

Highly Effective Pincer-Ligated Iridium Catalysts for Alkane Dehydrogenation. DFT Calculations of Relevant Thermodynamic, Kinetic, and Spectroscopic Properties

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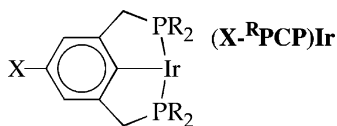
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Abstract: The *p*-methoxy-substituted pincer-ligated iridium complexes, (MeO-^tBuPCP)IrH₄ (^RPCP = κ^3 -C₆H₃-2,6-(CH₂PR₂)₂) and (MeO-ⁱPrPCP)IrH₄, are found to be highly effective catalysts for the dehydrogenation of alkanes (both with and without the use of sacrificial hydrogen acceptors). These complexes offer an interesting comparison with the recently reported bis-phosphinite "POCOP" (^RPOCOP = κ^3 -C₆H₃-2,6-(OPR₂)₂) pincer-ligated catalysts, which also show catalytic activity higher than unsubstituted PCP analogues (Göttker-Schnetmann, I.; White, P.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 1804). On the basis of ν_{CO} values of the respective CO adducts, the MeO-PCP complexes appear to be more electron-rich than the parent PCP complexes, whereas the POCOP complexes appear to be more electron-poor. However, the MeO-PCP and POCOP ligands are calculated (DFT) to show effects in the same directions, relative to the parent PCP ligand, for the kinetics and thermodynamics of a broad range of reactions including the addition of C-H and H-H bonds and CO. In general, both ligands favor (relative to unsubstituted PCP) addition to the 14e (pincer)Ir fragments but *disfavor* addition to the 16e complexes (pincer)IrH₂ or (pincer)Ir(CO). These kinetic and thermodynamic effects are all largely attributable to the same electronic feature: O → C(aryl) π -donation, from the methoxy or phosphinito groups of the respective ligands. DFT calculations also indicate that the kinetics (but not the thermodynamics) of C-H addition to (pincer)Ir are favored by σ -withdrawal from the phosphorus atoms. The high ν_{CO} value of (POCOP)Ir(CO) is attributable to electrostatic effects, rather than decreased Ir-CO π -donation or increased OC-Ir σ -donation.

Introduction

The development of systems for the selective catalytic functionalization of alkanes, and "unactivated" C-H bonds more generally, is one of the most significant challenges in modern catalysis. Organometallic systems have demonstrated great promise in this context. Particular progress has been made over the past two decades in the development of catalysts for the dehydrogenation of alkanes, either with or without the use of sacrificial olefins as hydrogen acceptors.^{1,2} Presently, the most promising systems seem to be (κ^3 -P,C,P-pincer)-ligated iridium catalysts (e.g., complexes of the form (X-^RPCP)Ir (^RPCP = κ^3 -C₆H₃-2,6-(CH₂PR₂)₂), first introduced as catalysts for transfer dehydrogenation³ and later found to be highly effective for acceptorless dehydrogenation as well.⁴



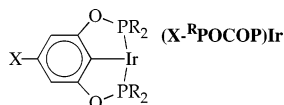
We recently reported the synthesis of iridium complexes bearing a *p*-methoxy-substituted PCP ligand (MeO-^tBuPCP) and

experimental and computational studies of the effect of *p*-methoxy and other *p*-substituents on the thermodynamics of addition reactions.⁵⁻⁷ DFT calculations predicted that additions of C-H bonds and H₂ to the 14-electron fragments (X-PCP)-Ir are favored by π -donating X groups such as methoxy. The mechanism of dehydrogenation by "(^tBuPCP)Ir" precursors⁸ has been shown to operate via C-H addition to this 14e fragment (which is rate-determining under certain conditions) and to proceed via formation of (^tBuPCP)IrH₂.⁹ Thus, factors that favor addition of either C-H bonds or H₂ are of obvious relevance in this context. Herein we report that *p*-methoxy-PCP derivatives, in particular the previously unreported complex (MeO-ⁱPrPCP)Ir,¹⁰ afford unprecedented levels of catalytic dehydrogenation activity under suitable conditions.

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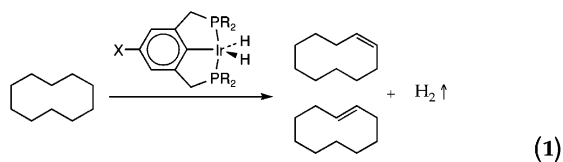
Very recently, Brookhart and co-workers reported that the bis-phosphinite catalysts ($X-tBuPOCOP$)IrH₂ ($RPOCOP = \kappa^3-C_6H_3-2,6-(OPR_2)_2$) are more effective than ($tBuPCP$)IrH₂ for cyclooctane/*tert*-butylethylene (COA/TBE) transfer dehydrogenation.¹¹ The metal centers of the POCOP complexes might



be expected to be less electron-rich than their PCP analogues. This expectation was supported by measurement of the C–O stretching frequencies of the respective CO adducts,¹² the standard indicator for electron richness of metal centers. These observations seemed at odds with the greater catalytic effectiveness of the *p*-methoxy-PCP derivatives (as described below), since the latter complexes are *more* electron-rich than the parent catalysts. Computational results, however, resolve this apparent contradiction. We demonstrate in this work that key thermodynamic and kinetic properties are affected similarly by the presence of *p*-methoxy substituents or by the substitution of the phosphorus-linked methylenes of PCP by oxygen atoms (to give POCOP), even though these substitutions affect ν_{CO} values in opposite directions. We believe these kinetic and thermodynamic similarities are closely linked to the greater catalytic activity of both POCOP and MeO–PCP catalysts.

Results and Discussion

1. Experiments with ($X-tBuPCP$)Ir Catalysts. 1.1. Acceptorless Dehydrogenation of Cyclodecane. Acceptorless dehydrogenation is a reaction that is potentially even more valuable than transfer dehydrogenation.^{4,13,14} Cyclodecane (CDA) is a convenient substrate for screening this reaction owing to the equivalence of all HCCH units and its high boiling point (201 °C).^{4,14} CDA solutions of ($tBuPCP$)IrH₂ and ($MeO-tBuPCP$)IrH₂ (1.0 mM) were prepared and subjected to vigorous reflux with argon flowing above the condenser to permit loss of H₂, as described previously.^{4,14}



As seen in Table 1, the initial rate of dehydrogenation was greater with the MeO– $tBuPCP$ complex than with the parent

Table 1. Acceptorless Dehydrogenation of CDA (bp 201 °C)^a Catalyzed by ($X-tBuPCP$)IrH₂^a

time/h	catalyst; total turnovers (= mM)		
	X = H; R = <i>t</i> -Bu	X = MeO; R = <i>t</i> -Bu	X = MeO; R = <i>i</i> -Pr
1	60	158	357
2	110	275	450
4	170	430	714
6	220	575	868
24	360	820	2120
48	360	820	2970
78	–	–	3050

^a Conditions: catalyst, 1.0 mM; 1.5 mL of CDA; 250 °C oil bath; concentrations determined by GC.

$tBuPCP$ complex (158 turnovers (TO) vs 60 TO after 1 h¹⁵). After 24 h, the *p*-methoxy-substituted catalyst afforded 820 TO as compared with 360 TO from the parent catalyst. These values obtained using the MeO– $tBuPCP$ catalyst are essentially equal (within 20%) to those previously reported using the bis(di-isopropylphosphino) catalyst (with no methoxy substituent), ($iPrPCP$)IrH₄. The latter complex was reported to give turnover numbers (TONs) higher than any previously reported alkane dehydrogenation catalyst.¹⁴

Since the *p*-methoxy substitution of the aryl ring and the presence of *i*-Pr groups on phosphorus (in lieu of *t*-Bu) each lead to significant improvements in rate and TONs, we naturally wished to explore the effect of both these substitutions on the same complex. ($MeO-iPrPCP$)IrH₄ was synthesized (see Experimental Section) and indeed found to be extremely effective for CDA dehydrogenation. Under conditions identical to those described above, 360 TO are obtained with ($MeO-iPrPCP$)IrH₄ after 1 h of reflux. After 24 h, 2100 TO are obtained, and after 72 h a total of 3050 TO is observed (see Table 1). These are the highest turnover numbers, by a factor of ca. 3, reported to date for homogeneous acceptorless alkane dehydrogenation.

1.2. Acceptorless Dehydrogenation of an *n*-Alkane. The superiority of ($MeO-tBuPCP$)IrH₂ over ($tBuPCP$)IrH₂ was not reproduced with the acceptorless dehydrogenation of *n*-undecane (bp 196 °C). There was little difference in rates at early reaction times (18 vs 23 TO, respectively, after 0.5 h) and only a slight advantage at longer times (108 vs 83 turnovers after 24 h). Even more disappointing, ($MeO-iPrPCP$)IrH₂ gave significantly poorer results for acceptorless *n*-undecane dehydrogenation than did either of the $tBuPCP$ -based catalysts (see Table 2).

1.3. Transfer Dehydrogenation of *n*-Alkanes. Despite the poor results obtained for acceptorless dehydrogenation of *n*-alkane, ($MeO-iPrPCP$)IrH₂ has proven to be a highly effective catalyst for *transfer* dehydrogenation of *n*-alkanes (and also for other *n*-alkyl group containing species¹⁶). For example, in runs with 0.79 M norbornene (NBE) added to *n*-octane catalyst

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- (8) Both ($X-tBuPCP$)IrH₄ and ($X-tBuPCP$)IrH₂ are suitable precursors of “($X-tBuPCP$)Ir”. The tetrahydrides lose H₂ reversibly and rapidly under even ambient conditions. We have never observed any difference in catalytic activity with the two precursors (although presumably an additional mole of sacrificial acceptor is consumed with the tetrahydrides). The tetrahydrides are more stable and are stored more conveniently. The difference in ease of isolation is more pronounced for the $X-iPrPCP$ complexes; preliminary attempts to isolate the ($MeO-iPrPCP$)IrH₂ were unsuccessful. Thus, all reactions of “($MeO-iPrPCP$)Ir” reported in this work use the tetrahydride precursor.
- (9) Renkema, K. B.; Kissin, Y. V.; Goldman, A. S. *J. Am. Chem. Soc.* **2003**, *125*, 7770–7771.
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- (13) (a) Fujii, T.; Saito, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 757–758. (b) Fujii, T.; Higashino, Y.; Saito, Y. *J. Chem. Soc., Dalton. Trans.* **1993**, 517–520. (c) Aoki, T.; Crabtree, R. H. *Organometallics* **1993**, *12*, 294–298.
- (14) Liu, F.; Goldman, A. S. *Chem. Commun.* **1999**, 655–656.
- (15) One TO = 1 mol product/mol iridium; products are *cis*- and *trans*-cyclodecene and 1,2-diethylcyclohexane, which is formed via dehydrogenation/Cope rearrangement/hydrogenation, as reported previously (ref 14).

Table 2. Acceptorless Dehydrogenation of *n*-Undecane (bp 196 °C)^a Catalyzed by (X-^RPCP)IrH₂^a

time/h	catalyst; total turnovers (= mM)		
	X = H; R = <i>t</i> -Bu	X = MeO; R = <i>t</i> -Bu	X = MeO; R = <i>i</i> -Pr
0.5	23	18	21
1	44	42	31
2	66	66	—
4	76	91	30
17	83	108	—

^a Conditions: catalyst, 1.0 mM; 1.5 mL of *n*-undecane; 250 °C oil bath; concentrations determined by GC.

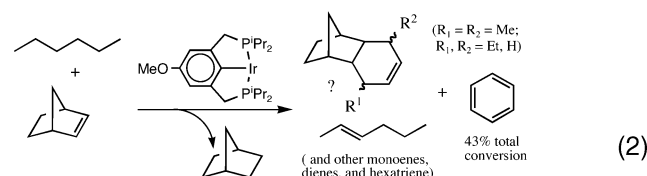
Table 3. *n*-Octane Transfer Dehydrogenation Catalyzed by (X-^RPCP)IrH₂ (150 °C)^a

time/min	(^t BuPCP)Ir		(MeO- ^t BuPCP)Ir		(MeO- ⁱ PrPCP)Ir	
	octenes	NBE	octenes	NBE	octenes	NBE
0	0	790	0	790	0	790
10	163	615	113	638	234	560
20	234	550	167	580	435	350
30	277	503	211	540	612	181
60	393	378	352	390	787	0
120	502	272	511	247	—	—
180	536	215	—	—	—	—

^a Conditions: catalyst, 15.0 mM; initial [NBE], 0.79 M; 0.5 mL of *n*-octane; concentrations determined by GC.

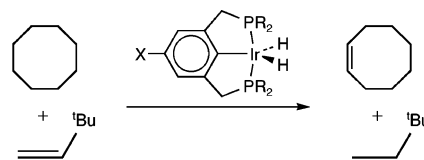
solutions (15 mM), (MeO-ⁱPrPCP)IrH₂ afforded 100% hydrogenation of NBE within 60 min (150 °C) as compared with 65% NBE conversion after 120 min with (^tBuPCP)IrH₂ (or 68% after 120 min with (MeO-^tBuPCP)IrH₂) (Table 3).

The new catalyst (MeO-ⁱPrPCP)IrH₄ has proven to be particularly effective in yielding high (and unprecedented) conversions of *n*-alkanes. For example, in a run with 0.37 g of NBE (3.9 mmol) added to a solution of 4.2 mg of (MeO-ⁱPrPCP)IrH₄ (0.0075 mmol) in 0.5 mL of *n*-octane (3.6 mmol), essentially all (>99%) NBE and 40% of the *n*-octane was consumed after 12 h at 150 °C. The mixture of products was complex, including products suspected to result from dehydrocyclization. Accordingly, the product distribution was simpler when *n*-hexane was the substrate. In a run with 0.5 mL of *n*-hexane (3.9 mmol), 4.5 mg of (MeO-ⁱPrPCP)IrH₄, and 0.48 g of NBE (5.1 mmol), the conversion of *n*-hexane was 43% after 30 h at 150 °C. Of the various products, 78.5% was linear hexenes (including dienes and triene) and 5.4% was benzene-derived from cycloaromatization (confirmed by comparison with authentic benzene by GC, GC-MS, and NMR). The remaining 16% was high boiling point compounds, predominantly with MW 176; these were presumed to be NBE/hexadiene adducts.



1.4. Transfer Dehydrogenation of Cyclooctane. The prototypical substrate-acceptor couple for organometallic-catalyzed transfer dehydrogenation is COA/TBE, first introduced by Crabtree for the purpose of screening and developing such catalysts. The COA/TBE couple is of particular interest in the context of the following section of this article, since, as noted

above, Brookhart et al. have used it for screening (POCOP)Ir catalysts.



When 1:1 (mol:mol) COA/TBE solutions of catalyst (1.2 mM) were simultaneously heated for 8 min in a 200 °C oil bath, the respective TONs were as follows: (^tBuPCP)IrH₂, 47; (MeO-^tBuPCP)IrH₂, 79; (MeO-ⁱPrPCP)IrH₂, 542. Thus, the *p*-methoxy group enhances the reaction rate slightly while the substitution of the *t*-butyl groups by *i*-propyl groups has a more significant favorable effect. On the basis of the relative TONs vs (^tBuPCP)IrH₂ (1.0:1.7:11.5), for this particular substrate couple under this particular set of conditions, (MeO-^tBuPCP)IrH₂ appears somewhat less effective than (^tBuPOCOP)IrH₂, while (MeO-ⁱPrPCP)IrH₂ appears comparable to the ^tBuPOCOP complex.¹⁷ Using NBE as acceptor gave somewhat greater TONs than TBE in the same time interval with use of the bis(*t*-butyl)phosphino catalysts: (^tBuPCP)IrH₂, 180; (MeO-^tBuPCP)IrH₂, 211. (It was not possible to use NBE for transfer dehydrogenation catalyzed by (MeO-ⁱPrPCP)IrH₂ under these conditions.¹⁸)

1.5. Comparisons between the Various Catalysts. There appears to be no simple unifying explanation for all of the above results. Consider, for example, that (MeO-ⁱPrPCP)IrH₂ is highly effective for transfer dehydrogenation of *n*-alkane and acceptorless dehydrogenation of cyclodecane, but not for the acceptorless dehydrogenation of *n*-alkane. It is not surprising that these derivatizations of the catalyst do not yield a single, simple outcome. Even in work with a single catalyst, “(^tBuPCP)Ir”, and a single donor/acceptor pair (COA/TBE), we find that the catalyst resting state is dependent upon TBE concentration and temperature.⁹ At high [TBE] the major resting state is (^tBuPCP)Ir(CH=CH^tBu)(H), while at low [TBE] it is (^tBuPCP)IrH₂ (high temperature favors the dihydride).¹⁹ Obviously, the identity of the resting state will be dependent on the nature of the acceptor as well as the dehydrogenated products present in the mixture. Likewise, the nature of the transition state will be variable. In the (^tBuPCP)IrH₂/COA/TBE system, we found that the transition states for C–H elimination (of TBA) and C–H addition (of COA) were rate-determining at low and high TBE concentrations, respectively. Furthermore, the transition state (TS) for

- (16) Using (MeO-ⁱPrPCP)IrH₄, much higher yields have been obtained for the dehydrogenation of tertiary amines to give enamines (Zhang, X.; Goldman, A. S. Unpublished results) and the partial dehydrogenation of saturated polyolefins (Ray, A.; Goldman, A. S. Unpublished results, 2003).
- (17) Brookhart has found (ref 11) that (^tBuPCP)IrH₂ gives TONs 5.9 times greater than “(^tBuPCP)Ir” generated in situ from dehydrohalogenation of the hydrido chloride. Presumably this value would be no greater (and possibly less) by comparison with the (^tBuPCP)IrH₂; this compares with the factor of 11.5 obtained for (MeO-ⁱPrPCP)IrH₂. However, the absolute TONs obtained by Brookhart et al. are roughly double those reported herein for (MeO-ⁱPrPCP)IrH₂. Given the lack of reliability in comparing runs conducted using different sets of apparatus (aluminum block vs oil bath) in different labs, it seems reasonable to simply consider these catalysts as being “comparably” effective.
- (18) Attempts to obtain comparable values for (MeO-ⁱPrPCP)IrH₂-catalyzed COA/NBE dehydrogenation were stymied by polymerization of NBE by the iridium catalyst. This surprising reactivity is currently under further investigation. Zhang, X.; Goldman, A. S. Unpublished observation, 2003.
- (19) The temperature dependence of the resting state in (^tBuPCP)Ir-catalyzed COA/TBE transfer dehydrogenation can be understood by considering that the formation of (^tBuPCP)Ir(CH=CH^tBu)(H) and TBA, from (^tBuPCP)Ir and 2 mol TBE is a reaction in which 3 mol reagent gives 2 mol product.

Table 4. Calculated and Experimental C–O Stretching Frequencies (ν_{CO} , cm^{-1}) and Ir–CO Bond Dissociation Energies (BDE, kcal/mol) for Pincer Complexes

	ν_{CO} (cm^{-1})		$\Delta\nu$		BDE	ΔBDE
	expt (R = <i>t</i> -Bu)	calcd (R = Me)	$\Delta\nu_{\text{expt}}$	$\Delta\nu_{\text{calcd}}$		
(H– ^R PCP)Ir(CO)	1927.7 ^a	2015.4	0.0	0.0	62.2	0.0
(H– ^R POCOP)Ir(CO)	1949 ^b	2030.1	21.3	14.6	63.1	0.9
(MeO– ^R PCP)Ir(CO)	1925.5 ^a	2012.7	–2.2	–2.7	63.3	1.1
(MeO– ^R POCOP)Ir(CO)	1947 ^b	2026.5	19.3	11.1	64.1	1.9
1a-CO		2029.1		13.6	60.7	–1.5
1b-CO		2024.4		9.0	60.9	–1.3

^a Cyclooctane solution, ref 5. ^b Pentane solution, ref 12.

TBE insertion into an Ir–H bond was fairly close in energy.⁹ The same derivatizations that might favor one particular TS or resting state, operative under a particular set of conditions, could very easily *disfavor* a different rate-determining TS or a different resting state that may be operative under a different set of conditions.

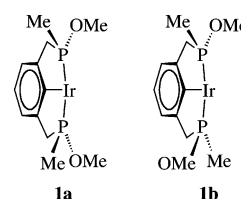
Consequently, the effect of catalyst derivatizations on catalytic activity is not easily rationalized. Nevertheless, the increased electron richness of the *p*-methoxy complexes appeared to be a factor generally favorable to catalytic activity. We were therefore intrigued by the recent discovery, by Brookhart et al., that the POCOP complexes were more catalytically active than their PCP analogues despite being apparently less electron-rich.¹¹ We have therefore undertaken a comparative study of these two catalyst classes using computational (DFT) methods. As elaborated below, we find that the catalytically relevant kinetics and thermodynamics of the (MeO–PCP)Ir and (POCOP)Ir fragments (as compared with unsubstituted (PCP)Ir) bear very strong similarities.

2. Computational Studies of (PCP)Ir and (POCOP)Ir Complexes. DFT calculations were conducted on all pincer complexes in both PCP and POCOP ligand classes with methyl groups on phosphorus in place of the *t*-butyl (or *i*-propyl) groups in the experimentally studied catalysts. Although such truncations of alkyl groups can dramatically affect absolute energies, largely because of steric factors, they do allow us to elucidate substituent electronic effects with high accuracy.⁵

2.1. C–O Stretching Frequencies and Ir–CO Bond Dissociation Energies. The experimentally observed greater C–O stretching frequency of the POCOP carbonyl complexes vis-à-vis the PCP analogues is reproduced by the calculations (Table 4), though the computed shift ($\sim 13 \text{ cm}^{-1}$) is not quite as large as the measured shifts ($\sim 20 \text{ cm}^{-1}$). The calculations reproduce the slightly lowered C–O stretching frequency of (MeO–PCP)Ir(CO) relative to that of (PCP)Ir(CO) extremely well (computed $\Delta\nu_{\text{CO}} = -2.7 \text{ cm}^{-1}$; measured $\Delta\nu_{\text{CO}} = -2.2 \text{ cm}^{-1}$). Thus, the calculations appear to successfully capture the major effects responsible for the shifted ν_{CO} values. In the case of POCOP, this is presumed to be the greater positive charge on the iridium center engendered by the greater electron-withdrawing ability of oxygen relative to methylene. However, we should also consider the possibility that the oxygen atoms would *donate* electron density to the pincer aryl ring and, through that, further on to Ir; this is the factor presumably responsible for the low-energy shift in ν_{CO} in the case of (*p*-MeO–PCP)Ir(CO). In an effort to assess the relative contributions of these two effects in the POCOP complexes, we ran calculations on several complexes that contained phosphinite

groups (as in POCOP) but in which phosphorus remains bound to the aryl through a methylene unit (as in PCP).

There are two possible stereoisomeric fragments of the composition $\{2,6\text{-C}_6\text{H}_3[\text{CH}_2\text{PMe}(\text{OMe})_2]\text{Ir}$: **1a** and **1b**; **1a** possesses a meso-type structure of near C_3 symmetry, whereas **1b** attains rigorous C_2 symmetry.



We did not expect to find any major differences in the electronic properties of the two stereoisomers; but independent calculations of the properties for both species provided a self-consistency check and some indication of the level of “random error” in the calculations.

The C–O stretching frequencies of the CO adducts of **1a** and **1b** (**1a-CO** and **1b-CO**) were calculated to be close to each other (2029.1 and 2024.4 cm^{-1} , respectively; Table 4) and close to that of (^{Me}POCOP)Ir(CO) (2030.1 cm^{-1}). These values are all higher than that calculated for (^{Me}PCP)Ir(CO), 2015.4 cm^{-1} , in accord with the experimental ^tBuPCP and ^tBuPOCOP¹² values. In contrast, the presence of a *p*-methoxy substituent on the aryl ring of PCP (or added to POCOP) leads to a slightly lowered ν_{CO} value (2026.5 and 2012.7 cm^{-1} , respectively),¹² attributable to O \rightarrow aryl π -donation. Thus, the greater ν_{CO} value of (POCOP)Ir(CO) appears to reflect effects exerted largely through the phosphorus atoms rather than through the aryl ring. However, these results certainly do not rule out O \rightarrow aryl π -donation in (POCOP)Ir; although this would contribute to a lowering of ν_{CO} , the effect might easily be offset by other factors.

Support for the importance of O \rightarrow aryl donation in (POCOP)Ir is obtained from calculations on the thermodynamics of Ir–CO bond formation (Table 4). The relative values of the Ir–CO bond dissociation energies (BDEs) show no correlation with the ν_{CO} values. For example, whereas the POCOP iridium carbonyl shows a higher ν_{CO} value than (^{Me}PCP)Ir(CO) and the *p*-methoxy-substituted PCP complex shows a slightly lower ν_{CO} , both the POCOP and MeO–PCP complexes show similarly high Ir–CO BDEs, which are, respectively, 0.9 and 1.1 kcal/mol greater than that of (^{Me}PCP)Ir. In contrast, the Ir–CO BDEs of **1a-CO** and **1b-CO** are weaker (by ~ 1.4 kcal/mol) than that of the parent complex, even though their ν_{CO} values are similar to that of (^{Me}POCOP)Ir(CO). Thus, O-substitution on phosphorus (as seen with **1a** and **1b**) raises ν_{CO} and lowers the Ir–CO BDE.

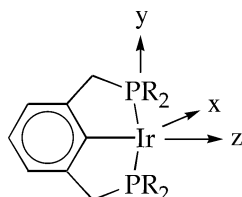


Figure 1. Labeling of axes for (pincer)Ir complexes.

The effects of O-substitution at the aryl para position of (pincer)Ir are opposite; however, the magnitude of the BDE effect is greater (per substituent), while the effect on ν_{CO} is much less. Assuming that ortho and para aryl effects are similar, the properties of the POCOP carbonyl are consistent with the combination of aryl and phosphorus substituent effects that would be expected on the basis of the above observations: a significantly raised ν_{CO} value and a higher Ir–CO BDE.²⁰

2.2. Thermodynamics of C–H and H–H Addition (Ir(I) → Ir(III)). We have previously demonstrated that aryl → Ir π -donation into the *d* orbitals of the *xz* plane (i.e., the plane orthogonal to and bisecting the approximately collinear P–Ir–P linkage; see Figure 1) strongly influences the thermodynamics of C–H and H–H addition to either (PCP)Ir or (PCP)IrH₂.⁵

This follows seminal work by Eisenstein and co-workers, who demonstrated the critical role of π -bonding from the X ligand in 5-coordinate *d*⁶ complexes of the form L₂IrXRH (R = H or hydrocarbyl). We found the thermodynamic effects from σ -donation along the *z*-axis plane to be significantly less pronounced.^{5,21,22} The effect of π -donation into the *x,y* or *y,z* planes, or σ -donation along the *y*-axis, has not previously been investigated systematically, although replacing PH₃ ligands with PMe₃ was calculated to favor addition of C–H or H₂ to Ir(PR₃)₂-Cl.²²

We have calculated the reaction and activation energies for addition of CH₃–H and *n*-C₃H₇–H to several fragments, including (MePCP)Ir, (MeO–MePCP)Ir, (MePOCOP)Ir, (MeO–MePOCOP)Ir, **1a**, and **1b**. As noted above, the calculated ν_{CO} values of the CO adducts of the complexes with P-bound O atoms (POCOP and **1**) are nearly equal to each other and significantly higher than those of the phosphino complexes, in accord with the experimental ν_{CO} values of (t^{Bu}POCOP)Ir(CO) and (t^{Bu}PCP)Ir(CO). By contrast, the *p*-methoxy-substituted PCP and POCOP carbonyls (experimental and computational) have ν_{CO} values lower than the parent complexes. We find, however, that the energetics of C–H and H–H addition conform to a pattern completely different from that displayed by the ν_{CO} values.

Looking first at the thermodynamics of C–H addition, the results in Table 5 show that the effect of the O-for-CH₂ substitution to give (MePOCOP)Ir (using (MePCP)Ir as the reference point) favors Me–H and Pr–H addition by $\Delta\Delta E = -3.0$ and -3.5 kcal/mol, respectively. This product stabilization

(20) In fact, if we rather crudely assume additivity and equal para and ortho effects, we could expect the Ir–CO bond (MePOCOP)Ir(CO) to be about 0.7 kcal/mol stronger than that of (MePCP)Ir(CO) (-1.5 kcal/mol (O on P, meso) + 2×1.1 kcal/mol (O on aryl)); the computed value is 0.9 kcal/mol (Table 2). Similarly, the expected ν_{CO} shift in (MePOCOP)Ir(CO) would be about 8 cm⁻¹ (13.6 cm⁻¹ (O on P, meso) + $2 \times (-2.7$ cm⁻¹) (O on aryl)), and the computed $\Delta\nu_{\text{CO}}$ is 14.6 cm⁻¹ (Table 4).

(21) Krogh-Jespersen, K.; Goldman, A. S. In *Transition State Modeling for Catalysis*; Truhlar, D. G., Morokuma, K., Eds.; ACS Symposium Series 721; American Chemical Society: Washington, DC, 1999; pp 151–162.

(22) Rosini, G. P.; Liu, F.; Krogh-Jespersen, K.; Goldman, A. S.; Li, C.; Nolan, S. P. *J. Am. Chem. Soc.* **1998**, *120*, 9256–9266.

Table 5. Reaction and Activation Energies (kcal/mol) for Addition of Methane and Propane to Pincer Complexes

pincer complex (M)	M + CH ₄ → M(CH ₃)(H)				M + C ₃ H ₈ → M(C ₃ H ₇)(H)			
	TS		product		TS		product	
	ΔE^\ddagger	$\Delta\Delta E^\ddagger$	ΔE	$\Delta\Delta E$	ΔE^\ddagger	$\Delta\Delta E^\ddagger$	ΔE	$\Delta\Delta E$
(MePCP)Ir	4.0	0.0	-1.6	0.0	6.5	0.0	-1.3	0.0
(MePOCOP)Ir	1.2	-2.8	-4.6	-3.0	3.7	-2.8	-4.8	-3.5
(MeO–MePCP)Ir	3.1	-0.9	-2.9	-1.3	5.7	-0.8	-2.7	-1.4
(MeO–MePOCOP)Ir	0.4	-3.6	-6.2	-4.6	2.8	-3.7	-6.2	-4.9
1a	4.5	0.5	-0.4	1.2	6.7	0.2	0.6	1.9
1b	3.6	-0.4	0.3	1.9	5.7	-0.8	0.8	2.1

Table 6. Reaction Energies (kcal/mol) for Addition of H₂ and Benzene to Pincer complexes

pincer complex (M)	M + H ₂ → M(H) ₂		M + PhH → M(Ph)(H)	
	ΔE	$\Delta\Delta E$	ΔE	$\Delta\Delta E$
(MePCP)Ir	-28.8	0.0	-11.6	0.0
(MePOCOP)Ir	-31.7	-2.9	-13.3	-1.7
(MeO–MePCP)Ir	-30.5	-1.7	-12.7	-1.1
(MeO–MePOCOP)Ir	-33.7	-4.9	-14.9	-3.3
1a	-27.8	1.0	-8.5	3.1
1b	-27.9	0.9	-9.0	2.6

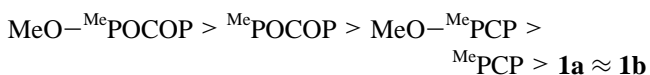
by the POCOP ligand is in the same direction but considerably larger than the effect of the *p*-methoxy substituent calculated for (MeO–MePCP)Ir ($\Delta\Delta E = -1.3$ and -1.4 kcal/mol). Thus, the same computational model that correctly produces a higher ν_{CO} value for (MePOCOP)Ir(CO) and a lower ν_{CO} value for (MeO–MePCP)Ir yields thermodynamics of C–H addition that are more favorable for both complexes than for the parent complex.

The calculated effects of a *p*-methoxy substituent on PCP and POCOP ligands are the same: reduced ν_{CO} values and thermodynamically more favorable additions of Me–H and Pr–H. It bears note in this context that Brookhart and co-workers have found that elimination of benzene from (MeO–t^{Bu}POCOP)Ir(Ph)(H) is slower than elimination from (t^{Bu}POCOP)Ir(Ph)(H).¹²

In contrast to the thermodynamically favorable effect on C–H addition engendered by the POCOP bis(phosphinite) ligand, the bis(phosphinite) complexes **1a** and **1b** are calculated to add methane and propane less favorably than the PCP analogues ($\Delta\Delta E \approx +1$ to $+2$ kcal/mol). Thus, the favorable thermodynamics of addition afforded by POCOP can apparently be attributed to effects transmitted through the aryl ring, not through the O–P linkage.

The trend for the thermodynamic effects calculated for Me–H and *n*-Pr–H addition to the pincer fragments is reproduced for addition of H–H and for addition of phenyl-H as well (Table 6).

The computed exoergicities ($-\Delta E$) for all four addition reactions (methane, propane, benzene, dihydrogen) show the following order:



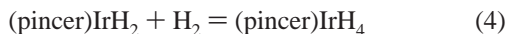
Essentially the same order is found for CO addition as well. As previously demonstrated,⁵ C–H and H–H additions to (PCP)Ir fragments (addition to Ir(I) to afford Ir(III)) are thermodynamically favored by increasing π -donation from the pincer aryl group. The marked difference between the thermodynamic effects of POCOP versus the phosphinite ligands of **1**

Table 7. Reaction Energies (kcal/mol) for Addition of H₂ and CO to (Pincer)IrH₂ Complexes To Afford 18e Complexes

pincer complex (M)	MH ₂ + H ₂ → MH ₄		MH ₂ + CO → MH ₂ (CO)		M(CO) + H ₂ → MH ₂ (CO)	
	ΔE	ΔΔE	ΔE	ΔΔE	ΔE	ΔΔE
(^{Me} PCP)Ir	-19.8	0.0	-46.7	0.0	-13.4	0.0
(^{Me} POCOP)Ir	-16.4	3.4	-43.6	3.1	-12.3	1.1
(MeO- ^{Me} PCP)Ir	-18.4	1.4	-45.4	1.3	-12.6	0.8
(MeO- ^{Me} POCOP)Ir	-14.4	5.4	-41.6	5.1	-11.1	2.3
1a	-19.7	0.1	-45.7	1.0	-12.8	0.6
1b	-20.4	-0.6	-47.4	-0.7	-14.3	-0.9

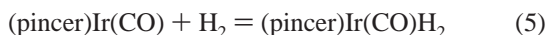
can accordingly be attributed to O → aryl π-donation. The magnitudes of the thermodynamic POCOP/PCP differences are, very roughly, twice the effects of a single *p*-methoxy substituent. The fact that such effects must presumably counteract unfavorable effects transmitted via phosphorus suggests that the total O → aryl π-donation operative in POCOP is at least twice that of the MeO-PCP ligand. This conclusion is further supported by electronic population analyses (see Section 2.5).

2.3. Thermodynamics of H-H Addition to (Pincer)IrH₂ (Ir(III) → Ir(V)). The Formation of (Pincer)IrH₄ and Other 18-Electron Products. (^tBuPCP)IrH₂ readily adds H₂ to give (^tBuPCP)IrH₄, a classical (i.e., Ir(V)) tetrahydride.²³



While we are aware of no isolated (pincer)Ir(V) species other than the tetrahydrides, (pincer)Ir(V) species have been clearly implicated as intermediates, for example, in the H/D exchange reactions of (^tBuPCP)IrH₂ with either hydrocarbon solvent or with the phosphino *tert*-butyl groups.^{5,24}

Although increased π-donation by substituents on the aryl ring favors addition to pincer-ligated iridium(I), we have previously shown, both by experimental and computational means, that this same factor *disfavors* addition to the Ir(III) dihydrides (eq 4).⁵ We have also shown (both experimentally and computationally) that the exothermicity of H₂ addition to (X-^RPCP)Ir(CO) (eq 5) decreases with increasing π-donation from X.⁵ Coordination of CO to the Ir(III) species (X-PCP)-IrH₂ (eq 6) is similarly calculated to be disfavored by π-donation from X.⁵



The favorable thermodynamics of addition to 14e (POCOP)-Ir, as well as the charge distributions discussed in Section 2.5, suggest that the POCOP aryl ring is in fact more π-electron-donating than that of PCP. If so, then (POCOP)IrH₂ should add H₂ and CO *less* favorably than the PCP analogues. This is indeed calculated to be the case (Table 7).

The thermodynamic substituent effects calculated for addition to (pincer)IrH₂ (Table 7) are approximately the opposite of those observed for addition to the 14e Ir(I) fragments (Table 6). Addition to the Ir(III) dihydrides and to the 16e carbonyls is

least favorable for the MeO-PCP and POCOP complexes, while methoxy substituents on phosphorus exert a relatively small effect.

Thus, for all three addition reactions examined (eqs 4–6), formation of the 18-electron species is disfavored by POCOP as well as by the *p*-methoxy derivatization. We propose that this may be very significant in the context of catalysis: increased π-donation to the metal is likely to disfavor (kinetically and/or thermodynamically) the formation of inactive out-of-cycle 18e resting states. At the very least, this result offers additional evidence that (POCOP)Ir bears a closer resemblance to (MeO-PCP)Ir than to the parent (PCP)Ir fragment.

2.4. Kinetics of C-H Addition and Elimination. We have thus far focused on the thermodynamics of C-H addition, although catalysis is intrinsically a kinetic phenomenon. The kinetics of C-H addition, however, only impact catalytic rates if the TS of the rate-determining reaction step is that of C-H addition. At least in the case of (^tBuPCP)Ir-catalyzed transfer dehydrogenation of COA/TBE, this appears to be the case. In the limit of low [TBE] the rate-determining step is C-H elimination, which, of course, proceeds via the same TS as that of addition. In the limit of high [TBE] we infer that C-H addition is rate-determining.^{9,25}

The kinetics of methane and propane C-H bond addition to either (^{Me}POCOP)Ir or (MeO-^{Me}PCP)Ir are calculated to be more favorable than to (^{Me}PCP)Ir (Table 5). This correlates with the thermodynamics and is in accordance with the Hammond Postulate. Consequently, with respect to both thermodynamic and kinetic parameters studied in the course of this work, the POCOP and MeO-PCP ligands show, in *all* cases, the same effects relative to unsubstituted PCP.

Unlike the Hammond behavior calculated for POCOP and MeO-PCP, the kinetics and thermodynamics for C-H addition to complexes **1a** and **1b** correlate poorly. Although the thermodynamics of C-H addition are distinctly disfavored by the phosphinite ligands (Tables 5 and 6), the kinetics of addition are comparable to that of (^{Me}PCP)Ir (Table 5). The values in question are small, but we believe they do reflect a real effect. If we view the TS for C-H addition as possessing some alkane σ-complex character, we would expect that *lowering* the energy of the d_{z²} (σ) acceptor orbital should favor formation of the TS. TS formation should also be favored by *raising* the energy of the d_{yz} orbital by promoting π-donation into the C-H σ* orbital. Thus, the favorable effects of both the π-donating *p*-methoxy group on the aryl ring and the σ-withdrawing methoxy groups on phosphorus are not at all inconsistent.

We have begun to test this hypothesis further using fluoro-substituted phosphines. This will be elaborated upon in a subsequent publication, but preliminary results support the notion of an inverse correlation between kinetic and thermodynamic effects resulting from σ-withdrawing groups on the pincer phosphorus atoms. We calculate that H₃C-H additions to fluorinated derivatives **2a** and **2b** are 0.5 and 1.0 kcal/mol kinetically *more* favorable than H₃C-H addition to ^{Me}PCP (independent of this work, the Brookhart lab has initiated

(23) Evidence for the classical (Ir(V)) nature of (^tBuPCP)IrH₄ has been obtained from T₁(min) measurements (Gupta, M. Ph.D. Thesis, University of Hawaii, 1997) and more recently, crystallographic data (Zhang, X.; Emge, T.; Goldman, A. S. Unpublished results, 2003).

(24) Lee, D. W.; Kaska, W. C.; Jensen, C. M. *Organometallics* **1998**, *17*, 1–3.

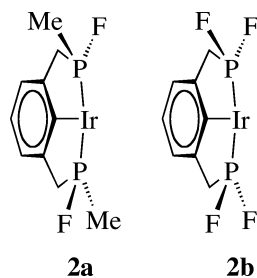
(25) Goldman, A. S.; Renkema, K. B.; Czerw, M.; Krogh-Jespersen, K. Alkane Transfer-Dehydrogenation Catalyzed by a Pincer-Ligated Iridium Complex. In *Activation and Functionalization of C-H Bonds*; Goldberg, K. I., Goldman, A. S., Eds.; ACS Symposium Series 885; American Chemical Society: Washington, DC, 2004; pp 198–215.

Table 8. Atomic Net Charges and Natural Atomic Orbital Populations

	(pincer)Ir				(pincer)Ir(CO)			
	atomic net charges				atomic net charges			
	(PCP)Ir (C _{2v})	(MeO-PCP)Ir (C _s)	(POCOP)Ir (C _{2v})	(MeO-POCOP)Ir (C _s)	(PCP)Ir(CO) (C _{2v})	(MeO-PCP)Ir(CO) (C _s)	(POCOP)Ir(CO) (C _{2v})	(MeO-POCOP)Ir(CO) (C _s)
Ir	-0.344	-0.344	-0.353	-0.355	-0.264	-0.262	-0.299	-0.295
P	0.937	0.937	1.255	1.252	0.988	0.988	1.301	1.298
C ₂	-0.086	-0.116	-0.234	-0.264	-0.364	-0.394	-0.475	-0.504
CH ₂ or O	-0.220	-0.219	-0.808	-0.804	-0.215	-0.214	-0.809	-0.804
C ₇	-0.070	-0.048	0.316	0.336	-0.034	-0.013	0.349	0.367
C ₈	-0.219	-0.290	-0.283	-0.353	-0.229	-0.300	-0.290	-0.360
C ₉	-0.225	0.350	-0.207	0.364	-0.202	0.369	-0.187	0.382
O(Me)		-0.577		-0.573		-0.574		-0.568
C(Me)		-0.229		-0.230		-0.230		-0.232
C					0.487	0.483	0.482	0.477
O					-0.539	-0.542	-0.523	-0.527
CO total					-0.052	-0.059	-0.041	-0.050

	natural atomic orbital populations							
	(PCP)Ir (C _{2v})	(MeO-PCP)Ir (C _s)	(POCOP)Ir (C _{2v})	(MeO-POCOP)Ir (C _s)	(PCP)Ir-CO (C _{2v})	(MeO-PCP)Ir-CO (C _s)	(POCOP)Ir(CO) (C _{2v})	(MeO-POCOP)Ir(CO) (C _s)
	Ir(6s)	0.762	0.761	0.757	0.756	0.657	0.655	0.665
Ir(d _{xy})	1.859	1.856	1.879	1.877	1.903	1.901	1.914	1.913
Ir(d _{yz})	1.885	1.900	1.900	1.913	1.711	1.710	1.728	1.727
Ir(d _{yz})	1.901	1.898	1.862	1.859	1.769	1.769	1.757	1.756
Ir(d _{x²-y²})	1.780	1.778	1.783	1.782	1.801	1.805	1.805	1.805
Ir(d _{z²})	1.176	1.170	1.189	1.185	1.432	1.433	1.438	1.438
P(p _x)	0.768	0.769	0.759	0.760	0.768	0.769	0.759	0.760
O(p _x)			1.867	1.865			1.865	1.864
C ₂ (p _x)	0.958	0.992	1.059	1.095	0.941	0.978	1.051	1.090
C ₇ (p _x)	1.044	1.031	1.019	1.008	1.015	1.003	0.992	0.977
C ₈ (p _x)	1.018	1.073	1.071	1.128	1.020	1.076	1.073	1.130
C ₉ (p _x)	1.036	1.006	1.021	0.994	1.007	0.983	0.995	0.972
O(p _x) _{MeO}		1.861		1.856		1.854		1.848
C(p _x) _{CO}					0.682	0.687	0.678	0.685
C(p _y) _{CO}					0.655	0.654	0.657	0.656
C(p _z) _{CO}					0.876	0.876	0.882	0.882
O(p _x) _{CO}					1.586	1.589	1.578	1.582
O(p _y) _{CO}					1.570	1.569	1.563	1.563
O(p _z) _{CO}					1.652	1.652	1.651	1.651

the synthesis of fluoroaryl derivatives of POCOP²⁶). Additions of the more electron-rich *n*-Pr-H bond to **2a** and **2b** are calculated to be even more kinetically favorable relative to ^{Me}PCP, by 1.4 and 2.8 kcal/mol, respectively. These favorable kinetics are in contrast with the thermodynamics, which, in all cases, are less favorable for the fluoro analogues than for addition to (^{Me}PCP)Ir.



2.5. Natural Atomic Charges and Atomic Orbital Occupations. Atomic net charges and natural atomic orbital populations were calculated for several (^{Me}PCP)Ir and (^{Me}POCOP)Ir complexes as well as for the methoxy derivatives. The effects of the various derivatizations on electronic populations are found to be generally similar for the (pincer)Ir, (pincer)Ir(CO), and (pincer)IrH₂ complexes; results for the former two sets of complexes are shown in Table 8. Overall, the calculations

are fully supportive of the conclusions drawn above strictly on the basis of thermodynamic considerations, namely that π -donation by the aryl-bound oxygen atoms of MeO-^{Me}PCP, ^{Me}POCOP, and MeO-^{Me}POCOP plays a dominant role in the relative thermodynamics and kinetics of the corresponding (pincer)Ir complexes. However, a more detailed analysis reveals additional aspects of interest.

We first consider the *p*-methoxy derivatization. Formally, the methoxy oxygen donates about 0.14e to the aryl π -system, and thus, predictably, the most marked effect of the *p*-methoxy group is an increase in π -density at the relative ortho (C₈, \sim 0.05₅e) and para (C₂, \sim 0.03₅e) positions (see Figure 2). This places an

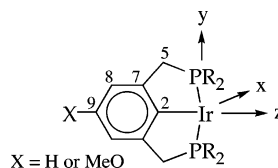


Figure 2. Numbering of carbon atoms for PCP and POCOP complexes (C5 methylene group replaced with O in POCOP complexes), with axis labels shown.

additional total charge of 0.03₀e on C₂ in (MeO-^{Me}PCP)Ir vs (^{Me}PCP)Ir; the increase in electron population on C₂ is similar for the corresponding carbonyl complexes. The electronic structure of the P atoms is essentially unperturbed by the presence of a *p*-methoxy group on the aryl ring. The Ir(d) orbital conjugating with the aryl π -system, Ir(d_{yz}), is calculated to have

(26) Brookhart, M., University of North Carolina, Chapel Hill, NC, 2003, personal communication.

a slightly increased population of 0.01_{5e}, but the overall charge on Ir remains unchanged. The general picture reflects significant MeO → C(aryl) π -donation. Figure 2 shows the numbering of the carbon atoms for PCP and POCOP complexes.

The effects of the oxygen atoms present in POCOP are more complex. Formally, each O in POCOP donates about 0.13e to the aryl π -system, just as the single *p*-methoxy oxygen does. Thus, the conclusion drawn above, based on thermodynamics, that the total O → C(aryl) π -donation is significantly greater in (POCOP)Ir than in (*p*-MeO-PCP)Ir, is readily substantiated. The greatest difference in net charge is found at the aryl C atoms located ortho to Ir (C₇; +0.38_{6e}), a result of C(aryl) → O σ -donation. The increased π -donation from *o*-positions leads to a significant buildup of negative charge, -0.14_{8e}, on C₂ in (^{Me}POCOP)Ir relative to (^{Me}PCP)Ir. The total population of the (^{Me}POCOP)Ir C₂(p_x) orbital is 0.10_{1e} greater than that of (^{Me}PCP)Ir; a difference of only 0.03_{4e} is computed for the analogous C₂(p_x) orbital of (MeO-^{Me}PCP)Ir. Substantial P → O σ -donation leads to a large positive net charge on the P atoms, +0.31_{8e}. Consistent with the opposing effects of increased positive charge on P and increased negative charge on C₂, the overall charge on the iridium center of (POCOP)Ir is nearly the same as that in the (PCP)Ir complexes.

The calculated POCOP atomic charges and orbital occupancies appear consistent with the calculated energetics of the various addition reactions; in particular, the greater π -electron density at the Ir-bound aryl carbon has been demonstrated to lead to more favorable energetics of C-H and H-H addition.⁵

Experimentally and computationally, a significant increase of the CO stretching frequency results in POCOP complexes (relative to analogous PCP complexes). The underlying “mechanism” for this is less obvious than that behind the thermodynamic effects. Detailed examination of the population data indicates that the O-for-CH₂ substitution engenders only minimal changes in Ir orbital populations or in net charge on the CO unit. Net Ir → CO charge transfer appears miniscule. However, changes occur internally in the C-O charge distribution. The major difference when comparing the CO ligands in (^{Me}POCOP)Ir(CO) and (^{Me}PCP)Ir(CO) is that the former shows more polarization toward carbon.

This polarization of the (^{Me}POCOP)Ir(CO) carbonyl ligand is most easily explained in terms of an *electrostatic* effect. The calculated dipole moment of (^{Me}POCOP)Ir is 3.9 D (pointing along the *z*-axis), while that of (^{Me}PCP)Ir is only 1.9 D and that of (MeO-^{Me}PCP)Ir is 1.7 D (1.5 D along the *z*-axis). Thus, although the *p*-methoxy and O-for-CH₂ derivatizations similarly affect the orbital occupancies of iridium (and the kinetics and thermodynamics of C-H and H-H additions), they have opposite effects on the magnitude of the dipole moment. It has been previously demonstrated that increased polarization of a carbonyl ligand (toward carbon), operating via purely electrostatic effects, can dramatically increase C-O stretching frequencies.²⁷ The large calculated difference in dipole moment (~2 D) can easily explain the observed (and calculated) (POCOP)Ir blue shift of approximately 20 cm⁻¹.²⁷ Calculations on model dipolar systems, in which there is no covalent bonding to CO, support this contention.²⁸ This result highlights the crude

approximation that C-O stretching frequencies afford as a gauge of “electron-density” on a metal center; unfortunately, we are not aware of any other experimental tool that conveniently offers more precise information.

Concluding Remarks

We report two new, *p*-methoxy-substituted, PCP-pincer catalysts, which are found to give unprecedented TONs for dehydrogenation of alkanes (both with and without sacrificial acceptors) under several different sets of conditions. The generally favorable effect of the methoxy group is demonstrated by comparisons with the parent complex, (^{tBu}PCP)IrH₂. Isopropyl groups on phosphorus, which were previously demonstrated to yield more favorable results for acceptorless dehydrogenation,¹⁴ are found to afford an excellent catalyst for *n*-alkane transfer dehydrogenation when combined with the *p*-methoxy substituent on the aryl ring. The effect of the methoxy groups is undoubtedly electronic, engendered largely by O → C(aryl) π -donation. We presume that the effects of isopropyl groups on phosphorus, in place of *t*-butyl groups, are largely steric in nature.

It is very difficult to elucidate with any certainty the factor directly responsible for the generally “favorable” effect that the *p*-methoxy substituent has upon catalytic activity. Any simple explanation should be generally applicable (e.g., for all alkanes), but we find that in several cases (e.g., acceptorless dehydrogenation of *n*-undecane) the new catalysts do not produce particularly good results. Given that the nature of the resting states (and possibly TSs as well) is expected to depend on the particular set of conditions, this is not too surprising. However, computational studies of key parameters, particularly the kinetics and thermodynamics of C-H addition to Ir(I) and the thermodynamics of H₂ addition to both Ir(I) and Ir(III), afford insight into the properties that are likely to play a role in leading to improved catalytic activity.

During the course of this work, Brookhart and co-workers discovered that another variation on the PCP motif (replacement of the methylene linkage with O atoms) also resulted in excellent catalytic activity.^{11,12} However, on the basis of ν_{CO} values of the respective CO adducts, the POCOP catalysts appeared to be relatively electron-poor in contrast with the electron-rich *p*-methoxy-substituted catalysts. We were intrigued by this contrast and included the POCOP system in our computational studies. The POCOP and MeO-PCP ligands show effects in the same direction, relative to the parent PCP ligand, for the entire range of kinetic and thermodynamic parameters studied. We believe this is not coincidental. The aryl groups of both ligands are more π -donating than the parent, and we believe this property is closely tied to the improved catalytic activity displayed by both families of complexes.

The high ν_{CO} value of (POCOP)Ir(CO) is attributable to electrostatic effects, rather than decreased M-CO π -donation. A very different distribution of charge is calculated for the (POCOP)Ir fragment vis-à-vis (PCP)Ir, as reflected in a much greater dipole moment (3.9 D vs 1.9 D). This results in polarization of a CO ligand, to give greater C-O triple-bond character, as was shown previously for cationic metal centers.²⁷

The thermodynamics and kinetics of C-H addition to the 14e “(pincer)Ir” fragment are favored by both the POCOP and MeO-PCP ligands, relative to the parent. However, likely

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resting states (e.g., (pincer)IrH₂) are also thermodynamically favored by the substitutions; this factor should inhibit catalytic activity. A comparison of relative stabilization of resting states vs stabilization of TSs by the different ligands is probably not meaningful. Such differences in *relative* stabilization are calculated to be very small (ca. several tenths of a kilocalorie per mole) and probably too small to be meaningful. Extrapolating these difference to the alkanes, acceptors, and phosphinoalkyl groups (*t*-butyl or *i*-propyl) used experimentally, seems particularly unreasonable. It is especially important to note in this context that completely nonanalogous resting states might be operative in different systems. Only a very detailed comparative kinetic study (including the determination of resting states) will allow the key differences to be elucidated.

Resistance to the formation of catalytically inactive species (either reversible deactivation or decomposition) may be as important as the relative kinetics of various steps within the catalytic cycle. It seems likely that potential inactive species would typically have an 18e configuration. Both POCOP and MeO-PCP ligands are calculated to disfavor all reactions that yield 18e species which we have studied, including the addition of either H₂ or CO to (pincer)IrH₂ and the addition of H₂ to (pincer)Ir(CO).

Finally, we note that the calculations, in combination with the experimental observations, offer indications that the kinetics of C-H addition are favored by both O → C(aryl) π -donation to the aryl ring and by σ -withdrawal from the phosphorus atoms. In reference to POCOP, it is noteworthy that the oxygen atoms presumably afford both these effects. The effect of σ -withdrawal from the phosphorus atoms, if indeed it favors the TS for C-H addition and elimination while disfavoring resting states such as C-H addition products and dihydrides, is of particular interest with respect to the design of future pincer catalysts.

Computational Methods

All calculations used DFT methodology²⁹ as implemented in the Gaussian98 series of computer programs.³⁰ We have made use of the three-parameter exchange functional of Becke³¹ and the correlation functional of Lee, Yang, and Parr (B3LYP).³² The Hay-Wadt relativistic, small core ECP, and corresponding basis sets (split valence double- ζ) were used for the Ir atom (LANL2DZ model);³³ all-electron, full double- ζ plus polarization function basis sets were applied to the elements C, O, and P (Dunning-Huzinaga D95(d)).³⁴ Hydrogen atoms in H₂ or in a hydrocarbon, which formally become hydrides in the product complexes, were described by the triple- ζ plus polarization 311G** basis set;³⁵ other hydrogen atoms in alkyl or aryl groups,

including those on the pincer ligand, were assigned a double- ζ quality 21G basis set.³⁶

Reactant, transition state, and product geometries were fully optimized using gradient methods with the ECP/basis set combination described above. The exact nature of a particular stationary point on the potential energy surface was ascertained via standard vibrational frequency/normal-mode analysis. Additional single-point calculations used a more extended basis set for Ir in which the default LANL2DZ functions for the Ir(6p) orbital were replaced by the functions reoptimized by Couty and Hall,³⁷ and sets of diffuse d functions (exponent = 0.07) and f functions (exponent = 0.938) were added as well. All computed energy values discussed in the text or presented in the tables are based on data from the extended basis set calculations.

The parent (POCOP)Ir complex optimizes to a structure of C_{2v} symmetry as do the simple dihydride and carbonyl complexes. The (*p*-MeO-POCOP)Ir complexes tend to possess C_s symmetry. The complexes containing PCP pincer ligands optimize so that the aryl group is canted away from alignment with the P-Ir-P axis to give structures of C₂ molecular symmetry for the parent, the carbonyl, and the dihydride complexes; most substituted (PCP)Ir complexes possess no symmetry (C₁). On all pincer ligands, methyl groups were attached to the phosphorus atoms. This represents a compromise between the use of hydrogen atoms and the alkyl groups (*i*-Pr or *t*-Bu) that are typically employed in experimental systems. Methyl groups capture most of the electronic effects of the larger alkyl groups, but do not fully represent the steric bulk exerted by those systems. However, steric effects are not expected to play a role in the comparisons of reactions considered here.

Electronic population analysis was carried out with the NBO module incorporated into Gaussian98.³⁸ Higher symmetry (C_s, C_{2v}) was imposed on the (PCP)Ir complexes to more clearly illustrate the σ - vs π -effects. The energetic cost of regularizing the structures of these molecules was in all cases less than 1.5 kcal/mol, and a comparison of net atomic charges on corresponding symmetric (constrained) and asymmetric (relaxed) structures showed a maximum difference of 0.01e.

Experimental Section

General Experimental. (^tBuPCP)IrH₄^{3a} and (MeO-^tBuPCP)IrH₄⁵ were prepared as described previously. All manipulations were conducted under an argon atmosphere (note: dinitrogen will poison all catalysts in this work²⁴) either in a glovebox or using standard Schlenk techniques. All solvents (COA, *n*-octane, *n*-hexane) were distilled under vacuum from Na/K alloy. NBE was purified by vacuum sublimation. Catalytic reactions were monitored using a Varian 3400 gas chromatograph with a 60 m × 0.32 mm SUPELCO SPB-5 capillary column. Calibration curves were prepared using authentic samples. GC-MS was performed using a Hewlett-Packard 5980 Series II gas chromatograph with an HP5971 mass spectrometer. All NMR spectra were recorded with Varian Mercury and Inova spectrometers operating at 300 or 400 MHz, respectively.

Transfer Dehydrogenation. Alkane transfer dehydrogenation experiments were typically conducted as follows. A 5-mL reactor vessel was fitted with a Kontes high-vacuum stopcock, which allows freeze-pump-thaw cycling and addition of argon, and an Ace Glass "Adjustable Electrode Ace-Thred Adapter", which allows removal of 0.5- μ L samples. In the argon-atmosphere glovebox, 0.5 mL of alkane solution (15 mM catalyst, and acceptor) was charged into the reactor. The charged apparatus was removed from the glovebox, and additional argon was added on a vacuum line to give a total pressure of 800 Torr. The reactor was put into a GC oven at the desired temperature. Samples were periodically taken by microliter syringe for GC analysis. After

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the reactions were monitored in this manner, the apparatus was typically returned to the glovebox where the solution was transferred to an NMR tube. ^1H NMR was used to confirm the identity and approximate concentration of the products.

Acceptorless Dehydrogenation of Alkanes. In a typical experiment, in the argon-atmosphere glovebox, 1.5 mL of catalyst solution (1 mM) was charged into a reactor consisting of a 5-mL round-bottom cylindrical flask fused to a water-jacketed condenser (ca. 15 cm). The top of the condenser was fused to two Kontes high-vacuum valves and an Ace Glass "Adjustable Electrode Ace-Thred Adapter". The solution was refluxed in an oil bath held ca. 50 °C above the alkane boiling point: 200 °C (COA) or 250 °C (CDA or *n*-undecane). Escape of H_2 from the system is facilitated by a continuous argon stream above the condenser. The reaction was monitored by GC.

Synthesis of Diisopropylphosphine. A solution of ClP^iPr_2 (20 g, 0.131 mol) in 100 mL of degassed dry ether was added dropwise to a slurry of LiAlH_4 (4.0 g, 0.421 mol) in 250 mL of degassed dry ether in ice/water bath. This mixture was then stirred overnight at room temperature until the reaction was complete as indicated by ^{31}P NMR and GC. The excess LiAlH_4 was quenched following a literature procedure,³⁹ and the gray precipitate was removed by filtration and washed with dry ether and dried by MgSO_4 . Distillation (bp = 118 °C) yielded 14.35 g of product (92.8%) as a clear liquid ($d = 0.800$ g/mL). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta -16.49$. ^1H NMR (C_6D_6): $\delta 2.91$ (dt, $J_{\text{HP}} = 192.3$ Hz, $^3J_{\text{HH}} = 6.0$ Hz, 1H, P-H), 1.78 (m, 2H, 2 C-H), 1.02 (m, 12H, 4 CH_3). MS: m/z 118.

Synthesis of 1,3-Bis-[(di(isopropyl)phosphino)methyl]-5-methoxybenzene ($\text{MeO}-i\text{PrPCP}-\text{H}$). To 7.0 g of 1,3-bis-bromomethyl-5-methoxybenzene (23.81 mmol), prepared as described previously,⁵ in 100 mL of degassed acetone was added 6.18 g of HP^iPr_2 (52.38 mmol) at room temperature. This mixture was heated under reflux with stirring for 8 h under argon atmosphere, and the solvent was removed in vacuo (note: precipitated gel rapidly expands to fill the flask under vacuum). The solid was dissolved in degassed methanol (50 mL) and treated with triethylamine (8.28 mL, 59.4 mmol). The product was crystallized out in cold methanol and filtrated and vacuum-line dried overnight, giving 7.58 g (86.5%) of the ligand as white crystals. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta 9.23$ (s). ^1H NMR (C_6D_6): $\delta 7.04$ (s, 1H, Ar-H), 6.88 (s,

2H, 2 Ar-H), 3.40 (s, 3H, CH_3O), 2.68 (s, 4H, 2 CH_2), 1.61 (m, 4H, 4 CH), 1.02(d, $J_{\text{HH}} = 7.2$ Hz, 12H, 4 CH_3), 0.98 (d, $J_{\text{HH}} = 7.2$ Hz, 12H, 4 CH_3). MS: m/z 368.

Synthesis of ($\text{MeO}-i\text{PrPCP}$) IrHCl . To 0.21 g of $\text{MeO}-i\text{PrPCP}-\text{H}$ (0.57 mmol) in 10 mL of toluene was added 0.21 g of $[\text{IrCl}(\text{1,5-cyclooctadiene})_2]$ (0.31 mmol) at room temperature. This mixture was heated to 70 °C and stirred for 1 h under H_2 atmosphere; the solvent was then removed in vacuo overnight, giving 0.24 g (94.7%) of ($\text{MeO}-i\text{PrPCP}$) IrHCl as a dark-red solid. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta 58.68$. ^1H NMR (C_6D_6): $\delta 6.72$ (s, 2H, Ar-H), 3.56 (s, 3H, CH_3O), 2.82 (dvt, downfield signal of AB pattern, $^2J_{\text{HH}} = 18.0$ Hz, $J_{\text{HP}} = 3.3$ Hz, 4H, 2 CH_2), 2.71 (dvt, upfield signal of AB pattern, $^2J_{\text{HH}} = 18.0$ Hz, $J_{\text{HP}} = 3.3$ Hz, 4H, 2 CH_2), 2.11 (m, 2H, 2 CH), 1.97 (m, 2H, 2 CH), 1.22 (m, 12H, 4 CH_3), 0.92 (m, 12H, 4 CH_3), -37.06 (t, $J_{\text{HP}} = 12.6$ Hz, 1H, Ir-H).

Synthesis of ($\text{MeO}-i\text{PrPCP}$) IrH_4 . A quantity of 0.17 g of ($\text{MeO}-i\text{PrPCP}$) IrHCl (0.285 mmol) was dissolved in 70 mL of pentane. A volume of 0.29 mL of 1 M LiBEt_3H in THF (0.29 mmol) was added dropwise to the solution at room temperature under H_2 atmosphere. The solution turned lighter color, and some white precipitate formed at the bottom of the flask. After the addition of LiBEt_3H was completed, the solution was stirred for 1 h at room temperature under H_2 , and the precipitate was then filtered out. The solvent was removed by purging the solution with a stream of H_2 and then dried by vacuum, giving 0.08 g (50%) of ($\text{MeO}-i\text{PrPCP}$) IrH_4 as brown solid. NMR data for ($\text{MeO}-i\text{PrPCP}$) IrH_4 : $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta 54.60$ (s). ^1H NMR (C_6D_6): $\delta 6.82$ (s, 2H, Ar-H), 3.59 (s, 3H, CH_3O), 3.11 (vt, $J_{\text{HP}} = 3.6$ Hz, 4H, CH_2), 1.53 (m, 4H, 4 CH), 1.00 (app. quart., $J_{\text{HP}} = 7.2$ Hz, 12H, 4 CH_3), 0.93 (app. quart., $J_{\text{HP}} = 6.8$ Hz, 12H, 4 CH_3), -9.32 (t, $J_{\text{HP}} = 10.0$ Hz, 4H, IrH_4).

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