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Article

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(ⁱPr)₄ pincer-supported iridium complex (PNP(ⁱPr)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 $\alpha_{,\beta}$ -dehydrogenation of alkyl amines.^{16,17} More recently, Brookhart¹⁸ and Huang¹⁹ demonstrated that neutral PCP pincer-supported iridium complexes catalyze the transfer dehydrogenation of alkyl ethers to vinyl ether products. The $\alpha_{\mu}\beta$ -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 CO₂, 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 highlying, filled d_{z^2} orbital in reactions of d^8 alkoxycarbenes.²²

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 metalalkoxycarbene 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

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Figure 1. Recent ether-derived alkoxycarbenes.

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 atomand 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 $[(cod)_2Ir]BAr_4^F$ with 2,6bis((diisopropylphosphino)methyl)pyridine (L1) gives complex 1 (eq 1) which undergoes hydrogenation to an iridium



dihydride complex 2 (eq 2). Dehydrogenation of 2 with *tert*butylethylene in CPME yields a product with a single ³¹P{¹H} NMR signal and a broad, downfield-shifted ¹H resonance at 13.5 ppm. This signal is in the range expected for an alkoxymethylidene Ir=CHOR resonance,^{28–30} which along with the appearance of a ¹³C{¹H} 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 nonpincer complex.³¹ Numerous attempts at confirmation of this assignment through X-ray crystallography ultimately led to a structure solution for 3 from samples crystallizing as 3-component merohedral twins in the P2₁ 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), and 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 (eq 3),



which can be distinguished by a shift of the Ir=CHOR ¹³C 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}



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), and O- $C_{carbene}$ 1.342(4).

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. 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 toward 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 toward group-transfer reactions.

Indeed, both 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 (eqs 4



and 5). N₂ 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)IrN₂ 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) for complex 6 (Ir— N_2 1.915(5), Ir— N_{py} 1.994(5), N \equiv N 1.105(8)) and complex 7 (Ir— N_2 1.881(5), Ir— N_{py} 2.053(4), N \equiv 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, four turnovers could be obtained over several days.²⁶ These conditions were subsequently improved through the slow addition of $Ad\text{-}N_3$ over 30 h, leading to a catalytic system capable of 10 turnovers. 21,27

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,



\bigcirc	∼O- ^{CH} 3 ^{Ad} 、N [,] N neat 1 equi	tl v.	Bu 5 equiv. alyst (n %		N Ad
entry	catalyst (mol %)	$T(^{\circ}C)$	<i>t</i> (h)	light source	yield"
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
^{<i>a</i>} NMR yield. ^{<i>b</i>} Average of two experiments.					

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-N₃ 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 ³¹P{¹H} NMR after exposure to blue light at 90 °C for 5 or 15 min, complex 6 appears to be the major metal-containing species in solution. This observation supports a role for light in N₂ 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

Scheme 1. Proposed Catalytic Cycle for Group Transfer Imination of \mbox{CPME}^a



^{*a*}Both $[2 + 2]^{26}$ (B) and $[2 + 3]^{38}$ azide-carbene cycloaddition mechanisms have been previously proposed.

complex 7 shows sensitivity to excess Ad-N₃, degrading to several unidentified species over minutes to hours under irradiation. In the case of catalysis by the cationic complex 3, total turnover numbers appear to be limited by catalyst degradation, as ${}^{31}P{}^{1}H$ 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 '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-N₃ could proceed via either initial $[2 + 2]^{26}$ (B) or $[2 + 3]^{38}$ cycloaddition, after which extrusion of formimidate 5 would give N₂ 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.

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 d⁸ metal ions, 3 and 4 bear a filled high-lying d_z^2 orbital which has been implicated in socalled Roper-type carbene chemistry of which group-transfer reactions of azides represent one example.^{21,22,39,40} Other electrophiles including CO₂, 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 grouptransfer reactions via what has been proposed as an initial $\begin{bmatrix} 2 + 1 \end{bmatrix}$ 2] cycloaddition²² 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 ketenes41-45 might serve as carbene equivalents to give the products of formal carbene-carbene cross-coupling.

Surprisingly, complex 3 is largely unreactive toward 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 N₂ adduct 6 is observed only in trace quantities and no organic product of carbene transfer was detected. In contrast, treatment of 3 with 25 equiv of phenyl ethyl ketene gives cyclopentyl formate and two new iridium-containing species in a ratio of 95:5 by ³¹P{¹H}NMR (eq 6).

We have characterized the minor product as the Ir(I)–CO complex 9 by doping with an authentic sample of 9 generated independently⁴⁶ (see the Supporting Information). The major product was separable by crystallization and found to be the unexpected cationic iridium vinylidene complex 8 (Figure 5).



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), and Ir- N_{py} 2.124(4).

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- $\kappa^2 O, C^1$)iridium(I) complex reported by Grotjahn is also consistent with this proposal, though O atom transfer from a diphenylketene- $\kappa^2 C^1, C^2$ adduct may also be possible.⁵¹

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 nonconcerted 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 ³¹P{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 $123.0(5)^{\circ}$ 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



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 (deg): Ir— C_{α} 2.040(6), Ir— N_{py} 2.167(5), O— C_{α} —O 110.2(5), Ir—N=O 123.0(5).

10 in solution has precluded the collection of high quality ¹H and ¹³C{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 ³¹P decoupling. This is in good agreement with the reported manganese dialkoxyalkyl which resonates at 7.38 ppm. There is no reported ¹³C chemical shift for the manganese dialkoxyalkyl; however, an HSQC experiment with **10** shows a correlation with a ¹³C 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 Ncoordinated alkyl nitrite via alkoxide attack at a metal nitrosyl, has been previously observed at Ir.⁶¹

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-N₃ to form the corresponding Ir-N₂ 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 h for comparable turnover numbers. The precursor complex $[(PNP(^{i}Pr)_{4})Ir(\eta^{2}-cod)]BAr_{4}^{F}(1)$ 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 d⁸ metal ions and show promise for future development for new functionalization reactions of ethers that proceed through alkoxycarbene intermediates.

ASSOCIATED CONTENT

③ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00609.

Experimental procedures, X-ray crystallographic data, and compound characterization data (PDF)

Accession Codes

CCDC 1986273–1986281 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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