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The quest for stable σ -methane complexes: computational and experimental studies[†]

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A series of cationic late transition metal pincer complexes with tridentate, neutral pincer ligands and their corresponding metal methyl complexes have been investigated by density functional theory (DFT). The key calculated quantities of interest for each metal-ligand pair were the energy of the metal methyl hydride relative to the metal σ -methane complex and the methane dissociation enthalpy and free energy. A few promising pincer ligand frameworks emerged as candidates for the syntheses of σ -methane complexes with enhanced thermal stability. The calculational predictions have been tested experimentally, and new iridium and rhodium complexes of a tridentate pincer ligand, 2,6-bis(di-tert-butylphosphinito)-3,5-diphenylpyrazine (N-PONOP) have been prepared as well as a cationic palladium methyl complex with 2.6-bis(di-tert-butylphosphinito)pyridine (PONOP) and subjected to several protonation experiments. Protonation of the (N-PONOP)Ir methyl complex yielded the corresponding five-coordinate iridium(III) methyl hydride cation. Kinetic studies of the C-H bond coupling and reductive elimination have been carried out. Line broadening NMR spectroscopic techniques have been established a barrier of 7.9(1) kcal mol⁻¹ for H–C_{alkvl} bond coupling in the iridium(III) methyl hydride (-100 °C). A protonation of the iridium pincer complexes at the uncoordinated pyrazine-N atom was not achieved.

Introduction

Carbon-hydrogen bond activation processes are not only reactions of fundamental importance but also have wide potential utility for conversion of alkane feedstocks to value-added chemical intermediates and in catalytic synthesis of fine chemicals and pharmaceuticals.¹⁻⁸ While many researchers concentrate their efforts on the development of practical organometallic oxidation catalysts,9-14 the fundamental aspects of the C-H bond activation are still not fully understood. For instance, it is now generally accepted that σ -alkane complexes are key intermediates in C-H activation reactions whether involving oxidative addition (and the reverse reductive elimination) reaction, 15,16 metathesis processes especially via σ -CAM,¹⁷ protonation of metal alkyls,^{18,19} simple ligand substitution processes^{15,20} or alkane adsorption on metal surfaces.²¹ Such σ -complexes have been detected and investigated by low-temperature experiments. Organometallic alkane complexes were observed and characterized following

photodissociation of CO from metal carbonyl precursors such as $M(CO)_6$ (M = Cr, Mo and W) in methane matrices at very low temperature (12 K) in the 1970s,^{22,23} even before the more stable dihydrogen complexes were discovered.²⁴

Sophisticated techniques such as fast time-resolved infrared (TRIR) spectroscopy have been developed and applied to these highly reactive systems. A systematic study of related metal carbonyl alkane complexes by TRIR spectroscopy showed an increased lifetime of these σ -alkane complexes on going both across and down Groups 5-7.25 The increased stability of this class of compounds subsequently allowed their characterization with ¹H NMR spectroscopy.^{25–32} Photolysis of CpRe(CO)₃ in cyclopentane at 180 K yielded the corresponding alkane complex which was the first alkane complex to be characterized by ¹H NMR spectroscopy.²⁶ However, while there is strong evidence of intermolecular metal-alkane interactions in solution, these systems have up to now defied isolation and solid state structural characterization.33 Intermolecular metal-alkane complexes are therefore one of the most attractive targets in the investigation of fundamental aspects of C-H bond activation. Furthermore, a more detailed understanding of the mechanisms of C-H bond activation should allow better reaction control, and is thus crucial for the advancement of this chemistry.

We have recently reported the isolation of an unusually stable five-coordinate 16VE Ir(III) hydrido methyl cation, [(PONOP)-Ir(H)(CH₃)][B(Ar_F)₄] {where PONOP is $2,6-(tBu_2PO)_2C_5H_3N$;

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tBu is C(CH₃)₃; and B(Ar_F)₄ is B[3,5-(F₃C)₂C₆H₃]₄} which is isoelectronic with the Pt(IV) methyl hydride species proposed in the Shilov cycle.³⁴ Additionally, rapid interchange between the Ir-H and Ir-CH₃ protons was observed and established reversible formation of a σ -methane complex. Density functional theory (DFT) calculations suggested that the $[(PONOP)Ir(H)(CH_3)]^+$ ground state lies only ~5 kcal mol⁻¹ below the $[(PONOP)Ir(\sigma-CH_4)]^+$ complex.¹⁸ However, the small ground state free energy difference between [(PONOP)- $Ir(H)(CH_3)$ ⁺ and $[(PONOP)Ir(\sigma-CH_4)]^+$ and the substantial binding energy of the σ -methane led us to investigate the Rh analogue in which the Rh(I) oxidation state was stabilized relative to the Rh(III) state. Indeed, protonation of [(PONOP)-Rh(CH₃)] at low temperature permitted the observation and full characterization by NMR spectroscopy of a relatively long-lived σ -methane complex, [(PONOP)Rh(CH₄)][B(Ar_F)₄], which is isoelectronic with the Pt(II)- σ -methane complexes postulated as intermediates in the Shilov-type oxidation of methane.18

In our synthetic approach, the σ -bound alkane is generated in the coordination sphere by protonation of the neutral metal–alkyl complex. The cationic charge of the complex gives rise to a significantly increased lifetime of the corresponding σ -alkane complex compared to the neutral complexes. However, even weakly coordinating solvents such as CHCl₂F bind more strongly than the corresponding alkane to the cationic metal center, and therefore loss of bound alkane is an irreversible process.¹⁸

Intrigued by these initial results we report herein on our computational efforts to screen a series of methane complexes of cationic late transition metal pincer complexes supported by various tridentate, neutral pincer ligands. Density functional theory (DFT) methods were used to estimate the binding energy of methane and the relative stabilities of the metal methyl hydride complexes *vs.* the methane σ -complexes. These computational predictions were probed experimentally with several selected examples.

Results and discussion

Computational results

Modern DFT calculations are a valuable tool for synthetic chemists in their efforts to optimize catalytic reactions and to explain the nature of the metal–ligand interaction and reactivity patterns.³⁵⁻⁴⁰ Computational models can also be used to examine a large number of potential synthetic targets and identify the most promising complexes for synthesis and further study. In this vein, we set out to probe a series of tridentate, neutral pincer ligands and their corresponding metal complexes by DFT methods with the goals of identifying the metal and ligand combination that is computed to yield the most stable σ -methane complex (eqn (1)).

$$LM^{n*} + CH_4 \xrightarrow{H_1} M^{H_1} H_2 \xrightarrow{\dots H} H$$
(1)

Additionally, the relative energy of the corresponding metal methyl hydride complex relative to the σ -methane complex was calculated (eqn (2)), which is a prediction of the ground state for a particular metal–ligand combination.

$$LM(CH_4)^{n^+} \rightleftharpoons LM(H)(Me)^{n^+}$$
 (2)

The ligand set examined, a trimmed version of the PONOP ligand in which t-Bu groups are replaced by Me groups, is shown in Scheme 1. Computations as a function of metal (M = Rh, Ir, Pd, Pt) were only carried out for the parent ligand, I-H, and Table 1 shows the calculated enthalpies (ΔH°) and free energies (ΔG°) of methane binding for this set. The charge on the metal complex has a pronounced effect on the methane binding enthalpy and free energy, with the dicationic group 10 metal complex binding methane more strongly than the group 9 metal complex (4.4 kcal mol⁻¹ for Pd/Rh and 5.9 kcal mol⁻¹ for Pt/Ir). For both group 9 and group 10 pairs, the third row transition metal is the stronger binder of methane (by 6 kcal mol⁻¹ for Pt/Pd and 4.6 kcal mol⁻¹ for Ir/Rh pair).

For Ir and Rh pincer complexes, a series structural modifications of the parent pincer were examined computationally. In set I, a variety of substituents were introduced in the *para* position on the pyridine ring ranging from the electrondonating NMe_2 group to the highly electron-withdrawing cationic NMe_3^+ group. In ligand II, the substituents on phosphorus in the parent ligand were changed from CH₃ to CF₃. In ligand III, the pyridine ring is replaced by a pyrazine ring. This ligand offers the opportunity to examine the impact

 Table 1
 Calculated methane binding enthalpies and free energies^{a,b}

Complex	ΔH°	ΔG°
$\begin{array}{c} \left[Rh(I-H) \right]^{+} \\ \left[Pd(I-H) \right]^{2+} \\ \left[Ir(I-H) \right]^{+} \\ \left[Pt(I-H) \right]^{2+} \end{array}$	-17.2 -21.6 -21.8 -27.7	-7.8 (-11.8) -12.7 -11.9 (-16.1) -18.1

 a Energies in kcal mol⁻¹. b Free energies at 298.15 K and 173 K (in parenthesis).

	Ir		Rh			
Ligand	ΔH°	ΔG°	ΔH°	ΔG°		
I-NMe ₂	-21.5	-11.5	-16.9	-7.4		
I-H -	-21.8	-11.9	-17.2	-7.8		
I-CF ₃	-22.4	-12.4	-17.7	-8.4		
I-NMe ₃ ⁺	-24.8	-14.8	-19.6	-12.2		
II	-27.0	-16.4	-21.6	-11.4		
III	-22.4	-12.5	-17.8	-8.8		
$III-H^+$	-27.9	-18.4	-21.6	-12.2		
^{<i>a</i>} Energies in kcal mol ⁻¹ . ^{<i>b</i>} Free Energies at 298.15 K.						

on methane binding of protonating the uncoordinated nitrogen of the pyrazine ring.

The calculated methane binding enthalpies and free energies for the Rh and Ir complexes as a function of ligand are reported in Table 2. For ligand set I, as expected, ligands with the more electron-withdrawing substituent in the para position gives rise to stronger methane binding. The methane binding energy is only modestly impacted ($\sim 1 \text{ kcal mol}^{-1}$) by the range of neutral substituents examined (I-NMe₂ to I-CF₃), while the introduction of a cationic substituent has the largest impact (from 3.3 kcal mol^{-1} (Ir) to 4.8 kcal mol^{-1} (Rh) for I-NMe₂ compared to I-NMe₃⁺). Placing more electron withdrawing substituents on phosphorus, cis to the methane binding site, has a favorable influence on the methane binding energy of 4.5 kcal mol⁻¹ and 3.6 kcal mol⁻¹ for Ir and Rh, respectively. The pyrazine ligand, III, has methane binding energies similar to I-CF₃ for both Rh and Ir. As expected, protonation of the pyrazine ligand increases the methane binding by $5.9 \text{ kcal mol}^{-1}$ for Ir and 3.4 kcal mol^{-1} for Rh.

The computed enthalpies and free energies for the oxidative addition reaction as shown in eqn (2) are reported in Table 3. Of the group 9 pair, the Rh-methane complex is substantially stabilized relative to the methyl hydride complex (by 8.7-14.9 kcal mol⁻¹), while for Ir, the energy difference is smaller (-5.1 to +1.8 kcal mol⁻¹). The trends in the enthalpy and free energy for the oxidative addition reaction as a function of ligand remarkably parallel those for methane binding, with the oxidative addition being less favored when electron withdrawing substituents are introduced. The Ir complex carrying the ligand III-H⁺ is the only complex that is computationally predicted to have a methane complex ground state. The group 10 metals were not included in this comparison

Table 3 Calculated oxidative addition enthalpies and free energies a,b

	Ir		Rh			
Ligand	ΔH°	ΔG°	ΔH°	ΔG°		
I-NMe ₂	-5.0	-5.3	8.5	8.7		
I-H	-4.9	-5.1	8.9	9.4		
I-CF ₃	-4.7	-4.9	9.2	9.7		
I-NMe ₃ ⁺	-2.5	-2.6	11.4	13.9		
II	-0.9	-0.3	12.9	13.7		
III	-4.1	-4.2	10.0	10.9		
$III-H^+$	1.4	1.8	14.3	14.9		
^{<i>a</i>} Energies in kcal mol ⁻¹ . ^{<i>b</i>} Free Energies at 298.15 K.						

for the oxidative addition reaction since for both Pd and Pt, the methyl hydride complex is not a minimum on the potential energy surface, and the methane complex is the ground state.

The structural parameters of the methane complexes as a function of metal and ligand are given in Table 4. The numbering scheme for the coordinated methane ligand is given in eqn (1). In all of the complexes except for those of ligand III-H⁺, a single C-H bond of the methane ligand is coordinated to the metal as signified by relative values of M-H₁ and M-H₂ as well as the corresponding C-H distances. For the group 9 set, the Ir complexes, which have more favorable methane binding free energies, have longer C-H₁ bonds (1.163–1.179 Å) than the corresponding Rh complexes (1.129–1.138 Å). The electron-withdrawing para substituents on the pyridine ring for a given metal shorten the C-H₁ distance, while electron-withdrawing substituents on phosphorus have the opposite effect, although both substituent positions have a favorable influence on the methane binding free energy. A similar trend is observed for the group 10 pair, with Pt having a substantially longer C-H bond (1.164 Å) than Pd (1.133 Å). Comparison of the group 9/10 pairs shows the cationic group 10 methane complex, with a more favorable methane binding free energy, has the shorter $C-H_1$ bond. The C-H₁ bond length for the pyrazine-based ligand, III, is similar to $I-NMe_3^+$ for both Rh and Ir. Interestingly, the methane ligand adopts a symmetrical binding mode with two C-H bonds equally coordinated in the Rh and Ir complexes of the cationic ligand, III-H⁺. Based on the computational screening, systems modeled after the promising candidates $[Pd(I-H)]^{2+}$ and $[M(III-H)]^{2+}$ (M = Rh, Ir) were selected for synthetic studies. For the case of Ir, $[Ir(III-H)]^{2+}$ was the only iridium complex computed that was predicted to have a σ -methane ground state. The experimental work on derivatives related to these complexes is described below.

New ligand system

The new neutral, tridentate pyrazine-based N-PONOP ligand 1, a derivative of III, was prepared from 2,6-dihydroxo-3,

Table 4 Structural parameters for methane complexes^{*a,b*}

Metal	Ligand	$C-H_1$	$C-H_2$	М–С	$M\!-\!H_1$	$M–H_2$	M–N	M–P
Rh	I-H	1.135	1.109	2.367	1.897	2.135	2.012	2.263
Pd	I-H	1.133	1.103	2.388	1.910	2.222	2.009	2.327
Ir	I-H	1.171	1.100	2.359	1.797	2.281	2.009	2.266
Pt	I-H	1.164	1.097	2.391	1.811	2.371	2.004	2.326
Rh	I-NMe ₂	1.138	1.106	2.374	1.875	2.169	2.009	2.261
	I-H ¯	1.135	1.109	2.367	1.897	2.135	2.012	2.263
	I-CF ₃	1.134	1.110	2.364	1.904	2.122	2.010	2.265
	I-NMe ₃ ⁺	1.130	1.114	2.357	1.943	2.079	2.002	2.270
	II	1.140	1.105	2.362	1.872	2.188	2.022	2.230
	III	1.129	1.113	2.362	1.935	2.083	1.998	2.270
	$III-H^+$	1.123	1.123	2.343	2.004	2.005	1.971	2.285
Ir	I-NMe ₂	1.179	1.098	2.362	1.777	2.319	2.009	2.264
	I-H ¯	1.171	1.100	2.359	1.797	2.281	2.009	2.266
	I-CF ₃	1.169	1.101	2.358	1.803	2.270	2.006	2.268
	I-NMe ₃ ⁺	1.163	1.104	2.354	1.826	2.240	1.995	2.273
	II	1.171	1.100	2.353	1.800	2.296	2.021	2.233
	III	1.164	1.103	2.358	1.820	2.244	1.993	2.273
	$III-H^+$	1.133	1.133	2.318	1.986	1.987	1.955	2.291
^a Bond	^{<i>a</i>} Bond distances given in Å. ^{<i>b</i>} Numbering scheme given in eqn (1)							(1).

5-diphenylpyrazine⁴¹ with di-*tert*-butylchlorophosphine in the presence of excess of NEt₃ at 65 °C in THF (eqn (3)) and characterized by multinuclear NMR spectroscopy and elemental analysis.



Metallation of **1** with Ir and Rh was readily accomplished by treatment with either $[(C_2H_4)_2IrCl]_2$ or $[(COE)_2RhCl]_2$, affording (*N*-PONOP)IrCl (**1-IrCl**) and (*N*-PONOP)RhCl (**1-RhCl**), respectively, in good yields (Scheme 2). Complex **1-IrCl** was isolated as dark purple powder and characterized by ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopy and elemental analysis. The ¹H NMR spectrum of **1-IrCl** is consistent with a molecular C_{2v} symmetry. The ³¹P{¹H} NMR spectrum displays a singlet at δ 185.9 which is downfield shifted relative to the free ligand **1** (δ 162.8). Complex **1-RhCl** was obtained as dark red powder and characterized by multinuclear NMR spectroscopy. A benzene-d₆ solution of **1-RhCl** shows the expected number of resonances, and the ³¹P{¹H} NMR spectrum displays a doublet at δ 206.3 (¹ J_{Rh-P} = 149 Hz).

Complexes 1-IrCl and 1-RhCl were methylated using MgMe₂ in a toluene/THF solution to afford (*N*-PONOP)-IrCH₃ (1-IrMe) and (*N*-PONOP)RhCH₃ (1-RhMe), respectively (Scheme 3). Complexes 1-IrMe and 1-RhMe were characterized

The solid state structure of **1-IrMe** is shown in Fig. 1 with relevant metrical parameters listed in the figure caption.[‡] The isostructural complex **1-RhMe** is shown in ESI (Fig. S2), and selected bond distances and angles are given in the figure caption. The X-ray diffraction data are consistent with the expected square planar geometry about the metal center.

Preparation of the cationic 2-PdMe⁺ complex

The other promising candidates for protonation identified were the dicationic PONOP-based Pd/Pt(II) methyl complexes. The DFT calculations (vide supra) suggested a σ -methane ground state and methane binding energies sufficient to allow observation of the σ -methane complexes at ambient temperature. These complexes are of particular significance since they are very closely related to Shilov Pt(II) catalytic systems for methane conversion.42-46 Within the scope of this paper we will only discuss investigations on 2-PdMe⁺. The synthesis of 2-PdMe⁺ has been accomplished in a straightforward manner from the reaction of the precursor (COD)Pd(Cl)(Me) with $Na[B(Ar_F)_4]$ and ligand 2 in CH₂Cl₂ at -40 °C (Scheme 4). Crystallization from pentane/CH₂Cl₂ afforded **2-PdMe⁺** as pale vellow crystals. which were characterized by multidimensional NMR spectroscopy, elemental analysis and a single crystal X-ray diffraction study (Fig. 2).[±]

Protonation attempts

The double protonation of **1-IrMe** and protonation of **2-PdMe**⁺ was attempted at various temperatures and using different acids and acid concentrations.

Protonation of 1-IrMe. Protonation at the Ir-center with $[H(OEt_2)_2][B(Ar_F)_4]$, was readily accomplished as previously



Scheme 2 Preparation of 1-RhCl and 1-IrCl.

by NMR spectroscopy, elemental analysis and X-ray diffraction. The presence of a M–CH₃ moiety was confirmed by the observation of a 3H triplet at δ 2.36 (${}^{3}J_{P-H} = 4.9$ Hz) and a 3H doublet of triplets at δ 0.73 (${}^{3}J_{P-H} = 4.9$ Hz, ${}^{2}J_{Rh-H} =$ 3.1 Hz) for **1-IrMe** and **1-RhMe**, respectively. Additionally, the ${}^{31}P{}^{1}H{}$ NMR spectra display a single resonance at δ 192.3 for **1-IrMe** and a doublet at δ 208.5 (${}^{1}J_{Rh-P} = 171$ Hz) for **1-RhMe**. In both cases the resonances are slightly shifted downfield relative to the starting materials **1-IrCl** and **1-RhCl**. It should be noted that trace impurities of MgI₂ in MgMe₂ cause problems in the synthesis of **1-RhMe**. In this case, **1-RhI** is formed which does not metathesis with MgMe₂ to **1-RhMe** (see ESI, Fig. S1, and Experimental Section for details).

‡ Crystal data for 1-IrMe: C₃₃H₄₉IrN₂O₂P₂, *M* = 759.88, monoclinic, *a* = 11.1882(3) Å, *b* = 12.8593(3) Å, *c* = 23.2460(6) Å, *α* = 90.00°, *β* = 94.8910(10)°, *γ* = 90.00°, *V* = 3332.28(15) Å³, *T* = 100(2)K, space group *P*2₁/*c*, *Z* = 4, μ (Cu-K*α*) = 8.896 mm⁻¹, 22.893 reflections measured, 6154 independent reflections (*R*_{int} = 0.0303). The final *R*₁ values were 0.0257 (*I* > 2 σ (*I*)). The final *wR*(*F*²) values were 0.0616 (*I* > 2 σ (*I*)). The final *R*₁ values were 0.0313 (all data). The final *wR*(*F*²) values were 0.0641 (all data). The goodness of fit on *F*² was 1.028. Crystal data for **2-PdMe**⁺: C₅₅H₅₆BCl₂F₂₄NO₂P₂Pd, *M* = 1469.06, monoclinic, *a* = 13.7687(5) Å, *b* = 23.5697(9) Å, *c* = 19.7027(7) Å, *α* = 90.00°, *β* = 98.591(2)°, *γ* = 90.00°, *V* = 6322.3(4) Å³, *T* = 100(2)K, space group *P*2₁/*c*, *Z* = 4, μ (Cu-K*α*) = 4.631 mm⁻¹, 59.378 reflections measured, 11956 independent reflections (*R*_{int} = 0.0310). The final *R*₁ values were 0.0463 (*I* > 2 σ (*I*)). The final *wR*(*F*²) values were 0.1241 (*I* > 2 σ (*I*)). The final *R*₁ values were 0.0502 (all data). The final *wR*(*F*²) values were 0.1273 (all data). The goodness of fit on *F*² was 1.034.







Fig. 1 ORTEP diagram of 1-IrMe (50% probability ellipsoids). Selected bond distances (Å): Ir1–N1 2.030(3), Ir1–C33 2.107(3), Ir1–P1 2.2391(8), Ir1–P2 2.2302(8).

described for **2-IrMe**. However, protonation at the *p*-nitrogen of the pyrazol-backbone did not occur even in the presence of excess acid, and above -40 °C, the excess acid induced phosphinite (O–P) bond cleavage. An excess of HN(SO₂CF₃)₂ gives rise to the formation of a 6-coordinate species in CD₂Cl₂ or CDCl₂F solvent as suggested by a downfield shift of the Ir–H resonance from δ –40.9 in **1-Ir(H)Me**⁺ to δ –16.6. This downfield shift is consistent with a sixth ligand *trans* to the Ir–H axis.

Since no double protonation was achieved, the focus of these investigations was shifted to study of the stability and reversible C–H activation process in 1-Ir(H)(Me)⁺ and the comparison to 2-Ir(H)(Me)⁺ and our computational predictions. The product of methane loss was tentatively assigned as the iridium(1) solvate cation, [(*N*-PONOP)Ir(CDCl₂F)]⁺. Free methane was detected concomitant with and roughly proportional



Fig. 2 ORTEP diagram of **2-PdMe**⁺ (50% probability ellipsoids). Selected bond distances (Å): Pd1–N1 2.064(2), Pd1–C22 2.060(3), Pd1–P1 2.2932(8), Pd1–P2 2.2896(8).

to the formation of $[(N-\text{PONOP})\text{Ir}(\text{CDCl}_2\text{F})]^+$. The rate of methane loss was monitored by ³¹P{¹H} NMR spectroscopy, and yields a first-order rate constant of $k = 4.3(1) \times 10^{-5} \text{ s}^{-1}$ at 19 °C, corresponding to a barrier of $\Delta G^{\ddagger} = 22.9(2)$ kcal mol⁻¹ (see ESI for details, Fig. S3). The barrier for methane loss from **1-Ir(H)(Me)**⁺ is very similar to the barrier for **2-Ir(H)(Me)**⁺ of $\Delta G^{\ddagger} = 22.4(2)$ kcal mol⁻¹, therefore this modification of the pincer backbone has no pronounced effect on the complex stability.

Cation **1-Ir(H)(Me)**⁺ was characterized by multinuclear, low-temperature NMR spectroscopy. At -130 °C in CDCl₂F solution the ¹H NMR spectrum of **1-Ir(H)(Me)**⁺ displays a triplet resonance at δ -40.90 (²J_{P-H} = 13.3 Hz) assigned to the Ir–H and a broad resonance at δ 2.15 assigned to the Ir–CH₃ moiety. When the temperature is increased to -90 °C, the Ir–H and Ir–CH₃ resonances exhibit significant line broadening. The rate of site exchange between the Ir–H and Ir–CH₃ positions was examined by line shape analysis⁴⁷ of selectively



decoupled ¹H{³¹P}-NMR spectra. At -100 °C in CDCl₂F solvent, a rate constant of 630(10) s⁻¹ was observed for the Ir–H and Ir–CH₃ exchange, which corresponds to a barrier of 7.9(1) kcal mol⁻¹ for the interchange of the iridium-hydride and iridium-methyl protons by reductive coupling and oxidative addition. It is interesting to note that the new pincer backbone slightly stabilizes **1-Ir(H)(Me)**⁺ with respect to methane elimination while the barrier to Ir–H and Ir–CH₃ exchange is lower ($\Delta G^{\ddagger} = 7.9(1)$ kcal mol⁻¹ vs. 9.3(4) kcal mol⁻¹).

The experimental result is consistent with a lower lying 1-Ir(σ -CH₄)⁺ state relative to 2-Ir(σ -CH₄)⁺ as initially predicted by DFT calculations ($\Delta\Delta G^{\circ} = 0.9 \text{ kcal mol}^{-1}$). The computed barriers to exchange are 7.2 kcal mol^{-1} for $[(\mathbf{III})\mathbf{Ir}(\mathbf{H})(\mathbf{Me})]^+$ and 7.4 kcal mol⁻¹ for $[(\mathbf{I-H})\mathbf{Ir}(\mathbf{H})(\mathbf{Me})]^+$, and therefore of similar magnitude to the experimental result for the untrimmed ligand. For the iridium complexes, since the ground state is the methyl hydride, a computed barrier to methane loss can be estimated by summing the energy difference between the $[(L)Ir(H)(Me)]^+$ and $[(L)Ir(\sigma-CH_4)]^+$ with an appropriately weighted entropic contribution to the free energy of methane loss from $[(L)Ir(\sigma-CH_4)]^+$ (see computational methods section). Based on the assumption that 40% of the reaction entropy is realized at the transition state for methane loss, the computed barriers for methane loss are 20.8 for $[Ir(I-H)(H)(Me)]^+$ and 20.6 kcal mol⁻¹ for $[Ir(III)(H)(Me)]^+$, which are in reasonable agreement with the experimental results for the untrimmed ligands.

Protonation of 2-PdMe⁺. No protonation of 2-PdMe⁺ occurred with an excess of $[H(OEt_2)_2][B(Ar_F)_4]$ or $HN(SO_2CF_3)_2$ in CD_2Cl_2 or $CDCl_2F$ solvent at -80 °C. More importantly, no significant protonation of 2-PdMe⁺ was observed on warming of the sample to ambient temperature or after storing the reaction mixture for several days at room temperature. We then resorted to the superacidic conditions, *i.e.* magic acid (HSO₃F/SbF₅, 1:1 ratio) with $H_0 = -20^{48}$ as the proton source. Cation 2-PdMe⁺ was protonated under these conditions at -80 °C in triffic anhydride, (CF₃SO₂)₂O, solvent. Unfortunately, a solvent coordinated species was formed, and no dicationic 2-Pd(HMe)²⁺ complex was observed. This result suggests that the stability of the methane complex may have been overestimated by DFT calculations. Further, it demonstrates that significantly stronger acids are required to protonate a monocationic methyl species in comparison to a neutral species.

Conclusions

Computational studies were used to identify pincer ligands and metal complexes expected to yield more stable σ -methane complexes. Among the ligands explored computationally, a pyrazine-based pincer ligand **III** was predicted to give rise to a more stable σ -methane complex upon protonation of the uncoordinated nitrogen. Further, in the parent pincer ligand system, **I**, dicationic group 10 analogues were predicted to form more stable σ -methane complexes than the group 9 analogues. Experimental difficulties in realizing the computational predictions were encountered. In the metal complexes of the pyrazine-based ligand, **1-IrMe**, monoprotation occurs at the metal, but addition

of a second proton to the uncoordinated nitrogen was not observed before ligand degradation via P-O bond cleavage. For 2-PdMe⁺, the same acids used to protonate the group 9 analogues were not sufficiently strong to protonate the group 10 complex, Protonation of 2-PdMe⁺ was achieved under superacid conditions, but the methane complex was not stable in this solvent system. These experimental results illustrate the limitations of a protonation strategy to yield complexes of a weak ligand like methane. Metals sufficiently electrophilic to bind methane strongly will make the methyl group less subject to protonation, thereby requiring superacids. A more electrophilic metal complex can also be generated by protonation of a coordinated ligand, but the site of protonation must be the most basic site in the molecule after protonation at metal to avoid undesired site reactions. Our quest continues for a methane complex stable at room temperature.

Experimental details

General considerations

All reactions, unless otherwise stated, were conducted under an atmosphere of dry, oxygen free argon using standard highvacuum, Schlenk, or drybox techniques. Argon was purified by passage through BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. ¹H, ¹³C{¹H}, ¹H-¹H COSY, ¹H-¹³C HSQC, ¹H-¹H NOESY, ¹H-¹H TOCSY and ¹³C DEPT135 NMR spectra were recorded on a Bruker DRX 500 MHz, a Bruker DRX 400 MHz, or a Bruker 400 MHz AVANCE spectrometer. ¹H and ¹³C Chemical shifts are referenced relative to residual CHCl₃ (δ 7.24 for ¹H), CH(D)Cl₂ (δ 5.32 for ¹H), CHCl₂F (δ 7.47 for ¹H), C₆HD₅ (δ 7.15 for ¹H), ¹³CD₂Cl₂ (δ 53.8 for ¹³C), ¹³CDCl₃(δ 77.0 for ¹³C), ¹³CDCl₂F (δ 104.2 for ¹³C) and ¹³C₆D₆ (δ 128.0 for ¹³C); ³¹P chemical shifts are referenced to an external standard of H₃PO₄. Probe temperatures were calibrated using ethylene glycol and methanol as previously described.⁴⁹ Due to strong ³¹P-³¹P coupling in the pincer ligand, many ¹H and ¹³C $\{^{1}H\}$ NMR signals appear as virtual triplets (vt) and are reported as such with the apparent coupling noted. Elemental analyses were carried out by Robertson Microlit Laboratories of Madison, NJ.

Materials

All solvents were deoxygenated and dried by passage over columns of activated alumina.^{50,51} CD₂Cl₂, purchased from Cambridge Laboratories, Inc., was dried over CaH₂, vacuum transferred to a Teflon sealable Schlenk flask containing 4 Å molecular sieves, and degassed *via* three freeze-pump-thaw cycles. Freon (CDCl₂F) was prepared according to a literature procedure and stored over activated 4 Å molecular sieves at $-25 \,^{\circ}\text{C}.^{52}$ IrCl₃ and RhCl₃ were purchased from J&J Materials or obtained from W. C. Heraeus GmbH and used as received. [H(OEt₂)₂][B(Ar_F)₄],⁵³ Na[B(Ar_F)₄],⁵⁴ [(COE)₂MCl]₂ (M = Ir,⁵⁵ Rh⁵⁶), [(COD)Pd(Me)(Cl)],⁵⁷ MgMe₂,⁵⁸ 2,6-Dihydroxy.3,5-diphenylpyrazine,⁴¹ 2,6-(*I*Bu₂PO)₂C₅H₃N (PONOP),³⁴ were synthesized according to literature methods. All other reagents were purchased from Aldrich, Acros, Alphar Aesar or Strem Chemicals and used as received.

Computational details

All density functional theory (DFT) calculations were performed by using the Gaussian 03 package.⁵⁹ The basis-set/ functional selection was based on a prior study of methane binding.¹⁸ and consists of the built-in 6-31G** basis set for all non-transition metal atoms, the Stuttgart-Dresden basis set-pseudo relativistic effective core potential combination for the transition metals^{60,61} with a single f-type polarization function for Rh and Ir (exponent = 1.062 (Rh); 0.685 (Ir)), which are the geometric average of the two f exponents given in the appendix of reference 61, and the functional PBE0, the hybrid variant of PBE that contains 25% Hartree-Fock exchange⁶² for geometry optimizations. The PBE0 functional was found to yield results in better agreement with experimental data than the B3LYP functional in an Ir pincer system,⁶³ and has been endorsed as one of the best performing functionals for late transition metal systems.⁶⁴ A similar basis set combined with the PBE0 functional was used to calculate weak Rh...H-C interactions in another system,⁶⁵ and in our recent study of methane binding energies.¹⁸ For each metal-ligand combination, geometries were optimized in the gas phase for $[(L)M]^{n+}$, $[(L)M(Me)(H)]^{n+}$ and the agostic complexes $[(L)M(\sigma-CH_4)]^{n+}$. Frequency calculations were carried out on all minimum structures, and the resulting frequencies all had positive values. The non-scaled vibrational frequencies formed the basis for the calculation of vibrational zero point corrections and the standard thermodynamic corrections for the conversion of electronic energies to enthalpies and free energies at 298.15 K and 1 atm.

For $[(I-H)Ir(\sigma-CH_4)]^+$ and $[(III)Ir(\sigma-CH_4)]^+$, the transition state for the oxidative addition reactions were optimized in the gas phase using the Synchronous Transit-Guided Quasi-Newton (STQN) method implemented in Gaussian. Frequency calculations yielded one imaginary frequency for all transition states, and IRC calculations were carried out to confirm that the transition state identified connected the correct minima.

Calculation of the barrier for methane loss at room temperature is not directly obtained from the calculations. For dissociation of a neutral ligand from a transition metal complex that does not rearrange following dissociation like the complexes calculated in this manuscript, assuming the recoordination of methane is enthalpically barrierless, the methane dissociation enthalpy (ΔH^0) is an upper limit to the ΔG^{\ddagger} for methane dissociation (Fig. 3). The actual ΔG^{\ddagger} for methane release will be determined by the degree to which the favorable entropy of methane dissociation is reflected in the transition state.⁶⁶ For comparison to experimental data for $[(I-H)Ir(\sigma-CH_4)]^+$ and $[(III)Ir(\sigma-CH_4)]^+$, it is assumed that 40% of the reaction entropy is realized in the transition state as calculated for κ^3 -TpPt(Me)(CH₄).⁶⁶



Fig. 3 Reaction coordinate diagram for methane dissociation. The marked quantities are for the forward methane dissociation reaction.

A table of calculated electronic energies, enthalpies, and free energies in the gas phase for all ground states and transition state calculated, and tables of Cartesian coordinates (Å) for the optimized structures and transition states in the gas phase are included as ESI.



Preparation of N-PONOP (1)

2,6-Dihydroxo-3,5-diphenylpyrazine (1.2 g, 4.54 mmol), di-tert-butylchlorophosphine (1.64 g, 9.1 mmol), triethylamine (5 mL), and THF (10 mL) were combined in a Schlenk flask. A colorless precipitate immediately formed and the reaction mixture was heated to 65 °C for 2 h. The volatiles were removed under dynamic vacuum, leaving a yellow solid. The solid was extracted into toluene and filtered. The solvent was removed under dynamic vacuum, leaving a bright yellow crystalline solid. Yield: 1.52 g (3.32 mmol, 73%). ¹H NMR (C_6D_6, RT) : δ 8.33 (d, 2H, ${}^3J_{HH} = 8.4$ Hz, $o-C_6H_5$), 7.33 (d, 4H, ${}^{3}J_{HH} = 7.8$ Hz, *m*-C₆*H*₅), 7.20 (t, 2H, ${}^{3}J_{HH} = 7.6$ Hz, $p-C_6H_5$), 1.15 (d, 36 H, ${}^{3}J_{P-H} = 12.0$ Hz, C(CH₃)₃). ${}^{31}P{}^{1}H{}^{1}$ NMR (C_6D_6 , RT): δ 162.8 (s). ¹³C{¹H} NMR (C_6D_6 , RT): δ 155.3 (d, ²J_{CP} = 9.0 Hz, C₃), 135.7 (s, C₄), 129.7 (s, C₆), 128.34 (s, C_8), 128.3 (s, C_7), 35.8 (d, ${}^{1}J_{CP} = 30.4$ Hz, C_2), 27.9 $(d, {}^{2}J_{CP} = 17.6 \text{ Hz}, C_{2})$. Anal. Calcd for $C_{24}H_{46}P_{2}O_{2}N_{2}$: C, 63.15; H, 10.15; N, 6.14. Found: C, 63.05; H, 10.02; N, 5.99.

Preparation of (N-PONOP)IrCl (1-IrCl)

A Schlenk tube was charged with [(COE)₂IrCl]₂ (0.4 g, 0.45 mmol) and diethyl ether (10 mL). On a Schlenk line, the orange solution was stirred under 1 atm of C_2H_4 at -40 °C until the solution became very pale yellow. Then a solution of N-PONOP (0.25 g, 0.95 mmol) dissolved in Et₂O was added via cannula to the reaction mixture, and immediate color change to dark purple was observed. The reaction vessel was slowly warmed to ambient temperature, and the volatiles were removed under dynamic vacuum. The resulting deep purple powder was extracted with toluene, fitered, and the solvent removed. The resulting red-purple powder was washed with cold pentane (10 mL) yielding 0.45 g (0.65 mmol, 73%) of **1-IrCl.** ¹H NMR (C₆D₆, RT): δ 8.27 (d, 2H, ³J_{HH} = 8.3 Hz, $o-C_6H_5$), 7.31 (t, 4H, ${}^3J_{HH} = 7.7$ Hz, $m-C_6H_5$), 7.16 (t, 2H, ${}^{3}J_{\text{HH}} = 7.3 \text{ Hz}, p-C_{6}H_{5}$, 1.42 (vt, 36 H, $J_{\text{P-H}} = 7.3 \text{ Hz}$, C(CH₃)₃). ³¹P{¹H} NMR (C₆D₆, RT): δ 185.9 (s). ¹³C{¹H} NMR (C₆D₆, RT): δ 159.1 (vt, $J_{CP} = 4.2$ Hz, C₃), 135.7 $(s, C_5), 135.7 (vt, J_{CP} = 1.7 Hz, C_4), 129.2 (s, C_6), 128.4 (s, C_8),$ 128.3 (s, C_7), 41.2 (vt, $J_{CP} = 8.4$ Hz, C_2), 27.9 (vt, ${}^2J_{CP} =$ 3.7 Hz, C₂). Anal. Calcd for C₂₄H₄₆P₂O₂N₂IrCl: C, 42.13; H, 6.78; N, 4.09. Found: C, 42.02; H, 6.65; N, 4.15.

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Preparation of (N-PONOP)RhCl (1-RhCl)

A 50 mL Schlenk tube was charged with N-PONOP (0.35 g, 1.32 mmol), [(COE)₂RhCl]₂ (0.47 g, 0.65 mmol) and 20 mL of toluene. The dark red solution was stirred at ambient temperature for 24 h, volatiles were removed *in vacuo*, and the dark red powder was washed with cold pentane affording 0.52 g (0.874 mmol, 66%) of **1-RhCl**. ¹H NMR (CD₂Cl₂, RT): δ 8.11 (d, 2H, ³J_{HH} = 7.5 Hz, *o*-C₆H₅), 7.50 (t, 4H, ³J_{HH} = 7.8 Hz, *m*-C₆H₅), 7.42 (t, 2H, ³J_{HH} = 7.3 Hz, *p*-C₆H₅), 1.49 (vt, 36 H, *J*_{P-H} = 7.3 Hz, C(CH₃)₃). ³¹P{¹H} NMR (CD₂Cl₂, RT): δ 157.5 (vt, *J*_{P-C} = 4.2 Hz, C₃), 136.7 (s, C₅), 135.7 (vt, *J*_{CP} = 1.5 Hz, C₄), 129.1 (s, C₈), 128.9 (s, C₇), 128.5 (s, C₆), 41.2 (dvt, *J*_{P-C} = 4.1 Hz, *J*_{Rh-C} = 2.1 Hz, C₂), 27.9 (vt, ²*J*_{CP} = 4.2 Hz, C₂). Anal. Calcd for C₂₄H₄₆P₂O₂N₂RhCl: C, 48.45; H, 7.79; N, 4.71. Found: C, 48.53; H, 7.50; N, 4.65.

Preparation of (N-PONOP)IrCH₃ (1-IrMe)

Under an argon atmosphere a heavy walled glass reaction vessel was charged with 1-IrMe (0.25 g, 0.37 mmol) and Mg(CH₃)₂ (0.020 g, 0.37 mmol). A solvent mixture of THF (ca. 0.1 mL) and toluene (ca. 4 mL) was added via cannula. The reaction mixture was heated to 130 °C for 3 days and a color change to purple was observed. Volatiles were removed under dynamic vacuum, and the residue was extracted with toluene. The deep purple toluene extracts were concentrated, a layer of pentane added and cooled to -35 °C. Dark purple blocks formed within a few days. Yield: 0.12 (0.18 mmol, 49%). ¹H NMR (C₆D₆, RT): δ 8.42 (d, 2H, ³J_{HH} = 7.7 Hz, $o-C_6H_5$), 7.36 (t, 4H, ${}^{3}J_{HH} = 7.8$ Hz, $m-C_6H_5$), 7.18 (t, 2H, ${}^{3}J_{\text{HH}}$ = 7.3 Hz, *p*-C₆H₅), 2.36 (t, 3H, ${}^{2}J_{\text{P-H}}$ = 4.9 Hz, Ir–CH₃), 1.36 (vt, 36 H, $J_{P-H} = 7.0$ Hz, C(CH₃)₃). ³¹P{¹H} NMR (C₆D₆, RT): δ 192.3 (s). ¹³C{¹H} NMR (CD₂Cl₂, RT): δ 156.5 (vt, $J_{P-C} = 4.0$ Hz, C_3), 137.2 (s, C_5), 134.5 (vt, $J_{CP} =$ 1.7 Hz, C₄), 129.1 (s, C₆), 128.6 (s, C₈), 128.3 (s, C₇), 40.6 (vt, $J_{P-C} = 8.4$ Hz, C_2), 27.8 (vt, ${}^2J_{CP} = 4.8$ Hz, C_2), -22.9 (t, ${}^{2}J_{PC} = 6.6$ Hz, Ir–CH₃). Anal. Calcd for C₂₅H₄₉P₂O₂N₂Ir: C, 45.23; H, 7.44; N, 4.22. Found: C, 45.16; H, 7.35; N, 4.15.

Preparation of (N-PONOP)RhCH₃ (1-RhMe)

Under an argon atmosphere a heavy walled glass reaction vessel was charged with 1-RhCl (0.25 g, 0.4 mmol), Mg(CH₃)₂ (0.022 g, 0.4 mmol) and THF solvent (ca. 2 mL). The reaction mixture was heated to 65 °C for 2 d. The conversion was monitored by ${}^{31}P{}^{1}H$ NMR spectroscopy, and it was found that the reaction time was strongly dependent on the amount of solvents. With more concentrated solutions faster conversion was observed. Volatiles were removed under dynamic vacuum, and the residue was extracted with toluene. The deep red toluene extracts were concentrated, a layer of pentane added and cooled to -35 °C. Dark red-brown blocks of 1-RhMe formed within a few days. Yield: 0.13 g (0.28 mmol, 57%). ¹H NMR (C₆D₆, RT): δ 8.46 (d, 2H, ³J_{HH} = 7.8 Hz, $o-C_6H_5$), 7.36 (t, 4H, ${}^{3}J_{HH} = 7.4$ Hz, $m-C_6H_5$), 7.19 (t, 2H, ${}^{3}J_{\text{HH}} = 7.4 \text{ Hz}, p-C_{6}H_{5}$, 1.35 (vt, 36 H, $J_{\text{P-H}} = 6.7 \text{ Hz}, \text{C}(\text{C}H_{3})_{3}$), 0.73 (dt, 3H, ${}^{2}J_{Rh-H} = 3.1$ Hz, ${}^{3}J_{P-H} = 4.9$ Hz, Rh–CH₃).

³¹P{¹H} NMR (C₆D₆, RT): δ 208.5 (d, ¹J_{Rh-P} = 171 Hz). ¹³C{¹H} NMR (C₆D₆, RT): δ 155.1 (vt, J_{P-C} = 4.3 Hz, C₃), 136.8 (s, C₅), 132.6 (s, C₄), 128.8 (s, C₆), 128.4 (s, C₈), 128.2 (s, C₇), 41.2 (dvt, J_{P-C} = 3.3 Hz, J_{Rh-C} = 3.5 Hz, C₂), 27.9 (vt, ²J_{CP} = 4.7 Hz, C₂). Anal. Calcd for C₂₅H₄₉P₂O₂-N₂Rh: C, 52.26; H, 8.60; N, 4.88. Found: C, 52.45; H, 8.45; N, 4.62.

Preparation of (N-PONOP)RhI (1-RhI)

Under an argon atmosphere a heavy walled glass reaction vessel was charged with 1-RhCl (0.10 g, 0.17 mmol), MgI₂ (0.047 g, 0.17 mmol) and THF solvent (ca. 2 mL). The reaction mixture was heated to 65 °C for 2 d. Volatiles were removed under dynamic vacuum, and the residue was extracted with toluene. The deep red toluene extracts were concentrated, a layer of pentane added and cooled to -35 °C. Dark red-brown blocks of 1-RhI formed within a few days. Yield: 0.105 g (0.158 mmol, 93%). ¹H NMR (C_6D_6 , RT): δ 8.14 (d, 2H, ${}^{3}J_{\text{HH}} = 7.7$ Hz, o-C₆H₅), 7.51 (t, 4H, ${}^{3}J_{\text{HH}} = 7.6$ Hz, m-C₆ H_5), 7.43 (t, 2H, ${}^{3}J_{HH} = 7.3$ Hz, p-C₆ H_5), 1.52 (vt, 36 H, $J_{\rm P-H} = 7.2$ Hz, C(CH₃)₃). ³¹P{¹H} NMR (C₆D₆, RT): δ 215.4 (d, ${}^{1}J_{Rh-P} = 140$ Hz). ${}^{13}C{}^{1}H{}$ NMR (C₆D₆, RT): δ 156.7 (vt, $J_{P-C} = 4.2$ Hz, C_3), 136.0 (s, C_5), 133.5 (vt, $J_{CP} = 1.7$ Hz, C_4), 129.2 (s, C_8), 128.6 (s, C_7), 128.3 (s, C_6), 40.9 (dvt, J_{P-C} = 4.4 Hz, $J_{\text{Rh-C}} = 2.3$ Hz, C_2), 27.9 (vt, ${}^2J_{\text{CP}} = 3.9$ Hz, C_2). Anal. Calcd for C24H46P2O2N2RhI: C, 42.0; H, 6.75; N, 4.08. Found: C, 42.12; H, 6.85; N, 3.95.

Observation of [(N-PONOP)Ir(H)(CH₃)][B(Ar_F)₄] (1-Ir(H)(Me)⁺)

A screw cap NMR tube was charged with $[H(OEt_2)_2][B(Ar_F)_4]$ (0.027 g, 0.027 mmol) and 1-IrMe (0.017 g, 0.026 mmol). At 77 K approximately 500 µL CDCl₂F was transferred onto the tube via a cannula. The NMR tube was transferred into a cooling bath which was precooled to -100 °C. After the sample thawed, the screw cap was removed and the sample was mixed under a flow of argon with glass rod until a homogeneous solution formed. The NMR tube was capped again and cooled to 77 K. The sample was maintained at 77 K until inserted into the precooled NMR probe at -143 °C. After the sample thawed, 1-Ir(H)(Me)⁺ was monitored by multinuclear NMR spectroscopy. A typical experiment yielded 100% conversion of 1-IrMe to 1-Ir(H)(Me)⁺. ¹H NMR (CDCl₂F, -130 °C): δ 8.16 (d, 2H, ³J_{HH} = 7.5 Hz, *o*-C₆H₅), 7.80 (s, 8H, o-Ar, B(Ar_F)₄), 7.61 (t, 4H, ${}^{3}J_{HH} = 7.2$ Hz, m-C₆ H_5), 7.55 (p-C₆ H_5 , overlapped with p-Ar B(Ar_F)₄ resonance), 2.15 (br.s, 3H, CH₃), 1.37 (br.s., 36H, C(CH₃)₃), -40.9 (t, 1H, ${}^{2}J_{P-H} = 13.3$ Hz, Ir-H). ¹H NMR (CDCl₂F, -30 °C): δ 8.21 (d, 1H, ${}^{3}J_{\text{HH}} = 8.2$ Hz, o-C₆H₅), 7.61 (t, 1H, ${}^{3}J_{\rm HH} = 7.5$ Hz, $m-C_{6}H_{5}$), 7.58 (p-C₆H₅, overlapped with *p*-Ar B(Ar_F)₄ resonance), 1.42 (vt, 36H, J = 8.1 Hz, $C(CH_3)_3$, no Ir-H and Ir-CH₃ resonances detected. ³¹P{¹H} NMR (CDCl₂F, -110 °C): δ 192.7. ¹³C{¹H} NMR (CDCl₂F, -120 °C): δ 162.2 (q, 37 Hz, *ipso*-Ar, B(Ar_F)₄), 153.5 (br.s, C₃), 136.3 (br. s, C₄), 135.2 (o-Ar, B(Ar_F)₄), 133.9 (s, C₅), 130.9 (s, C₈), 129.4 (s, C₆), 129.3 (q, 31 Hz, m-Ar, B(Ar_F)₄), 128.8 (s, C₇), 125.0 (q, 273 Hz, CF_3 , $B(Ar_F)_4$), 117.9 (*p*-Ar, $B(Ar_F)_4$), 43.7 (br.s, C_{2a}), 41.1 (br.s, C_{2b}), 26.9 (br. s, $C_{1a}+b$), -19.9 (t, ${}^{2}J_{PC} = 6.5$ Hz, Ir–CH₃).



Preparation of [(PONOP)PdMe][B(Ar_F)₄] (2-PdMe⁺)

Under an argon atmosphere a Schlenk tube was charged with **2** (0.2 g, 0.5 mmol), Na[B(Ar_F)₄] (0.44 g, 0.5 mmol) and [(COD)Pd(Me)(Cl)] (0.132 g, 0.5 mmol) and cooled to -78 °C. To this precooled CH₂Cl₂ (ca. 15 mL) was added via cannula to form a yellow suspension. The reaction mixture was stirred at -78 °C for 10 min, and then slowly warmed to room temperature. The yellow solution was filtered, concentrated and a layer of pentane added. Slow cooling to -30 °C yielded pale yellow crystals of 2-PdMe⁺, which incorporate one molecule of CH₂Cl₂. Yield: 0.44 g (0.30 mmol, 60%). ¹H NMR (CD₂Cl₂, RT): δ 7.82 (t, ³J_{HH} = 8.0 Hz, 1H, p-C₆H₃N), 7.80 (s, 8H, o-Ar, B(Ar_F)₄), 7.56 (s, 4H, p-Ar, $B(Ar_F)_4$), 6.91 (d, ${}^3J_{HH} = 8.3$ Hz, 2H, $m-C_6H_3N$), 1.36 (vt, 36H, $J_{P-H} = 8.1$ Hz, C(CH₃)₃), 0.87 (t, ${}^{3}J_{PH} = 4.8$ Hz, 3H, Pd-CH₃). ³¹P{¹H} NMR (CD₂Cl₂, RT): δ 191.0 (s). ¹³C{¹H} NMR (CD₂Cl₂, RT): δ 162.2 (q, 37 Hz, *ipso*-Ar, $B(Ar_F)_4$, 161.0 (vt, $J_{PC} = 1.8$ Hz, C_3), 145.4 (s, C_5), 135.2 (o-Ar, B(Ar_F)₄), 129.3 (q, 31 Hz, m-Ar, B(Ar_F)₄), 125.0 (q, 273 Hz, CF₃, B(Ar_F)₄), 117.9 (*p*-Ar, B(Ar_F)₄), 103.7 (s, C₄), 40.7 (vt, $J_{PC} = 5.7$ Hz, C_2), 27.3 (vt, $J_{PC} = 3.8$ Hz, C_1), -22.9 (t, ${}^{2}J_{PC} = 6.6$ Hz, Pd-CH₃). Anal. Calcd for C₅₄H₅₄BF₂₄NO₂P₂Pd*CH₂Cl₂: C, 44.97; H, 3.84; N, 0.95. Found: C, 44.65; H, 3.93; N, 0.88.

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