Available online at www.sciencedirect.com

ELSEVIER

SCIENCE DIRECT

Coordination Chemistry Reviews 238–239 (2003) 315–331

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

De Novo design in organometallic chemistry: stabilizing iridium(V)

Charles Edwin Webster, Michael B. Hall *

Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA

Received 3 July 2002; accepted 2 December 2002

Contents

Abstract

Modern density functional theory (DFT) calculations are well suited for designing and testing alternative ligand schemes for transition-metal organometallic complexes. DFT methods have been applied to a variety of ligand systems and substrates (alkanes and silane) for the reaction $(\eta^x\text{-L})\text{L}'\text{Ir}^{\text{III}}\text{R} + \text{R}'\text{H} \Leftrightarrow (\eta^x\text{-L})\text{L}'\text{Ir}^{\text{V}}\text{RR}'\text{H}$ (η^x-L = Cp^R, Tp, and carborane; L′ = PR_3, CR_3^-, SiR_3^-, and SnR_3^-; R = CH_3, H; R′ = Aryl, CR_3, and H) with the goal of finding ligand–substrate combinations that will stabilize the Ir(V) species. This species is of particular interest, as it is the putative intermediate in the C–H bond activation by Ir(III) complexes. Among the donor ligands examined were various multihapto ligands (η^x-L), alternative phosphines, anionic silanes (SiR_3^-) and stannanes (SnR_3^-), and chelating ligands. Cationic Ir(V) intermediates produced by oxidative addition of an alkane are not easily stabilized when compared with their Ir(III) counterparts. Replacing the phosphine donor ligands with more covalent inorganic ligands, specifically silyl and stannyl ligands (AR_3), produces neutral Ir(V) complexes that are more stable than the Ir(III) reactants but would be subject to alkane elimination except at very low temperatures. Reacting the unsaturated 16 e$^-$ species $[\text{CpIr}^{\text{III}}\text{PR}_3\text{LR}_3]^+$ (where R = H, CH_3 and L = C, Si) with the appropriate amount of silane ($HSiR'_3$) might also afford Ir(V) complexes $[\text{CpIr}^{\text{V}}\text{PR}_3\text{LR}_3\text{SiR}'_3\text{H}]^+$ that are stable enough to be observed spectroscopically, and in some instances, possibly isolated.

Keywords: Carbon–hydrogen bond activation; Density functional theory; Iridium complexes; Ir(V) intermediates; Organometallic reaction mechanisms; Oxidative addition

---

* Corresponding author. Tel.: +1-979-845-1843.
E-mail address: hall@mail.chem.tamu.edu (M.B. Hall).

0010-8545/03/$ - see front matter
doi:10.1016/S0010-8545(02)00329-6

1. Introduction

Full utilization of our methane reserves will require facile functionalization of strong C–H bonds. Numerous experimental [1] and theoretical [2] studies on a variety of transition metal systems have been directed toward the goal of C–H bond activation. The first reports of C–H bond activation followed two general routes, photoinitiation of CpMLL′, M = Rh(I), Ir(I), L = CO, PR_3, L′ = CO, H_2 [1l–q,s–w,y–bb], which produces stable oxidative-addition products, and thermal initiation of early d^0 metal complexes such as Cp_2La, which activates through a σ-bond metathesis [1r,1x].

Following Bergman and co-workers' report of low-temperature C–H bond activation of methane by a cationic iridium(III) complex $[(Cp^*Ir^{III}P(CH_3)_3CH_3)]^+$ [1j], Hall and co-workers used density functional calculations to show that the mechanism begins with hydrocarbon oxidative addition (OA), proceeds through an iridium(V) intermediate, and finishes by reductive elimination (RE) [2g]. This OA/RE mechanism was preferred over a four-center σ-bond metathesis pathway, which could not be located after a systematic search for its transition state on the potential energy surface (PES) [2g,2h]. Subsequently, Su and Chu reported MP2 and QCISD studies of both the Ir and the analogous Rh systems and came to similar conclusions for the Ir system but concluded that the Rh complex could proceed via a metathesis transition state [2e]. Previously unpublished results reported in a recent review of theoretical studies of transition-metal reactions by Niu and Hall [2a] illustrate that, while the C–H bond activation by the Ir(III) complex prefers an OA/RE pathway, the Co system follows a σ-bond metathesis pathway with a high activation energy. For the Rh system, Niu and Hall found a transitional pathway somewhere between the two paths [2a]. Very recently, Klei et al. have isolated a silyl Ir(V) metallocycle complex that they propose 'lends convincing experimental support' [1e] to the conclusion by Hall and co-workers for the OA/RE mechanism involving the Ir(V) intermediate.

The work described here is centered at finding a system for stabilizing the Ir(V) oxidative addition intermediate (i.e. an Ir(V) complex with adjacent Ir–X and Ir–H bonds, where X = C, Si, Sn, etc. especially X = C) as an observable product or as a long-lived intermediate. Various donor ligands have been studied in the hope that better donor ligands might stabilize the higher oxidation-state intermediate. Modified Cp ligands, carboranes, alternative phosphines, silanes, and stannanes, as well as an alternative substrate (silane) have been examined in the hope that the Ir(V) intermediate can be stabilized enough to be observed. Stabilizing the Ir(V) intermediate by utilizing the chelate effect through formation of a metallocycloalkane was also examined. Intriguing results are reported for improved donors, an alternative substrate, and metal chelation.

2. Theoretical calculations and methodology

Density functional theory (DFT) implicitly treats electron correlation by utilizing an energy functional, some with empirically adjusted parameters. Modern functionals, such as the generalized gradient approximation (GGA) or gradient corrected functionals and so-called hybrid functionals with an admixture of exact or Hartree–Fock (HF) exchange, have been shown to provide accurate geometries and reasonable energetics for a variety of systems at a cost similar to HF theory. DFT has a distinct advantage over traditional wavefunction based techniques (ab initio) where the explicit addition of electron correlation (correlation beyond HF exchange) becomes quite computationally expensive.

Most of the theoretical calculations reported here have been carried out using the GAUSSIAN 98 [3] implementation of B3LYP [Becke three-parameter exchange functional (B3) [4] and the Lee–Yang–Parr correlation functional (LYP) [5]] density functional theory [6] with default pruned fine grids for energies (75, 302), default pruned course grids for gradients and Hessians (35, 110) (unpruned for iridium), and default SCF convergence for geometry optimizations (10^{-8}). All structures were fully optimized, and analytical frequency calculations were performed on transition state structures to ensure that a first order saddle point was achieved. In cases where single-point energy calculations have been used to compare relative energies, literature standard notation has been used to denote the level of theory and basis set used for both the geometry optimization and the single-point calculation [7], i.e. BP86/BS2//B3LYP/BS1 denotes single point energy calculations with the BP86 functional and basis set BS2 at the geometry optimization with the B3LYP functional and basis set BS1. Non-default SCF convergence was used for GAUSSIAN 98 single-point calculations (10^{-8}). In some instances, single-point BP86 (the Becke exchange functional (B) [8] and the Perdew correlation functional (P86) [9]) calculations performed with the GAUSSIAN 98 implementation of BP86 and with the Amsterdam density functional (ADF) program implementation of BP86 (ADF, ver 2000.02) [10]. ADF uses Slater-type orbital (STO) basis sets rather than Gaussian type orbitals (GTO) and contains a density fitting procedure using auxiliary functions (fit functions) for the evaluation of the Coulomb potential and molecular density. All reported ADF calculations used a post-SCF gradient correction to the local density approximation (LDA) density functional energy (VWN, version V [11]) with the BP86 exchange-correlation potential (as implemented in ADF) and with the standard single-point grid accuracy factor (4.0) and SCF convergence (10^{-6}). For our reaction prototype (see below), relativistic corrections are significant and the results from the relativistic effective core potential (ECP) used in GAUSSIAN 98 are quite similar to those of scalar relativistic effects from the zeroth-order regular approximation (ZORA) [12] used in ADF. For ADF ZORA calculations, the frozen core approximation was used. All geometries used in ADF and GAUSSIAN 98 BP86 single point calculations were from GAUSSIAN 98 B3LYP optimizations.

Notations for relative energies used in this article are as follows: ΔE are the 'raw' relative energies from the PES; ΔE_o include zero-point energy; ΔH are the relative enthalpies; ΔG are the relative free energies (which include the temperature dependent entropic contribution, $T\Delta S$), and ΔH° and ΔG° are the relative enthalpies and relative free energies at standard conditions. Entropy, of course, favors the higher molecularity side of a reaction. Throughout the article, relative energies are ΔE from B3LYP optimizations (unless otherwise noted) because frequency calculations were not performed on every species calculated in this work, particularly those calculated with the basis set used for initial potential energy surveys (BS1) and/or when the intermediate analogue was considered to be too unstable for further consideration.

Generally, double-zeta (DZ) basis sets should be considered the minimum requirement to provide enough flexibility in the atomic functions to describe bonding correctly, although smaller basis sets can sometimes be used for atoms distant from the chemically active ones. Tables 1 and 2 include summaries of the basis sets used in the current study and results on a prototypical reaction. (Basis sets 1–6 were used in GAUSSIAN 98 calculations, and basis sets 7 and 8 were used in ADF calculations.) In BS1, the basis set for iridium is the ECP of Hay and Wadt (LanL2DZ) [13] as modified by Couty and Hall (341/541/21), where the two outermost *p* functions have been replaced by a (41) split of the optimized iridium 6*p* function [14]. This replacement of the original valence *p* with these reoptimized functions has been shown to be quite important in reactions involving bond breaking and bond formation, such as oxidative addition. The energetics of simple substitutions or relative energies of molecular isomers are not nearly as sensitive to the choice of this valence *p* set. Spherical harmonic *d* and *f* functions were used, i.e. there are five angular (contracted) basis functions per *d* function and there are seven angular basis functions per *f* function. BS1 utilized the standard LanL2DZ basis sets for phosphorus [13] and the D95V basis set [15] for nitrogen, oxygen, carbon, boron, and hydrogen.

BS2 utilizes the Couty and Hall modified LanL2DZ with an *f* polarization function [16a] for Ir, the LanL2DZ basis set augmented with a *d* polarization function 16b for phosphorus (DZ plus polarization (P), ECP, DZP–ECP), double zeta plus polarization (DZP) basis sets for all C and N and H atoms (D95* for C and N [15] and D95** for H [15]). BS3 utilizes the metal basis set and ECP of BS1 for iridium, the basis set and ECP of BS2 for phosphorus, the cc-pVDZ [17] for iridium bound carbons and hydrogens, and D95 for the peripheral atoms. BS4 is identical to BS3 but has the DZ basis set of hydrogens of the iridium bound methyl groups replaced with a DZP basis set (cc-pVDZ). BS5 is identical to BS3 but replaces the ECP basis set of the phosphorus and silicon with an all electron double zeta (DZ) plus polarization basis set (cc-pVDZ). BS6 utilized the basis set and ECP of BS1 for iridium, the LanL2DZ basis set augmented with a *d* polarization function 16b for phosphorus, silicon, and tin (DZP–ECP), DZP basis sets for all atoms bound directly to the metal center (D95* for C[15] and D95** for H[15]), and DZ for the peripheral atoms (D95 on C and H) [15]. The cc-pVDZ basis sets have had the redundant functions removed

Table 1
Summary of the basis sets used in the current study

	Metal	P, Si, Sn	Other atoms α to M [a]	Atoms ≥β to M [b]
BS1	mod-LanL2DZ(ECP)	DZ(ECP)	VDZ	VDZ
BS2	mod-LanL2DZ*(ECP)	DZP(ECP)	DZP	DZP
BS3	mod-LanL2DZ(ECP)	DZP(ECP)	VDZP	DZ
BS4	mod-LanL2DZ(ECP)	DZP(ECP)	VDZP	VDZ[c]
BS5	mod-LanL2DZ(ECP)	DZP(AE)	VDZP	DZ
BS6	mod-LanL2DZ(ECP)	DZP(ECP)	DZP	DZ
BS7	STZ(AE)	SDZP(AE)	SDZP	SDZP
BS8	STZ(AE)	SDZP(AE)	SDZP	SDZP

ECP, effective core potential; S(prefix), Slater type orbital; AE, all electron; VDZ, valence double zeta; DZ, double zeta; DZP, double zeta plus polarazation; VDZP, valence double zeta plus polarazation; TZ, triple zeta.

[a] Atoms that are connected to the metal, other than P, Si, and/or Sn.

[b] All atoms that are at least one atom away from the metal.

[c] The β-hydrogens on the iridium-bound methyl groups are VDZP.

Table 2
The reaction of $[Cp^{R}Ir^{III}PR_3CH_3]^+$ with CH_4 (kcal mol^{-1})

		Reactant $CpIr(PH_3)(CH_3)^+ + CH_4$	σ-Complex $[CpIr(PH_3)(CH_3){-}CH_4]^+$	TS	Intermediate $[CpIr(PH_3)(CH_3)_2H]^+$
BS1	ΔE	0.0	−1.6	+10.3	+3.4
BS2	ΔE	0.0	−0.8	+9.4	+3.5
	ΔE_o	0.0	−0.1	+10.5	+6.1
	$\Delta H^{\circ,\ddagger}$	0.0	−0.2	+9.3	+4.9
	$\Delta G^{\circ,\ddagger}$	0.0	+7.2	+20.6	+16.4
BS5	ΔE	0.0	−1.3	+7.3	+1.5
	ΔE_o	0.0	−0.5	+8.7	+4.2
	$\Delta H^{\circ,\ddagger}$	0.0	−1.98	+6.6	+2.1
	$\Delta G^{\circ,\ddagger}$	0.0	+7.1	+20.2	+15.8
BS3	ΔE	0.0	–	–	+1.1
	ΔE_o	0.0	–	–	+4.1
	ΔH_o	0.0	–	–	+2.8
	ΔG°	0.0	–	–	+16
BS4	ΔE	0.0	–	–	+2.6
	ΔE_o	0.0	–	–	+5.5
	ΔH°	0.0	–	–	+4.2
	ΔG°	0.0	–	–	+16
BS2//BS5	ΔE	0.0	−0.8	+9.4	+3.5
BP86/BS2//B3LYP/BS2	ΔE	0.0	−0.7	+4.0	−1.9
BP86(ZORA)/BS7//B3LYP/BS2	ΔE	0.0	−1.39	+3.2	−2.1
BP86(ZORA)/BS7//B3LYP/BS5	ΔE	0.0	−1.0	+3.2	−2.1
BP86(Non-Rel)/BS8//B3LYP/BS2	ΔE	0.0	−6.0	−12.6	−18.3
		$Cp^{*}Ir(PH_3)(CH_3)^+ + CH_4$			$[Cp^{*}Ir(PH_3)(CH_3)_2H]^+$
BS1	ΔE	0.0	–	–	+9.5
BS3	ΔE	0.0	–	–	+7.5
	ΔE_o	0.0	–	–	+10.9
	ΔH°	0.0	–	–	+9.1
	ΔG°	0.0	–	–	+23.6
		$CpIr(PMe_3)(CH_3)^+ + CH_4$			$[CpIr(PMe_3)(CH_3)_2H]^+$
BS1	ΔE	0.0	–	–	+4.6
BS3	ΔE	0.0	–	–	+3.5
	ΔE_o	0.0	–	–	+6.0
	ΔH°	0.0	–	–	+5.0
	ΔG°	0.0	–	–	+16.0
		$Cp^{*}Ir(PMe_3)(CH_3)^+ + CH_4$			$[Cp^{*}Ir(PMe_3)(CH_3)_2H]^+$
BS1	ΔE	0.0	–	–	+9.6
BS3	ΔE	0.0	–	–	+9.0
	ΔE_o	0.0	–	–	+11.8
	ΔH°	0.0	–	–	+10.4
	ΔG°	0.0	–	–	+23.4

and have been linearly transformed as suggested by Davidson [18]. In cases where an atom becomes metal bound during the course of a reaction, polarization functions are added to that atom for all species involved, e.g. when one H of SiH_3 in a starting material becomes a metal bound hydride, polarization functions are added to that one hydrogen for all species. BS7 utilized the standard ADF ZORA III basis set (an uncontracted double-zeta STO basis set with one polarization function, DZP) for all phosphorus, silicon (if present), carbon, and hydrogen; and the ADF ZORA IV basis set (TZP) with frozen core orbitals up to 4*f* for the metal. ADF ZORA basis sets have been optimized for use within the ZORA relativistic calculations. BS8 utilized the standard ADF III basis set (an uncontracted double-zeta STO basis set with one polarization function, DZP) for all phosphorus, carbon, and hydrogen; and the ADF IV basis set (TZP) with frozen core orbitals up to 4*d* for the metal.

Often, simplification of the ligands of a given system not only expedites results but also is required in order to perform the number of calculations needed to appropriately describe the species involved in the reaction system under study. However, this simplification can and sometimes does lead to problematic interpretations of the predictions. For example, replacement of an experimental pentamethyl-Cp (Cp*) or pentaphenyl-Cp with a simple Cp ligand may make the calculation tractable, but one must consider the steric and/or electronic consequences of this ligand trimming. The effects of ligand trimming are separate from and can compound with the effects of an incomplete basis set and an imperfect energy functional. Another consideration involves entropy and temperature effects ($T\Delta S$) and their role on the calculated changes in the free energy (ΔG). To illustrate these sometimes subtle differences in results, consider the original Bergman Ir(III) reactant complex, $(\mathrm{Cp^{*}Ir^{III}P(CH_3)_3CH_3})^+$, which has Cp* as well as trimethylphosphine as ligands (see Table 2). In their original report, Hall and workers trimmed the system by using plain Cp and simple phosphine $(\mathrm{CpIr^{III}PH_3CH_3})^+$ reacting with methane and used a DZ quality basis set, BS1. Reoptimization of the stationary points of the PES for this reaction with a mixed DZ/DZP quality basis set (BS5) reduces slightly the endoergicity of the transition state (the barrier (ΔE) for C–H bond activation is reduced from +11.9 to +8.6 kcal mol^{-1}) and the Ir(V) intermediate (+1.5 kcal mol^{-1} above the separated reactants rather than +3.4 kcal mol^{-1} as calculated from BS1).

Changing from an all electron DZP basis set (cc-pVDZ) on the phosphorus to an ECP plus valence basis set (BS3) or adding polarization to the iridium bound methyl hydrogens (BS4) produces small differences in the calculated relative energies. Other slightly larger differences appear when comparing the relative energies of the reactant and intermediate of the substituted complexes, Cp versus Cp* and $\mathrm{PH_3}$ versus $\mathrm{P(CH_3)_3}$. For example, the $\mathrm{P(CH_3)_3}$ intermediate is slightly less stable than the simple phosphine intermediate (~2 kcal mol^{-1}), and the steric effects of the Cp* ligand have an even greater destabilizing effect on Ir(V) intermediates (~5 kcal mol^{-1}). We might use these results to our advantage while searching for an Ir(V) intermediate analogue—although simple $\mathrm{PH_3}$ complexes would be difficult, simple Cp complexes might be isolatable.

When one considers $T\Delta S$, the gas-phase σ-complex (agostic complex) becomes unstable by +7.1 kcal mol^{-1} (ΔG°), compared with −2.0 kcal mol^{-1} for ΔH°. The $\Delta G^{\ddagger/\circ}$ of the transition state and the intermediate are +20.2 and +15.8 kcal mol^{-1}! The relative energy differences between the ΔE, ΔE_o, ΔH°, and ΔG° can sometimes be quite large when the molecularity of the reaction changes or the vibrational structures of the species differs dramatically. In some cases, solvent effects can become important. Generally, higher dielectric solvents favor species with higher dipole moments, but specific solvent coordination can affect an observed equilibrium in ways other than those expected from the bulk solvent properties. In the current study, solvent effects should be minimal, as low dieletric alkane solvents are generally used for the systems described here.

3. Background results

The identification of an accessible and observable Ir(III)–Ir(V) system with a stable Ir(V) analogue to the intermediate proposed by Hall and coworkers [2a] is a nontrivial task. In this section, we will illustrate two fundamental points that have an impact on this goal: (1) high oxidation metal complexes with hydride ligands are more stable than the corresponding complex with alkyl ligands and (2) reductive elimination from $\mathrm{M(H)_2}$ and M(H)(R) are much easier (lower barriers) than reductive elimination from $\mathrm{M(R)_2}$.

While several cationic [19] and neutral [20,21] Ir(V) complexes have been reported in the literature, their stability is connected to the energetic pattern described above and shown in Fig. 1. The simplest Ir(V) intermediate analogue is the neutral cyclopentadienyl-tetrahydride, $\mathrm{CpIr(H)_4}$, which has been known since 1983 [21a]. Here, the Ir(III) dihydride produced by reductive elimination of $\mathrm{H_2}$ from this Ir(V) tetrahydride is energetically unfavorable by 44.1 kcal mol^{-1} (ΔE, BS1). While both the methyltrihydride and dimethyldihydride Ir(V) complexes have low-energy barriers for $\mathrm{CH_4}$ reductive-elimination, they are still both stable with respect to this transformation [+16.1 for the trihydride Ir(V) and +5.8 kcal mol^{-1} (ΔE, BS1) for the dihydride Ir(V)] (entropy may, of course, make this dimethyldihydride Ir(V) complex difficult to prepare) [22]. In this series, the closest neutral Ir analogue to the previously proposed cationic intermediate $[\mathrm{CpIr^{V}PR_3(CH_3)_2H}]^+$, $\mathrm{CpIrH(CH_3)_3}$, is not only unstable to the species produced by the reductive elimination of $\mathrm{CH_4}$ but also has a low barrier for that elimination. The ease of elimination of $\mathrm{CH_4}$ from this monohydride complex clearly illustrates the dilemma in the search for a suitable complex where the Ir(V) intermediate can be experimentally observed or ‘trapped’. The next analogue, the tetramethyl Ir(V) complex, which is known experimentally [21b], is thermodynamically unstable with respect to reductive elimination of $\mathrm{C_2H_6}$; but elimination will not occur because the barrier (transition state) for this process is exceedingly high, +41.9 kcal mol^{-1} (ΔE, BS1). Low and Goddard studied the elimination of $\mathrm{C_2H_6}$ from $\mathrm{Pd^{II}(CH_3)_2}$ and $\mathrm{Pt^{II}(CH_3)_2}$ and found similar results and attributed the high barrier to the directionality of the methyl sp^3 hybrid orbital when coupling two $\mathrm{CH_3}$ to form ethane [2h,2i,2j]. One might note that in the Ir(V) complexes as an alkyl group is replaced by a hydride, the relative stability progressively increases, but the first H provides a dramatically lower barrier to elimination. Thus, the monohydride complex with a

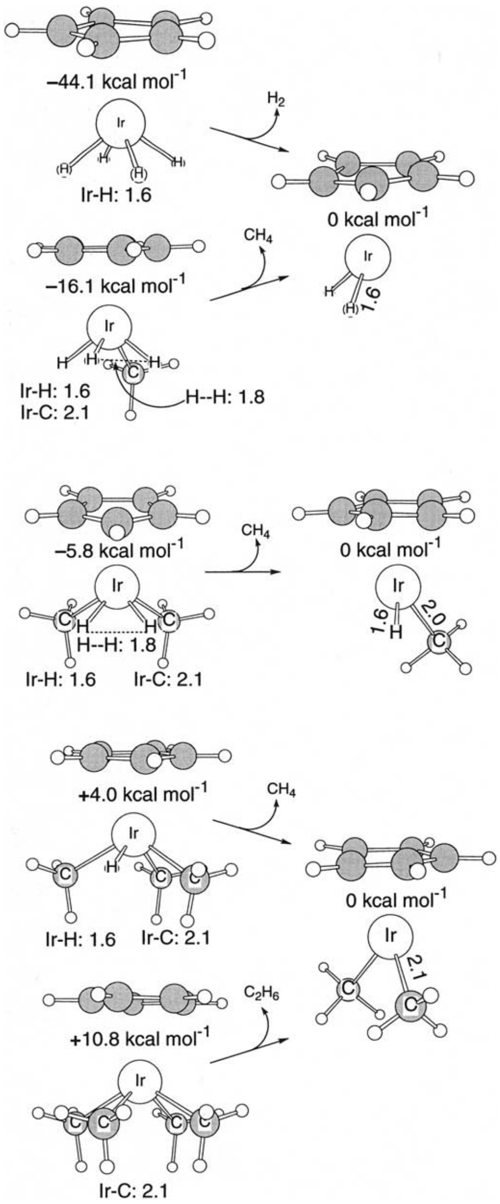


Fig. 1. The B3LYP/BS1 stability (ΔE) of various hydrido and alkyl substituted Ir(V) complexes, $\mathrm{CpIr^{V}(X)_4}$ (where X = H, $\mathrm{CH_3}$), with respect to the species produced by the reductive elimination of H_2, CH_4, or C_2H_6. All distances are in Å.

methyl ligand is the ‘worst case’ for the purposes of stabilizing an Ir(V) intermediate analogue.

Another system, similar to the cationic $(\mathrm{CpIr^{III}PR_3CH_3})^+$–$[\mathrm{CpIr^{V}PR_3(CH_3)_2H}]^+$ pair, is the hydride analogue pair, $(\mathrm{CpIr^{III}PR_3H})^+$–$[\mathrm{CpIr^{V}PR_3CH_3(H)_2}]^+$. When compared with the reactants, CH_4 and $(\mathrm{CpIr^{III}PH_3H})^+$, the Ir(V) *cis*-dihydride intermediate analogue model complex ($[\mathrm{CpIr^{V}PH_3CH_3(H)_2}]^+$) is stable by −8.9 kcal mol^{-1} (ΔE, BS1); and the barrier for oxidative addition of CH_4 is low. Our calculations show that for the hydride–trihydride model pair, $(\mathrm{CpIr^{III}PH_3H})^+$–$[\mathrm{CpIr^{V}PH_3(H)_3}]^+$), the Ir(V) complex is stable by −34.6 kcal mol^{-1} (ΔE, BS1). The di and trihydride complexes produce fairly stable Ir(V) intermediate analogues, but their stability alone does not prove the dimethylhydride intermediate is involved in the experimental system as the relative stability is drastically decreased with the replacement of a single hydride with a methyl group. The relative high stability of the trihydride complex compared with the monohydride ($[\mathrm{CpIr^{V}PR_3(H)_3}]^+$–$[\mathrm{CpIr^{III}PR_3H}]^+$), the difference in electronegativity between H (2.20) and C (2.55) when compared with Ir (2.20), and the *s* hybridization of H versus the sp^3 hybridization of CH_3 have all been purported to make the stability of a trihydride or a methyl dihydride complex (compared with the Ir(III) reactant and substrate) unsuitable as direct evidence for the stability of a similar Ir(V) dimethyl hydride complex [19]. Although the stability of these Ir(V) analogues is suggestive, the need for a closer analogue to better illustrate the proposed reaction pathway is clearly evident.

Consider the silyl model complex for the experimental cyclometalated silyl Ir(V) intermediate analogue recently reported by Klei et al. [1e]. Calculations on a simplified model $[\mathrm{Cp}\overline{\mathrm{Ir^{V}(PH_3)(Si(H)_2C}}\mathrm{_6H_4)H}]^+$ concur with the reported stability of the cyclometalated silyl Ir(V) complex, $[\mathrm{Cp^{*}}\overline{\mathrm{Ir^{V}(P(CH_3)_3)Si(Ph_2{-}C}}\mathrm{_6H_4)(H)}]^+$ (see Fig. 2). The model complex for this Ir(V) intermediate analogue (plus CH_4) is calculated to be 27.0 kcal mol^{-1} (BS5) more stable than the starting materials (ΔE_o is −27.1, ΔH° is −26.7, and ΔG° is −21.3 kcal mol^{-1}; for BP86(ZORA)/BS7//B3LYP/BS5, $\Delta E = -34.1$ kcal mol^{-1}). The high stability of the complex allowed the authors to isolate it and to determine its X-ray structure. The stabilization of this complex comes from several factors, the weakness of the Si–H bond, [23] the strength of the Ir–Si bond, the strength of the Ir–$\mathrm{C_{Ph}}$ bond, and the inherent entropic and steric favorability of orthometalation.

We shall next consider if orthometalation itself can improve the stability of an Ir(V) intermediate. Orthometalated phosphine $\mathrm{Cp^R}$ iridium(III) complexes have been synthesized and characterized [24]. Reacting CH_4 with an orthometalated phosphine model complex $[\mathrm{Cp}\overline{\mathrm{Ir^{III}(P(H_2{-}C}}\mathrm{_6H_4)}]^+$ produces an Ir(V) intermediate

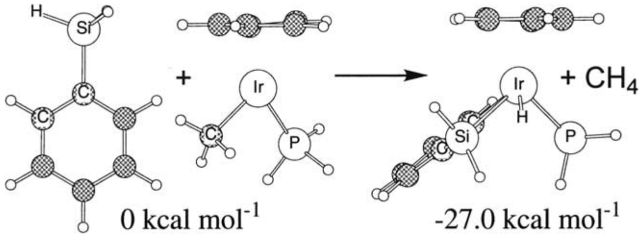


Fig. 2. The B3LYP/BS5 calculated stability (ΔE) for a cationic model complex of Bergman’s orthometalated silyl Ir(V) complex. The BP86(ZORA)/BS7//B3LYP/BS5 calculated stability (ΔE) is −34.1 kcal mol^{-1}.

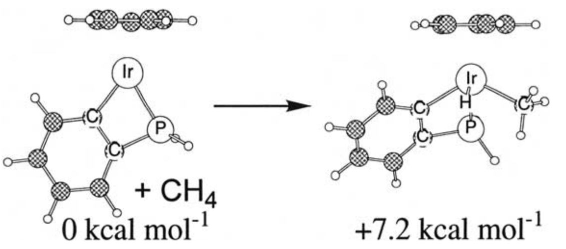


Fig. 3. The B3LYP/BS5 calculated stability (ΔE) for a cationic orthometalated phosphine Ir(V) model complex.

complex which is $+7.2$ kcal mol^{-1} (ΔE, BS5; $\Delta E_o = +8.7$, $\Delta H^\circ = +7.6$, and $\Delta G^\circ = +19.5$) less stable than the reactants (see Fig. 3). Thus, orthometalation alone is not sufficient to stabilize the Ir(V) intermediate. However, a Ir(V) hydrido complex with terminal silane and an orthometallated aryl or alkyl phosphine might be stable enough to be characterized and/or isolated [25].

In our search for other analogues, we may need to consider less stable species such that spectroscopic observation of an Ir(V) species would also be supportive of the oxidative-addition mechanism. Disregarding any systematic errors in the calculations, our goal is to find a system that has a $\Delta G^\circ \leq 0$ kcal mol^{-1}, which corresponds to a $\Delta E \leq -10$ kcal mol^{-1} for the reaction $\mathrm{LIr^{III}} + \mathrm{AH} \Leftrightarrow \mathrm{LIr^{V}(A)(H)}$. Of course, the more stable the Ir(V) intermediate analogue is calculated to be, the more likely it can be observed. ΔE could be closer to zero if the entropic disadvantage of the reaction were reduced by temperature, pressure, and/or chelation.

4. Results and discussion

A variety of ligand strategies have been attempted in our search for a system that will stabilize an analogue for the Ir(V) intermediate. Presumably, a superior donor ligand could provide more electron density to a metal center in a high oxidation state that is taxed by multiple covalent bonds. In that regard, we have explored alternative η^x ligands for Cp$^-$, such as Tp$^-$ and dianionic capping carboranes, alternative phosphines with better σ-donor properties, and anionic replacements for the phosphines, such as $\mathrm{SiR_3^-}$. Other strategies are also reported, such as chelation to reduce steric repulsions and to increase entropic favorability and other substrates that have H–A bonds that are weaker than the H–C bonds in simple hydrocarbons.

4.1. Metallocarboranes

Replacing the monoanionic Cp$^-$ ligand with a dianionic η^5-carborane cage ligand (specifically η^5-7,8-$\mathrm{C_2B_9H_{11}^{2-}}$, **B1**) could stabilize Ir(V) if the carborane cage is a better donor that than Cp (or Cp*). Several examples of various metallocarborane complexes have been reported in the literature [26]. Fig. 4 contains the geometric results for several of the various metallocarborane complexes that were studied. Replacing the Cp ligand in the original model complex $(\mathrm{CpIr^{III}PH_3CH_3})^+$ with η^5-7,8-$\mathrm{C_2B_9H_{11}^{2-}}$ ($\mathrm{C_2B_9H_{11}}$) produced a neutral Ir(V) intermediate, $\mathrm{C_2B_9H_{11}Ir^VPH_3(CH_3)_2H}$, that is 16.4 kcal mol^{-1} (ΔE, BS1) higher in energy than the Ir(III) complex and uncoordinated methane, increasing the unfavorability of the Ir(V) complex even further.

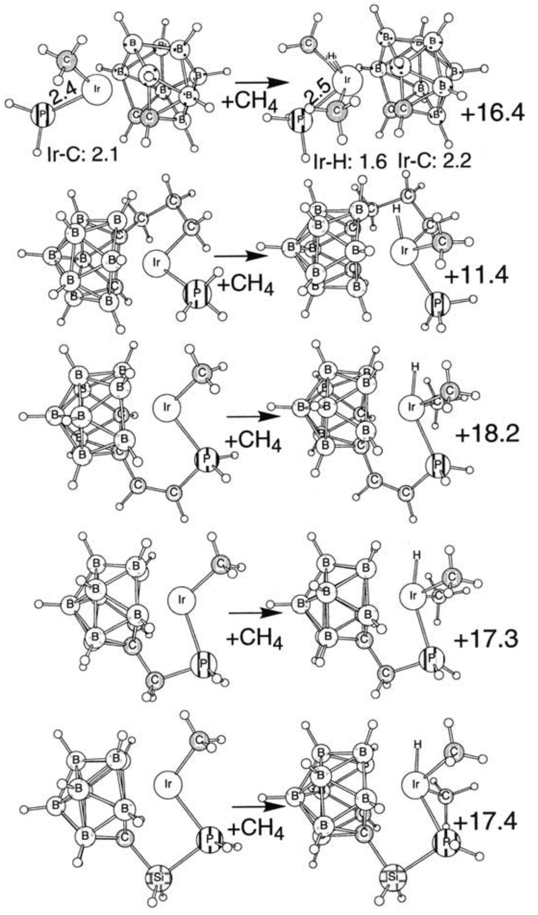
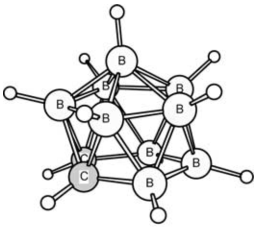


Fig. 4. The B3LYP/BS1 calculated stability (ΔE) for various neutral carborane cage Ir(V) model complexes for the oxidative addition of CH_4. All distances are in Å, and energies are in kcal mol^{-1}.

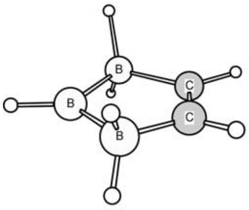


B1

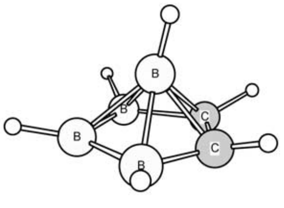
In order to determine if steric effects and/or donor effects destabilize the carborane Ir(V) intermediate, a simple test case has been considered. Loss of H_2 from the tetrahydride complex, η^5-7,8-$\mathrm{C_2B_9H_{11}Ir^VH_4}$, requires 37.2 kcal mol^{-1} (ΔE, BS1), while the loss of H_2

from the Cp analogue, CpIr^{V}H$_4$ requires 44.1 kcal mol^{-1} (ΔE, BS1) (see Fig. 1). Thus, the Ir(V) tetrahydride is stabilized more by η^5-Cp$^-$ than by η^5-7,8-C$_2$B$_9$H$_{11}^{2-}$. This comparison leads to the conclusion that while a nominal steric influence of the carborane ligand may exist in these iridium systems, the η^5-Cp$^-$ ligand is a better donor than the η^5-7,8-C$_2$B$_9$H$_{11}^{2-}$ ligand. Apparently, the larger cage delocalizes the additional negative charge such that less is available to the metal.

Perhaps, smaller dianionic carboranes surrogates, such as C$_2$B$_3$H$_7^{2-}$ (**B2**) and the boron capped C$_2$B$_4$H$_6^{2-}$ (**B3**) could be better [27]. When the C$_2$B$_3$H$_7^{2-}$ ligand attaches in a η^5 fashion to the metal, two H's become B–B bridged (see Fig. 5) [27b]. For the **B2** ligand, the Ir(V) intermediate analogue, (η^5-C$_2$B$_3$H$_7$)IrPH$_3$(CH$_3$)$_2$H, was found to be 9.3 kcal mol^{-1} (ΔE, BS1) above the separated Ir(III) precursor and CH$_4$; and for the **B3** ligand, (η^5-C$_2$B$_4$H$_6$)Ir^{V}PH$_3$(CH$_3$)$_2$H was found to be 15.9 kcal mol^{-1} (ΔE, BS1) higher in energy (see Fig. 5).



B2



B3

While these dianonic carborane ligands are apparently unable to stabilize the Ir(V) intermediate analogues, their destabilization of the Ir(V) complex might be a useful property, as the destabilization of Ir(V) by pincer ligands may be a key feature in their ability to catalyze the dehydrogenation of alkanes [28].

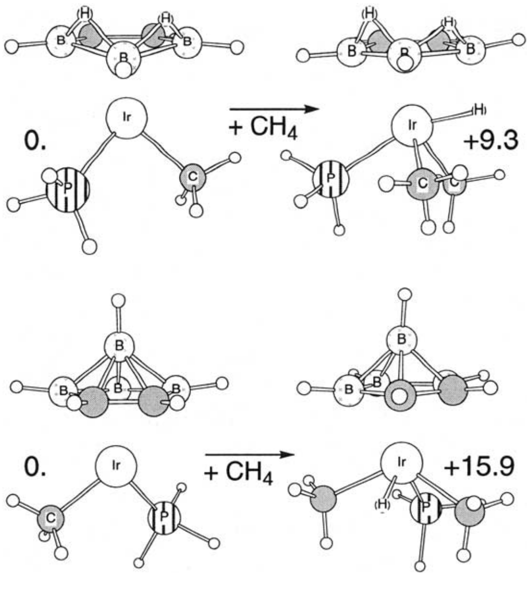


Fig. 5. The B3LYP/BS1 calculated stability (ΔE) for two neutral carborane Ir(V) model complexes for the oxidative addition of CH$_4$. All energies are in kcal mol^{-1}.

4.2. Tris(pyrazolyl)borate ligands

An increasing amount of recent work on tris(pyrazolyl)borate ligand has yielded structurally interesting organometallic complexes with important catalytic properties [29]. Several studies have been made to better understand the steric versus electronic requirements of this borate ligand [30–33]. Tris(pyrazolyl)borates are considered to be strong donor ligands, whose complexes have demonstrated many similarities with their Cp analogues but some non-parallel behaviors with respect to their reactivity [30–32]. These ligands also prefer the chelated metal to be six-coordinate, pseudo-octahedral complexes. Our studies of the tris-(pyrazol-1-yl)borate Ir analogue of CpIr^{V}H$_4$ have afforded similar conclusions to these differences from the Cp complex in reactivity and structure [33]. For example, while the Cp tetrahydride (CpIrH$_4$) adopts a four-legged piano stool geometry, the Tp ligand induces two geometries of approximately equal energy for the TpIrH$_4$ complex, an edge-bridged octahedral geometry (tetrahydride) and a η^2-dihydrogen, dihydride complex [33].

In the case of the cationic Ir(III) phosphine methyl tris(pyrazolyl)borate complex (TpIrPH$_3$CH$_3^+$) reacting with CH$_4$, a notably strong σ-C–H interaction has been calculated, -8.8 kcal mol^{-1} (ΔE, BS1). However, due to the preference for an octahedral environment by the Tp ligand, the Ir(V) intermediate was found to be less stable than the Ir(III) complex by $+6.9$ kcal mol^{-1} (ΔE, BS1) (see Fig. 6).

4.3. Improved donor phosphines

An alternative route to stabilizing the high-oxidation state intermediate complex could involve phosphine ligands with improved donor ability. However, the P(CH$_3$)$_3$ ligand in the Bergman complex is already a strong σ-donor [34]. Phosphines with a heteroatom in a position such that its lone pair could destabilize the P lone pair might be good candidates. The phosphines were first screened by a simple proton affinity (PA) test, which concluded that P(CH$_3$)$_3$ (PA$_{\text{HF/6-31G*}} = +236.9$ kcal mol^{-1}) is a better donor than PH$_3$ (PA $= +196.8$ kcal mol^{-1}). Each phosphine was optimized at the HF/6-31G* level; and after being protonated and reoptimized, the energy was compared with the unprotonated phosphine. The structures of several uncoordinated phosphine ligands and their relative proton affinities are given below.

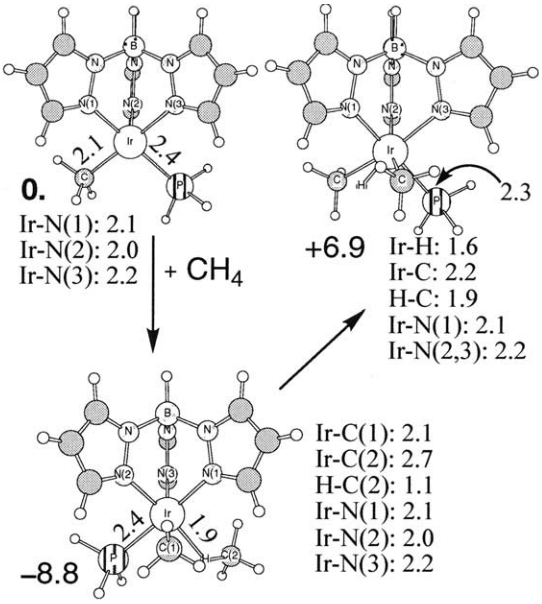
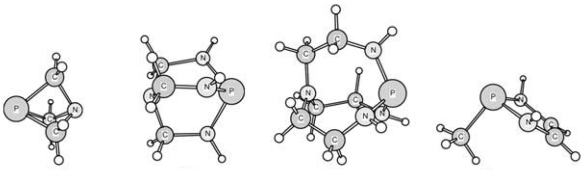


Fig. 6. The B3LYP/BS1 calculated stability (ΔE) for neutral Tp methane σ-complex and the Ir(V) oxidative addition intermediate model complex. All distances are in Å, and energies are in kcal mol^{-1}.



	P1	**P2**	**P3**	**P4**
PA (kcal mol^{-1})	+210.9	+223.9	+263.8	+266.2

After screening, four selected donor ligands were tested with the fragment metal complex, $[(\eta^5\text{-Cp})Ir^{V}L(CH_3)_2H]^+$, and the relative energies compared with the Ir(III) complex and methane (see Fig. 7). Several phosphines were found to be better donors to the iridium fragment than $P(CH_3)_3$ and formed more stable Ir(V) intermediates [35]. One, as yet unprepared, phosphine, 2,3-dihydro-1-methyl-1,3,2-diazaphosphole (**P4**), [36] produced particularly interesting results. The Ir(V) intermediate with **P4** $[CpIr^{V}(\overline{P(CH_3)(N}HCH)_2)(CH_3)_2H]^+$ was within +1.56 kcal mol^{-1} (ΔE, BS1) of the analogous Ir(III) complex, unfortunately a lower energy conformer of the Ir(III) complex (with the methyl group of $P(CH_3)(NHCH)_2$ eclipsing the iridium bound hydrogen) increases this difference to +2.87 kcal mol^{-1} (ΔE, BS1) (see Fig. 7). Compared with +4.59 kcal mol^{-1} (ΔE, BS1) for the $[CpIr^{III}P(CH_3)_3]^+$ system, this new ligand is an improvement, but only a small one.

Fig. 7 also shows the results for three other promising phosphine ligands for the Ir(III)–Ir(V) OA reaction. The Ir(III) complex with the $P(NH(CH_2)_2)_3N$ (2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane, **P3**) ligand was more stable than its Ir(V) counterpart by 3.61 kcal mol^{-1} (ΔE, BS1), while the Ir(III) complex with a similar phosphine ligand (2,4,6,7-tetraaza-1-phosphabicyclo[2.2.2]octane, **P2**, with a methylene spacer instead of an ethylene spacer) was also unstable, by 2.61 kcal mol^{-1} (ΔE, BS1). The last Ir(III) complex included in Fig. 7, with another, as yet unknown, phosphine (3-aza-1-phosphabicyclo[1.1.1]pentane, **P1**), was less stable by only 1.49 kcal mol^{-1} (ΔE, BS1).

Better success was encountered when combining these improved donor phosphines with modified cyclopentadienyl ligands capable of chelation similar to those explored with the carborane ligands (vide infra).

4.4. Chelation: modified carborane ligands

Several variants of the $C_2B_9H_{11}$ carborane ligand were examined with appropriately spaced ‘chelating arms’ $(-(CH_2)_xCH_3)$ that could then undergo the appropriate OA/RE to form a more stable complex. Using hydrocarbon substituted ligands in this fashion stabilizes the Ir(V) product for two reasons: (1) it reduces the steric repulsion for the high coordination number of the Ir(V) intermediate and (2) an entropic advantage results from the chelate effect because the OA reaction to form Ir(V) is intramolecular. Incorporating a propyl linker between the carborane cage and the Ir metal center created a complex, $7\text{-}\overline{C_3H_6\text{-}7,8\text{-}C_2B_9H_{10}Ir}^{V}PH_3(CH_3)_2H$, which lowered the difference by several kcal mol^{-1}, but the difference remained high at 11.4 kcal mol^{-1} (ΔE, BS1, for the less stable Ir(V) complex).

Ligand systems that incorporated the phosphorus donor in the bridging arm were also examined—our motivation for this type of chelating linker, which could reduce the overall sterics, came from an interesting complex identified by Greenwood and co-workers [37]. Several of these carborane ligands with the phosphine in the chelating arm were investigated ($7\text{-}PH_2C_2H_2\text{-}7,8\text{-}C_2B_9H_{10}^{2-}$: +18.2 kcal mol^{-1} ($\Delta E$, BS1); $7\text{-}PH_2CH_2\text{-}7,8\text{-}C_2B_9H_{10}^{2-}$: +17.3 kcal mol^{-1}; $7\text{-}PH_2SiH_2\text{-}7,8\text{-}C_2B_9H_{10}^{2-}$: +17.4 kcal mol^{-1}), but none were predicted to increase the probability for the observation of an Ir(V) intermediate analogue (see Fig. 4).

4.5. Chelation: modified cyclopentadienyl ligands

While the steric effect of the Cp ligand is less than the caged carborane, the seven-coordinate Ir(V) intermediate may still be crowded, and there is still an entropic advantage to a chelating ligand [38]. Several modified Cp-ligands were investigated. The Ir(V) intermediate created from the oxidative addition of a chelating propyl arm on the coordinated Cp ring $[\overline{C_3H_6CpIr}^{V}(PH_3)CH_3H]^+$ was found to be far less stable (+7.7 kcal mol^{-1}, ΔE, BS1) than the non-chelated Ir(III) reactant complex $[C_3H_7CpIr(PH_3)CH_3]^+$, but this same Ir(V) complex was slightly more stable (−0.82 kcal mol^{-1}, ΔE, BS1) than the Ir(III) complex

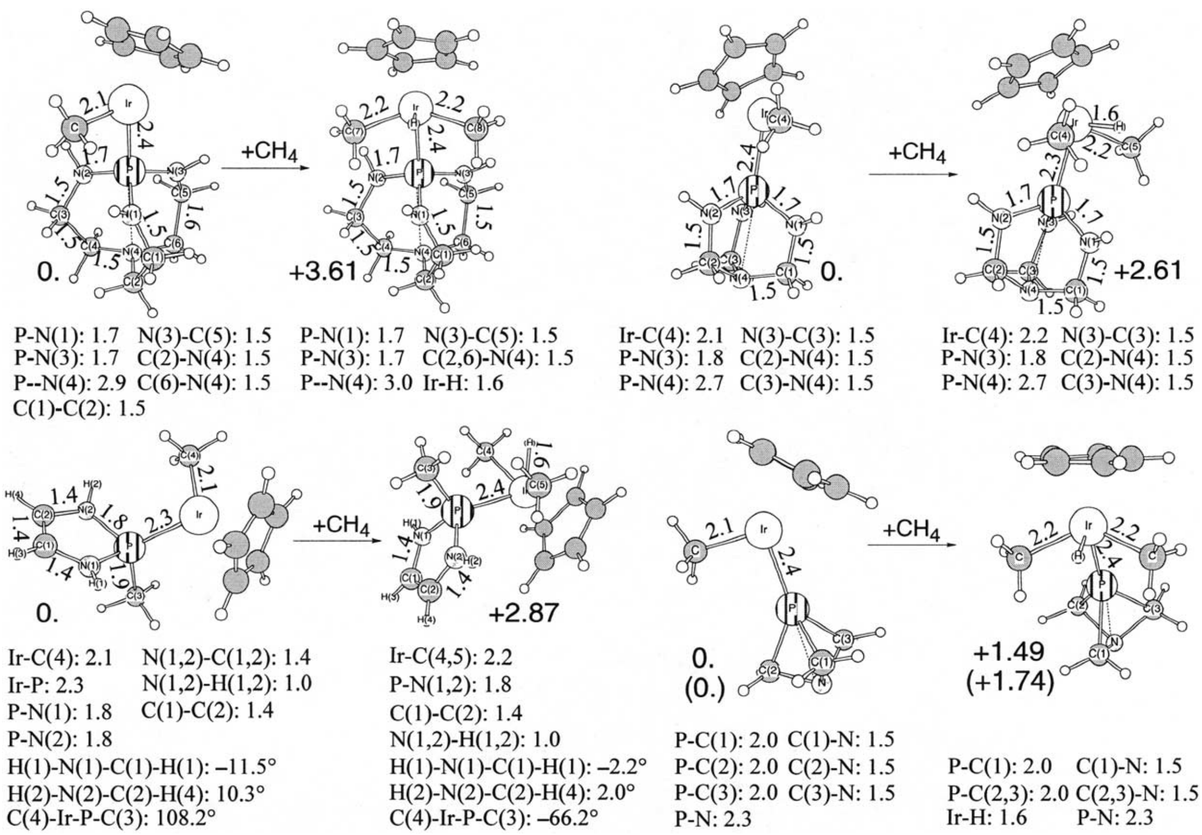


Fig. 7. The B3LYP/BS1 calculated stability (ΔE) for various cationic substituted phosphine Ir(V) model complexes for the oxidative addition of CH_4. The energy in parentheses is BS2//BS1. All distances are in Å, and energies are in kcal mol^{-1}.

created by the reductive elimination of CH_4, $[C_3H_6CpIr^{III}(PH_3)]^+$ (not pictured).

The analogous Ir(V) intermediate with trimethylphosphine (instead of a simple phosphine) was only slightly less stable (+0.19 kcal mol^{-1}, ΔE, BS1) than the Ir(III) elimination product (not pictured). Two of the improved donor phosphines (**P1** and **P4**) were tested with these chelating Cp Ir(V) complexes to determine their relative stability (see Fig. 8). Unfortunately, the reactants (unchelated Ir(III) starting complexes) are still more stable than all of the Ir(V) intermediate analogue complexes.

In an attempt to discover a more stable Ir–C bond for a linked group of the modified Cp ligand, the propyl group was made to be a propenyl group, $Cp(CH_2{-}CH{=}CH{-}Ir)$. The rationale behind this alteration followed from the fact that the C of a propylene group attached to the Ir would only have one α-hydrogen, and the orientation of this H could create a high barrier for reductive elimination. However, this modification did not produce an Ir(V) intermediate more stable (+3.54 kcal mol^{-1}, ΔE, BS1) than the reactants (not pictured). Another modification of this propyl ligand involved a $Cp(CH{=}CH{-}CH_2{-}Ir)$ chelating ligand. The OA of methane by this $Cp(CH{=}CH{-}CH_2)Ir^{III}(PH_3)^+$ complex also produced an Ir(V) intermediate slightly less stabile (+3.94 kcal mol^{-1}, ΔE, BS1) than the reactants (not pictured).

4.6. Ir(III) hydride reactants

When the methyl group of the Ir(III) starting material is replaced by a hydride, the energetics of the corresponding Ir(III)–Ir(V) species change drastically. This reactant, $[Cp^*Ir^{III}P(CH_3)_3H]^+$, has been synthesized, [1p] and calculations on the reaction with methane produces a methyl dihydride Ir(V) intermediate analogue that is more stable than the starting materials, ΔE −2.7 kcal mol^{-1} (BS1). In order to obtain more accurate relative energies, single point calculations were performed with basis set BS2. Again, the calculations indicated that the Ir(V) intermediate analogue is more stable with an energy difference of −2.4 kcal mol^{-1} (ΔE, BS2//BS1) (see Fig. 9) [39].

The same oxidative addition of methane with the analogous simple phosphine, plain Cp Ir(III) complex produces similar results: an Ir(V) complex, $[CpIr^{V}PH_3CH_3(H)_2]^+$, that is −8.9 kcal mol^{-1} (ΔE, BS1) more stable than the reactants, CH_4 and $(CpIr^{III}PH_3H)^+$ (see Fig. 9). Even though the conversion from a dihydride to a dihydrogen complex often has a low barrier, the total elimination of H_2 from

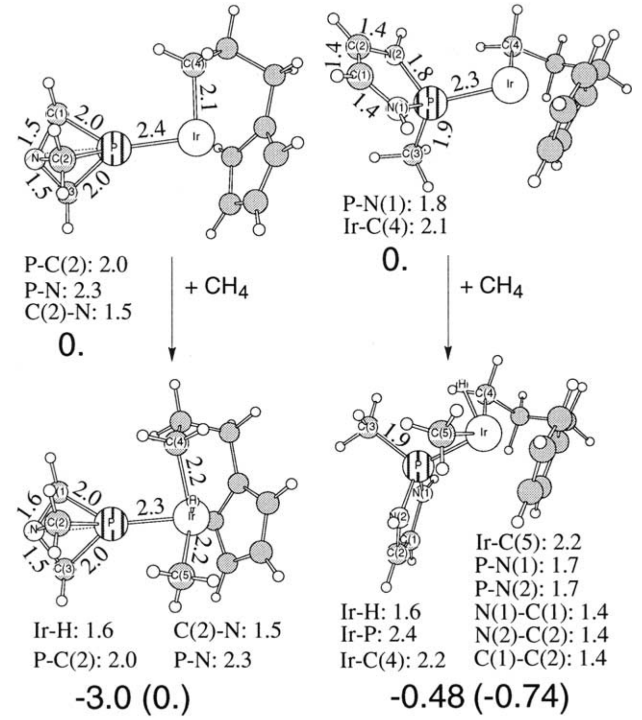


Fig. 8. The B3LYP/BS1 calculated stability (ΔE) for various cationic chelated Cp, substituted phosphine Ir(V) model complexes for the oxidative addition of CH_4. The energy in parentheses is BS2//BS1. All distances are in Å.

$[CpIr^{III}PH_3CH_3(H)_2]^+$ will not be favorable because the overall elimination is endothermic by 23.9 kcal mol^{-1} (ΔE, BS1). The reaction of dihydrogen with the Ir(III) hydride produces a very stable Ir(V) intermediate analogue, $[CpIr^{V}PH_3(H)_3]^+$ (exothermic by -34.6 kcal mol^{-1}, ΔE, BS1), and the stability of the trihydrido trimethyl phosphine complex, $[Cp^*Ir^{V}P(CH_3)_3(H)_3]^+$ has been noted experimentally [1p].

4.7. Metallocycloalkanes

Another conceivable route to an Ir(V) intermediate analogue would be to cyclize the metal center with an alkane by a reductive elimination of methane amid two successive oxidative additions of a single alkane, thus producing a metallocycloalkane. Such structures have been postulated in various organometallic reaction mechanisms and in some instances isolated [40]. This type of reaction also makes use of $T\Delta S$ to drive the reaction to the desired Ir(V) complex. The addition of propane, butane, pentane, and hexane to form, a metallocyclobutane, -cyclopentane, -cyclohexane, and -cycloheptane, respectively, have been considered. For each of these complexes after an oxidative addition of alkane and a reductive elimination of CH_4, the second oxidative addition of the coordinated alkyl group can produce two different isomers—one with the hydride 'inside' the metallocycle and the other has the hydride 'outside' the metallocycle. The relative stabilities (BS1) of the Ir(V) intermediates with the hydride 'outside' the metallocycle for the metallocyclobutane, -cyclopentane, -cyclohexane, and -cycloheptane complexes are $+2.68$, $+9.03$, -0.99, and $+15.0$ kcal mol^{-1}, respectively (not pictured). The relative stability (BS1) of the complexes with the hydride 'inside' the metallocycle are $+19.3$ and $+10.0$ kcal mol^{-1} for metallocyclobutane and -cyclopentane complexes, respectively (not pictured). Because the reaction of butane with $(CpIr^{III}PH_3CH_3)^+$ produced the 'outside' Ir(V) metallocyclopentane isomer slightly more stable than the Ir(III) precursor (-0.99 kcal mol^{-1}, ΔE, BS1), the corresponding $P(CH_3)_3$ metallocyclopentane complex (BS2//BS1) was tested. This $P(CH_3)_3$ Ir(V) intermediate analogue is more stable (-3.36 kcal mol^{-1}, ΔE, BS2//BS1) than the reactants, $[CpIr^{III}P(CH_3)_3CH_3]^+$ and butane (see Fig. 10). Unfortunately, the coordinatively unsaturated Ir(III) butyl complex produced by reductive elimination of one side of the metallocyclopentane is even more favorable (-5.8 kcal mol^{-1}, BS1), in part, because of a strong internal agostic bond from the CH_3 of the butyl group to Ir.

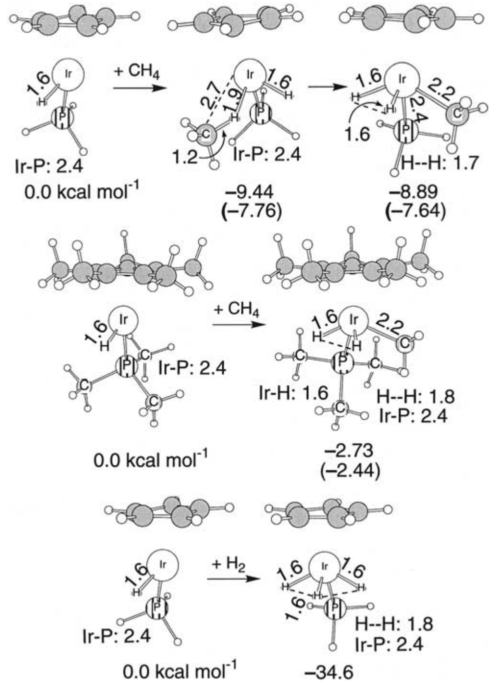


Fig. 9. The B3LYP/BS1 calculated stability (ΔE) for various cationic hydrido Ir(V) model complexes for the oxidative addition of H_2 and CH_4. The energies in parentheses are BS2//BS1. All distances are in Å, and energies are in kcal mol^{-1}.

A plausible synthetic route to an analogue of the more stable $[CpIr^{V}P(CH_3)_3HC_4H_8]^+$ product involves using a substituted butane, 2,3-tetramethylbutane. This methyl substitution produces a reactant that will not undergo a β-hydride elimination through a β-agostic pathway, the product here $[CpIr^{V}P(CH_3)_3(H)C_2H_4C_2(CH_3)_4]^+$ is stable by −2.6 kcal mol^{-1} (Δ*E*, BS2//BS1) when compared with the reactants (see Fig. 10). At best, this Ir(V) intermediate analogue could be observed in an experimental system under optimal conditions.

Another plausible synthetic route involves the hydride reactant analogues. For the hydride starting material, $(CpIr^{III}PH_3H)^+$, the reaction with cyclobutane and cyclopropane each produce two isomers of a Ir(V) intermediate analogue that are more stable. The metallocyclopentane product of the reaction between cyclobutane and $[CpIr^{III}P(CH_3)_3H]^+$ is also more stable (see Fig. 10). The addition of cyclopropane to $(CpIr^{III}PH_3CH_3)^+$ which ultimately forms an η^3-allyl complex has been treated elsewhere [41].

4.8. Covalent ligands

After consideration of various modified Cp and phosphine donor ligands (described above), our attention turned to systems with other reasonable ligands, particularly ligands with more covalent bonding character [42]. Also, the experimental existence of Ir(V) trihydride silyl and stannyl complexes [20c] suggested the use of similar ligands for the isolation of Ir(V) intermediate analogues.

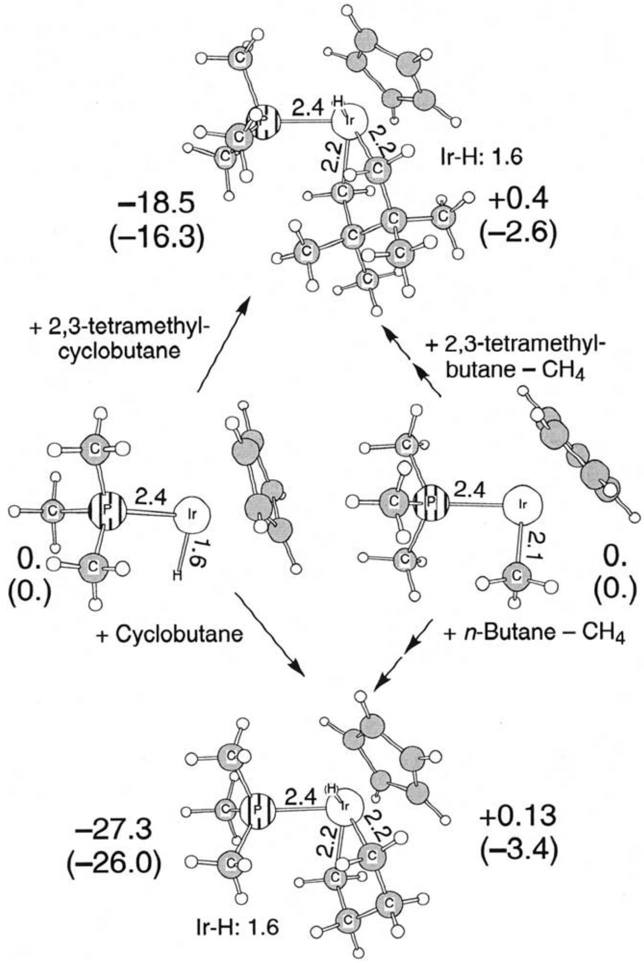


Fig. 10. The B3LYP/BS1 calculated stability (Δ*E*) for various cationic Ir(V) model complexes for the oxidative addition of non-substituted and substituted cyclobutane and *n*-butane. The energies in parentheses are BS2//BS1. All distances are in Å, and energies are in kcal mol^{-1}.

The same computational scheme was used for these neutral Ir(III) reactants and Ir(V) intermediate analogues as was used for the cationic phosphine complexes, except that BS6 basis set was used here for geometries and energies. Both of the model complex pairs with hydrogen substituted donors ($CpIr^{III}AH_3CH_3$–$CpIr^{V}$-$AH_3(CH_3)_2H$, where A = Si (**1**) or Sn (**6**)) yielded an Ir(V) intermediate analogue (**2** and **9**) that was more stable than the reactants by a few kcal mol^{-1}. Subsequently, the experimentally accessible trimethyl substituted donor complexes (**3** and **10**) ($CpIr^{V}$-$(A(CH_3)_3)(CH_3)_2H$, where A = Si or Sn) were tested. The two Ir(V) oxidative-addition intermediate analogue isomers from the trimethylsilyl pair (**4** and **5**) are very close in energy to the starting materials (+1.3 and +0.5 kcal mol^{-1}, BS6), and the two trimethylstannyl Ir(V) intermediate analogue isomers (**11** and **12**) were more stable with relative stabilities of −2.0 and −2.0 kcal mol^{-1} (Δ*E*, BS6, see Fig. 11 and Table 3). These pairs of Ir(V) isomers (**4/5** and **11/12**) are close in energy and differing only by the Cp orientation. Unfortunately, the inclusion of temperature effects, especially *T*Δ*S*, overcomes the calculated stability of the Ir(V) intermediate analogues; the calculated relative free energies (ΔG°) favor the separated reactants.

Based on our experience earlier in this paper with the phosphine hydride complexes $[CpIr^{III}(PR_3)(H)^+]$, we can conclude that the reaction of CH_4 with silyl and stannyl hydride analogues, like $CpIr^{III}(AR_3)H$, will produce stable Ir(V) intermediates, like $CpIr^{V}$-$(AR_3)(CH_3)(H)_2$. However, these silyl and stannyl dihydride complexes do not meet our goal of finding a monohydride Ir(V) complex; therefore, we have not performed any calculations on these hydride analogues, $CpIr^{III}(AR_3)H$, or their Ir(V) partners.

Another consideration for a silyl type ligand is the replacement of the methyl group in the original cationic complex $[(CpIr^{III}PR_3CH_3)^+]$, producing the analogous $[(CpIr^{III}PR_3SiR'_3)^+]$ silyl reactants (See Fig. 12 and Table 3). This type of silyl reactant (which has been postulated as an intermediate by Bergman and coworkers, [1k] vide infra) can be produced from the reaction of the original methyl iridium complex with a silane. The Si–H activation of silane by both the simple phosphine (**13**) and the trimethylphosphine (**23**) complexes ($[CpIrPR_3CH_3]^+$ where R = H, CH_3) affords methylsilyl Ir(V) intermediates complexes $[CpIrPR_3SiH_3CH_3H]^+$ (**17** and **24**) that are stable with respect to silane elimination, but not alkane elimination [43]. Furthermore, two different pathways for producing these methylsilyl intermediate analogues exist, one

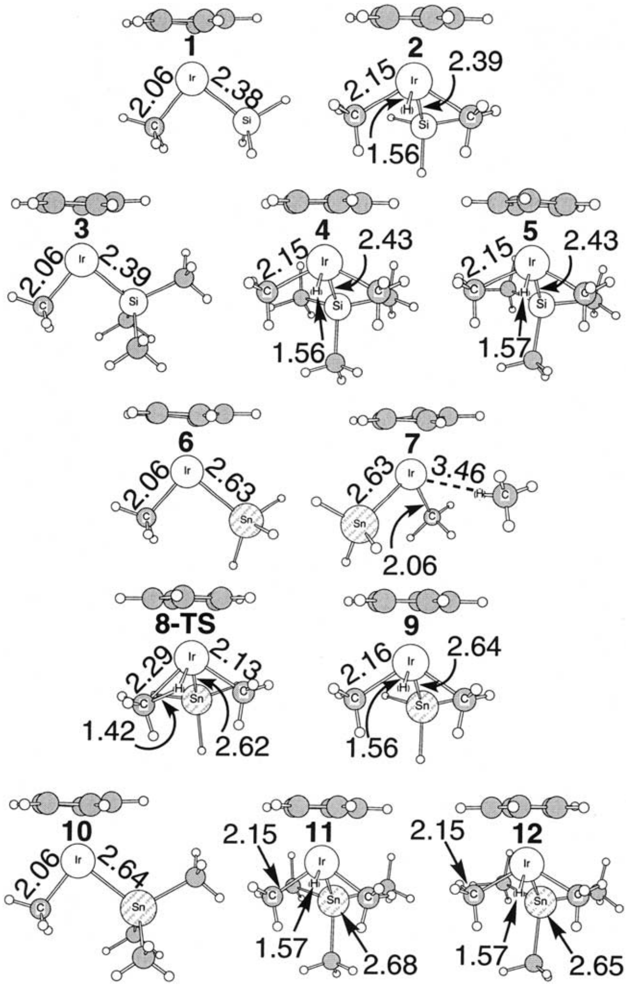


Fig. 11. The B3LYP/BS6 calculated neutral silyl and stannyl Ir(V) model complexes for the oxidative addition of CH_4. All distances are in Å. See Table 3 for relative energies.

reacting $(CpIrPR_3SiH_3)^+$ with CH_4 and the other reacting $(CpIrPR_3CH_3)^+$ with SiH_4. The methylsilyl iridium(V) intermediate analogue, $(CpIrPR_3CH_3SiH_3H)^+$, is much more stable than its dimethyl iridium hydride counterpart $[CpIr^{V}PR_3(CH_3)_2H^+]$. This difference in relative stability is attributable to the C–H bond strength versus the Si–H bond strength, which is about 15 kcal mol^{-1} weaker [23].

Unfortunately for our purposes, the subsequent loss of methane from the methylsilyl complex yields the previously mentioned more stable silyl reactant, $[CpIr^{III}PR_3SiH_3]^+$ (**13** and **23**). After this loss of methane, 1,2 hydride migration (**21-TS** and **26-TS**) produces very stable iridium hydride silylene complexes (**22** and **27**), which have been observed experimentally [1k]. However, our calculations indicate that a second equivalent of silane (SiH_4) reacting with $[CpIr^{III}PR_3SiH_3]^+$ could produce disilyl Ir(V) hydrides (**20** and **25**) that are more stable than the silylene complexes. In spite of this reaction's reduction in molecularity, the ΔG is still favorable. Bergman and coworkers have considered Si–H activation of various silanes by $(Cp^*Ir^{III}P(CH_3)_3CH_3)^+$ and postulated the intermediacy of a $[Cp^*Ir^{III}P(CH_3)_3Si(CH_3)_3]^+$ complex in the production of the β-H transfer ($[Cp^*IrPMe_3(SiMe_2CH_2)H]^+$) and 1, 2 migration products ($[Cp^*IrPMe_3(=SiMe_2)CH_3]^+$) [44]. Under appropriate conditions, Bergman's postulated intermediate silyl complex might react with another equivalent of silane, producing the disilyl Ir(V) intermediate analogue complex, $[Cp^RIr^VPR_3(SiR_3)_2(H)]^+$ (our **20** and **25**). Our calculations indicate that the disilyl complexes (**20** and **25**) are 3–5 kcal mol^{-1} ($-\Delta G$, BS5) more stable than the silylene hydride complexes and separated SiH_4. In comparison to Bergman's original methyl complex $[CpIr^{III}PR_3CH_3]^+$, the addition of two equivalents of SiH_4 produces very stable Ir(V) complexes, **20** and **25** $[CpIr^VPR_3(SiH_3)_2H]^+$, which with release of CH_4 are 36–38 kcal mol^{-1} ($-\Delta G$, BS5) more stable than the reactants.

5. Conclusions

Density functional methods have been applied to a variety of ligand systems (various multihapto ligands (η^x-L = Cp^R, Tp, and carborane), L = alternative phosphines, L′ = anionic silanes (SiR_3^-) and stannanes (SnR_3^-), and chelating ligands) as well as the reaction of different alkanes with the cationic and neutral $Ir^{III}\eta^xLL'(CH_3/H)$ to predict the corresponding Ir(V) intermediate analogue. Finding an alternative ligand set that allows 'trapping' of an Ir(V) intermediate from the C–H bond activation of alkanes by the cationic Ir(III) complex has proved to be more elusive than we originally expected, but several encouraging possibilities have been predicted. The calculated stability of the Ir(V) 'intermediate' lead to a reasonable expectation that new intermediate analogues could be observed spectroscopically, and in some instances, possibly isolated.

Despite its dianionic charge, the η^5-carborane systems did not stabilize the Ir(V) metallocarborane complex. Although the problems were partly steric because of the angle required at the pentagonal face, the dianionic charge of the ligand is delocalized so that it is not a particularly strong donor. Metallocyclic Cp systems (substituted Cp with arms linked to the metal center) produced an Ir(V) intermediate analogue lower in energy only when compared with the elimination of methane, not elimination of the linked arm itself (which reproduces the starting material).

Improved stability of an Ir(V) intermediate analogue has been found for the reaction of CH_4 with the hydride Ir(III) starting material, $[Cp^*Ir^{III}P(CH_3)_3H]^+$. The predicted stability of the Ir(V) trihydride complex, $[CpIr^VPH_3(H)_3]^+$, when compared with the Ir(III)

Table 3
The reaction of various cationic and neutral Ir(III) complexes with CH_4 and SiH_4

	Charge/basis set	ΔE (kcal mol^{-1})	ΔE_o (kcal mol^{-1})	$\Delta H^{\circ,\ddagger}$ (kcal mol^{-1})	$\Delta G^{\circ,\ddagger}$ (kcal mol^{-1})
1+CH_4	0/BS6	0.0	0.0	0.0	0.0
2 (intermediate analogue)	0/BS6	−1.0	+1.9	+0.5	+12.2
3+CH_4	0/BS6	0.0	0.0	0.0	0.0
4 (intermediate)	0/BS6	+1.3	+3.6	+1.4	+16.4
5 (intermediate)	0/BS6	+0.5	+3.3	+2.0	+14.8
6+CH_4	0/BS6	0.0	0.0	0.0	0.0
7 (σ-CH_4 complex)	0/BS6	−0.3	+0.2	+0.4	+6.9
8-TS (oxidative addition TS)	0/BS6	+8.6	+9.3	+8.1	+20.6
9 (intermediate analogue)	0/BS6	−1.7	+0.8	−0.49	+12.2
10+CH_4	0/BS6	0.0	0.0	0.0	0.0
11 (intermediate analogue)	0/BS6	−2.0	+0.4	−1.4	+12.3
12 (intermediate analogue)	0/BS6	−2.0	+0.6	−0.7	+12.7
13+CH_4	+1/BS5	0.0	0.0	0.0	0.0
14 (σ-CH_4 complex)	+1/BS5	−8.7	−6.8	−7.5	+3.3
15 (σ-CH_4 complex)	+1/BS5	−8.8	−7.1	−7.6	+2.8
16-TS (oxidative addition TS)	+1/BS5	−3.2	−2.7	−3.8	+7.6
17 (intermediate analogue)	+1/BS5	−10.9	−8.6	−10.0	+2.4
18 (intermediate analogue)	+1/BS5	−10.2	−8.1	−9.5	+2.9
19 (intermediate analogue)	+1/BS5	−6.8	−4.4	−5.8	+6.7
23+CH_4	+1/BS5	0.0	0.0	0.0	0.0
24 (intermediate analogue)	+1/BS5	−8.5	+6.4	−4.6	+4.5
13	+1/BS5	0.0	0.0	0.0	0.0
21-TS (hydride transfer TS)	+1/BS5	+0.4	0.0	−0.4	+0.5
22 (silylene hydride)	+1/BS5	−21.0	−20.4	−20.8	−19.7
13+SiH_4	+1/BS5	0.0	0.0	0.0	0.0
22+SiH_4	+1/BS5	−21.1	−20.4	−19.7	−20.0
20 (intermediate analogue)	+1/BS5	−38.0	−35.1	−35.8	−24.3
23	+1/BS5	0.0	0.0	0.0	0.0
26-TS (hydride transfer TS)	+1/BS5	+0.7	+0.2	−0.2	+0.6
27 (silylene hydride)	+1/BS5	−19.8	−19.2	−19.6	−18.5
23+SiH_4	+1/BS5	0.0	0.0	0.0	0.0
27+SiH_4	+1/BS5	−19.7	−19.2	−19.7	−17.6
25 (intermediate analogue)	+1/BS5	−35.1	−32.2	−33.1	−21.4
17+SiH_4	+1/BS5	0.0	0.0	0.0	0.0
20+CH_4	+1/BS5	−27.2	−26.6	−26.0	−27.1
24+SiH_4	+1/BS5	0.0	0.0	0.0	0.0
25+CH_4	+1/BS5	−26.9	−25.8	−25.9	−25.9
$[CpIrPH_3CH_3]^+$ +SiH_4	+1/BS5	0.0	0.0	0.0	0.0
17 (intermediate analogue)	+1/BS5	−27.1	−23.3	−24.2	−11.3
$[CpIrPMe_3CH_3]^+$ +SiH_4	+1/BS5	0.0	0.0	0.0	0.0
24 (intermediate analogue)	+1/BS5	−25.0	−21.3	−22.3	−10.1
$[CpIrPMe_3(CH_3)_2(H)]^+$ +SiH_4	+1/BS5	0.0	0.0	0.0	0.0
25+CH_4	+1/BS5	−26.9	−25.8	−25.4	−25.9
$[CpIrPH_3CH_3]^+$ +2 SiH_4	+1/BS5	0.0	0.0	0.0	0.0
20+CH_4	+1/BS5	−54.3	−49.9	−50.2	−38.4
$[CpIrPMe_3CH_3]^+$ +2 SiH_4	+1/BS5	0.0	0.0	0.0	0.0
25+CH_4	+1/BS5	−51.9	−47.2	−47.6	−36.1

reactant and H_2 (see Fig. 9) is experimentally corroborated by the previous isolation of $Cp^*Ir^{III}PMe_3(H)_3$.

For hydrocarbon ligands with conventional Cp and phosphine Ir complexes, our most conclusive results came from considering metallocycloalkane structures formed by two successive oxidative additions (with an intervening reductive elimination of CH_4) of substituted alkanes such as 2,3-tetramethylbutane. This alkane reacting with the methyl-substituted phosphine, cyclopentadienyl cationic Ir(III) starting material produced a

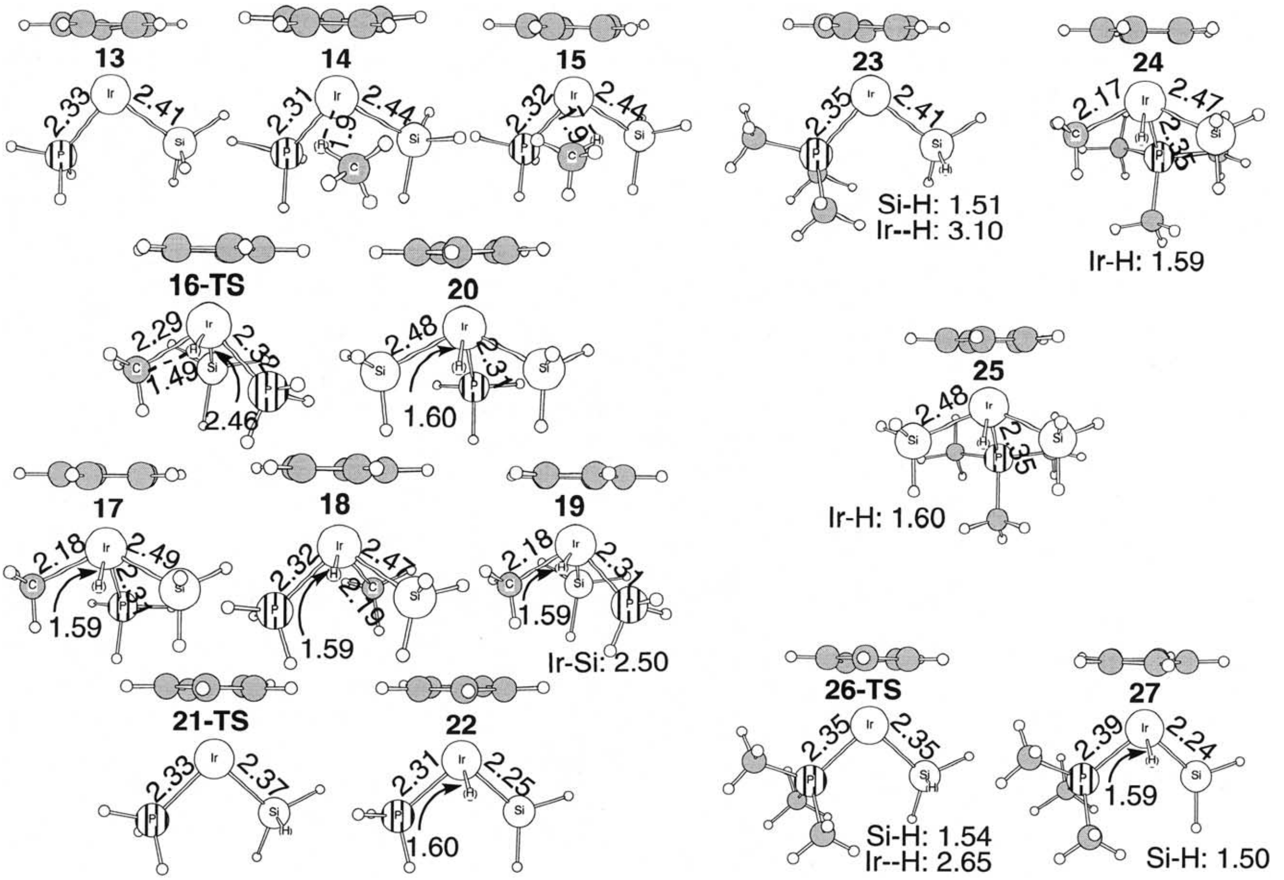


Fig. 12. The B3LYP/BS5 calculated cationic silyl and disilyl Ir(V) model complexes for the oxidative addition of CH_4 and SiH_4. All distances are in Å. See Table 3 for relative energies.

hydridometallocyclopentane Ir(V) complex, $[CpIr^{V}\text{-}P(CH_3)_3HC_2H_4C_2(CH_3)_4]^+$, that is slightly more stable than the reactants (see Fig. 10), but not stable with respect to reductive elimination of one arm from the metallocycle.

Although replacing the trimethyl phosphine donor ligands with alternative phosphines was not very successful in stabilizing Ir(V) intermediate analogues, when more covalent inorganic ligands, specifically silyl and stannyl ligands (AR_3^-, $R = H$, CH_3) were used, the neutral Ir(V) complexes produced are slightly more stable than the Ir(III) reactant and alkane ($\Delta E < 0$, but $\Delta G > 0$). These neutral reactant Ir(III) complexes could possibly be synthesized, and the Ir(V) complexes might be spectroscopically observable at low temperature (see Fig. 11).

The replacement of the iridium bound methyl group with a silyl group produces a cationic unsaturated 16 e^- species, $[CpIr^{III}PR_3SiH_3]^+$ where $R = H$, CH_3, that can react with methane to form a methylsilyl Ir(V) intermediate analogue $[CpIr^{III}PR_3CH_3SiH_3H]^+$, which, driven by $T\Delta S$, unfortunately decomposes and re-releases methane. Reacting $[CpIr^{III}PR_3SiH_3]^+$ with silane forms a disilyl Ir(V) intermediate analogue, $[CpIr^{V}PR_3(SiH_3)_2H]^+$, which is more stable than the reactants, even considering entropy effects.

Our calculations indicate that the aforementioned cationic disilyl complex can be obtained from a second pathway in two steps: (1) Si–H bond activation of $HSiR_3$ by the conventional reactant, $[CpIr^{III}PR_3CH_3]^+$, followed by CH_4 loss, which is driven by $T\Delta S$ and (2) Si–H bond activation of a second equivalent of $HSiR_3$ by $[CpIr^{III}PR_3SiR_3]^+$ to form the disilyl Ir(V) intermediate analogue $[CpIr^{V}PR_3(SiR_3)_2H]^+$ (see Fig. 12).

Acknowledgements

We would like to thank the National Science Foundation (Grant No. CHE 98-00184) and the Welch Foundation (Grant No. A-648) for financial support.

References

[1] (a) A.E. Shilov, G.B. Shulp'in, Chem. Rev. 97 (1997) 2879;
(b) Y.-X. Chen, T.J. Marks, Organometallics 16 (1997) 3649;
(c) R.H. Crabtree, Chem. Rev. 95 (1995) 987; 2599.;
(d) R.H. Crabtree, Chem. Rev. 85 (1985) 245;

(e) S.R. Klei, T.D. Tilley, R.G. Bergman, J. Am. Chem. Soc. 122 (2000) 1816;
(f) D.D. Wick, T.O. Northcutt, R.J. Lachicotte, W.D. Jones, Organometallics 17 (1998) 4484;
(g) K. McNeill, A. Richard, R.A. Andersen, R.G. Bergman, J. Am. Chem. Soc. 119 (1997) 11244;
(h) P.J. Alaimo, B.A. Arndtsen, R.G. Bergman, J. Am. Chem. Soc. 119 (1997) 5269;
(i) H.F. Luecke, B.A. Arndtsen, P. Burger, R.G. Bergman, J. Am. Chem. Soc. 118 (1996) 2517;
(j) B.A. Arndtsen, R.G. Bergman, Science 270 (1995) 1970;
(k) P. Burger, R.G. Bergman, J. Am. Chem. Soc. 115 (1993) 10462;
(l) W.D. McGhee, R.G. Bergman, J. Am. Chem. Soc. 110 (1988) 4246;
(m) D.P. Klein, J.C. Hayes, R.G. Bergman, J. Am. Chem. Soc. 110 (1988) 3704;
(n) R.A. Periana, R.G. Bergman, J. Am. Chem. Soc. 108 (1986) 7346;
(o) R.A. Periana, R.G. Bergman, J. Am. Chem. Soc. 108 (1986) 7332;
(p) T.M. Gilbert, R.G. Bergman, J. Am. Chem. Soc. 107 (1985) 3502;
(q) W.D. McGhee, R.G. Bergman, J. Am. Chem. Soc. 107 (1985) 3388;
(r) P.L. Watson, G.W. Parshall, Acc. Chem. Res. 18 (1985) 51;
(s) R.A. Periana, R.G. Bergman, J. Am. Chem. Soc. 106 (1984) 7272;
(t) W.D. Jones, F.J. Feher, J. Am. Chem. Soc. 106 (1984) 1650;
(u) R.A. Periana, R.G. Bergman, Organometallics 3 (1984) 508;
(v) A.H. Janowicz, R.G. Bergman, J. Am. Chem. Soc. 105 (1983) 3929;
(w) W.D. Jones, F.J. Feher, Organometallics 2 (1983) 562;
(x) P.L. Watson, J. Am. Chem. Soc. 105 (1983) 6491;
(y) A.H. Janowicz, R.G. Bergman, J. Am. Chem. Soc. 104 (1982) 352;
(z) J.K. Hoyano, W.A.G. Graham, J. Am. Chem. Soc. 104 (1982) 3722;
(aa) R.H. Crabtree, M.F. Mellea, J.M. Minelsie, J.M. Quick, J. Am. Chem. Soc. 104 (1982) 107;
(bb) W.D. Jones, F.J. Feher, J. Am. Chem.Soc. 104 (1982) 4240.

[2] (a) S.Q. Niu, M.B. Hall, Chem. Rev. 100 (2000) 353;
(b) M.-D. Su, S.-Y. Chu, J. Am. Chem. Soc. 121 (1999) 1045;
(c) S. Sakaki, S. Kai, M. Sugimoto, Organometallics 18 (1999) 4825;
(d) A.L. Sargent, E.P. Titus, Organometallics 17 (1998) 65;
(e) M.-D. Su, S.-Y. Chu, J. Am. Chem. Soc. 119 (1997) 5373;
(f) Y.Z. Han, L.Q. Deng, T. Ziegler, J. Am. Chem. Soc. 119 (1997) 5939;
(g) D.L. Strout, S. Zaric, S. Niu, M.B. Hall, J. Am. Chem. Soc. 118 (1996) 6068;
(h) S.Q. Niu, M.B. Hall, J. Am. Chem. Soc. 121 (1999) 3992;
(i) L. Deng, T. Ziegler, Organometallics 15 (1996) 3011;
(j) J.J. Low, W.A. Goddard, J. Am. Chem. Soc. 108 (1986) 6115;
(k) J.J. Low, W.A. Goddard, Organometallics 5 (1986) 609;
(l) J.J. Low, W.A. Goddard, J. Am. Chem. Soc. 106 (1984) 8323;
(m) J. Song, M.B. Hall, Organometallics 12 (1993) 3118.

[3] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, A.C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98, Revision A.6, A.7, and A.9, Gaussian, Incorporation, Pittsburgh, PA, 1998.

[4] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[5] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.

[6] R.G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.

[7] W.J. Hehre, L. Radom, P.V.R. Schleyer, J.A. Pople, Ab initio Molecular Orbital Theory, Wiley, New York, 1986, p. 96.

[8] A.D. Becke, Phys. Rev. A 38 (1988) 3098.

[9] (a) J.P. Perdew, Phys. Rev. B 33 (1986) 8822;
(b) J.P. Perdew, Phys. Rev. B 33 (1986) 7406.

[10] (a) E.J. Baerends, D.E. Ellis, P. Ros, Chem. Phys. 2 (1973) 41;
(b) E.J. Baerends, P. Ros, Chem. Phys. 2 (1973) 52;
(c) L. Versluis, T. Ziegler, J. Chem. Phys. 88 (1988) 322;
(d) G. te Velde, E.J. Baerends, J. Comput. Phys. 99 (1992) 84;
(e) C. Fonseca Guerra, J.G. Snijders, G. te Velde, E.J. Baerends, Theor. Chem. Acc. 99 (1998) 391;
(f) E.J. Baerends, A. Bérces, C. Bo, P.M. Boerrigter, L. Cavallo, L. Deng, R.M. Dickson, D.E. Ellis, L. Fan, T.H. Fischer, C. Fonseca Guerra, S.J.A. van Gisbergen, J.A. Groeneveld, O.V. Gritsenko, F.E. Harris, P. van den Hoek, H. Jacobsen, G. van Kessel, F. Koostra, E. van Lenthe, V.P. Osinga, P.H.T. Philipsen, D. Post, C.C. Pye, W. Ravenek, P. Ros, P.R.T. Schipper, G. Schreckenbach, J.G. Snijders, M. Sola, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, O. Visser, E. van Wezenbeek, G. Wiesenekker, S.K. Wolff, T.K. Woo, T. Ziegler, ADF 2000.02; Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, 2000.

[11] S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200.

[12] (a) C. Chang, M. Pellisier, P. Durand, Phys. Ser. 34 (1986) 394;
(b) E. van Lenthe, E.J. Baerends, J.G. Snijders, J. Chem. Phys. 99 (1993) 4597;
(c) E. van Lenthe, E.J. Baerends, J.G. Snijders, J. Chem. Phys. 101 (1994) 9783;
(d) E. van Lenthe, R. van Leeuwen, E.J. Baerends, Int. J. Quantum Chem. 57 (1996) 281;
(e) S.K. Wolff, T. Ziegler, E. van Lenthe, E.J. Baerends, J. Chem. Phys. 110 (1999) 7689.

[13] (a) P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270;
(b) W.R. Wadt, P.J. Hay, J. Chem. Phys. 82 (1985) 284.

[14] M. Couty, M.B. Hall, J. Comp. Chem. 17 (1996) 1359.

[15] T.H. Dunning, P.J. Hay, in: H.F. Schaefer, III (Ed.), Modern Theoretical Chemistry, Plenum Press, New York, 1976, pp. 1–28.

[16] (a) A.W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K.F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, Chem. Phys. Lett. 208 (1993) 111;
(b) A. Höllwarth, M. Böhme, S. Dapprich, A.W. Ehlers, A. Gobbi, V. Jonas, K.F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, Chem. Phys. Lett. 208 (1993) 237; 224 (1994) 603.

[17] T.H. Dunning, J. Chem. Phys. 90 (1989) 1007.

[18] E.R. Davidson, Chem. Phys. Lett. 260 (1996) 514.

[19] P.J. Alaimo, R.G. Bergman, Organometallics 18 (1999) 2707 (and references therein).

[20] (a) J.S. Ricci, T.F. Koetzle, M.-J. Fernandez, P.M. Maitlis, J.C. Green, J. Organomet. Chem. 299 (1986) 383;
(b) L. Garlaschelli, S.I. Khan, R. Bau, G. Longoni, T.F. Koetzle, J. Am. Chem. Soc. 107 (1985) 7212;
(c) T.M. Gilbert, F.J. Hollander, R.G. Bergman, J. Am. Chem. Soc. 107 (1985) 3508;
(d) K. Isobe, A.V.D. Miguel, A. Nutton, P.M. Maitlis, J. Chem. Soc. Dalton (1984) 929.

[21] (a) $Cp^*Ir(H)_4$: T.M. Gilbert, R.G. Bergman, Organometallics 2 (1983) 1458.;

(b) Cp^*IrMe_4: K. Isobe, P.M. Bailey, P.M. Maitlis, J. Chem. Soc. Chem. Commun. (1981) 808.

[22] There are two dimethyldihydride Ir(V) isomers—one *cis* dihydride, one *trans*—the *cis* isomer is lower in energy.

[23] The C–H bond strength of the first carbon hydrogen bond in CH_4 is 104.8 kcal mol^{-1}, while the analogous Si–H bond in SiH_4 is 14.5 kcal lower at 90.3 kcal mol^{-1}. D.R. Lide (Ed.), 71st CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 1990, pp. 9–87, 9–88.

[24] (a) H.F. Luecke, R.G. Bergman, J. Am. Chem. Soc. 119 (1997) 11538;
(b) L. Andreucci, P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti, V. Adovasio, M. Nardelli, J. Chem. Soc. Dalton Trans. (1986) 803.

[25] The terminal methyl orthometallated phosphine complex has been previously described: C. Hinderling, D. Feichtinger, D.A. Plattner, P. Chen, J. Am. Chem. Soc. 119 (1997) 10793.

[26] (a) F. Teixidor, M.A. Flores, C. Viñas, R. Sillanpää, R. Kivekäs, J. Am. Chem. Soc. 122 (2000) 1963;
(b) C. Viñas, R. Núñez, F. Teixidor, R. Sillanpää, R. Kivekäs, Organometallics 18 (1999) 4712;
(c) D.D. Ellis, P.A. Jelliss, F.G.A. Stone, Organometallics 18 (1999) 4982;
(d) I.T. Chizhevsky, I.A. Lobanova, P.V. Petrovskii, V.I. Bregadze, F.M. Dolgushin, A.I. Yanovsky, Y.T. Struchkov, A.L. Chistyakov, I.V. Stankevich, C.B. Knobler, M.F. Hawthorne, Organometallics 18 (1999) 726.

[27] (a) R.N. Grimes, J. Am. Chem. Soc. 93 (1971) 261;
(b) J.P. Brennan, R.N. Grimes, R. Schaeffer, L.G. Sneddon, Inorg. Chem. 12 (1973) 2266;
(c) D.A. Franz, V.R. Miller, R.N. Grimes, J. Am. Chem. Soc. 94 (1972) 412;
(d) K.E. Stockman, E.A. Boring, M. Sabat, M.G. Finn, R.N. Grimes, Organometallics 19 (2000) 2200.

[28] (a) M.W. Haenel, S. Oevers, K. Angermund, W.C. Kaska, H.J. Fan, M.B. Hall, Angew. Chem. Int. Ed. 40 (2001) 3596;
(b) S. Niu, M.B. Hall, J. Am. Chem. Soc. 121 (1999) 3992;
(c) S. Li, M.B. Hall, Organometallics 20 (2001) 2153–3210;
(d) M. Kanzelberger, B. Singh, M. Czerw, K. Krogh-Jespersen, A.S. Goldman, J. Am. Chem. Soc. 122 (2000) 11017;
(e) M. Krogh-Jespersen, M. Czerw, K. Kanzelberger, A.S. Goldman, J. Chem. Inf. Comput. Sci. 41 (2001) 56.

[29] S.E. Bromberg, H. Yang, M.C. Asplund, T. Lian, B.K. McNamara, K.T. Kotz, J.S. Yeston, M. Wilkens, H. Frei, R.G. Bergman, C.B. Harris, Science 278 (1997) 260.

[30] S. Zaric, M.B. Hall, J. Phys. Chem. A 102 (1998) 1963.

[31] R. Jiménez-Cataño, S. Niu, M.B. Hall, Organometallics 16 (1997) 1962.

[32] D.M. Tellers, S.J. Skoog, R.G. Bergman, T.B. Gunnoe, W.D. Harman, Organometallics 19 (2000) 2428.

[33] C.E. Webster, D.A. Singleton, M.J. Szymanski, M.B. Hall, C.Y. Zhao, G.C. Jia, Z.Y. Lin, J. Am. Chem. Soc. 123 (2001) 9822.

[34] L. Perrin, E. Clot, O. Eisenstein, J. Loch, R.H. Crabtree, Inorg. Chem. 40 (2001) 5806.

[35] Simple phosphine oxide was also tested as a ligand (with BS2), but it did not improve the results—the Ir(V) intermediate analogue was 10.9 kcal mol^{-1} above the starting materials. Trimethylphosphite was also tested with BS1 (+1.9 kcal mol^{-1}) and BS2//BS1 (+4.6 kcal mol^{-1}), and it did not improve the results either.

[36] This ligand has been previously considered theoretically. (a) R.R. Sauers, Tetrahedron 53 (1997) 2357.(b) D. Gudat, A. Haghverdi, H. Hupfer, M. Nieger, Chem. Eur. J. 6 (2000) 3414.

[37] J. Bould, N.N. Greenwood, J.D. Kennedy, W.S. McDonald, J. Chem. Soc. Chem. Commun. (1982) 465.

[38] One such modified Cp ligand system (with the phosphine connected to the Cp ring by a substituted ethyl linkage) has been reported by Mobley and Bergman. T.A. Mobley, R.G. Bergman, J. Am. Chem. Soc. 120 (1998) 3253.

[39] Stable Ir(V) intermediate analogues are also formed from the reaction of cycloalkanes with the hydride analogue starting material by carbon–carbon bond activation forming metallocycloalkanes.

[40] (a) B.C. Gates, Catalytic Chemistry, Wiley, New York, 1992, p. 102;
(b) R.H. Crabtree, The Organometallic Chemistry of the Transition Metals (and references cited therein), Wiley, New York, 1988, pp. 267–275;
(c) J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry (and references cited therein), University Science Books, Mill Valley, CA, 1987, pp. 460–495;
(d) F.U. Axe, J.W. Andzelm, J. Am. Chem. Soc. 121 (1999) 5396;
(e) A.K. Rappé, W.A. Goddard, J. Am. Chem. Soc. 104 (1982) 297;
(f) M. Ephritikhine, M.L.H. Green, R.E. MacKenzie, J. Chem. Soc. Chem. Commun. (1976) 619.

[41] C.E. Webster, M.B. Hall, Organometallics 20 (2001) 5606.

[42] Replacement of the coordinated phosphine with a cyano group produced a neutral Ir(V) complex that is 5.6 kcal mol^{-1} (ΔE, BS1) less stable than the Ir(III) reactant and methane.

[43] Golden, Andersen, and Bergman synthesized $[Cp^*Ir^{V}PMe_3SiMe_3(H)_2]^+$ and, in agreement with the current calculations, were unable to isolate $[Cp^*Ir^{V}PMe_3SiMe_3(R)(H)]^+$ from direct activation of alkane. J.T. Golden, R.A. Andersen, R.G. Bergman, J. Am. Chem. Soc. 123 (2001) 5837. Klei, Tilley, and Bergman have synthesized $[Cp^*Ir^{V}PMe_3SiPh_3(H)_2]^+$ from an alternative route [44c].

[44] (a) S.R. Klei, T.D. Tilley, R.G. Bergman, Organometallics 20 (2001) 3220;
(b) S.R. Klei, T.D. Tilley, R.G. Bergman, Organometallics 21 (2002) 3376;
(c) S.R. Klei, T.D. Tilley, R.G. Bergman, Organometallics 21 (2002) 4648.