Group-transfer reactions of a cationic iridium alkoxycarbene generated by ether dehydrogenation

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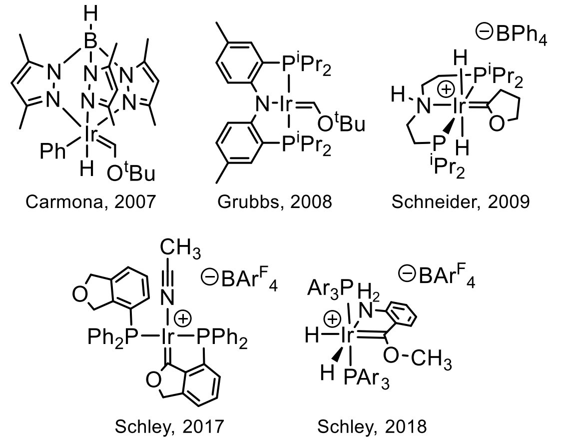
ABSTRACT: Despite broad interest in metal carbene complexes, there remain few examples of catalytic transformations of ethers that proceed via alkoxycarbene intermediates generated by α,α-dehydrogenation. We demonstrate that both neutral and cationic alkoxycarbene derivatives are accessible via ether dehydrogenation at a PNP(^{i}Pr)$_4$ pincer-supported iridium complex (PNP(^{i}Pr)$_4$ = 2,6-bis((diisopropylphosphino)methyl)pyridine). Both cationic and neutral alkoxycarbene complexes undergo group transfer imination with azides, with the cationic derivative serving as a more efficient catalyst for cyclopentyl ether imination. Mechanistic studies support an iridium(I)dinitrogen complex as the resting state in the dark and a role for light-promoted N_2 dissociation. Isoamyl nitrite and phenyl ethyl ketene are also found to engage with the cationic alkoxycarbene complex in formal alkoxide- and O-atom transfer reactions respectively. In the former case an isolable dialkoxyalkyliridium complex is obtained, representing only the second example of a structurally-characterized dialkoxyalkyl complex of a transition metal.

Introduction

The selective activation and functionalization of inert C-H bonds by homogeneous metal complexes has been an area of significant interest since pioneering studies on alkane C-H oxidative addition and alkane dehydrogenation.[1-4] These foundational stoichiometric systems led the way to early examples of catalytic alkane transfer dehydrogenation.[5-9] Further development of alkane dehydrogenation over the intervening decades has revealed design criteria that favor neutral, electron-rich and thermally-stable pincer iridium complexes analogous to those initially applied to alkane dehydrogenation by Kaska and Jensen in 1996.[10-14]

In contrast to the large body of work on alkane dehydrogenation, the dehydrogenation of compounds bearing heteroatom functionality has seen considerably less attention. Jensen and Kaska reported the transfer dehydrogenation of THF to a mixture of furan and dihydrofurans[15] and Goldman has reported the α,β-dehydrogenation of alkyl amines.[16-17] More recently, Brookhart[18] and Huang[19] demonstrated that neutral PCP pincer-supported iridium complexes catalyze the transfer dehydrogenation of alkyl ethers to vinyl ether products. The α,β-dehydrogenation of amines and ethers is complicated by competing α,α-dehydrogenation to give aminocarbene and alkoxycarbene complexes respectively. The formation of iridium alkoxycarbene complexes via ether dehydrogenation and their reactivity has been studied extensively both by Carmona and by Whited and Grubbs.[20-21] Grubbs' work demonstrated that neutral iridium alkoxycarbenes undergo group-transfer reactions with heterocumulenes and certain 1,3-dipolar reagents including CO_2, phenyl isocyanate and adamantyl azide (Ad-N_3). These transformations were proposed to occur via initial [2+2] cyclization to give a 4-membered iridacyclic intermediate. This reactivity is distinct from that of canonical group 6 alkoxycarbenes, and argues for a significant role for the high-lying, filled d_{z^2} orbital in reactions of d^8 alkoxycarbenes.[22]


Carmona, 2007 Grubbs, 2008 Schneider, 2009

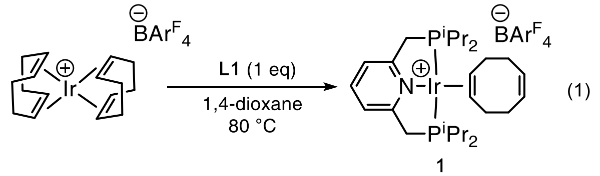
Schley, 2017 Schley, 2018

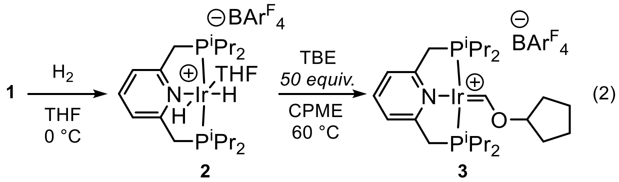
Figure 1. Recent ether-derived alkoxycarbenes.

In this context our group has been exploring the chemistry of *cationic* bis(phosphine)iridium alkoxycarbene complexes with the aim of developing systems with reduced metal-alkoxycarbene backbonding and enhanced electrophilicity relative to neutral variants. Prior to our studies, a single example of THF dehydrogenation to give a cationic iridium alkoxycarbene over a period of days had been reported by Schneider (Figure 1).[23] We have since demonstrated facile formation of cationic alkoxycarbene complexes via ether dehydrogenation in Lewis base-directed intra- and intermolecular examples, with evidence for reversible α-hydride insertion and C-O bond cleavage reactions in certain cases.[24-25] Despite the body of work on the generation of alkoxycarbene complexes via ether dehydrogenation, few stoichiometric transformations and only a single catalytic reaction have been reported.[21, 26-27] We now report the synthesis of a cationic pincer-supported Ir(I) alkoxycarbene complex generated by α,α-dehydrogenation of cyclopentyl methyl ether (CPME) and demonstrate its reactivity in atom- and group-transfer reactions with an alkyl azide, a ketene and an alkyl nitrite. This complex serves as a catalyst in ether imination, showing that cationic iridium complexes are sufficiently competent at ether dehydrogenation to support catalytic transformations.

Results and Discussion

Treatment of commercially-available [(cod)$_2$Ir]BAr$^F_4$ with 2,6-bis((diisopropylphosphino)methyl)pyridine (**L1**) gives complex **1** (eqn. 1) which undergoes hydrogenation to an iridium dihydride complex **2** (eqn. 2). Dehydrogenation of **2** with *tert*-butylethylene in CPME yields a product with a single ^{31}P{^{1}H} NMR signal and a broad, downfield-shifted ^{1}H resonance at 13.5 ppm. This signal is in the range expected for an alkoxymethylidene Ir=C*H*OR resonance,[28-30] which along with the appearance of a ^{13}C{^{1}H} resonance at 234.7 ppm led us to assign the product as cationic alkoxycarbene complex **3**, a site of CPME activation distinct from the 3,4-dehydrogenation observed in a related non-pincer complex.[31] Numerous attempts at confirmation of this assignment through X-ray crystallography ultimately led to a structure solution for **3** from samples crystalizing as 3-component merohedral twins in the P2$_1$ space group (Figure 2). The unambiguous characterization of **3** represents one of only a few cationic iridium alkoxycarbene complexes generated by ether dehydrogenation.[23-25, 32]





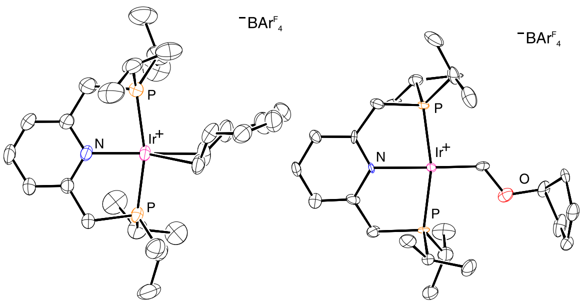
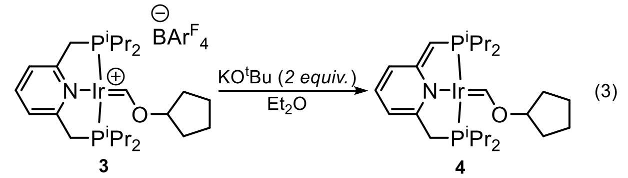


Figure 2. ORTEP diagrams of **1** (left) and **3** (right) shown at 50% probability. Full disorder models are omitted for clarity. Selected bond distances in **3** (Å): Ir=C 1.880(12), Ir-N$_{py}$ 2.179(8), O-C$_{carbene}$ 1.342(16).

Work by Milstein has shown that metal-bound bis(phosphinomethyl)pyridines like **L1** can undergo deprotonation at the α-phosphino methylene position to give a formally monoanionic PNP ligand.[33] Treatment of **3** with potassium *tert*-butoxide gives the neutral alkoxycarbene complex **4** (eqn. 3), which can be distinguished by a shift of the Ir=*C*HOR ^{13}C resonance from 234.7 to 221.5 ppm. The bond metrical parameters obtained from the crystal structure of **4** show significant Kekulé distortion of the pyridine moiety and contraction of one exocyclic C-C bond consistent with those observed in other systems (Figure 3).[34-35] The Ir=C$_{carbene}$ bond length in **4** is 1.882(3) Å, which is indistinguishable from the bond length of 1.880(12) Å in **3** and similar to that of a neutral (PNP)Ir(I) alkoxycarbene complex reported by Grubbs (1.884(4) Å)[30] as well as a cationic iridium(I)alkoxycarbene (1.912(4) Å) we have previously reported.[24] Thus the iridium carbene bond length in **3** and **4** appear insensitive to the net ionic charge. In contrast, these values are shorter than those observed for a cationic iridium(III) alkoxycarbene reported by Schneider (1.938(3) Å)[23] as well as a trio of cationic iridium(III) alkoxybenzylidenes we have previously reported (1.997(3), 1.997(8) and 2.001(2)).[24-25] These observations suggest that iridium alkoxycarbene bond lengths are most sensitive to the formal oxidation state.



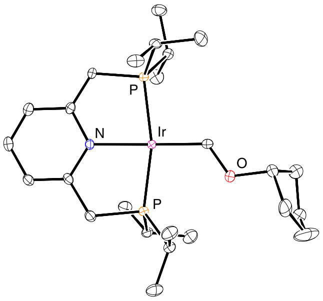
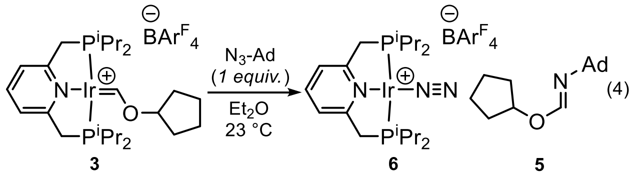
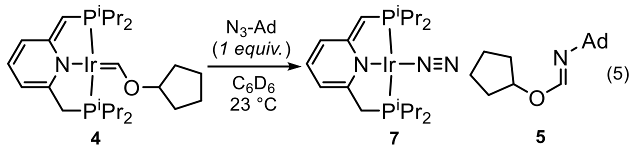


Figure 3. ORTEP diagram of **4** shown at 50% probability. Selected bond distances (Å): Ir=C$_{carbene}$ 1.882(3), Ir-N$_{py}$ 2.096(3). O-C$_{carbene}$ 1.342(4).

The structural similarity of complex **4** to the family of neutral PNP(Ir) alkoxycarbenes prepared by Whited and Grubbs via ether dehydrogenation encouraged a closer comparison of the two systems. In particular, we were interested in whether the reactivity of the neutral complex **4** towards alkyl azides would match that observed by Grubbs for the analogous complex shown in Figure 1. Additionally, cationic derivative **3** could be compared directly to **4** in order to ascertain whether the net ionic charge modulates the reactivity of alkoxycarbenes towards group-transfer reactions.

Indeed, both complexes **3** and **4** react rapidly with Ad-N$_3$ at room temperature to give N-adamantyl formimidate **5** and the corresponding Ir-N$_2$ complexes **6** and **7** respectively (eqns. 4 and 5). N$_2$ binding can be confirmed by analysis of their infrared spectra, which show an Ir-N$_2$ band at 2141 cm^{-1} for **6** and 2076 cm^{-1} for complex **7**. For comparison, a neutral (PNP)IrN$_2$ complex reported by Grubbs absorbs at 2067 cm^{-1}, demonstrating a clear decrease in Ir-N$_2$ backbonding for the cationic variant **6**. The assignment of **6** and **7** was confirmed by single crystal X-ray diffraction of both species (Figure 4) and by conversion of **6** to **7** on treatment with potassium *tert*-butoxide.





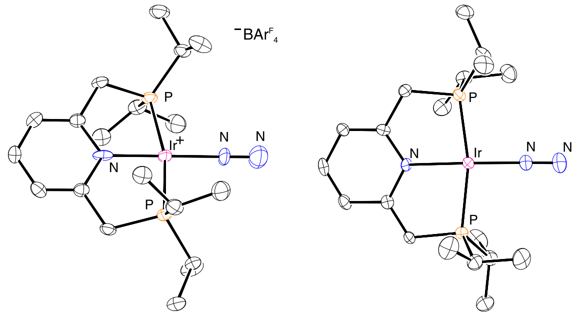
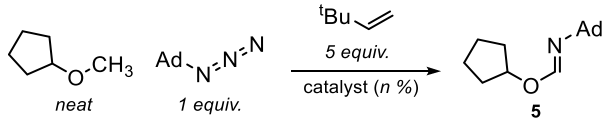


Figure 4. ORTEP diagrams of **6** (left) and **7** (right) shown at 50% probability. Selected bond distances (Å), Complex **6**: Ir-N$_2$ 1.915(5), Ir-N$_{py}$ 1.994(5), N≡N 1.105(8). Complex **7**: Ir-N$_2$ 1.881(5), Ir-N$_{py}$ 2.053(4), N≡N 1.083(7).

An analogous azide-alkoxycarbene group-transfer reaction has been used previously as part of a synthetic cycle for the imination of ethers to formimidates. The incompatibility of the system with excess azide reagent initially precluded the development of a true catalytic reaction, but through stepwise addition under photolysis, 4 turnovers could be obtained over several days.[26] These conditions were subsequently improved through the slow addition of Ad-N$_3$ over 30 hours, leading to a catalytic system capable of 10 turnovers.[21, 27]

Table 1. Evaluation of Reaction Conditions



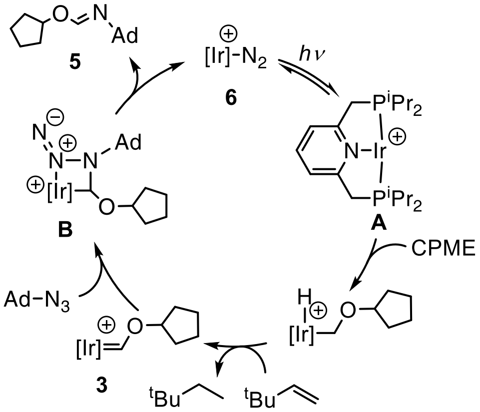
Entry	Catalyst (mol %)	Temp. (°C)	Time (hr.)	Light source	Yield[a]
1	**3** (10%)	23	22	blue	0.4%
2	**3** (10%)	90	22	none	0.8%
3	**3** (10%)	90	22	blue	83%[b]
4	**3** (5%)	90	22	blue	39%[b]
5	**3** (10%)	80	22	blue	70%[b]
6	**4** (10%)	90	22	blue	29%[b]
7	**3** (10%)	90	1	blue	68%[b]
8	**1** (10%)	90	22	blue	84%[b]

[a] NMR yield. [b] Average of two experiments.

By comparison, cationic complex **3** serves as a competent catalyst for the group-transfer imination of CPME under batch conditions without requirement for slow azide addition. Under optimized conditions under blue light irradiation we observe 8.3 turnovers to give 83% yield of formimidate **5** (Table 1, entry 3). The majority of turnovers occur within the first hour (entry 7), demonstrating rapid catalysis without the sensitivity to excess azide observed in the neutral Grubbs system. In a series of experiments we found that **3** reacts productively with Ad-N$_3$ to give **5** at 23 °C, but that a reaction temperature of 90 °C under blue light irradiation is required for productive catalysis. When a catalytic reaction is examined in the dark by $^{31}P\{^1H\}$ NMR after exposure to blue light at 90 °C for 5 or 15 minutes, complex **6** appears to be the major metal-containing species in solution. This observation supports a role for light in N$_2$ dissociation and is consistent with **6** being on-path intermediate in catalysis (Scheme 1). Although **3** closely matches the total turnover number achieved by the Grubbs system, the tolerance of batch conditions rather than a requirement for azide slow addition is a marked improvement. In contrast, the neutral complex **4** achieves only 2.9 turnovers under comparable batch conditions (entry 7). The neutral N$_2$ complex **7** shows sensitivity to excess Ad-N$_3$, degrading to several unidentified species over minutes to hours under irradiation. In the case of the catalysis by the cationic complex **3**, total turnover numbers appear to be limited by catalyst degradation, as $^{31}P\{^1H\}$ NMR analyses show numerous unidentified products after cessation of catalysis.

The success of complex **3** as an ether imination catalyst inspired us to examine the precursor, complex **1** for the same transformation. Dissociation of 1,5-cyclooctadiene would provide access to a three coordinate 14 e$^-$ Ir(I) fragment **A** (Scheme 1) analogous to those proposed as reactive intermediates in both α-C-H activation of CPME and C-H activation of alkanes.[12-14, 23, 36] Under our optimized conditions complex **1** shows comparable activity to **3** with 8.4 TON (84%) (Table 1, entry 8). This observation should simplify future reaction development since derivatives of ligands related to **L1** can be accessed in one step from commercially available iridium starting materials. Indeed the ^{t}Bu analogue of **1** has been previously reported.[37]

A proposed mechanism for catalytic CPME imination by **3** is given in Scheme 1. Reaction of **3** with Ad-N$_3$ could proceed via either initial [2+2][26] (**B**) or [2+3][**38**] cycloaddition, after which extrusion of formimidate **5** would give N$_2$ complex **6**. Light-promoted dissociation of dinitrogen would give the 14 e$^-$ Ir(I) fragment **A**, which is likely the species responsible for CPME activation to regenerate **3**.

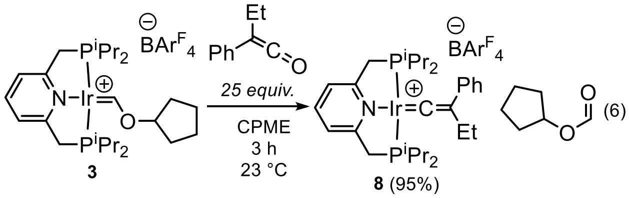


Scheme 1. Proposed catalytic cycle for group transfer imination of CPME. Both [2+2][26] (**B**) and [2+3][38] azide-carbene cycloaddition mechanisms have been previously proposed.

In total, the stoichiometric reactivity of alkoxycarbene complexes **3** and **4** with Ad-N$_3$ closely mirrors observations made by Whited and Grubbs. In our case, complex **3** was found to serve as a catalyst for group transfer imination of CPME without requirement for portionwise or slow addition of azide, while the neutral complex **4** appears to share the Grubbs system's reported sensitivity to excess azide.[26]

As complexes of square planar d^8 metal ions, **3** and **4** bear a filled high-lying d_{z^2} orbital which has been implicated in so-called Roper-type carbene chemistry of which group-transfer reactions of azides represent one example.[21-22, 39-40] Other electrophiles including CO_2, carbonyl sulfide, and phenyl isocyanate have been demonstrated to give formate esters, thioformates and formimidates, respectively.[22, 30] We suspected that other substrates might undergo similar group-transfer reactions via what has been proposed as an initial [2+2] cycloaddition[22] to alkoxycarbene **3**, and identified diazoalkanes, ketenes and alkyl nitrites as possible candidates for C-C or C-O bond-forming chemistry. Just as alkyl azides are observed to transfer a formal nitrene equivalent, we hypothesized that diazoalkanes and alkyl aryl ketenes[41-45] might serve as carbene equivalents to give the products of formal carbene-carbene cross-coupling.

Surprisingly, complex **3** is largely unreactive towards either one equivalent or an excess of trimethylsilyldiazomethane at room temperature. While elevated temperatures or irradiation with blue light did lead to partial consumption of **3**, the N_2 adduct **6** is observed only in trace quantities and no organic product of carbene transfer was detected. In contrast, treatment of **3** with 25 equivalents of phenyl ethyl ketene gives cyclopentyl formate and two new iridium-containing species in a ratio of 95:5 by $^{31}P\{^1H\}$NMR (eqn. 6).



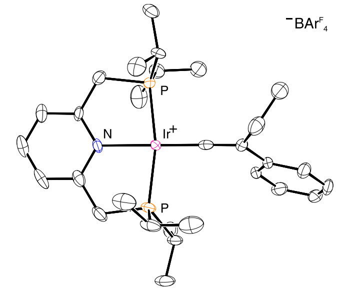
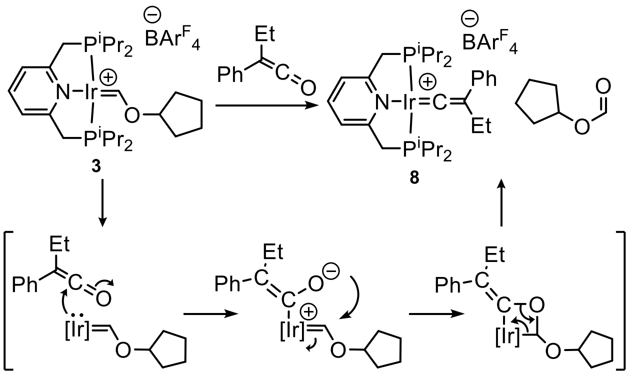


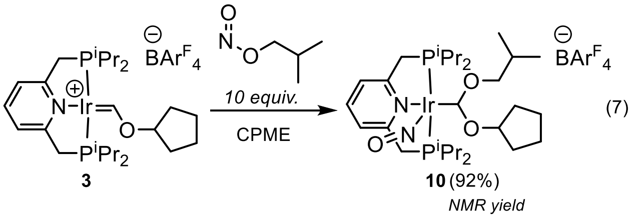
Figure 5. ORTEP diagram of **8** shown at 50% probability. The full disorder model and anion are omitted for clarity. Selected bond distances (Å): Ir=C_α 1.828(5), C_α=C_β 1.304(6), Ir-N_{py} 2.124(4).

We have characterized the minor product as the Ir(I)-CO complex **9** by doping with an authentic sample of **9** generated independently[46] (see the supporting information). The major product was separable by crystallization and found to be the unexpected cationic iridium vinylidene complex **8** (Figure 5). Thus, phenyl ethyl ketene appears to serve as an oxygen atom donor rather than a carbene equivalent. This outcome is interesting when considered alongside the reported reactivity of phenyl isocyanate with a related neutral alkoxycarbene,[30] which serves as a nitrene source despite the electronic similarity of ketenes and isocyanates.[47] Ketenes undergo thermal [2+2] reactions with a variety of substrates including simple olefins, but such reactivity engages the C=C fragment of the ketene moiety.[48] In our case the observed group transfer reaction of phenyl ethyl ketene likely requires that initial [2+2] cycloaddition occur via the C=O fragment, implicating the pair of stepwise or concerted, asynchronous nucleophilic additions shown in Scheme 2 rather than a concerted, synchronous [2+2] process. A closely-related mechanism has been proposed for a series of oxygen atom transfer reactions of an isolable niobocene ketene complex,[49-50] demonstrating the O-nucleophilicity of α-metalloketenes. The structure of a (diphenylketene-κ^2O,C^1)iridium(I) complex reported by Grotjahn is also consistent with this proposal, though O-atom transfer from a diphenylketene-κ^2C^1,C^2 adduct may also be possible.[51]



Scheme 2. Proposal for ketene O-atom transfer

Previous studies by Whited and Grubbs were limited to group- or atom-transfer reactions of heterocumulenes, but the possibility that **3** might be capable of non-concerted group transfer reactions encouraged us to explore other electrophiles. One promising reagent – isobutyl nitrite was found to react with **3** to give a single new complex with a major $^{31}P\{^1H\}$ NMR signal at 34 ppm in 92% yield. We have characterized this species as the iridium dialkoxyalkyl nitrosyl complex **10** resulting from formal alkoxide group-transfer and scission of the N-O bond. Transition metal dialkoxyalkyls are proposed as tetrahedral intermediates in the alkoxide exchange of alkoxycarbene complexes, however there is only a single report of a transition metal dialkoxyalkyl complex in the Cambridge crystallographic database. In that case, nucleophilic attack of NaMn(CO)$_5$ on di(phenoxy)chloromethane gave the corresponding manganese diphenoxyalkoxyalkyl,[52] making **10** the only isolable dialkoxyalkyl generated by alkoxide transfer to an alkoxycarbene.



The solid-state structure of **10** shows a square pyramidal complex containing a bent nitrosyl with an Ir-N-O angle of 123.0(5)° and a vacant site *trans* to the nitrosyl ligand, an arrangement shared by all other reported bent, 5-coordinate iridium nitrosyls.[53-58] Though we have been successful in characterizing **10** in the solid state by both single-crystal X-ray diffraction (Figure 6) and elemental analysis, the instability of **10** in solution has precluded the collection of high quality ^1H and $^{13}C\{^1H\}$ NMR data. Nonetheless, the dialkoxyalkyl ^1H resonance can be identified as a triplet occurring at 7.18 ppm with $^3J_{HP}$ = 4.7 Hz, which collapses to a broad singlet on ^{31}P decoupling. This is in good agreement with the reported manganese dialkoxyalkyl which resonates at 7.38 ppm. There is no reported ^{13}C chemical shift for the manganese dialkoxyalkyl, however an HSQC experiment with **10** shows a correlation with a ^{13}C resonance at 94.2 ppm, which aligns well with an iridium hydroxyaminoalkyl reported to resonate at 96.9 ppm.[59]

The conversion of **3** to **10** presumably occurs via initial binding of Ir to the electrophilic N atom of isobutyl nitrite. This binding mode has been inferred previously on the basis of IR and NMR data at complexes of Ru[60] and Ir,[61] and shown in a single crystallographically characterized example on Pd.[62] Subsequent alkoxide transfer to the alkoxycarbene would give **10**. A related reverse reaction – the formation of an N-coordinated alkyl nitrite via alkoxide attack at a metal nitrosyl has been previously observed at Ir.[61]

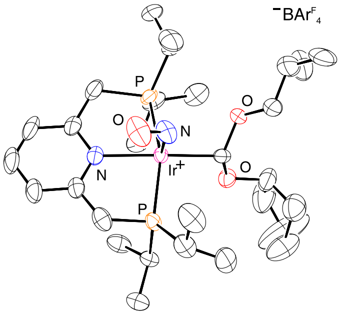


Figure 6. ORTEP diagram of **10** shown at 50% probability. The full disorder model and anion are omitted for clarity. Selected bond distances (Å) and angles (°): Ir-C$_\alpha$ 2.040(6), Ir-N$_{py}$ 2.167(5), O-C$_\alpha$-O 110.2(5), Ir-N=O 123.0(5).

Conclusion

In summary, we report the synthesis of cationic and neutral PNP(^{i}Pr)$_4$ iridium alkoxycarbene complexes via transfer dehydrogenation of CPME. Both alkoxycarbene complexes react with Ad-N$_3$ to form the corresponding Ir-N$_2$ complex and a formimidate resulting from formal nitrene transfer to the alkoxycarbene. This reactivity mirrors observations by Whited and Grubbs on a related neutral iridium alkoxycarbene system. We have translated this stoichiometric reactivity to catalysis in both the cationic and neutral alkoxycarbene cases, however the cationic complex **3** shows superior performance. Under optimized batch conditions **3** displays 7 TON within the first hour, comparing favorably against the previously reported system which requires slow addition of azide over more than 24 hours for comparable turnover numbers. The precursor complex [(PNP(^{i}Pr)$_4$)Ir(η^2-cod)]BAr$^F_4$ (**1**) is also found to serve as an active catalyst with similar performance.

In addition, we have further expanded the scope of reagents which undergo atom or group-transfer reactions with iridium alkoxycarbenes to include phenyl ethyl ketene and isobutyl nitrite. These experiments have led to the isolation of a ketene-derived iridium vinylidene complex and the first late transition metal dialkoxyalkyl complex to be structurally characterized. The reactivity of **3** with phenyl ethyl ketene and isobutyl nitrite is suggestive of stepwise processes rather than a concerted [2+2] process. These results add to our understanding of alkoxycarbene complexes of d^8 metal ions and show promise for future development for new functionalization reactions of ethers that proceed through alkoxycarbene intermediates.

ASSOCIATED CONTENT

The Supporting Information is available free of charge at the ACS publications website at “http://pubs.acs.org.”

Experimental procedures, X-ray crystallographic data, and compound characterization data,.

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Notes

The authors declare no competing financial interest.

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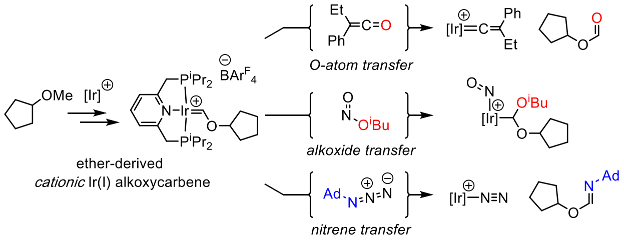

Synopsis

We report the synthesis of a cationic pincer-supported Ir(I) alkoxycarbene complex generated by α,α-dehydrogenation of cyclopentyl methyl ether and demonstrate its reactivity in atom- and group-transfer reactions with an alkyl azide, a ketene and an alkyl nitrite. This complex serves as a catalyst for ether imination, showing that cationic iridium complexes are competent to support catalytic transformations of ethers that proceed through alkoxycarbene complexes.