

Ancillary Ligand Effects on C–H Bond Activation Reactions Promoted by β -Diiminate Iridium Complexes

Wesley H. Bernskoetter, Emil Lobkovsky, and Paul J. Chirik*

Department of Chemistry and Chemical Biology, Baker Laboratory,
Cornell University, Ithaca, New York 14853

Received August 15, 2005

A series of β -diiminate iridium(I) olefin, diolefin, and hydride complexes have been synthesized and evaluated in carbon–hydrogen bond activation reactions. Treatment of $[\text{Ir}(\text{COE})_2\text{Cl}]_2$ (COE = cyclooctene) with the lithio β -diiminate anions $[\text{Li}(\text{OEt}_2)][\text{BDI}]$ (BDI = $\text{ArNC}(\text{Me})\text{CH}(\text{Me})\text{CNAr}$; Ar = 2,6-Me₂C₆H₃, 2,6-Et₂C₆H₃, 2,6-ⁱPr₂C₆H₃) under an N₂ atmosphere furnished the corresponding iridium(I) cyclooctene dinitrogen complexes. Using a similar procedure, the analogous β -diiminate iridium(I) cyclooctadiene compounds have also been prepared and characterized. Addition of the sterically demanding β -diiminate anion (2,6-Me₂C₆H₃)NC(CMe₃)CH(CMe₃)CN(2,6-Me₂C₆H₃) to $[\text{Ir}(\text{COD})\text{Cl}]_2$ (COD = 1,5-cyclooctadiene) yielded an unusual η^5 -arene complex that is stabilized by a significant contribution from an iminocyclohexadienyl resonance form. The relative electronic influence of each β -diiminate ligand has been evaluated by preparation of the corresponding iridium dicarbonyl complexes and reveals little electronic perturbation among alkyl substituents on the aryl rings. With respect to C–H bond activation, warming the β -diiminate iridium(I) cyclooctene dinitrogen compounds to 50 °C resulted in intramolecular dehydrogenation chemistry, the outcome of which is dependent on the β -diiminate aryl substituents. For the 2,6-dimethyl-substituted complex, transfer dehydrogenation of the cyclooctene ligand is observed, while for the larger diethyl- and diisopropyl-substituted variants, dehydrogenation of the aryl substituents occurs.

Introduction

The activation and functionalization of saturated carbon–hydrogen bonds by soluble transition-metal compounds continues to be an area of active interest, given the potential of these reactions to selectively convert abundant feedstocks into value-added fine and commodity chemicals.^{1,2} Iridium complexes have emerged as attractive candidates in hydrocarbon functionalization processes, and examples of both stoichiometric³ and catalytic reactions such as isotopic exchange,⁴ arene borylation,⁵ alkane dehydrogenation,⁶ and olefin hydroarylation⁷ have been described. In general, most of these transformations have been dominated by “L₂X”-

type⁸ ligands such as cyclopentadienyl derivatives,⁹ tris(pyrazolyl)borate,¹⁰ and pincer-type anions.^{11–13}

Introduction of lower electron count, “LX-type” β -diiminate anions¹⁴ offers the possibility of generating more reactive transition-metal centers, owing to coordinative unsaturation imparted by a formally three-electron donor. Indeed, Goldberg and co-workers have reported the first examples of alkane dehydrogenation with platinum using β -diiminates as supporting ligands.

* To whom correspondence should be addressed. E-mail: pc92@cornell.edu.

(1) For general reviews on hydrocarbon activation, particularly with precious metal complexes, see: (a) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (b) Crabtree, R. H. *Dalton Trans.* **2001**, 2437. (c) Fekl, U.; Goldberg, K. I. *Adv. Inorg. Chem.* **2003**, *54*, 259. (d) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.

(2) Goldberg, K. I.; Goldman, A. S. *Activation and Functionalization of C–H Bonds*; American Chemical Society: Washington, DC, 2004.

(3) For recent examples see: (a) Bhalla, G.; Liu, X. Y.; Oxgaard, J.; Goddard, W. A.; Periana, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 11372. (b) Rodriguez, P.; Diaz-Requejo, M. M.; Belderrain, T. R.; Trofimenko, S.; Nicasio, M. C. *Organometallics* **2004**, *23*, 2162 and references therein.

(4) (a) Klei, S. R.; Golden, J. T.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 2092. (b) Yung, C. M.; Skaddan, M. B.; Bergman, R. G. *J. Am. Chem. Soc.* **2004**, *126*, 13033. (c) Slugovc, C.; Perner, B. *Inorg. Chim. Acta* **2004**, *357*, 3104. (d) Skaddan, M. B.; Yung, C. M.; Bergman, R. G. *Org. Lett.* **2004**, *6*, 11. (e) Kruger, J.; Manmontri, B.; Fels, G. *Eur. J. Org. Chem.* **2005**, *7*, 1402.

(5) (a) Iverson, C. N.; Smith, M. R., III. *J. Am. Chem. Soc.* **1999**, *121*, 7696. (b) Cho, J.-Y.; Iverson, C. N.; Smith, M. R., III. *J. Am. Chem. Soc.* **2000**, *122*, 12868. (c) Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390. (d) Cho, J. Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E., Jr.; Smith, M. R., III. *Science* **2002**, *295*, 305. (e) Ishiyama, T.; Takagi, J.; Hartwig, J. F.; Miyaura, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 3056. (f) Chotana, G. A.; Rak, M. A.; Smith, M. R. *J. Am. Chem. Soc.* **2005**, *127*, 10539.

(6) Jensen, C. M. *Chem. Commun.* **1999**, 2443.

(7) (a) Bhalla, G.; Oxgaard, J.; Goddard, W. A.; Periana, R. A. *Organometallics* **2005**, *24*, 3229. (b) Periana, R. A.; Lui, X. Y.; Bhalla, G. *Chem. Commun.* **2002**, 3000. (c) Matsumoto, T.; Taube, D. J.; Periana, R. A.; Taube, H.; Yoshida, H. *J. Am. Chem. Soc.* **2000**, *122*, 7414.

(8) For a description of the “L” and “X” formalism see: Green, M. L. H. *J. Organomet. Chem.* **1995**, *500*, 127.

(9) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970.

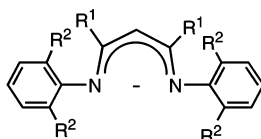
(10) Slugovc, C.; Padilla-Martinez, I.; Sirol, S.; Carmona, E. *Coord. Chem. Rev.* **2001**, *213*, 129.

(11) Haenel, M. W.; Oevers, S.; Angermund, K.; Kaska, W. C.; Fan, H.-J.; Hall, M. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3596.

(12) (a) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (b) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870.

(13) Weng, W.; Guo, C.; Moura, C.; Yang, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2005**, *24*, 3487.

(14) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031.



Ligand	R ¹	R ²
BDI-1	CH ₃	CH ₃
BDI-2	CH ₃	CH ₂ CH ₃
BDI-3	CH ₃	CHMe ₂
BDI-4	CF ₃	CHMe ₂
BDI-5	CMe ₃	CHMe ₂

Figure 1. β -Diiminate ligands and their shorthand designations.

Both stoichiometric dehydrogenation chemistry¹⁵ and H/D exchange in pentane¹⁶ have been observed. On the basis of these results and the high activity of iridium pincer complexes in catalytic dehydrogenation,⁶ we became interested in exploring the corresponding β -diiminate iridium chemistry. This area has been pioneered by Budzelaar and co-workers, who described the synthesis of (BDI-1)Ir(η^3 -C₈H₁₃)H (BDI-1 = ArNC(Me)-CH(Me)CNAr, Ar = 2,6-Me₂C₆H₃), arising from allylic C-H activation of the putative cyclooctene compound.¹⁷ Addition of dihydrogen to (BDI-1)Ir(η^3 -C₈H₁₃)H furnished the β -diiminate iridium(III) olefin dihydride (BDI-1)Ir(COE)H₂, a molecule that is unreactive toward olefins and excess H₂.¹⁸

Our laboratory has discovered that replacing the aryl methyl substituents with more sterically demanding isopropyl groups on the β -diiminate ligand dramatically changes the reactivity of the iridium center. Metalation of the lithio β -diiminate precursor BDI-3 (BDI-3 = ArNC(Me)CH(Me)CNAr, Ar = 2,6-ⁱPr₂C₆H₃), with [Ir(COE)₂Cl]₂ furnished the olefin dinitrogen complex (BDI-3)Ir(COE)N₂, with no evidence of allylic C-H activation to form the corresponding iridium octenyl hydride compound. Addition of dihydrogen to (BDI-3)Ir(COE)N₂ resulted in rapid olefin hydrogenation, yielding cyclooctane and the trigonal-prismatic β -diiminate iridium(V) tetrahydride (BDI-3)IrH₄.¹⁹ This compound and two phosphine dihydride adducts, (BDI-3)Ir(PR₃)H₂ (R = ⁱPr, Cy), promote the C-H activation and isotopic exchange in arene substrates such as benzene, toluene, and mesitylene.²⁰ In both cases mechanistic studies implicate oxidative addition of an aromatic C-H bond to a putative β -diiminate iridium(III) dihydride, in contrast with the preferred pathway for most saturated precursors such as (η^5 -C₅Me₅)Ir(PMe₃)H₂, where Ir(I)-Ir(III) redox couples are generally favored.^{1d}

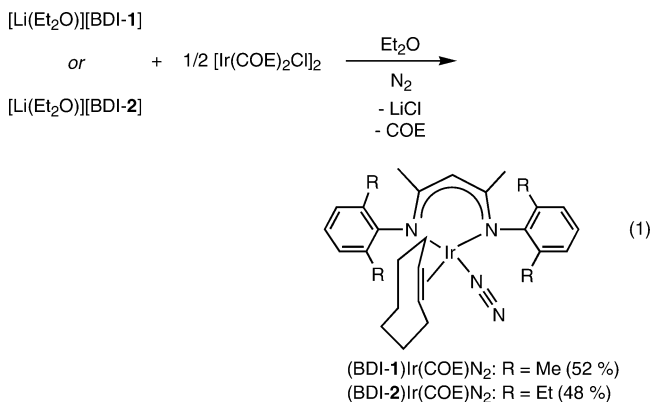
Intrigued by the profound reactivity differences associated with slight alterations in the aryl substituents, a more systematic study of ancillary ligand effects in β -diiminate iridium chemistry seemed warranted. Here we describe the synthesis, structural characterization, and electronic properties of a series of β -diiminate iridium(I) compounds. Several olefin complexes were

found to promote intramolecular dehydrogenation chemistry, the outcome of which is dependent on aryl group substitution.

Results and Discussion

Synthesis of β -Diiminate Iridium(I) Olefin Complexes. The family of β -diiminate ligands employed in this study is presented in Figure 1. Initial experiments focused on understanding the effect of aryl group substitution on the course of β -diiminate metalation. Budzelaar and co-workers¹⁷ reported that addition of the THF solvate of the lithio salt of the smallest member of the series, BDI-1, to [Ir(COE)Cl]₂ furnished the β -diiminate iridium(III) cyclooctenyl hydride (BDI-1)Ir(η^3 -C₈H₁₃)H, arising from allylic activation of the coordinated olefin. Our laboratory has reported that metalation of the β -diiminate ligand with isopropyl aryl substituents afforded the corresponding iridium(I) cyclooctene dinitrogen complex (BDI-3)Ir(COE)N₂.¹⁹ In an attempt to reconcile this apparent discrepancy, several additional metalation experiments were performed.

One likely possibility for the difference in metalation outcomes is a deficiency of dinitrogen, resulting in allylic C-H activation of the coordinated olefin and leading to isolation of the iridium(III) cyclooctenyl hydride (BDI-1)Ir(η^3 -C₈H₁₃)H. To explore this possibility, 1 equiv of [Li(OEt₂)]BDI-1 was added to a diethyl ether solution of [Ir(COE)₂Cl]₂ under 1 atm of dinitrogen. Following filtration and recrystallization from pentane at -35 °C, a yellow powder identified as the desired cyclooctene dinitrogen complex, (BDI-1)Ir(COE)N₂, was isolated in moderate yield (eq 1). Using a similar synthetic proce-



(15) Fekl, U.; Kaminsky, W.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 15286.

(16) Fekl, U.; Goldberg, K. I. *J. Am. Chem. Soc.* **2002**, *124*, 6804.

(17) Budzelaar, P. H. M.; de Gelder, R.; Gal, A. *Organometallics* **1998**, *17*, 4121.

(18) Budzelaar, P. H. M.; Moonen, N. N. P.; de Gelder, R.; Smits, J. M. M.; Gal, A. *Eur. J. Inorg. Chem.* **2000**, 753.

(19) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. *Chem. Commun.* **2004**, 764.

(20) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2005**, *24*, 4367.

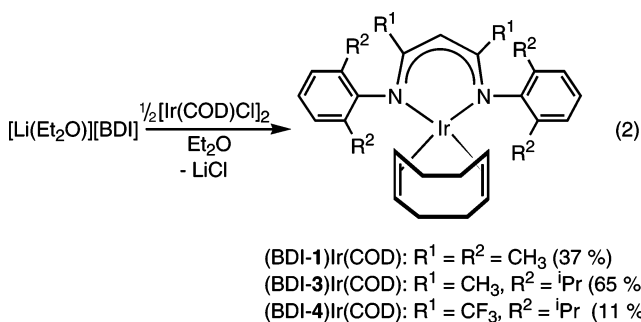
cedure, a β -diiminate iridium(I) cyclooctene dinitrogen complex containing 2,6-diethyl aryl substituents, (BDI-2)Ir(COE)N₂, was also prepared (eq 1). Both complexes have been characterized by NMR and IR spectroscopy

and combustion analysis. Diagnostic N–N stretches centered at 2120 and 2121 cm^{-1} are observed in the benzene solution infrared spectra of (BDI-1)Ir(COE)N₂ and (BDI-2)Ir(COE)N₂, respectively. These peaks are in agreement with the value of 2122 cm^{-1} observed for (BDI-3)Ir(COE)N₂¹⁹ and suggest only weak dinitrogen activation by the d⁸ iridium center.

One difference between our synthetic protocol and that described by Budzelaar is the solvate of the lithio β -diiminate precursor. To determine whether this influences the product distribution, the metalation of BDI-1 with [Ir(COE)₂Cl]₂ was carried out in THF. As with our other procedures, the reaction was performed in the presence of 1 atm of dinitrogen and, as a result, (BDI-1)Ir(COE)N₂ was again isolated. Accordingly, performing the metalation under vacuum furnished (BDI-1)Ir(η^3 -C₈H₁₃)H. Thus, the apparent differences in metalation are a result of dinitrogen availability rather than substituent or solvent effects.

Attempts to prepare other β -diiminate iridium cyclooctene dinitrogen complexes by addition of BDI-4 or BDI-5 to [Ir(COE)₂Cl]₂ have been unsuccessful. In the case of the fluorinated ligand BDI-4, no reaction was observed at ambient temperature and heating ultimately resulted in an unidentified mixture of iridium products and recovery of protio β -diiminate ligand. For the *tert*-butyl-substituted BDI-5, decomposition was observed upon addition of the lithio salt to [Ir(COE)₂Cl]₂.

The inability to prepare clean olefin dinitrogen complexes with the fluorinated and *tert*-butyl-substituted β -diiminate ligands prompted investigation into other iridium(I) olefin precursors as potential entry points for C–H bond activation chemistry. Addition of a stoichiometric quantity of the lithio salts of each of the following β -diiminate ligands, BDI-1, BDI-3, and BDI-4, to [Ir(COD)Cl]₂ (COD = 1,5-cyclooctadiene) furnished the desired β -diiminate iridium cyclooctadiene complexes, albeit in modest yields (eq 2). Each compound was



characterized by ¹H and ¹³C NMR spectroscopy and exhibits the number of resonances expected for a C_{2v} symmetric diolefin complex. For (BDI-4)Ir(COD), a ¹⁹F NMR resonance was observed at 108.10 ppm in benzene-*d*₆ for the equivalent CF₃ groups on the β -diiminate backbone. (BDI-3)Ir(COD) was also characterized by X-ray diffraction; a view of the solid structure and metrical parameters for this compound can be found in the Supporting Information.

Attempts to synthesize the corresponding β -diketiminate iridium(I) cyclooctadiene complex with the steri-

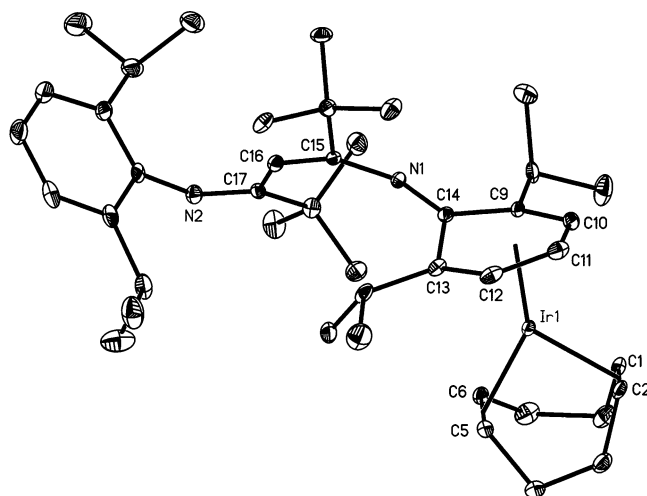
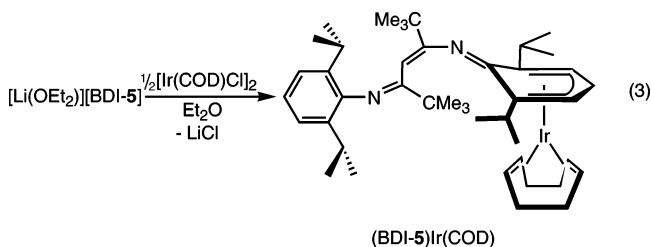


Figure 2. Partially labeled view of the molecular structure of (BDI-5)Ir(COD) with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) for (BDI-5)Ir(COD)

Ir(1)–C(9)	2.373(4)	C(9)–C(10)	1.413(6)
Ir(1)–C(10)	2.231(4)	C(10)–C(11)	1.404(6)
Ir(1)–C(11)	2.241(4)	C(11)–C(12)	1.399(6)
Ir(1)–C(12)	2.245(4)	C(12)–C(13)	1.434(5)
Ir(1)–C(13)	2.292(4)	C(13)–C(14)	1.479(5)
Ir(1)–C(14)	2.704(4)	N(1)–C(14)	1.295(4)
C(1)–C(2)	1.431(6)	N(2)–C(17)	1.288(4)
C(5)–C(6)	1.426(6)		

cally demanding *tert*-butyl-substituted ligand BDI-5 produced unexpected results. Treatment of [Ir(COD)Cl]₂ with a stoichiometric quantity of [Li(OEt₂)]+[BDI-5] furnished a yellow compound that exhibits the number of ¹H and ¹³C NMR peaks anticipated for a molecule with C_s rather than C_{2v} symmetry. In addition, a doublet and a triplet appear upfield at 4.64 and 5.04 ppm, respectively, and are assigned to the meta and para protons on one of the aryl rings, suggesting that the β -diiminate is bound to the iridium through one of the arene rings rather than the nitrogen atoms (eq 3).²¹



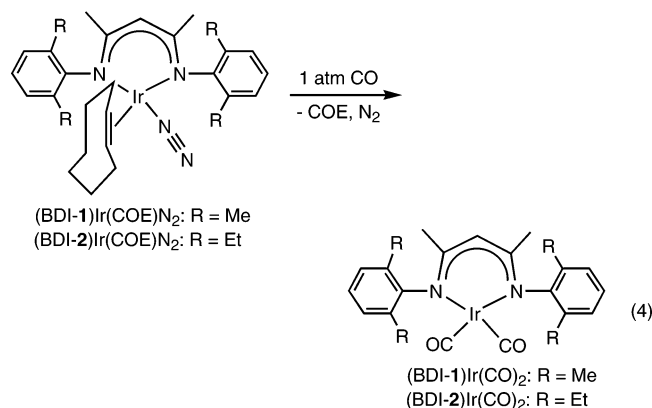
The solid-state structure (Figure 2) of (BDI-5)Ir(COD) was confirmed by X-ray diffraction, and selected metrical parameters are reported in Table 1. In agreement with the solution spectroscopic data, the iridium center is ligated by a cyclooctadiene ligand and one of the aryl substituents of the β -diiminate ligand. Inspection of the bond distances and the geometry of the arene reveal that only five of the six carbon atoms are engaged in bonding with the iridium center, suggesting the imi-

(21) Uson, R.; Oro, L. A.; Carmona, D.; Esteruelas, M. A.; Foces-Foces, C.; Cano, F. H.; Garcia-Blanco, S. *J. Organomet. Chem.* **1983**, *254*, 249.

nocyclohexadienyl resonance form as an important contributor to the overall hybrid. For the five carbons bound to the iridium, metal–carbon bond lengths range between 2.231(4) and 2.373(4) Å and are significantly shorter than the Ir(1)–C(14) distance of 2.704(4) Å. Also consistent with this bonding description is the puckering observed in the coordinated arene. A dihedral angle of 31.4(3)° is formed between the idealized planes defined by C(9)–C(14)–C(13) and C(9)–C(10)–C(11)–C(12)–C(13). Accordingly, the C(9)–C(14) and C(13)–C(14) distances are elongated to 1.468(5) and 1.479(5) Å, respectively, and are indicative of iminocyclohexadienyl character. It should be noted that the solid-state structure of (BDI-5)Ir(COD) lacks the symmetry observed by ¹H and ¹³C NMR spectroscopy. In solution fast rotation about any of the C–C or C–N bonds along the ligand backbone would render both sides of the aryl groups equivalent and result in a time-averaged structure.

There are several examples²² of iridium complexes with η^5 -cyclohexadienyl ligands, and these are generally stabilized by either an iminocyclohexadienyl or oxocyclohexadienyl resonance form. Of particular relevance to (BDI-5)Ir(COD) is the iridium diphenylamine complex (η^5 -PhNPh₂)Ir(TFB) (TFB = tetrafluorobarrelene), reported by Esteruelas and co-workers.²³ In this case, the dihedral puckering in the arene is 16.8(9)° and is stabilized by the iminocyclohexadienyl resonance contribution.

Comparison of the Electronic Structures of β -Diiminate Iridium(I) Complexes. With a family of β -diiminate iridium(I) complexes in hand, the relative electronic properties of each metal center were investigated. Because metal–carbonyl infrared stretching frequencies have proven useful in evaluating the relative electronic environments imparted by ancillary ligation,²⁴ the corresponding β -diiminate iridium(I) dicarbonyl complexes were synthesized. Treatment of (BDI-1)Ir(COE)N₂ or (BDI-2)Ir(COE)N₂ with 1 atm of carbon monoxide resulted in displacement of the olefin and dinitrogen ligands to furnish (BDI-1)Ir(CO)₂ and (BDI-2)Ir(CO)₂, respectively (eq 4).



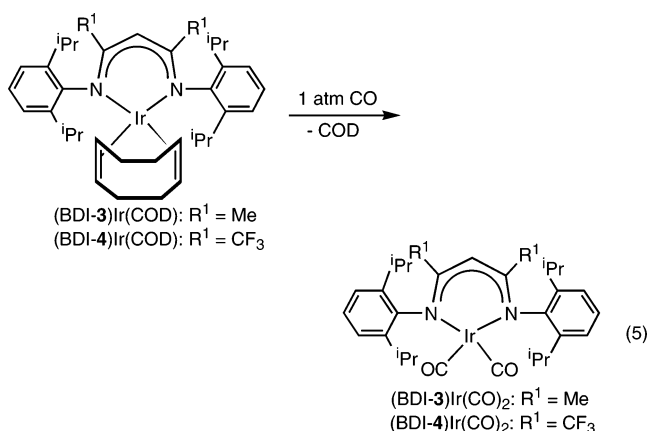
Similarly, addition of 1 atm of CO to (BDI-3)Ir(COD) and (BDI-4)Ir(COD) also afforded the corresponding dicarbonyl complexes, (BDI-3)Ir(CO)₂ and (BDI-4)Ir-

Table 2. Infrared CO Stretching Frequencies (cm⁻¹) of Various Iridium(I) Dicarbonyl Complexes

compound	$\nu(\text{CO})$	$\nu(\text{CO})$	$\nu(\text{CO})_{\text{av}}$	ref
Cp*Ir(CO) ₂ ^a	1953	2020	1986.5	25
Tp*Ir(CO) ₂ ^a	1960	2039	1999.5	25
(BDI-1)Ir(CO) ₂	1986	2054	2020	this work
(BDI-2)Ir(CO) ₂	1985	2054	2019.5	this work
(BDI-3)Ir(CO) ₂ ^b	1985	2053	2019	this work
(BDI-4)Ir(CO) ₂ ^b	2005	2069	2037	this work
(PCP ^t Bu ²)Ir(CO) ₂ ^{b,c}	1930		1930	26
(PCOP ^t Bu ²)Ir(CO) ₂ ^{b,d}	1949		1949	26

^a Recorded in hexanes. ^b Recorded in pentane. ^c PCP^tBu² = (C₆H₃)-1,3-(CH₂P^tBu)₂. ^d PCOP^tBu² = (C₆H₃)-1,3-(OP^tBu)₂

(CO)₂, concomitant with loss of 1,5-cyclooctadiene (eq 5). Treatment of (BDI-5)Ir(COD) with 1 atm of carbon



monoxide produced an intractable mixture of products.

The solution CO stretching frequencies of each dicarbonyl derivative were determined in pentane and are reported in Table 2. Also included are the CO bands of other iridium carbonyl complexes supported by monoanionic ancillary ligands. Inspection of the data establishes several salient trends. As expected, manipulation of the alkyl substituents in the ortho positions of the aryl rings has little effect on the CO stretching frequencies. Thus, the electronic environments imparted by BDI-1, BDI-2, and BDI-3 to the iridium center are very similar.

Replacement of the methyl groups with CF₃ substituents on the β -diiminate backbone has a pronounced electronic effect, resulting in an increase in the average carbonyl stretching frequency of 18 cm⁻¹, consistent with a more electron deficient metal center in (BDI-4)-

(22) (a) Grundy, S. L.; Smith, A. J.; Adams, H.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1747. (b) Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1990**, *9*, 969. (c) Le Bras, J.; Amouri, H.; Vaissermann, J. *Organometallics* **1996**, *15*, 5706. (d) Le Bras, J.; Rager, M. N.; Besace, Y.; Amouri, H.; Vaissermann, J. *Organometallics* **1997**, *16*, 1765. (e) Le Bras, J.; Amouri, H.; Vaissermann, J. *Organometallics* **1998**, *17*, 1116. (f) Le Bras, J.; Amouri, H.; Vaissermann, J. *Organometallics* **1998**, *17*, 5850. (g) Le Bras, J.; Amouri, H.; Vaissermann, J. *J. Organomet. Chem.* **1998**, *567*, 57. (h) Amouri, H.; Vaissermann, J.; Rager, M. N.; Besace, Y. *Inorg. Chem.* **1999**, *38*, 1211. (i) Mousi, J.; Guyard-Duhayon, C.; Herson, P.; Amouri, H.; Rager, M. N.; Jutand, A. *Organometallics* **2004**, *23*, 6231.

(23) Uson, R.; Oro, L. A.; Carmona, D.; Esteruelas, M. A.; Foces-Foces, C.; Cano, F. H.; Garcia-Blanco, S.; De Miguel, A. V. *J. Organomet. Chem.* **1984**, *273*, 111.

(24) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G. E.; Brandow, C. G.; Bercau, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Kiester, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525. (c) Bradley, C. A.; Flores-Torres, S.; Lobkovsky, E.; Abruña, H. D.; Chirik, P. J. *Organometallics* **2004**, *23*, 5332.

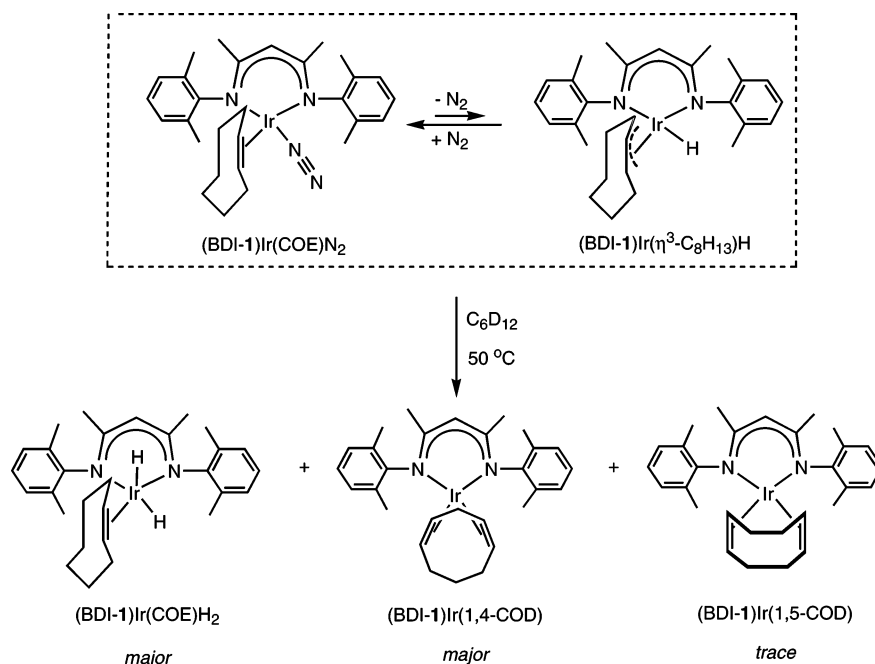


Figure 3. Cyclooctene dehydrogenation with (BDI)Ir(COE)N₂.

Ir(CO)₂. Comparison of the β -diiminate iridium dicarbonyl complexes to (C₅Me₅)Ir(CO)₂, tris(pyrazolyl)borate,²⁵ or the pincer complexes²⁶ demonstrates that the β -diiminates engender the most electron deficient metal centers in the series, consistent with a three-electron, LX-type ligand as compared to five-electron, L₂X-type donors.⁸

C–H Activation with β -Diiminate Iridium(I) Olefin Complexes. Each of the β -diiminate iridium(I) olefin complexes was evaluated for alkane dehydrogenation activity as well as other C–H bond activation chemistry. The cyclooctadiene complexes (BDI-1)Ir(COD), (BDI-3)Ir(COD), and (BDI-4)Ir(COD) are robust in solution, as no change in the ¹H NMR spectrum is observed upon heating to 110 °C in alkane or arene solvent for several days. Addition of dihydrogen to each compound also produced no reaction, even at elevated temperatures. In contrast, the analogous cyclooctene dinitrogen complexes participate in a range of C–H bond activation reactions, depending on the β -diiminate ligand.

Thermolysis of the least sterically hindered member of the series, (BDI-1)Ir(COE)N₂, at 50 °C in cyclohexane-*d*₁₂ or benzene-*d*₆ for 3 h under vacuum produced several new iridium products. It is important that the thermolysis reaction be carried out under vacuum, as performing the experiment under a dinitrogen atmosphere inhibits product formation. The initial kinetic product of the thermolysis procedure was identified as the β -diiminate iridium(III) cyclooctenyl hydride (BDI-1)Ir(η^3 -C₈H₁₃)H, previously reported by Budzelaar and co-workers.¹⁷ This compound results from N₂ loss and allylic C–H activation of the cyclooctene ligand (Figure

3). The C–H activation process is reversible, as addition of excess dinitrogen to (BDI-1)Ir(η^3 -C₈H₁₃)H regenerates (BDI-1)Ir(COE)N₂. These results again demonstrate that the isolation of the cyclooctenyl hydride from metalation of [Li(THF)][(BDI-1)] with [Ir(COE)₂Cl]₂ is a kinetic rather than thermodynamic phenomenon resulting from an N₂ deficiency.

Continuing the thermolysis resulted in consumption of (BDI-1)Ir(COE)N₂ and (BDI-1)Ir(η^3 -C₈H₁₃)H and produced two new major iridium products, arising from transfer dehydrogenation of the cyclooctene ligand (Figure 3). In addition, a trace product formed in approximately 5% yield has been identified as (BDI-1)Ir(COD). The two major products are formed in near-equimolar quantities. The first has been identified as the β -diiminate iridium(III) cyclooctene dihydride (BDI-1)Ir(COE)H₂, originally reported by Budzelaar and co-workers from hydrogenation of (BDI-1)Ir(η^3 -C₈H₁₃)H,¹⁸ while the second exhibits the number of ¹H and ¹³C NMR resonances expected for a C_{2v}-symmetric iridium diolefin complex. Treatment of the latter product with 1 atm of carbon monoxide afforded (BDI-1)Ir(CO)₂ and a stoichiometric quantity of 1,4-cyclooctadiene, identified by comparison to the spectrum of authentic material.²⁷ Attempts to perform the dehydrogenation with a traditional organic hydrogen acceptor such as *tert*-butylethylene produced no change in the product distribution.

The observed products derived from the thermolysis of (BDI-1)Ir(COE)N₂ are a result of transfer dehydrogenation of the cyclooctene ligand. Unfortunately, 1 equiv of the iridium starting material, (BDI-1)Ir(COE)N₂, serves as the stoichiometric hydrogen acceptor, forming (BDI-1)Ir(COE)H₂. Under the experimental conditions employed, this product may be a result of dinitrogen loss and transfer hydrogenation of (BDI-1)Ir(η^3 -C₈H₁₃)H (vide infra). The isolation and robust

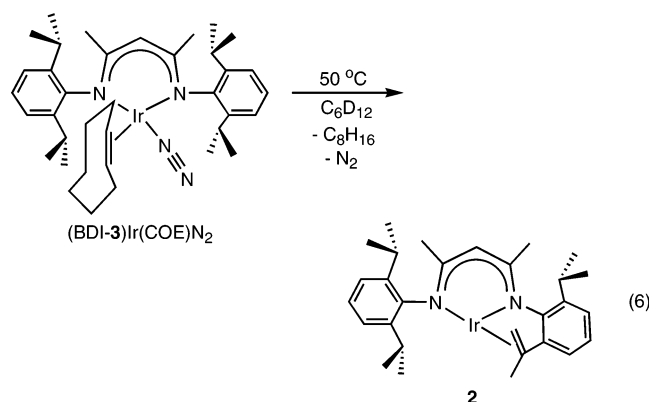
(25) Tellers, D. M.; Skoog, S. J.; Bergman, R. G.; Gunnoe, T. B.; Harman, W. D. *Organometallics* **2000**, *19*, 2428.

(26) Göttker-Schnetmann, I.; White, P. S.; Brookhart, M. *Organometallics* **2004**, *23*, 1766.

(27) Moon, S.; Ganz, C. R. *J. Org. Chem.* **1969**, *34*, 465.

nature of (BDI-1)Ir(1,5-COD) demonstrates that the observed major dehydrogenation product, (BDI-1)Ir(1,4-COD), is a result of selective C–H activation rather than diolefin isomerization. The preference for 1,4-diolefin formation is most likely due to the conformation of the COE ligand, which renders the C–H bonds in the 4-position more susceptible to oxidative addition than those in the 5-position of the olefin.

Thermolysis of the more sterically hindered β -diiminate iridium(I) precursor (BDI-3)Ir(COE)N₂ also produced intramolecular dehydrogenation chemistry but with a different C–H bond preference. Heating a cyclohexane-*d*₁₂ or benzene-*d*₆ solution of (BDI-3)Ir(COE)N₂ resulted in loss of cyclooctane and formation of a single new iridium compound identified as **2**, arising from dehydrogenation of an isopropyl aryl substituent (eq 6). Similar chemistry has been reported by Fekl and



Goldberg during the thermolysis of (BDI-3)PtMe₃, affording the analogous β -diiminate platinum olefin hydride.¹⁶ In the present case, the dehydrogenation reaction occurs at much lower temperature.

Accordingly, the ¹H NMR spectrum of **2** exhibits diagnostic, upfield-shifted resonances centered at 2.73 and 3.14 ppm for the methylene protons of the coordinated olefin. These values are similar to the spectral features reported for the corresponding platinum hydride compound. The iridium complex **2** was also characterized by X-ray diffraction. The solid-state structure, presented in Figure 4, reveals a pseudo-three-coordinate intramolecular olefin complex. Selected bond distances and angles are reported in Table 3. The iridium atom is positionally disordered and was successfully modeled. Unlike other iridium complexes containing BDI-3 ligation, the iridium atom is significantly displaced from the β -diiminate plane and the activated aryl substituent is rotated from its normal position orthogonal to the ligand plane. The C(27)–C(28) bond distance of 1.416(2) Å is elongated from that expected for a typical carbon–carbon double bond, a result of back-bonding from the d⁸ iridium(I) center. This value is similar to that reported for the corresponding platinum hydride complex.¹⁶ Interestingly, there is no evidence for N₂ coordination to **2** either in the solid state or in solution. Because (BDI-3)Ir(COE)-

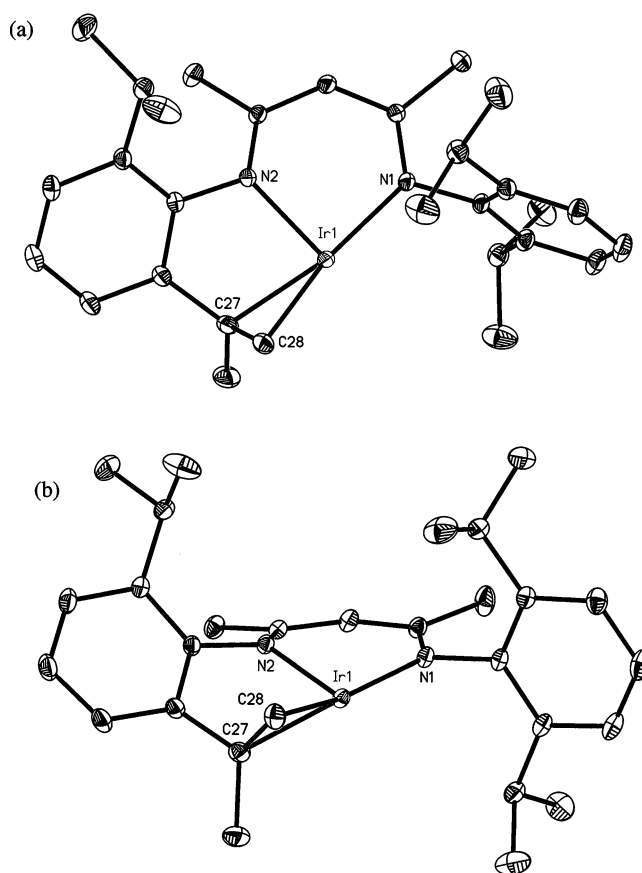


Figure 4. Partially labeled views of **2** with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2**

Ir(1)–N(1)	2.0431(12)	Ir(1)–C(28)	2.1260(15)
Ir(1)–N(2)	2.0528(12)	C(27)–C(28)	1.416(2)
Ir(1)–C(27)	2.1627(15)		
<hr/>			
N(1)–Ir(1)–N(2)	89.44(5)	C(4)–N(2)–Ir(1)	123.11(9)
C(28)–C(27)–C(29)	120.93(16)	C(4)–N(1)–Ir(1)	125.64(10)

N₂ is thermodynamically favored compared to its N₂-loss product, the lack of N₂ coordination by **2** is most likely steric in origin, arising from the orientation of the β -diiminate aryl substituents, a consequence of intramolecular olefin coordination.

Several additional experiments were conducted to gain insight into the intramolecular alkane dehydrogenation observed with (BDI-1)Ir(COE)N₂. Performing the thermolysis experiment in the presence of dinitrogen produced no reaction, demonstrating that N₂ loss is a prerequisite for C–H bond activation. Additionally, treatment of **2** with cyclooctane under an atmosphere of N₂ regenerated (BDI-3)Ir(COE)N₂, demonstrating the ability of β -diiminate iridium compounds to promote a stoichiometric dehydrogenation reaction. In this case, the coordinated olefin serves as the dihydrogen acceptor. Attempts to extend the dehydrogenation activity to other alkanes such as heptane and cyclohexane produced no reaction, even after heating to 65 °C for 12 h. We believe that the origin of this reactivity difference is due to the relative dehydrogenation enthalpy of COA as compared to other alkanes.²⁶

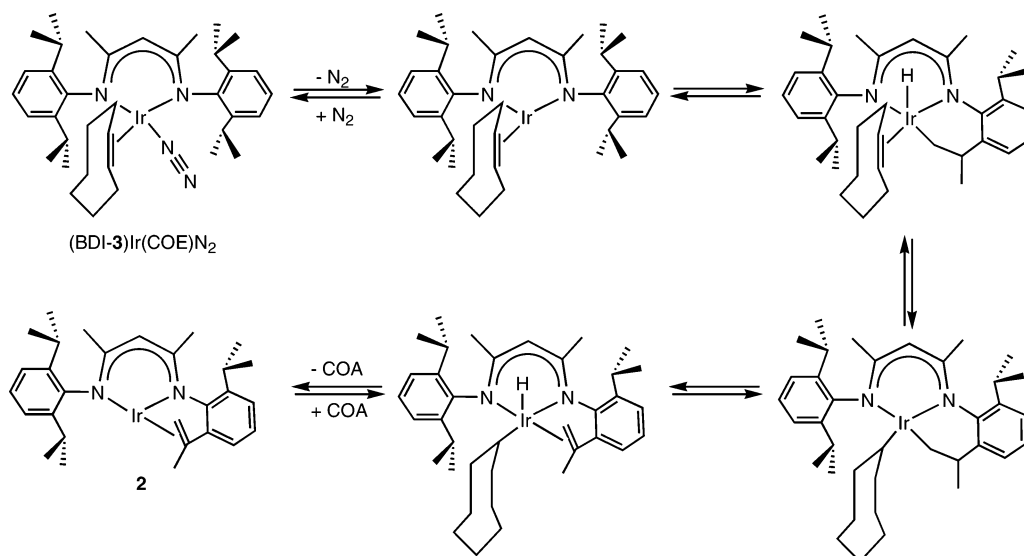


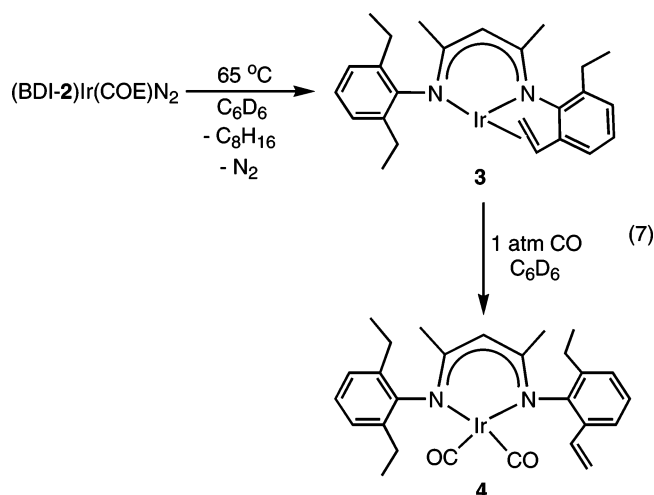
Figure 5. Proposed mechanism for the formation of **2**.

On the basis of the limited experimental data available, a mechanism to account for the observed dehydrogenation chemistry with $(\text{BDI-3})\text{Ir}(\text{COE})\text{N}_2$ is proposed in Figure 5. Following initial dissociation of dinitrogen, C–H activation of an isopropyl methyl substituent affords the β -diimine iridium(III) olefin alkyl hydride complex. Olefin insertion into the iridium hydride followed by β -hydrogen elimination and reductive elimination of cyclooctane yields the observed products. Other sequences of these transformations are possible and cannot be ruled out on the basis of our experimental observations.

Importantly, manipulation of the aryl substituents on the β -diimine ligand from methyl to isopropyl changes the preferred substrate for transfer dehydrogenation. For the less hindered compound $(\text{BDI-1})\text{Ir}(\text{COE})\text{N}_2$, C–H activation and dehydrogenation of the cyclooctene ligand is observed, whereas in the more hindered analogue $(\text{BDI-3})\text{Ir}(\text{COE})\text{N}_2$, cyclooctane formation and activation of an isopropyl aryl substituent occurs. The presence of aryl substituents with β -hydrogens offers the possibility for intramolecular dehydrogenation unavailable in the methyl-substituted variant. As will be demonstrated in a later section, the methyl groups on the BDI-1 ligand can participate in reversible cyclometalation reactions; however, the lack of β -hydrogens prevents dehydrogenation. In addition, the more open metal “pocket” offered by the less hindered β -diimine ligand may also account for the differences by accommodating the formation of the cyclooctadiene derivatives that are observed from the thermolysis of $(\text{BDI-1})\text{Ir}(\text{COE})\text{N}_2$.

In an attempt to determine if smaller aryl substituents containing β -hydrogens would accommodate cyclooctadiene formation, the thermolysis of $(\text{BDI-2})\text{Ir}(\text{COE})\text{N}_2$ was studied. Warming a benzene- d_6 solution of the iridium cyclooctene dinitrogen complex to 50 °C for 3 h liberated a stoichiometric quantity of cyclooctane

and furnished the intramolecular dehydrogenation compound **3** as the sole iridium product (eq 7). No evidence



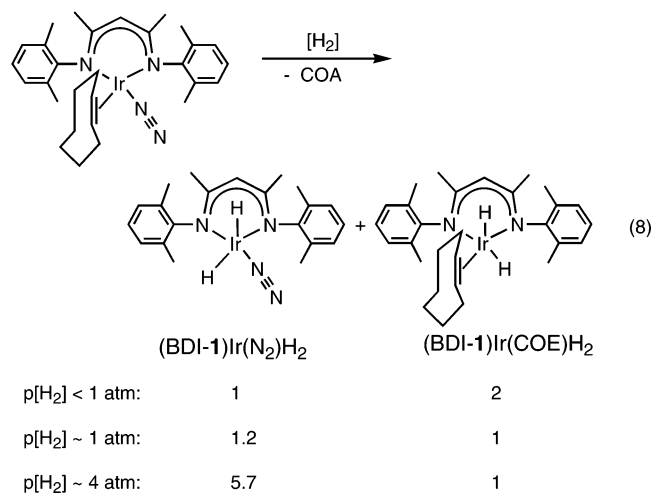
for β -diimine iridium cyclooctadiene complexes was obtained from the ^1H NMR spectrum. To confirm this assignment, **3** was treated with 1 atm of carbon monoxide to furnish the dicarbonyl complex **4** (eq 7). Significantly, no free cyclooctadiene was detected by ^1H NMR spectroscopy. It should be noted that both **3** and **4** have been isolated in very low yield and small quantities, thereby preventing combustion analysis.

The observation of aryl group dehydrogenation from the thermolysis of $(\text{BDI-2})\text{Ir}(\text{COE})\text{N}_2$ demonstrates the preference for β -diimine iridium complexes with β -hydrogen-containing aryl substituents to C–H activating these groups over cyclooctene. While the steric environment associated with BDI-2 is larger than that imposed by BDI-1, the presence of β -hydrogen-containing aryl substituents allows for a productive pathway for intramolecular olefin complex formation. Only when β -hydrogens are absent is cyclooctene dehydrogenation observed.

Ancillary Ligand Effects on the Hydrogenation of β -Diimine Iridium Olefin Complexes. Because

(BDI-1)Ir(COE)N₂ serves as the stoichiometric dihydrogen acceptor during the dehydrogenation of coordinated cyclooctene, its reactivity with H₂ was independently investigated. As with C–H activation, literature reports suggest that β -diimine aryl substitution has a profound effect on the outcome of olefin hydrogenation reactions. Budzelaar and co-workers reported that addition of H₂ to (BDI-1)Ir(η^3 -C₈H₁₃)H afforded (BDI-1)-Ir(COE)H₂ with no evidence for free alkane.¹⁷ In contrast, introduction of larger isopropyl aryl substituents in the case of (BDI-3)Ir(COE)N₂ resulted in facile olefin hydrogenation of the cyclooctene ligand to afford the trigonal-prismatic iridium(V) tetrahydride (BDI-3)-IrH₄.¹⁹

One possible reason for the difference in hydrogenation reactivity is the nature of the iridium starting material. The synthesis and isolation of (BDI-1)Ir(COE)N₂ allows direct comparison of its hydrogenation chemistry with that of (BDI-3)Ir(COE)N₂. Addition of 4 atm of H₂ to a benzene-*d*₆ solution of (BDI-1)Ir(COE)N₂ at 23 °C afforded an approximate 6:1 ratio of two new β -diimine iridium hydrides along with free cyclooctane (eq 8). Quantitation of the free alkane by ¹H NMR



spectroscopy indicated that it is derived from the formation of the major product. A combination of NMR and IR spectroscopy has been used to characterize the major product as the iridium dihydride dinitrogen complex (BDI-1)Ir(N₂)H₂. The minor product has been identified as the previously reported cyclooctene dihydride (BDI-1)Ir(COE)H₂.¹⁷ It should be noted that when the reaction is carried out under these conditions and run to complete conversion of starting material, significant decomposition (~15%) to free ligand and iridium black accompanies the hydrogenation. Isolation of small quantities of pure (BDI-1)Ir(N₂)H₂ has been accomplished by successive recrystallizations from pentane at –35 °C. (BDI-1)IrH₂N₂ is a relatively rare example of an Ir(III) dinitrogen complex. Bergman and co-workers have reported a cationic iridium(III) N₂ compound supported by a hydridotris(pyrazolyl)borate ligand.²⁸ The N₂ ligand in this compound can be displaced by dative ligands and H₂ and also promotes C–H activation in benzene and aldehydes.

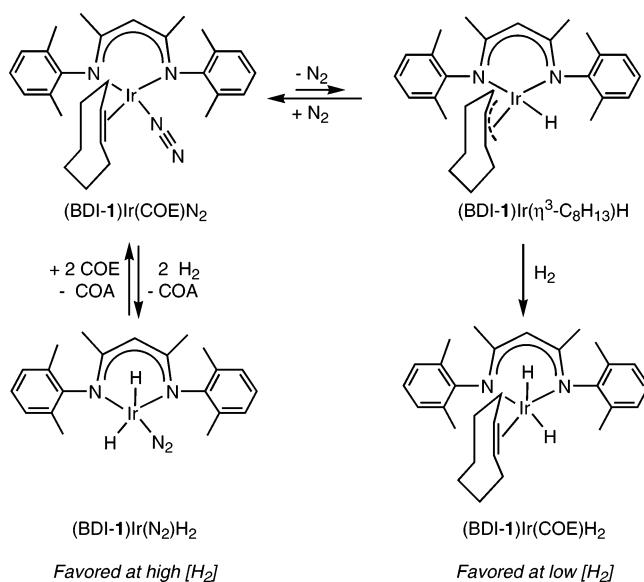


Figure 6. Proposed pathways for the formation of (BDI-1)Ir(COE)H₂ and (BDI-1)Ir(N₂)H₂ from (BDI-1)Ir(COE)N₂.

In an attempt to determine the origin of the two β -diimine iridium hydrides, the effect of H₂ pressure on the product distribution was studied. Each experiment was conducted at low conversion to minimize complications from decomposition reactions. Addition of approximately 0.25 atm of H₂ to an NMR tube containing a 0.01 M solution of (BDI-1)Ir(COE)N₂ furnished a 2:1 mixture of (BDI-1)Ir(COE)H₂ to (BDI-1)Ir(N₂)H₂. Performing similar hydrogenations with 1 and 4 atm increased the amount of the dinitrogen dihydride complex (BDI-1)Ir(N₂)H₂ to 1:1.2 and 1:5.7, respectively. Therefore, as the pressure of H₂ increases, the amount of (BDI-1)Ir(N₂)H₂ also increases (eq 8).

To determine whether the two hydride products can be interconverted, N₂ and H₂ were added to (BDI-1)Ir(COE)H₂. In agreement with previous reports,¹⁷ no change was observed in the ¹H NMR spectrum, indicating that dinitrogen does not trigger the conversion of (BDI-1)Ir(COE)H₂ to (BDI-1)Ir(N₂)H₂ with loss of cyclooctane. The lack of hydrogenation activity of (BDI-1)Ir(COE)H₂ was further investigated with an isotopic labeling experiment. Facile isotopic exchange occurs within the iridium hydride positions upon addition of 1 atm of D₂ to (BDI-1)Ir(COE)H₂, allowing synthesis of (BDI-1)Ir(COE)D₂. Monitoring benzene-*d*₆ solutions of the olefin dideuteride complex by ¹H NMR spectroscopy over the course of 4 days at ambient temperature resulted in no incorporation of the isotopic label into the cyclooctene ligand, demonstrating that olefin insertion and alkyl migration do not readily occur under these conditions.

The experimental results are consistent with the observed mixture of β -diimine iridium dihydrides arising from two independent pathways (Figure 6). On the basis of the limited experimental data available, we tentatively conclude that (BDI-1)Ir(N₂)H₂ arises from hydrogenation of (BDI-1)Ir(COE)N₂, while (BDI-1)Ir(COE)H₂ is derived from H₂ addition to (BDI-1)Ir(η^3 -C₈H₁₃)H. During the thermolysis experiments described earlier, the equilibrium between (BDI-1)Ir(COE)N₂ and (BDI-1)Ir(η^3 -C₈H₁₃)H and free N₂ was directly observed at 50 °C in benzene-*d*₆. To account for the observed

(28) (a) Tellers, D. M.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 954. (b) Tellers, D. M.; Bergman, R. G. *Organometallics* **2001**, *20*, 4819.

ratios of products as a function of H₂ and N₂ pressure, it appears that the absolute rate constant for the hydrogenation of (BDI-1)Ir(COE)N₂ is smaller than that for (BDI-1)Ir(η^3 -C₈H₁₃)H. Support for this hypothesis is the observation of (BDI-1)Ir(COE)H₂ as the sole product from stoichiometric transfer hydrogenation. However, the observation of increased quantities of (BDI-1)Ir(N₂)-H₂ as a function of increased H₂ pressure suggests a higher order in H₂ for the hydrogenation of (BDI-1)Ir(COE)N₂ compared to (BDI-1)Ir(η^3 -C₈H₁₃)H. This could be a consequence of cyclooctene hydrogenation for (BDI-1)Ir(COE)N₂ requiring additional equivalents of dihydrogen or a rate-determining reductive coupling process in (BDI-1)Ir(η^3 -C₈H₁₃)H that precedes H₂ addition. Another possibility is that the equilibration between (BDI-1)Ir(η^3 -C₈H₁₃)H and (BDI-1)Ir(COE)N₂ is relatively slow, occurring on a time scale competitive with hydrogenation. If (BDI-1)Ir(η^3 -C₈H₁₃)H undergoes faster hydrogenation but is present at a lower concentration, then the equilibrium between the two iridium starting materials would be continually reestablished as the hydrogenation proceeds, favoring (BDI-1)Ir(COE)H₂ at low dihydrogen pressures. At higher H₂ pressures, the equilibration could not compete and more (BDI-1)Ir(N₂)-H₂ would result. Unfortunately the presence of parallel reaction pathways in conjunction with a decomposition reaction prohibits a meaningful kinetic study.

Isolation of (BDI-1)Ir(N₂)H₂ from the addition of H₂ to (BDI-1)Ir(COE)N₂ is in contrast with the hydrogenation chemistry of (BDI-3)Ir(COE)N₂, where formation of the β -diiminate iridium(V) tetrahydride is observed. Because the electronic properties of the metal complexes with the two different β -diiminates are nearly identical, the observed difference in reactivity is most likely a result of steric effects. The smaller methyl substituents allow tighter N₂ binding, and as a result, oxidative addition of a second equivalent of dihydrogen to form the corresponding iridium(V) tetrahydride derivative is not observed. Accordingly, addition of 1 atm of dinitrogen to (BDI-3)IrH₄ does not induce reductive elimination of dihydrogen. In analogy to the case for (BDI-1)Ir(PR₃)-H₂ complexes,²⁰ (BDI-1)Ir(N₂)H₂ promotes H/D exchange in benzene-*d*₆ at ambient temperature. Analysis of the iridium complex by ²H NMR spectroscopy following isotopic exchange revealed deuterium incorporation into the metal hydride position and the methyl substituents of the β -diiminate ligand, demonstrating reversible cyclometalation of the ligand.

The ability of the β -diiminate iridium dinitrogen dihydride (BDI-1)Ir(N₂)H₂ to undergo insertion chemistry was also explored. Addition of 2 equiv of cyclooctene to a benzene-*d*₆ solution of (BDI-1)Ir(N₂)H₂ produced 1 equiv of cyclooctane along with (BDI-1)Ir(COE)N₂ (Figure 6). Performing the same experiment with a larger excess of COE also furnished (BDI-1)Ir(COE)N₂ and cyclooctane along with small quantities of (BDI-1)Ir(COE)H₂. Because conversion of (BDI-1)Ir(COE)N₂ to (BDI-1)Ir(COE)H₂ requires 1 equiv of dihydrogen, the observation of (BDI-1)Ir(COE)H₂ from (BDI-1)Ir(N₂)H₂ in the absence of H₂ suggests that the olefin dihydride is obtained from simple displacement of the dinitrogen ligand by cyclooctene. This side pathway is only detectable at higher concentrations of free olefin.

Concluding Remarks

This study highlights the importance of aryl group substitution on the reactivity of β -diiminate iridium complexes. When smaller methyl substituents are present, intramolecular transfer dehydrogenation of cyclooctene from the corresponding iridium(I) olefin dinitrogen complex affords two isomeric cyclooctadiene compounds along with an iridium cyclooctene dihydride complex. Increasing the size of the aryl substituents to ethyl or isopropyl groups changes the substrate for dehydrogenation, resulting in intramolecular olefin complexes derived from the aryl substituents. Hydrogenation is also subject to aryl group substituent effects, as addition of H₂ to the less hindered precursor (BDI-1)Ir(COE)N₂ yielded two products, depending on the dihydrogen pressure. One product, (BDI-1)Ir(N₂)H₂, is favored at higher H₂ pressures (4 atm) and is active for aromatic C–H bond cleavage, promoting H/D exchange with benzene-*d*₆. Significantly, deuterium incorporation is observed in the aryl methyl groups, demonstrating that all of the β -diiminate ligands undergo cyclometalation. Overall, this study highlights the significant impact subtle changes in aryl group substitution can have on C–H activation reactions promoted by β -diiminate iridium complexes.

Experimental Section²⁹

Preparation of (BDI-1)Ir(COE)N₂. A 20 mL scintillation vial was charged with 0.178 g (0.199 mmol) of [Ir(COE)₂Cl]₂ and approximately 12 mL of diethyl ether. The resulting orange solution was chilled to –35 °C, and 0.151 g (0.398 mmol) of Li[BDI-1]·Et₂O in approximately 5 mL of diethyl ether was added in small portions. The resulting reaction mixture was stirred for 2 days and the solvent was removed in vacuo, leaving a yellow solid. Extraction into pentane and filtration through a pad of Celite followed by solvent removal produced a yellow foam. Recrystallization from pentane at –35 °C afforded 0.132 g (52%) of yellow powder identified as (BDI-1)Ir(COE)N₂. Anal. Calcd for C₂₉H₃₉IrN₄: C, 54.78; H, 6.18; N, 8.81. Found: C, 54.50; H, 6.13; N, 8.69. ¹H NMR (benzene-*d*₆): δ 1.07–1.44 (m, 10H, COE CH₂), 1.36 (s, 6H, Ar Me), 1.58 (s, 6H, Ar Me), 1.67 (br s, 2H, COE CH₂), 2.15 (s, 3H, CH₃), 2.48 (s, 3H, CH₃), 2.64 (br d, 2H, COE CH), 5.26 (s, 1H, CH), 6.89–7.12 (Ar H). ¹³C NMR (benzene-*d*₆): δ 18.75, 19.24 (Ar Me), 23.28, 25.73, 26.78 (COE CH₂), 28.45, 31.40 (CMe), 59.12 (CH COE), 101.74 (CH), 126.16, 126.31 (*p*-Ar), 128.05, 128.19 (*m*-Ar), 132.29, 133.47 (*o*-Ar), N–C quaternary signals not located. IR (benzene-*d*₆): ν_{N-N} 2120 cm⁻¹.

Preparation of 2. A thick-walled glass vessel was charged with 0.058 g (0.091 mmol) of (BDI-3)Ir(COE)N₂ and approximately 20 mL of heptane. On the high-vacuum line, the vessel was submerged in liquid nitrogen and evacuated. The solution was thawed and the resulting yellow solution heated to 65 °C for 4–6 h. Periodically the vessel was again submerged in liquid nitrogen and the atmosphere removed in vacuo to remove any liberated dinitrogen. This process was repeated four times, after which the solvent was removed in vacuo. Pentane was vacuum-transferred onto the resulting solid and removed in vacuo. This process was repeated several times to remove residual cyclooctane. The solid was then recrystallized from pentane at –35 °C, yielding 0.019 g (36%) of yellow-orange crystals identified as 2. Anal. Calcd for C₂₉H₃₉IrN₂: C, 57.30; H, 6.78; N, 4.61. Found: C, 57.60; H, 7.36; N, 4.51. ¹H NMR (cyclohexane-*d*₁₂): δ 0.71 (d, 3H, 7 Hz, CHCH₃),

(29) General considerations and additional experimental details can be found in the Supporting Information.

1.10 (d, 3H, 7 Hz, CHCH₃), 1.16 (d, 3H, 7 Hz, CHCH₃), 1.23 (d, 3H, 7 Hz, CHCH₃), 1.25 (d, 3H, 7 Hz, CHCH₃), 1.35 (d, 3H, 7 Hz, CHCH₃), 1.74 (s, 3H, CH₃), 2.03 (s, 3H, CH₃), 2.16 (s, 3H, CH₃), 2.73 (s, 1H, olefinic CH), 2.85 (sept, 1H, 7 Hz, CHCH₃), 2.98 (sept, 1H, 7 Hz, CHCH₃), 3.14 (s, 1H, olefinic CH), 3.30 (sept, 1H, 7 Hz, CHCH₃), 5.13 (s, 1H, CH), 6.81–7.12 (Ar H). ¹³C NMR (benzene-*d*₆): δ 20.29, 22.23, 22.50, 23.56, 23.68, 28.78, 29.18, 33.23, 34.95 (CH₃), 24.69, 25.22, 25.61 (CH), 47.06 (C=CH₂), 51.41 (C=CH₂), 103.12 (CH), 123.43, 123.85, 124.04, 124.20, 124.49, 126.45 (*o*-, *p*-, *m*-Ar), N–C quaternary signals not located.

Preparation of (BDI-1)Ir(COD). A 20 mL scintillation vial was charged with 0.093 g (0.14 mmol) of [Ir(COD)Cl]₂ in approximately 5 mL of diethyl ether. The resulting orange slurry was chilled in a drybox freezer to –35 °C for about 20 min, after which time 0.105 g (0.280 mmol) Li[BDI-1]·Et₂O in approximately 5 mL of diethyl ether was added. The orange mixture was stirred for 16 h at ambient temperature. Filtration through Celite followed by solvent removal in vacuo and subsequent recrystallization from pentane at –35 °C affords 0.053 g (37%) of a yellow solid identified as (BDI-1)Ir(COD). Anal. Calcd for C₂₅H₃₇IrN₂: C, 57.49; H, 6.16; N, 4.62. Found: C, 57.40; H, 5.84; N, 4.36. ¹H NMR (benzene-*d*₆): δ 1.42 (br d, 4H, COD), 1.56 (s, 6H, CH₃), 2.08 (br s, 4H, COD), 2.28 (s, 12H, ArMe), 3.04 (br s, 4H, COD), 5.39 (s, 1H, CH), 6.95–7.04 (Ar H). ¹³C NMR (benzene-*d*₆): δ 19.28 (Ar Me), 25.77 (CMe), 31.89, 63.22 (COD), 102.21 (CH), 126.07 (*p*-Ar), 129.00 (*m*-Ar), 132.97 (*o*-Ar), N–C quaternary signals not located.

Preparation of (BDI-3)Ir(CO)₂. A thick-walled glass vessel was charged with 0.012 g (0.020 mmol) of (BDI-3)IrH₄ and approximately 15 mL of pentane. On the vacuum line, the vessel was submerged in liquid nitrogen and evacuated, and 1 atm of CO was added. The contents of the vessel were thawed, and the resulting solution was stirred for 24 h at ambient temperature. The pentane was removed in vacuo and the resulting yellow solid recrystallized from pentane at –35 °C, yielding 0.009 g (71%) of (BDI-3)Ir(CO)₂. Anal. Calcd for C₃₁H₄₁IrN₂O₂: C, 55.92; H, 6.21; N, 4.21. Found: C, 55.44; H, 5.69; N, 3.94. ¹H NMR (benzene-*d*₆): δ 1.08 (d, 12H, 7 Hz,

CHMe₂), 1.47 (d, 12H, 7 Hz, CHMe₂), 1.64 (s, 6H, CH₃), 3.30 (sept, 4H, 7 Hz, CHMe₂), 5.24 (s, 1H, CH), 7.10 (br s, 4H, Ar *m*-H), 7.11 (br s, 2H, Ar *p*-H). ¹³C NMR (benzene-*d*₆): δ 23.44, 24.49 (CHMe₂), 24.57 (CMe), 28.05 (CHMe₂), 100.97 (CH), 124.14 (*p*-Ar), 127.70 (*m*-Ar), 141.35 (*o*-Ar), 154.62 (NC), 160.47 (CMe), 198.50 (CO). IR (pentane): ν_{CO} 1985, 2053 cm⁻¹.

Preparation of (BDI-1)IrH₂N₂. A thick-walled glass vessel was charged with 0.098 g (0.15 mmol) of (BDI-1)Ir(COE)N₂ and approximately 10 mL of pentane. On the vacuum line, the vessel was submerged in liquid nitrogen and evacuated, and 1 atm of H₂ was admitted. The contents of the vessel were then thawed, and the resulting yellow solution was stirred at ambient temperature for 8 h. The resulting dark purple solution was transferred into the drybox and filtered through a glass frit. The filtrate was collected and the pentane removed in vacuo, yielding a dark foam. Recrystallization from pentane at –35 °C yielded 0.024 g (30%) of a black solid, identified as (BDI-1)IrH₂N₂. ¹H NMR (cyclohexane-*d*₁₂): δ 1.59 (s, 6H, Ar Me), 1.80 (s, 6H, Ar Me), 2.18 (s, 3H, CH₃), 2.26 (s, 3H, CH₃), 5.36 (s, 1H, CH), 6.93–7.08 (Ar H), –20.45 (s, 2H, Ir–H), –20.09 (t, 3.6 Hz, 1H, Ir–HD in benzene-*d*₆). ¹³C NMR (cyclohexane-*d*₁₂): δ 19.03, 19.27 (Ar Me), 22.29, 22.46 (CMe), 101.97 (CH), 124.76, 125.85 (*p*-Ar), 128.41, 128.43 (*m*-Ar), 130.91, 131.51 (*o*-Ar), N–C quaternary signals not located. IR (benzene-*d*₆): $\nu_{\text{N-N}}$ 2167 cm⁻¹. IR (KBr): $\nu_{\text{N-N}}$ 2170 cm⁻¹.

Acknowledgment. We thank Cornell University and the National Science Foundation (CAREER Award) for financial support. Christopher A. Bradley is also acknowledged for the initial preparation and crystallographic characterization of (BDI-3)Ir(COD).

Supporting Information Available: Text giving additional experimental procedures, figures giving additional NMR spectra, and CIF files giving crystal structure data for (BDI-3)Ir(COD), (BDI-5)Ir(COD), and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM050705F