaction between **2** and CO_2 under pseudo-first-order conditions. Crystallographic details for **2** and **3** are provided in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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