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A Highly Stable Adamantyl-Substituted Pincer-Ligated Iridium Catalyst for Alkane Dehydrogenation

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The adamantyl-substituted pincer-ligand precursor $^{\text{Ad}}\text{PCP-H}$ [$^{\text{Ad}}\text{PCP} = \kappa^3\text{-C}_6\text{H}_3\text{-2,6-(CH}_2\text{PAd)}_2$; Ad = 1-adamantyl] has been synthesized by the reaction of 1,3-dibromoxylene with di-1-adamantylphosphine in the presence of triethylamine. Treatment of $^{\text{Ad}}\text{PCP-H}$ with $[\text{Ir}(\text{COD})\text{Cl}]_2$ (COD = 1,5-cyclooctadiene) affords the pincer-ligated complex $(^{\text{Ad}}\text{PCP})\text{IrHCl}$, which was crystallographically characterized. Dehydrohalogenation of $(^{\text{Ad}}\text{PCP})\text{IrHCl}$ either with LiEt_3H or with KO^tBu , under hydrogen atmosphere, yields the hydrides $(^{\text{Ad}}\text{PCP})\text{IrH}_2$ and $(^{\text{Ad}}\text{PCP})\text{IrH}_4$. $(^{\text{Ad}}\text{PCP})\text{IrH}_2$ catalyzes dehydrogenation of alkanes with a level of activity comparable to that of the previously reported $(^t\text{BuPCP})\text{IrH}_2$, while it is thermally much more robust than the $^t\text{BuPCP}$ analogue, as well as $^{\text{iPr}}\text{PCP}$ or $^t\text{BuPOCOP}$ pincer complexes.

Introduction

The dehydrogenation of alkanes to give olefins is a reaction with great potential value in applications ranging from the synthesis of fine chemicals to fuels.^{1–3} Industrially, alkane dehydrogenations are currently confined to heterogeneous systems that operate at high temperatures (above 400 °C) and show a lack of selectivity.² However, in recent years progress has been made in the development of soluble molecular catalysts for alkane dehydrogenation that are active at relatively low temperatures.^{1,3} Of these, perhaps the most promising class developed thus far are the pincer-ligated⁴ iridium catalysts. Kaska, Jensen, and co-workers reported that $(^t\text{BuPCP})\text{IrH}_2$ ($^t\text{BuPCP} = \kappa^3\text{-C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^t\text{Bu)}_2$) (**1**) is active for the transfer dehydrogenation of alkanes using *tert*-butylethylene (TBE) as hydrogen acceptor (sacrificial olefin).⁵ This complex was later employed for the acceptorless

dehydrogenation of alkanes by refluxing in high-boiling alkane solvents under a flow of argon;⁶ in addition to not consuming any sacrificial reagent, this approach offers the advantage of an intrinsically simpler process. Mechanistic and computational studies of these catalysts have been reported.⁷ The less sterically demanding $^{\text{iPr}}\text{PCP}$ derivative $\{\kappa^3\text{-C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^{\text{iPr}}\text{Pr)}_2\}\text{IrH}_4$ (**2**) was found to be more effective than **1**, for both transfer and acceptorless dehydrogenation of alkanes.⁸ In addition to bis-phosphine systems, bis(phosphinite) ($^{\text{R}}\text{POCOP}$) systems have been reported,^{9,10} most notably $\{\kappa^3\text{-C}_6\text{H}_3\text{-2,6-(OP}^{\text{R}}\text{Bu)}_2\}\text{IrH}_2$ (**3**). Both $^{\text{R}}\text{POCOP}$ and $^{\text{R}}\text{PCP}$ pincer-ligated catalysts have been employed as cocatalysts (in tandem with olefin metathesis catalysts) for alkane metathesis.¹¹

Although pincer-ligated iridium catalysts are quite efficient for alkane transfer dehydrogenation and quite stable by comparison with most organometallic catalysts, decomposition is still a problem. This is particularly a concern for acceptorless dehydrogenation,^{6,12–14} which generally requires much higher

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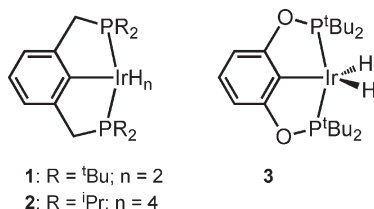
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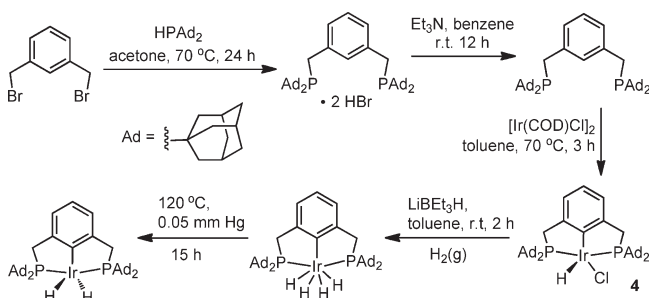
temperatures and longer reaction times to overcome the high enthalpic barrier (ca. 28–30 kcal/mol for *n*-alkanes), in contrast with transfer dehydrogenation or alkane metathesis, which are approximately thermoneutral. We report herein the introduction of the robust adamantyl group as the phosphinoalkyl substituent of a PCP-pincer ligand, in an effort to synthesize thermally more stable active catalysts for alkane dehydrogenation. We report the synthesis and characterization of (^{Ad}PCP)-IrH₂ [(κ^3 -C₆H₃-2,6-(CH₂PAd₂)₂IrH₂; Ad = 1-adamantyl) and a comparison of its stability and catalytic activity for alkane dehydrogenation with that of catalysts **1**–**3**.



Results and Discussion

Synthesis and Characterization. In analogy to the synthesis of 1,3-C₆H₃(CH₂P^tBu₂)₂,¹⁵ the bis(phosphine) pincer ligand precursor 1,3-bis(diadamantylphosphino)methyl)benzene (^{Ad}PCP-H) was synthesized from the reaction of 1,3-dibromomethylbenzene and di-1-adamantylphosphine in the presence of triethylamine in very good yield as a white crystalline solid (Scheme 1). Treatment of ^{Ad}PCP-H with 0.5 equiv of [Ir-

Scheme 1. Synthesis of (^{Ad}PCP)IrH₂ Catalyst



(COD)Cl]₂ (COD = 1,5-cyclooctadiene) in toluene at 70 °C for 3 h under hydrogen atmosphere yields (^{Ad}PCP)IrHCl (**4**) as a dark orange crystalline solid. The ³¹P{¹H} NMR spectrum of this complex shows a doublet at δ 58.5 ppm with an apparent ²J_{PH} coupling of 10.5 Hz (all ³¹P NMR spectra in this work were taken with selective decoupling of protons in the range δ 0–10). The hydride appears in the ¹H NMR spectrum as a triplet at δ –43.16 ppm with ²J_{PH} = 11.3 Hz. The (^{Ad}PCP)IrHCl complex is obtained with a minor amount of (^{Ad}PCP)IrHBr, presumably due to bromide impurity remaining from the ligand synthesis. The (^{Ad}PCP)IrHBr shows a doublet at δ 57.4 ppm in the ³¹P{¹H} NMR spectrum, with an apparent ²J_{PH} coupling of 10.1 Hz, and a triplet at δ –43.94 ppm with ²J_{PH} = 11.1 Hz in the ¹H NMR spectrum. Crystals of (^{Ad}PCP)-IrHX (X = Cl, Br) suitable for X-ray analysis were obtained by the slow evaporation of an *n*-hexane solution, which gave a 70:30 mixture of (^{Ad}PCP)IrHCl and (^{Ad}PCP)IrHBr (Figure 1 and Table 1).

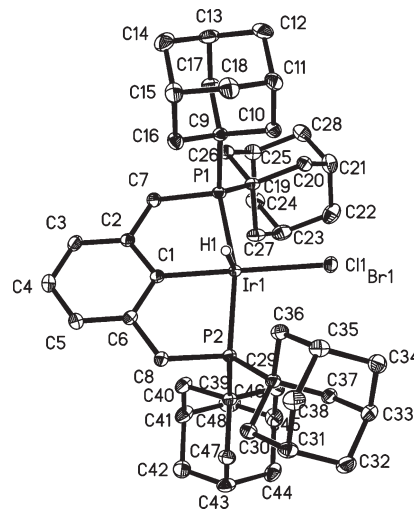


Figure 1. ORTEP diagram of the structure of (^{Ad}PCP)IrHX; X = Cl (70%), Br (30%).

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for (^{Ad}PCP)IrHX (X = Cl, Br) (**4**) and (^tBuPCP)IrHCl (**5**)

(^{Ad} PCP)IrHX (X = Cl, Br) (4)		(^t BuPCP)IrHCl (5)	
Ir(1)–C(1)	2.0285(15)	Ir(1)–C(1)	2.014(4)
Ir(1)–P(2)	2.3018(4)	Ir(1)–P(2)	2.3048(14)
Ir(1)–P(1)	2.3133(4)	Ir(1)–P(1)	2.3051(14)
Ir(1)–Cl(1)	2.4884(3)	Ir(1)–Cl(1)	2.4250(12)
Ir(1)–H(1)	1.571(9)	Ir(1)–H(1)	1.603(10)
P(1)–C(7)	1.8393(15)	P(1)–C(7)	1.838(5)
P(2)–C(8)	1.8382(15)	P(2)–C(8)	1.835(5)
C(1)–Ir(1)–P(2)	82.53(4)	C(1)–Ir(1)–P(2)	82.30(18)
C(1)–Ir(1)–P(1)	83.30(4)	C(1)–Ir(1)–P(1)	81.97(18)
P(2)–Ir(1)–P(1)	165.232(14)	P(2)–Ir(1)–P(1)	164.27(4)
C(1)–Ir(1)–Cl(1)	178.79(4)	C(1)–Ir(1)–Cl(1)	179.7(2)
C(1)–Ir(1)–H(1)	82.3(7)	C(1)–Ir(1)–H(1)	90(3)
C(9)–P(1)–Ir(1)	116.57(5)	C(9)–P(1)–Ir(1)	113.18(19)
C(19)–P(1)–Ir(1)	114.05(5)	C(13)–P(1)–Ir(1)	119.03(18)
C(29)–P(2)–Ir(1)	119.67(5)	C(17)–P(2)–Ir(1)	119.22(19)
C(39)–P(2)–Ir(1)	111.09(5)	C(21)–P(2)–Ir(1)	113.26(19)

The coordination geometry of (^{Ad}PCP)IrHCl is approximately square pyramidal around iridium, with the hydride located in the apical position (Figure 1). For comparison, the molecular structure of the known compound (^tBuPCP)IrHCl (**5**)¹⁵ was also determined crystallographically; the structures of **4** and **5** were found to be quite similar (Table 1). The Ir–P distances are essentially identical (average *d*_{Ir–P} = 2.308 Å in **4**; 2.305 Å in **5**), while the C_{aryl}–Ir distance Ir(1)–C(1) of **4** (2.0285(15) Å) is negligibly greater than that of **5** (2.015(3) Å). The P(1)–Ir–P(2) bond angle of **4** (165.232(14)°) is very slightly greater than that of **5** (164.27(4)°), but it is doubtful that this is of any significance, particularly since the P–Ir–P angle of the *p*-NO₂-substituted analogue of **5** has been reported to be 166.80(3)°.¹⁶

The mixture of (^{Ad}PCP)IrHCl and (^{Ad}PCP)IrHBr was converted to hydrides (^{Ad}PCP)IrH₂ and (^{Ad}PCP)IrH₄ by treatment with LiBEt₃H (1.0 M in THF) in toluene under a H₂ atmosphere at room temperature (Scheme 1). The same products were also synthesized by the reaction of (^{Ad}PCP)IrH(halide) with one equivalent of sublimed KO^tBu in benzene under

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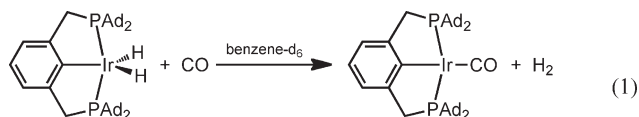
Table 2. Acceptorless Dehydrogenation of Cyclodecane by $(^R\text{PCP})\text{IrH}_n$ ^a

time (h)	total cyclodecenes (mM)		
	$(^{\text{Ad}}\text{PCP})\text{IrH}_2$	$(^{\text{tBu}}\text{PCP})\text{IrH}_2$	$(^{\text{iPr}}\text{PCP})\text{IrH}_4$
1	74	102	136
3	179	218	274
5	251	240	
24	509	267	364
48	526	294	
72	534	305	366
96	543	314	

^a Conditions: catalyst = 1.0 mM, cyclodecane = 1.5 mL, cyclodecane bp = 201 °C. Oil bath temp = 230 °C.

a H_2 atmosphere. The mixture of $(^{\text{Ad}}\text{PCP})\text{IrH}_2$ and $(^{\text{Ad}}\text{PCP})\text{IrH}_4$ was converted to pure $(^{\text{Ad}}\text{PCP})\text{IrH}_2$ by heating at 120 °C under vacuum for 15 h.⁵ The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $(^{\text{Ad}}\text{PCP})\text{IrH}_2$ and $(^{\text{Ad}}\text{PCP})\text{IrH}_4$ show single resonances at δ 81.2 and 73.9 ppm, respectively. In the ^1H NMR spectrum, $(^{\text{Ad}}\text{PCP})\text{IrH}_2$ and $(^{\text{Ad}}\text{PCP})\text{IrH}_4$ in toluene- d_8 appear as triplets at δ -19.15 ($^2J_{\text{HP}} = 9.3$ Hz) and -9.30 ppm ($^2J_{\text{HP}} = 9.5$ Hz), respectively, which is essentially the same as $(^{\text{tBu}}\text{PCP})\text{IrH}_2$ and $(^{\text{tBu}}\text{PCP})\text{IrH}_4$ (δ -19.21, $^2J_{\text{HP}} = 8.8$ Hz; δ -9.14, $^2J_{\text{HP}} = 9.8$ Hz, respectively).⁵

Treatment of $(^{\text{Ad}}\text{PCP})\text{IrH}_2$ with 1 atm of CO in benzene- d_6 gave $(^{\text{Ad}}\text{PCP})\text{Ir}(\text{CO})$ in quantitative yield (eq 1). The C–O stretching frequency, ν_{CO} , obtained for $(^{\text{Ad}}\text{PCP})\text{Ir}(\text{CO})$ in hexane solution is 1916 cm^{-1} , comparable to that observed for $(^{\text{tBu}}\text{PCP})\text{Ir}(\text{CO})$ (1914 cm^{-1}) and $(^{\text{iPr}}\text{PCP})\text{Ir}(\text{CO})$ (1918 cm^{-1}).



Catalytic Activity for Acceptorless Dehydrogenation of Alkanes. Acceptorless dehydrogenation of alkanes (eq 2) is in principle an ideal process for the formation of olefins, with respect to both simplicity of process (in that there are no added reagents or extraneous products such as hydrogenated acceptor) and “atom-economy”.¹⁷



Several pincer complexes $(^R\text{PCP})\text{Ir}$ have been found to be effective catalysts for eq 2.^{6,8,18} However, compared with transfer dehydrogenation, acceptorless dehydrogenation (which is highly endothermic) requires significantly higher temperatures and/or longer reaction times. Decomposition is therefore a particular concern in the context of acceptorless dehydrogenation.

The substitution of adamantyl for *tert*-butyl groups bound to phosphorus on a ^RPCP ligand was expected to exert a relatively small effect on steric and electronic properties at the metal center. However, as a derivative of the simplest “diamondoid”, the adamantyl group is considered to be particularly robust. Although the decomposition routes have not been characterized, we considered that the cage structure

Table 3. Acceptorless Dehydrogenation of *n*-Dodecane by $(^R\text{PCP})\text{IrH}_n$ ^a

time (h)	total dodecenes (mM)		
	$(^{\text{Ad}}\text{PCP})\text{IrH}_2$	$(^{\text{tBu}}\text{PCP})\text{IrH}_2$	$(^{\text{iPr}}\text{PCP})\text{IrH}_4$
1	26	35	26
2	39	39	28
5	45	40	35
24	61	42	
48	69	40	61
72	71		

^a Conditions: catalyst = 1.0 mM, *n*-dodecane = 1.5 mL, *n*-dodecane bp = 216 °C. Oil bath temp = 230 °C.

might be more resistant to cyclometalation, which could perhaps be responsible for decomposition.¹⁹ Additionally, the adamantyl–phosphorus bond is presumably stronger than the *tert*-butyl–phosphorus bond (in analogy with the corresponding C–H bonds²⁰); this might also potentially inhibit decomposition. Moreover, while we expected that the additional hydrocarbyl groups in adamantyl versus *tert*-butyl would probably exert no steric effect on the reactions with alkanes, the added bulk could conceivably inhibit intermolecular catalyst–catalyst interactions.

Owing to its low enthalpy of dehydrogenation²¹ and high boiling point, cyclodecane is a useful starting point for studies of homogeneous acceptorless dehydrogenation. Refluxing (201 °C) a cyclodecane solution of $(^{\text{Ad}}\text{PCP})\text{IrH}_2$ (1.0 mM) (230 °C oil bath temperature) gave *cis*- and *trans*-cyclodecene with 74 turnovers (TO's) obtained after 1 h as compared with 102 and 136 TO's using $(^{\text{tBu}}\text{PCP})\text{IrH}_2$ (**1**) and $(^{\text{iPr}}\text{PCP})\text{IrH}_4$ (**2**), respectively (Table 2; olefin yields determined by gas chromatography). But although the initial turnover frequency obtained with $(^{\text{Ad}}\text{PCP})\text{IrH}_2$ was no greater than that of **1**, total turnovers were noticeably greater than those obtained with **1** (543 vs 314) after 96 h.²²

Refluxing an *n*-dodecane solution of $(^{\text{Ad}}\text{PCP})\text{IrH}_2$ (1.0 mM) at 230 °C yields 26 mM dodecenes after 1 h compared to 35 and 26 mM with $(^{\text{tBu}}\text{PCP})\text{IrH}_2$ (**1**) and $(^{\text{iPr}}\text{PCP})\text{IrH}_4$ (**2**), respectively (Table 3). However, production of the linear olefins quickly leveled off in all three cases. This has previously been shown to be attributable to product inhibition, presumably due to both the strong binding of olefins to the catalyst and the back reaction (hydrogenation), which is significantly more exothermic than the corresponding reaction of cyclodecane.²¹

In general, product inhibition is a significant issue in the contexts of both transfer and acceptorless dehydrogenation by pincer-iridium catalysts.⁶ Thus, while the higher turnover numbers obtained for cyclodecane dehydrogenation with $(^{\text{Ad}}\text{PCP})\text{IrH}_2$ after longer reaction times are consistent with $(^{\text{Ad}}\text{PCP})\text{IrH}_2$ being more stable than **1** or **2**, there are reasonable alternative explanations as well. In our view, the most

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(22) This result is slightly different from that obtained previously for $(^{\text{tBu}}\text{PCP})\text{IrH}_2$ -catalyzed acceptorless dehydrogenation of cyclodecane, where 360 turnovers were obtained after 24 h (ref 6). In general, during acceptorless dehydrogenation, factors such as the rate of loss of hydrogen from solution and thermal homogeneity may play an important role in determining rates and turnover numbers. Thus when comparing different runs, it is important to ensure that they were conducted under identical conditions including identical reaction vessels, controlled oil bath temperature, and extent of immersion of the vessel in the oil bath.

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Table 4. Catalyst Stability in *n*-Octane at 250 °C^a

catalyst	time (min)	(^R PCP)IrH _n (%)	(^R PCP)Ir(olefin) (%) ^b	(^R PCP)Ir(CO) (%)	free ligand (%)	dec (%)
(AdPCP)IrH ₂	10	73	23	3	0	0
	30	64	26	4	2	4
	60	61	26	6	3	4
	180	57	28	6	4	5
	300	55	24	7	4	10
	1500	42	17	6	6	29
(tBuPCP)IrH ₂	10	93	0	2	0	5
	30	68	0	2	0	30
	60	50	0	3	2	45
	180	11	0	3	6	80
(iPrPCP)IrH ₄	10	84	5	0	0	11
	30	59	8	0	2	31
	60	51	12	2	4	34
	180	37	15	2	6	40
	300	33	8	4	6	49
(tBuPOCOP)IrH ₂	10	79	16	3	0	2
	30	59	32	3	0	6
	60	53	33	3	0	11
	180	35	36	2	0	27
	300	18	41	3	0	38
	1500	2	9	4	0	85

^aConditions: catalyst = 10 mM, *n*-octane = 0.5 mL, sand bath temp = 250 °C, % are calculated with respect to internal standard (Me₃P) capillary.
^b(AdPCP)Ir(H)(octenyl) complexes for (AdPCP)IrH₂

meaningful way to assess stability of the catalysts is to subject them to thermolysis under steady-state conditions mimicking those of the catalytic reactions.

Catalyst Stability Monitored by NMR. *n*-Octane solutions of (AdPCP)IrH₂, **1**, **2**, and **3** (10.0 mM) were each heated in sealed NMR tubes in a preheated sand bath inside an oven at 250 °C, which were then monitored by ³¹P NMR spectroscopy. Small amounts of (pincer)Ir(CO) invariably formed (Table 4). When the NMR tubes were not flame-dried prior to use, formation of (pincer)Ir(CO) was much more pronounced (up to 24% conversion), indicating that the source of the carbonyl oxygen was moisture and/or silica. Other than (pincer)IrH₂, (pincer)Ir(octene), (pincer)Ir(H)(octenyl) (see below and Experimental Section), and small amounts of (pincer)Ir(CO) and free pincer ligand, no measurable products were observed in the ³¹P NMR spectrum. Upon prolonged heating, however the total concentration of these species diminished in all cases, as determined by comparison with the PMe₃ standard present in the capillary. (The solutions turned black in the cases of tBuPCP and iPrPCP.) Addition of H₂ to the solutions did not result in the conversion of the “missing” (NMR-invisible) material to (pincer)IrH₄ or any other NMR-visible species. This strongly indicates that the loss of NMR-observable pincer complex can be safely considered as “decomposition”, as it is unlikely that any species that do not react with H₂ to give (pincer)Ir hydrides would abstract hydrogen from alkanes to regenerate the same hydrides.

After 180 min at 250 °C, 85% of the (AdPCP)Ir was observable by ³¹P NMR as (AdPCP)IrH₂ (57%) and three doublets (*J* = ca. 10 Hz) in the range δ 56–57 ppm (totaling 28%) (Table 4). Three hydride peaks were observed in the range δ –42 to –44 ppm. In analogy with (tBuPCP)Ir(CH=CH^tBu)(H),^{7a} we tentatively assign these species as products of vinylic C–H addition, viz., isomers/rotamers of (AdPCP)Ir(H)(octenyl). Accordingly conversion to the same species is observed upon addition of *cis*- or *trans*-2-octene to a *p*-xylene solution of the labile complex (AdPCP)Ir(norbornene) (see Experimental Section for further details). Importantly, upon addition of H₂ atmosphere, they are readily converted to

(AdPCP)IrH₄. In contrast, only 11% and 52% of the (tBuPCP)Ir and (iPrPCP)Ir complexes remained as species observable in the NMR spectrum, as well as 71% of (tBuPOCOP)Ir complexes. The contrast with the tBuPCP species is particularly noteworthy since the tBuPCP ligand is so commonly used and the AdPCP ligand is expected to be very similar with respect to electronic and steric effects. The (tBuPCP)Ir species was predominantly present as (tBuPCP)IrH₂, while the other complexes were present largely as dihydride along with some octene adduct (Table 4).^{9c} (Note that small amounts of free alkane dehydrogenation product are often observed to form in the presence of dehydrogenation catalysts at elevated temperatures, even in a sealed vessel in the absence of hydrogen acceptor.²³ Formation of coordinated olefin would be thermodynamically even more favorable.)

When the analogous experiments were carried out in cyclooctane instead of *n*-octane, the rates of decomposition were quite similar except that (iPrPCP)Ir seemed to be less stable (Table 5). Thus, after 180 min at 250 °C, 82% of the (AdPCP)Ir was observable in solution versus 15%, 25%, and 65% for the (tBuPCP)Ir, (iPrPCP)Ir, and (tBuPOCOP)Ir complexes, respectively. Interestingly, a significant fraction (13%) of the (AdPCP)Ir was present as two hydride complexes (**6a** and **6b**) with ¹H NMR chemical shifts of δ –43.98 ppm (t, ²*J*_{PH} = 11.2 Hz) and –43.19 ppm (t, ²*J*_{PH} = 11.7 Hz), clearly indicative of five-coordinate Ir(III) species; for example the chemical shift of (tBuPCP)Ir(CH=CH^tBu)(H) is δ –45.78 ppm. The ³¹P{¹H} NMR spectrum was also consistent with characterization as a monohydride, showing doublets at δ 56.6 and 55.9 ppm with apparent ²*J*_{PH} coupling values of 10.6 and 11.7 Hz, respectively.

We initially considered that the hydrides **6a** and **6b** were the products of cyclooctene C–H addition, analogous to (tBuPCP)Ir(CH=CH^tBu)(H)^{7a} and the (AdPCP)Ir(H)(octenyl) species noted above. However, no reaction was observed upon adding COE to a *p*-xylene solution of (AdPCP)Ir(norbornene)

(23) (a) Guo, N.; Li, H.; Baker, R. T.; Marshall, C. L.; Sattelberger, A. P. *Abstracts of Papers*, 236th ACS National Meeting, Philadelphia, PA, August 17–21, 2008, INOR-092. (b) Li, H.; Duran, B. L.; Janicke, M. T.; Kelly, D.; Baker, R. T.; Sattelberger, A. P. *Abstracts of Papers*, 233rd ACS National Meeting, Chicago, IL, March 25–29, 2007, INOR-645.

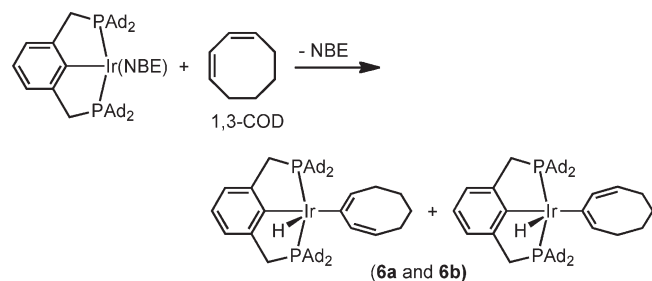
Table 5. Catalyst Stability in Cyclooctane at 250 °C^a

catalyst	time (min)	(^R PCP)IrH _n (%)	(^R PCP)Ir(olefin) (%) ^b	(^R PCP)Ir(CO) (%)	free ligand (%)	dec (%)
(AdPCP)IrH ₂	10	82	14	4	0	0
	30	72	17	3	4	4
	60	72	15	4	4	5
	180	69	13	4	4	10
	300	60	13	6	6	15
	1500	47	9	8	5	31
(tBuPCP)IrH ₂	10	85	0	0	0	15
	30	71	0	2	0	27
	60	53	0	4	3	40
	180	15	0	4	8	73
(iPrPCP)IrH ₄	10	61	14	0	0	25
	30	34	17	0	1	48
	60	16	15	0	3	66
	180	11	14	0	7	68
	300	7	12	0	10	71
(tBuPOCOP)IrH ₂	10	72	24	0	0	4
	30	57	36	1	0	6
	60	42	40	2	0	16
	180	31	34	4	0	29
	300	24	32	4	0	40
	720	5	26	5	0	64

^a Conditions: catalyst = 10 mM, cyclooctane = 0.5 mL, sand bath temp = 250 °C, % are calculated with respect to internal standard (Me₃P) capillary. ^b 6a and 6b in the case of (AdPCP)IrH₂.

until the mixture was heated at 80 °C for ca. 15 h, during which time 6a and 6b were formed. This argues against the likelihood that these hydrides are simple products of addition of a COE C–H bond to (AdPCP)Ir since olefin exchange reactions, as well as C–H addition/elimination reaction of (tBuPCP)Ir complexes, are generally very fast (on the order of seconds or less at room temperature or below).⁷

Considering both electronic and steric effects, we would expect that 1,3-cyclooctadiene (1,3-COD) would undergo C–H addition more favorably than does COE. Accordingly, in contrast with the very slow reactivity toward COE at 80 °C, when a *p*-xylene solution of (AdPCP)Ir(norbornene) (42 mM) was mixed with 1,3-COD (420 mM), the hydride signals of 6a and 6b appeared within ca. 3 h at room temperature. Therefore we propose that under the conditions of the thermolysis (250 °C), COE is disproportionated to give 1,3-COD, which undergoes C–H addition to (AdPCP)Ir, probably at the 1,3-COD 2-position, to give two possible rotamers. In the ¹H NMR spectrum, peaks in the vinylic region are consistent with this assignment (see Experimental Section).



The catalyst stabilities were also monitored under conditions mimicking transfer dehydrogenation, i.e., in alkane solution with olefin present. Cyclooctane solutions of complexes (^RPCP)IrH_n (R = Ad, tBu, iPr) and (tBuPOCOP)IrH₂ in the presence of 200 mM cyclooctene were heated at 250 °C. From the reaction of (tBuPOCOP)IrH₂, the major product was the pincer-iridium COE adducts (presumably η²-olefin complex).^{9c} The reaction of (iPrPCP)IrH₂, however, gave two species showing doublets in the ³¹P{¹H} NMR spectrum (δ 70.6 and 71.1 ppm, with apparent coupling constants of 138.5

and 129.5 Hz, respectively). These are not characteristic of η²-olefin complexes, which resonate significantly further upfield (ca. 45.2 ppm). These species, however, can be regenerated to (iPrPCP)IrH₄ by the addition of H₂. In the case of the (tBuPCP) complex, the major product observed was (tBuPCP)IrH₂ with some amount of apparently similar H₂-regeneratable products (δ 86.8 and 93.4 ppm, with apparent couplings of 124.2 and 133.4 Hz, respectively). In contrast (AdPCP)Ir was still mostly in the form of (AdPCP)IrH₂, although with greater amounts of 6a and 6b present than in the case of the experiments with pure cyclooctane. The (AdPCP)Ir species was again observed to be the most robust species, with 71% remaining as NMR-observable species after 1320 min. Decomposition was much more severe for the other complexes under these conditions, in particular for the closely related (tBuPCP)Ir species (only 6% NMR-observable species remaining after 180 min) (Table 6).

Similar results were obtained in *n*-octane solution at 250 °C with 1-octene added (200 mM; most of which was quickly isomerized to internal octenes under these conditions) (Table 7). The (AdPCP)Ir was present as the species assigned as (AdPCP)Ir(H)(octenyl), which was fairly stable; for example, 88% of the complex was present in this form after 180 min at 250 °C, and 69% after 1440 min. The (iPrPCP)Ir unit under these conditions was present as several unidentified species, showing doublets in the ³¹P{¹H} NMR spectrum (δ 70.9 and 71.6 ppm, with apparent coupling constants of 144.2 and 137.4 Hz, respectively), i.e., not the simple olefin adducts, which appear further upfield in the ³¹P NMR (ca. 49.8 ppm). When H₂ was added to these products (as well as to the olefin adduct from (AdPCP)Ir), they are regenerated to the corresponding hydrides, and we therefore do not characterize them as decomposition products. However, after 180 min under these conditions, only 19% of the (tBuPCP)Ir species remains as NMR-observable (showing doublets in the ³¹P{¹H} NMR spectrum at δ 86.8 and 93.3 ppm, with apparent coupling constants of 122.8 and 137.7 Hz, respectively). Addition of H₂ does not regenerate the remaining 81%. Decomposition is also much faster for the (iPrPCP)Ir and (tBuPOCOP)Ir species than for (AdPCP)Ir (see Table 7), although not as fast as in the case of (tBuPCP)Ir.

Table 6. Catalyst Stability Cyclooctane/Cyclooctene at 250 °C^a

catalyst	time (min)	(^R PCP)IrH _n (%)	(^R PCP)Ir(olefin) (%) ^b	unidentified regeneratable products (%)	(^R PCP)Ir(CO)(%)	free ligand (%)	dec (%)
(AdPCP)IrH ₂	10	72	25	0	2	0	1
	30	62	31	0	4	0	3
	60	56	33	0	5	1	5
	180	53	31	0	7	1	8
	300	52	27	0	9	3	9
	1320	50	21	0	9	3	17
(tBuPCP)IrH ₂	10	78	0	14	2	0	6
	30	26	0	40	3	2	29
	60	6	0	28	3	7	66
	180	0	0	6	4	11	79
(iPrPCP)IrH ₄	10	0	7	64	0	0	29
	30	0	2	61	0	0	37
	60	0	0	60	0	0	40
	180	0	0	58	0	1	41
	300	0	0	48	0	3	49
(tBuPOCOP)IrH ₂	10	0	93	0	0	0	7
	30	0	67	3	4	0	26
	60	0	52	7	5	0	36
	180	0	49	8	5	0	38
	300	0	40	5	5	0	50
	1320	0	34	5	8	0	53

^a Conditions: catalyst = 10 mM, cyclooctene = 200 mM, total solution = 0.5 mL, sand bath temp = 250 °C, % are calculated with respect to internal standard (Me₃P) capillary. ^b **6a** and **6b** in the case of (AdPCP)IrH₂.

Table 7. Catalyst Stability in *n*-Octane/1-Octene at 250 °C^a

catalyst	time (min)	(^R PCP)IrH _n (%)	(^R PCP)Ir(octene) (%) ^b	unidentified regeneratable products (%)	(^R PCP)Ir(CO) (%)	free ligand (%)	dec (%)
(AdPCP)IrH ₂	10	0	96	0	4	0	0
	30	0	93	0	4	0	3
	60	0	91	0	4	0	5
	180	0	88	0	3	0	9
	300	0	84	0	4	0	12
	1440	0	69	0	6	3	25
(tBuPCP)IrH ₂	10	0	9	63	2	0	26
	30	0	2	37	2	0	59
	60	0	0	28	2	3	67
	180	0	0	19	3	5	73
(iPrPCP)IrH ₄	10	0	0	88	0	0	12
	30	0	0	72	0	0	28
	60	0	0	67	1	0	32
	180	0	0	63	1	0	36
	300	0	0	58	3	0	39
(tBuPOCOP)IrH ₂	1440	0	0	21	3	0	76
	10	0	88	4	0	0	8
	30	0	77	5	0	0	18
	60	0	76	5	0	0	19
	180	0	74	4	2	0	20
	300	0	71	3	2	0	24
	1440	0	43	3	4	0	50

^a Conditions: catalyst = 10 mM, 1-octene = 200 mM, total solution = 0.5 mL, sand bath temp = 250 °C, % are calculated with respect to internal standard (Me₃P) capillary. ^b (AdPCP)Ir(H)(octenyl) complexes for (AdPCP)IrH₂.

Summary. The adamantyl-substituted complexes (AdPCP)-IrH_n have been synthesized and have been found to catalyze alkane dehydrogenation with turnover frequencies similar to those of the analogous (tBuPCP)Ir and (iPrPCP)Ir species. The (AdPCP)Ir complexes are found to be significantly more robust than the (tBuPCP)Ir and (iPrPCP)Ir analogues at high temperature (250 °C). With respect to potential large-scale and commodity-type applications of this class of catalysts, stability is clearly a critical parameter. Therefore the greater stability that is engendered by the adamantyl group offers promise with respect to PCP-pincer iridium complexes. This may perhaps be extrapolated more generally to other transition metal phosphine complexes for reactions in which high thermal stability is an important factor. In particular the

significantly greater stability of the (AdPCP) catalyst compared with the (tBuPCP) is noteworthy given that these two species have very similar electronic and steric parameters, and in view of the fairly widespread occurrence of phosphino-*tert*-butyl groups in organometallic catalysis. Attempts to characterize the decomposition pathways of the other catalysts, particularly the (tBuPCP)Ir species, are currently underway.

Experimental Section

General Experimental Procedures. All manipulations were conducted under an argon atmosphere either in a glovebox or using standard Schlenk techniques. All solvents were distilled under vacuum from Na/K alloy after several freeze–pump–thaw

cycles and stored in an argon-atmosphere glovebox. (^tBuPCP)-IrH₂,^{3,5} (ⁱPrPCP)IrH₄,⁸ and (^tBuPOCOP)IrH₂^{9,10} were prepared as described previously. Di-1-adamantylphosphine was used as purchased from Strem. All other reagents were obtained from commercial sources and used as received. Catalytic reactions were monitored using a Focus gas chromatograph with a 30 m × 0.25 mm capillary column. NMR spectra were recorded on 400 or 500 MHz Varian spectrometers, and ¹H NMR spectra are referenced to residual protio solvent. ³¹P{¹H} NMR chemical shifts are referenced to an external standard, Me₃P in mesitylene-*d*₁₂ solvent (δ −62.4 ppm), in a capillary tube.

Acceptorless Dehydrogenation of Alkanes. In a typical experiment, in the argon-atmosphere glovebox, an alkane solution of catalyst (1.0 mM) was charged into a reactor consisting of a 5 mL cylindrical bulb fused to a water-jacketed condenser (ca. 15 cm in length). The top of the condenser was fused to two Kontes high-vacuum valves and an Ace Glass “adjustable electrode ace-thred adapter”. The cylindrical bulb was fully immersed in an oil bath held at 230 °C, resulting in vigorous reflux of the reaction solution. Escape of H₂ from the system is enabled by a continuous argon stream above the condenser. The reaction was monitored by GC analysis.

Sealed-Tube Reactions. Sealed-tube reactions were conducted as follows. The catalyst solution, 10.0 mM in alkane or alkane/olefin, was charged into a long NMR tube, and a capillary, containing external standard solutions, was introduced into it inside the glovebox. The tube was flame-sealed under vacuum and then placed in a preheated sand bath inside an oven. The tube was periodically removed from the oven, and the reaction was monitored by NMR spectroscopy. After this periodic monitoring, the solution was transferred into a J-Young valved NMR tube inside the glovebox, H₂ gas was then added to the solution on a high-vacuum line, and the percentage of regenerated product (tetrahydride) was determined by NMR.

Synthesis of (^{Ad}PCP-H). A mixture of 1,3-dibromoxylene (0.44 g, 1.67 mmol) and di-1-adamantylphosphine (1 g, 3.33 mmol) in degassed acetone (40 mL) was heated to reflux for 24 h. The white precipitate formed was separated from the mother liquor by cannula filtration and then dried under vacuum. The white salt was brought into the glovebox, benzene (40 mL) and Et₃N (0.51 mL, 3.67 mmol) were added, and the mixture was stirred overnight and then filtered to remove the Et₃N·HBr salt. The mother liquor was then evaporated to dryness to obtain the white crystalline product, which was recrystallized from toluene. Yield: 1.04 g, (88%). Anal. Calcd for C₄₈H₆₈P₂: C, 81.54; H, 9.69. Found: C, 80.92; H, 9.41. ¹H NMR (500 MHz, C₆D₆): δ 7.83 (s, 1H, Ar-*H*), 7.39 (d, ³J_{HH} = 7.5 Hz, 2H, Ar-*H*), 7.26 (t, ³J_{HH} = 7.7 Hz, 1H, Ar-*H*), 2.87 (d, ²J_{PH} = 2.0 Hz, 4H, 2 CH₂), 1.96 (s, 24H, 12 Ad-CH₂(α)), 1.88 (s, 12H, 12 Ad-CH_β), 1.67 (s, 24H, 12 Ad-CH₂(γ)). ³¹P{¹H} NMR (202.3 MHz, C₆D₆): δ 29.6 (s). ¹³C{¹H} NMR (125.7 MHz, C₆D₆): δ 143.1 (d, ²J_{PC} = 13.8 Hz, 2C, aryl *ortho*-C), 132.2 (t, ³J_{PC} = 12.5 Hz, 1C, aryl *ipso* C), 128.7 (s, 2C, aryl *meta*-C), 127.5 (s, 1C, aryl *para*-C), 41.7 (d, ²J_{PC} = 11.4 Hz, 12C, Ad-CH₂), 37.7 (s, 12C, Ad-CH₂), 37.2 (d, ¹J_{PC} = 25.3 Hz, 4C, Ad-C-P), 29.5 (d, ³J_{PC} = 8.2 Hz, 12C, Ad-CH), 25.4 (d, ¹J_{PC} = 24.4 Hz, 2C, CH₂-P).

Synthesis of (^{Ad}PCP)IrHCl. A mixture of (^{Ad}PCP-H) (0.5 g, 0.71 mmol) and [Ir(COD)Cl]₂ (0.232 g, 0.35 mmol) in toluene (20 mL) was heated at 70 °C for 3 h under a H₂ atmosphere. The solution was cooled and solvent was removed under vacuum to obtain a dark red crystalline product. A small amount was recrystallized in *n*-hexane to obtain X-ray quality crystals. Yield: 0.59 g (90%). Anal. Calcd for C₄₈H₆₈Br_{0.3}Cl_{0.7}IrP₂: C, 60.81; H, 7.23; Br, 2.53; Cl, 2.62. Found: C, 61.27; H, 7.13; Br, 2.24; Cl, 2.94. ¹H NMR (500 MHz, C₆D₆): δ 7.11–7.21 (m, 3H, Ar-*H*), 3.32 (dvt, ²J_{HH} = 13.0 Hz, ²J_{PH} = 3.5 Hz, 2H, CH₂), 3.26 (dvt, ²J_{HH} = 13.0 Hz, ²J_{PH} = 3.5 Hz, 2H, CH₂), 2.17–2.51 (m, 24H, Ad-CH₂), 1.82–1.88 (m, 12H, Ad-CH), 1.52–1.70 (m, 24H, Ad-CH₂), −43.16 (t, ²J_{PH} = 11.25 Hz, 1H, Ir-*H*). ³¹P{¹H} NMR (202.3 MHz, C₆D₆): δ 58.5 (d, ²J_{PH} = 10.5 Hz). ¹³C{¹H}

NMR (125.7 MHz, C₆D₆): δ 138.2 (s br, 1C, Aryl-C), 134.5 (s br, 2C, Aryl-C), 129.6 (s br, 2C, Aryl-C), 129.2 (s, 1C, Aryl-C), 41.2 (s br, 12C, Ad-CH₂), 40.5 (s, 12C, Ad-CH₂), 37.3 (s br, 4C, Ad-C-P), 29.4 (vt, ²J_{PC} = 4.2 Hz, 12C, Ad-CH), 20.3 (vt, ²J_{PC} = 19.1 Hz, 2C, CH₂-P).

Synthesis of (^{Ad}PCP)IrH₂. To a solution of (^{Ad}PCP)IrHCl (0.5 g, 0.53 mmol) in toluene (20 mL) was added dropwise a solution (1.0 M in THF) of LiBEt₃H (0.53 mL, 0.53 mmol) at room temperature under a H₂ atmosphere. The dark orange reaction mixture became colorless upon stirring for 1 h and was then cannula-filtered to remove the precipitate. The filtrate was evaporated under vacuum and dried overnight to obtain a crystalline compound of (^{Ad}PCP)IrH₂ with a minor amount of (^{Ad}PCP)IrH₄. The mixture was dried under vacuum at 120 °C overnight to obtain exclusively (^{Ad}PCP)IrH₂. Yield: 0.35 g, (73%). Anal. Calcd for C₄₈H₆₉IrP₂: C, 64.04; H, 7.73. Found: C, 63.79; H, 7.39. ¹H NMR (500 MHz, toluene-*d*₈): δ 7.45 (d, ³J_{HH} = 7.5 Hz, 2H, Ar-*H*), 7.21 (t, ³J_{HH} = 6.8 Hz, 1H, Ar-*H*), 3.61 (vt, ²J_{PH} = 4.0 Hz, 4H, 2 CH₂), 2.14 (d, ²J_{HH'} = 12.0 Hz, 12H, Ad-CH_α), 2.08 (d, ²J_{HH'} = 11.0 Hz, 12H, Ad-CH_α), 1.83 (s, 12H, Ad-CH_β), 1.63 (d, ²J_{HH'} = 12.0 Hz, 12H, Ad-CH_γ), 1.57 (d, ²J_{HH'} = 10.5 Hz, 12H, Ad-CH_γ), −19.15 (t, ²J_{PH} = 9.25 Hz, 2H, Ir-*H*). ³¹P{¹H} NMR (202.3 MHz, toluene-*d*₈): δ 81.2 (s). ¹³C{¹H} NMR (125.7 MHz, C₆D₆): δ 137.6 (s br, Ar-C), 131.9 (s br, Ar-C), 126.7 (s br, 2C, Ar-C), 120.4 (m, Ar-C), 41.5 (s br, 12C, Ad-CH₂), 40.4 (s, 12C, Ad-CH₂), 37.6 (s br, 4C, Ad-C-P), 29.9 (m, 12C, Ad-CH), 29.4 (vt, ²J_{PC} = 4.3 Hz, 2C, CH₂-P).

Synthesis of (^{Ad}PCP)Ir(CO). To a solution of (^{Ad}PCP)IrH₂ (0.02 g, 0.022 mmol) in benzene-*d*₆ (0.6 mL) in a J-Young NMR tube was added norbornene (0.006 g, 0.063 mmol), and the reaction mixture was left at room temperature overnight to obtain (^{Ad}PCP)Ir(norbornene). The solvent and excess norbornene were removed under vacuum, and fresh solvent and CO (1 atm) were then added. The tube was shaken for 5 min as the solution turned yellow. ¹H NMR (400 MHz, C₆D₆): δ 7.39 (d, ³J_{HH} = 7.6 Hz, 2H, Ar-*H*), 7.18 (t, ³J_{HH} = 6.4 Hz, 1H, Ar-*H*), 3.54 (vt, ²J_{PH} = 3.4 Hz, 4H, 2 CH₂), 2.32 (d, ²J_{HH'} = 11.6 Hz, 12H, Ad-CH_α), 2.25 (d, ²J_{HH'} = 12.0 Hz, 12H, Ad-CH_α), 1.86 (s, 12H, Ad-CH_β), 1.67 (d, ²J_{HH'} = 11.6 Hz, 12H, Ad-CH_γ), 1.57 (d, ²J_{HH'} = 11.6 Hz, 12H, Ad-CH_γ). ³¹P{¹H} NMR (161.9 MHz, C₆D₆): δ 77.2 (s). ¹³C{¹H} NMR (125.7 MHz, C₆D₆): δ 182.2 (t, ²J_{PC} = 4.0 Hz, CO), 138.1 (vt, ²J_{PC} = 11.3 Hz, Ar-C), 128.9 (s, Ar-C), 126.0 (s, Ar-C), 120.6 (vt, ²J_{PC} = 8.5 Hz, 2C, Ar-C), 41.4 (s, 12C, Ad-CH₂), 37.5 (s, 12C, Ad-CH₂), 37.1 (vt, ²J_{PC} = 4.3 Hz, 12C, Ad-CH), 35.9 (vt, ²J_{PC} = 14.3 Hz, 4C, Ad-C-P), 29.4 (vt, ²J_{PC} = 2.3 Hz, 2C, CH₂-P). IR (hexane, cm^{−1}): ν_{CO} = 1916 cm^{−1}. The same complex was observed upon addition of CO directly to a solution of (^{Ad}PCP)IrH₂.

Synthesis of (^{Ad}PCP)IrH(η¹-1,3-cyclooctadienyl) (6a and 6b). To a solution of (^{Ad}PCP)IrH₂ (0.02 g, 0.022 mmol) in *p*-xylene-*d*₁₀ (0.5 mL) in a J-Young NMR tube was added norbornene (0.006 g, 0.063 mmol), and the reaction mixture was left at room temperature overnight to obtain (^{Ad}PCP)Ir(norbornene). The solvent and excess norbornene were removed under vacuum, and fresh solvent and 1,3-cyclooctadiene (0.028 mL, 0.22 mmol) were added in an argon-atmosphere glovebox. After allowing the solution to remain at room temperature for 3 h, the solvent and excess 1,3-cyclooctadiene were removed. The compound was then dissolved in fresh *p*-xylene-*d*₁₀, and NMR spectra were recorded. ¹H NMR (500 MHz, *p*-xylene-*d*₁₀): δ 7.26 (d, ³J_{HH} = 7.4 Hz, 2H, Ar-*H*), 7.07 (t, ³J_{HH} = 7.5 Hz, 1H, Ar-*H*), 5.81 (d, ²J_{HH} = 10.3 Hz, 1 H, vinyl-*H*), 5.53–5.58 (m, 2 H, vinyl-*H*), 3.27 (dvt, ²J_{HH} = 17.1 Hz, ²J_{PH} = 3.4 Hz, 2H, CH₂), 3.12 (dvt, ²J_{HH} = 16.9 Hz, ²J_{PH} = 3.3 Hz, 2H, CH₂), 2.16–2.95 (m, 8 H, cyclooctadienyl), 1.58–1.95 (m, 60H, Ad-CH), −43.98 (t, ²J_{PH} = 11.2 Hz, 1H, Ir-*H*), −43.19 (t, ²J_{PH} = 11.7 Hz, 1H, Ir-*H*, minor isomer). ³¹P{¹H} NMR (202.3 MHz, *p*-xylene-*d*₁₀): δ 56.6 (d, ²J_{PH} = 10.6 Hz), 55.9 (d, ²J_{PH} = 11.7 Hz, minor). ¹³C{¹H} NMR (125.7 MHz, *p*-xylene-*d*₁₀): δ 156.6 (br s), 155.1 (br s), 153.6 (s), 152.2 (s), 148.9 (s), 142.3 (s), 140.9 (s), 138.1 (s), 134.8 (s),

133.8 (s), 47.1 (s), 45.1 (s), 44.6 (s), 44.4 (s), 41.2 (m, 12C, Ad-CH₂), 40.7 (s, 12C, Ad-CH₂), 32.7 (s, 12C, Ad-CH), 30.6 (s, 4C, Ad-C-P), 30.1 (s, CH₂-P).

Synthesis of (^{Ad}PCP)Ir(H)(hexenyl). These experiments were conducted to help characterize the products obtained from the thermolysis reactions with octenes and octane. To reduce complexity due to possible olefin isomerization, hexenes were used instead of octenes. To a solution of (^{Ad}PCP)IrH₂ (0.01 g, 0.011 mmol) in *p*-xylene-*d*₁₀ (0.5 mL) in a J-Young NMR tube was added norbornene (0.0042 g, 0.044 mmol), and the reaction mixture was left at room temperature overnight to obtain (^{Ad}PCP)Ir(norbornene). The solvent and excess norbornene were removed under vacuum, and fresh solvent and *trans*-2-hexene (0.0042 mL, 0.033 mmol) were added in an argon-atmosphere glovebox. After 10 min at room temperature the NMR spectra were recorded. ¹H NMR (400 MHz, *p*-xylene-*d*₁₀): δ 7.21–7.65 (m, 9H, Ar-*H*, 3 isomers), 5.31 (br s, 1H, hexenyl-*H*), 5.22 (br s, 1H, hexenyl-*H*), 4.85 (br s, 1H, hexenyl-*H*), 3.08–3.72 (m, 12H, CH₂, 3 isomers), 0.92–2.51 (m, 30H, hexenyl-*H*,

180H, Ad-CH, 3 isomers), –42.25 (br s, 1H, Ir-*H*), –43.64 (br s, 1H, Ir-*H*), –43.89 (t, ²*J*_{PH} = 11.6 Hz, 1H, Ir-*H*). ³¹P{¹H} NMR (162.4 MHz, *p*-xylene-*d*₁₀): δ 56.8 (d, ²*J*_{PH} = 9.9 Hz), 56.4 (d, ²*J*_{PH} = 9.4 Hz), 56.1 (d, ²*J*_{PH} = 11.4 Hz). The same species were obtained from the reaction with *cis*-2-hexene, indicating that *cis*–*trans* isomerization is facile under these conditions. Reaction with *trans*-3-hexene, however, gave mostly (^{Ad}PCP)IrH₂.

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Supporting Information Available: Crystal structure data and cif files for (^{Ad}PCP)IrHX (X = Cl, Br) (**4**) and (^{tBu}PCP)IrHCl (**5**). This material is available free of charge via the Internet at <http://pubs.acs.org>.