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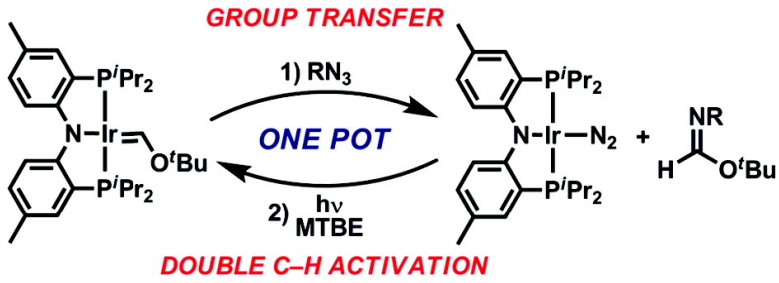

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A Catalytic Cycle for Oxidation of *tert*-Butyl Methyl Ether by a Double C−H Activation-Group Transfer Process

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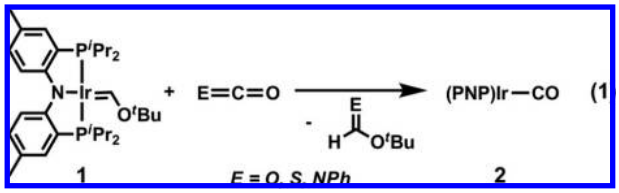
Despite numerous advances and decades of research, unactivated C−H bonds are still considered almost entirely inert to catalytic cleavage and functionalization. Such unactivated C−H bonds are ubiquitous in organic chemicals and hydrocarbon feedstocks, making their selective transformation an important goal. Myriad transition metal species have been reported that are capable of selective C−H activation,[1] typically by a single oxidative addition or σ-bond metathesis event, though other important mechanisms are known.[1d,f] In the cases where C_{sp^3}−H bonds are activated, these processes generally produce M−C_{sp^3} species, imposing limits on the types of products that can be obtained. In contrast, we envisioned an alternate strategy where multiple C−H activation events would generate M═C_{sp^2} species for further elaboration.[2] In light of the rich reactivity of metal-bound carbenes,[3] generation of such a species could open a new manifold of reactivity for catalytic C−H functionalization.

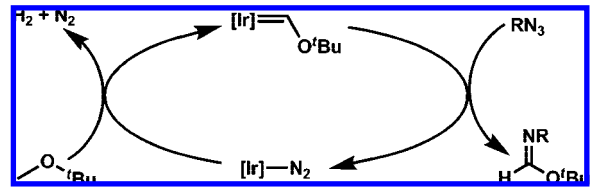
We have previously reported that pincer-type iridium complexes supported by Ozerov's PNP ligand (PNP = $[N(2\text{-}P^iPr_2\text{-}4\text{-}Me\text{-}C_6H_3)_2]^-$)[4] effect the double C−H activation of *tert*-butyl methyl ether (MTBE) to generate an unusual square-planar iridium(I) carbene (**1**) with loss of H_2.[5] Unlike most carbenes, which are nucleophilic or electrophilic at carbon, this complex possesses a high-lying Ir(d_{z^2}) orbital that renders it nucleophilic at iridium, effecting atom and group transfer to the carbene from electrophilic heterocumulenes (eq 1).[5a,6] In this contribution, we report that (PNP)Ir═C(H)O^{t}Bu (**1**) promotes analogous atom and group transfer from nitrous oxide and organic azides, allowing recycling of the resulting iridium complexes and suggesting a new catalytic cycle based on generation of M═C_{sp^2} species.[7]



In our previous investigations of atom and group transfer from heterocumulenes, we have noted that the generation of a stable (PNP)Ir−CO species (**2**) seems to provide the thermodynamic driving force for the cleavage of strong C═E bonds (E = O, S, NPh).[5a] Thermolysis and photolysis of complex **2** in MTBE produces no observable C−H activation products. Thus, the disadvantage inherent in these reactions is the difficulty in achieving catalytic turnover due to the reluctance of carbonyl complex **2** to serve as a precursor for C−H activation.

In light of our previous observation that C−H activation by (PNP)Ir is not hindered by the presence of N_2,[5] it seemed plausible that a change in oxidant from carbonyl reagents (E═C═O) to the isoelectronic diazo reagents (E═N═N) could offer a related route that circumvents unreactive carbonyl complex **2**. By analogy with earlier investigations,

Scheme 1. Proposed Cycle for MTBE Oxidation

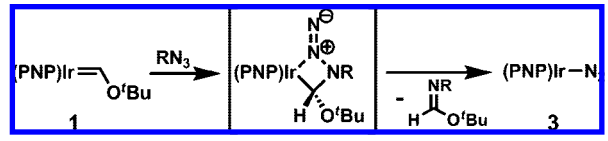


organic azides should react with nucleophilic complex **1** at the electrophilic central nitrogen.[6] Subsequent cyclization and elimination of formimidate would generate an iridium−dinitrogen complex, which could serve as a viable precursor for C−H activation to regenerate the iridium carbene, as depicted in Scheme 1. This reactivity would find precedent in the work of Hillhouse, wherein organic azides and nitrous oxide were shown to oxidize electron-rich Ni(II) dialkyls by nitrene-group and oxygen-atom insertion, respectively.[8,9]

As predicted, exposure of complex **1** to organic azides resulted in quantitative nitrene-group transfer to generate the expected formimidate and the previously unknown dinitrogen adduct (PNP)Ir−N_2 (**3**).[10] The transfer reaction proceeded cleanly with trimethylsilyl azide (TMS−N_3), 2,6-diisopropylphenyl azide (DIPP−N_3), and 1-azidoadamantane (AdN_3), with reaction rates reflecting the steric bulk of the azide substituent (DIPP > Ad > TMS). In accord with the isoelectronic analogy between CO_2 and N_2O, carbene **1** also reacted with nitrous oxide to effect oxygen-atom transfer, generating *tert*-butyl formate and **3**.

These reactions have few analogues in transition metal carbene chemistry,[11,12] presumably because Fischer carbenes are generally electrophilic at carbon and organic azides and N_2O are poor nucleophiles.[13] The closest precedent comes from elegant studies by Collman and co-workers on the generation of iridium(I)−dinitrogen complexes by nitrene transfer from organic azides to bound carbonyl ligands with release of isocyanate.[14] By analogy with our previous studies, we propose that the transformations proceed through a four-membered iridacyclic transition state (Scheme 2), and tentatively suggest that a similar mechanism is likely operative in the *trans*-Ir(Cl)(CO)(PR_3)$_2$ systems examined by Collman.[14]

Scheme 2



Dinitrogen complex **3** was characterized by NMR, IR, and single-crystal X-ray diffraction (XRD). XRD analysis (Figure 1) revealed a square-planar complex with metric parameters quite similar to the previously reported (PNP)Ir−CO (**2**). The dinitrogen ligand exhibits

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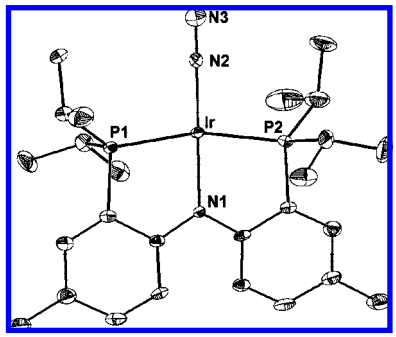
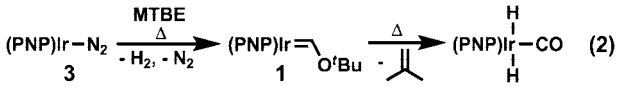


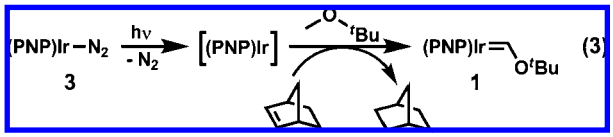
Figure 1. Displacement ellipsoid (30%) representation of (PNP)Ir−N_2 (**3**). Selected bond lengths (Å): Ir−N1, 2.041(3); Ir−N2, 1.859(4); Ir−P1, 2.282(1); Ir−P2, 2.283(1); N2−N3, 1.128(7).

an N−N bond length of 1.13 Å, indicating modest activation of the N_2 unit.[15] The diagnostic IR stretch (2067 cm^{-1}) is lower in energy than those previously reported for N_2 complexes of iridium(I),[5b,14,16] probably due to the trans disposition of the dinitrogen ligand to a strongly π-basic arylamido donor.

Dinitrogen complex **3** was found to be a suitable precursor for the double C−H activation of MTBE. Thermolysis of **3** in neat MTBE resulted in the slow formation of Fischer carbene **1** with loss of H_2 and N_2, though prolonged heating caused the gradual degradation of this complex to the previously reported *trans*-(PNP)Ir(H_2)(CO) (eq 2).[5b]



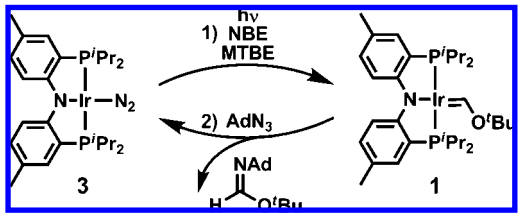
A photolysis route allowed the thermal decomposition of carbene **1** to be avoided. Irradiation of dinitrogen adduct **3** in MTBE at ambient temperature in the presence of norbornene (NBE) as a sacrificial hydrogen acceptor facilitated the quantitative conversion of **3** to **1** (eq 3). This process proceeded smoothly in the presence of *tert*-butyl formates and formimidates, indicating that a catalytic cycle based on double C−H activation of MTBE and subsequent group transfer from organic azides or N_2O would not be hampered by product inhibition.



The development of a continuous process for catalytic oxidation of MTBE to formimidate was hindered by the decomposition of **3** upon photolysis in the presence of organic azides, presumably due to preferential reaction with RN_3 over MTBE. However, the feasibility of a photocatalytic scheme was validated by a sequential method. A solution of **3** and excess NBE in MTBE was subjected to sequential AdN_3 addition (1 equiv) and photolysis, allowing four turnovers to be realized and affording *tert*-butyl *N*-adamantylformimidate in 93% yield (Scheme 3). Current efforts are directed toward the development of a continuous method based on these reactions.

In conclusion, we have presented a sequential process for the oxidation of MTBE based on double C−H activation to generate an alkoxycarbene complex of iridium(I). The active iridium species can be recycled via a one-pot protocol, suggesting that a catalytic process based on these reactions may be achievable. This scheme offers a conceptual alternative to traditional hydrocarbon functionalization pathways and reveals new possibilities for carbon−element multiple bond formation via nucleophilic-at-metal carbene complexes.

Scheme 3



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Supporting Information Available: Detailed experimental procedures and characterization data. Crystallographic details for **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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