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Reductive Elimination at an Ortho-Metalated Iridium(III) Hydride Bearing a Tripodal Tetraphosphorus Ligand

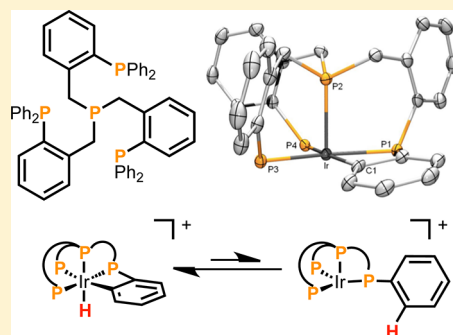
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S Supporting Information

ABSTRACT: The synthesis of the novel C_3 -symmetric tripodal, tetradentate ligand **1**, bearing only phosphorus atoms as donor groups, is described, starting from commercially available *o*-tolyldiphenylphosphine, and its molecular structure has been determined by X-ray crystallographic analysis. Coordination to the cationic Ir^I precursor $[\text{Ir}(\text{COE})_2(\text{acetone})_2]\text{PF}_6$ led to a highly unsymmetrical species (90% yield) with four inequivalent phosphorus atoms, as evidenced by ^{31}P NMR spectroscopy. The corresponding ^1H NMR spectrum exhibited a pseudo doublet of quartets at $\delta -5.9$ ppm with one large *trans* P–H coupling ($^2J_{\text{P-H}} = 115.4$ Hz) and a much smaller *cis* coupling ($^2J_{\text{P-H}} = 10.8$ Hz). X-ray crystallography confirmed the formation of complex **2**, $[\text{Ir}(\text{H})(\kappa^5\text{P},\text{P},\text{P},\text{P},\text{C}-1)]\text{PF}_6$, which is a rare example of a structurally characterized mononuclear Ir hydride species bearing an ortho-metalated phosphine ligand. This species does not react with hydride sources, but addition of 1 equiv of CF_3COOH resulted in facile overall formal protonation of the Ir–C bond. DFT calculations support a pathway involving initial reductive elimination, forming the highly distorted four-coordinate Ir^I species **2'**, followed by protonation at iridium to give the dicationic monohydride species **3**, with an activation barrier ΔG^\ddagger of 28.2 kcal mol^{−1}. Deuteration experiments support this mechanism. Reductive elimination can also be induced by reaction of **2** with carbon monoxide, yielding the monocationic carbonyl complex $[\text{Ir}^{\text{I}}(\text{CO})(\text{1})]\text{PF}_6$ as the sole product.

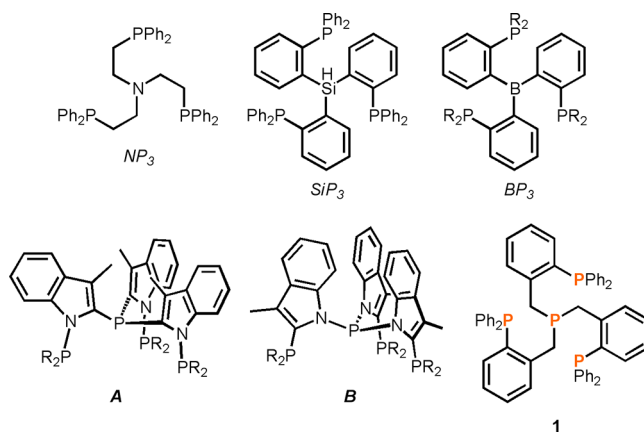


INTRODUCTION

Encapsulation of transition-metal complexes in well-defined environments, using either supramolecular or covalent approaches, is being actively pursued to stabilize and characterize species with unusual properties (reactivity, electronic structure, geometry) that may ultimately be exploited in, for example, catalytic reactions.¹ Concerning covalent frameworks, in particular C_3 -symmetric tripodal ligand systems have provided an ideal platform to investigate new phenomena in the reactivity of transition-metal complexes over the past few decades.² Among the plethora of binding motifs, ranging from neutral to trianionic scaffolds, triphosphine ligands have taken a prominent role, especially concerning the stabilization of late-transition-metal complexes.

An early, prominent tetradentate ligand bearing a coordinating noncarbon bridgehead atom is Sacconi's NP_3 system, wherein the pivot nitrogen atom is connected to three phosphine arms via ethylene spacers.³ However, this highly flexible tripodal structure shows hemilabile behavior of the nitrogen donor, which complicates the coordination chemistry. To counter this, tripodal triphosphine ligands with a strongly coordinating monoanionic bridgehead, such as SiP_3 , have been introduced (Chart 1),⁴ as well as the metalloboratrane analogue BP_3 , where additional metal-to-boron coordination induces structural rigidity.⁵ An alternative approach would be to employ

Chart 1. Structures of Tripodal Tetradentate Triphosphine Ligands NP_3 ,³ SiP_3 ,⁴ and BP_3 ,⁵ Linkage Isomers **A** and **B** of Tripodal Tetradentate All-Phosphorus Donor Ligands Based on 3-Methylinidole,⁵ and the Novel Ligand Scaffold **1**



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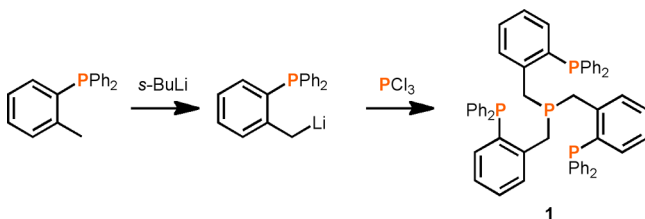
neutral tetradentate tripodal scaffolds wherein the position of the pivot donor is locked due to overall structural rigidity, forcing it to become part of the metal coordination sphere.

Typical examples feature five-membered “chelation”, which provides very favorable coordination to, for example, group 9 metals (Rh, Ir) but also automatically restricts the conformational freedom around the metal center. As an example, we have previously reported on the formation of two linkage isomers **A** and **B** of tripodal tetradentate all-phosphorus donor ligands based on an indolylphosphine scaffold as well as their sterically encumbered Rh^I, Rh^{II}, and Rh^{III} complexes.⁶ The highly constrained, rigid nature of the ligand was shown to dominate the overall geometry in these Rh complexes. Inspired by these results and building on the literature describing C₃-symmetric tetradentate ligands as well as our ongoing work on tridentate all-phosphorus donor ligands,^{7,8} we sought to construct a tripodal all-phosphorus donor with a slightly less rigid skeleton, enabling six-membered chelation while still possessing a strongly donating pivot, in order to accommodate a wider range of coordination geometries for the metal center and potentially induce additional reactivity pathways. Herein we describe the straightforward synthesis of novel PP₃ ligand **1** featuring benzyl spacers as well as its initial coordination chemistry to iridium and subsequent reactivity of the isolated ortho-metalated Ir^{III} hydrido species.

RESULTS AND DISCUSSION

Preparation and Characterization of Tripodal Tetradentate Ligand 1. Starting from 2-tolyldiphenylphosphine, simple lithiation of the methyl group afforded the corresponding organolithium building block. Upon reaction with an equimolar amount of PCl₃ and after extractive workup, ligand **1** was obtained as a white solid in moderate yield (Scheme 1).

Scheme 1. Synthetic Procedure to PP₃ Ligand **1**, Starting from Commercially Available Diphenyl-*o*-tolylphosphine



The ³¹P NMR spectrum of **1** reflected the anticipated highly symmetric nature of this compound, with a quartet at δ −4.0 and a doublet at −15.9 ppm in a relative ratio of 1:3 and both featuring a coupling constant *J*_{PP} of 25.0 Hz. The methylene spacer showed up nicely in the ¹H NMR spectrum at δ 3.54 ppm as a sharp singlet and as a pseudotriplet at δ 34.1 in the ¹³C NMR spectrum with a coupling constant ¹*J*_{PC} of 21.5 Hz. HR-MS also confirmed the formation of the intact PP₃ framework at *m/z* 857.3 for the parent molecular ion.

Single crystals suitable for X-ray crystallographic analysis were obtained from toluene at −20 °C; Figure 1 displays the resulting molecular structure and selected data. The intra-molecular P−P distances range from 3.4463(6) to 5.2926(7) Å, with the pivot P₁ atom in a typical pyramidal geometry and the lone pair oriented toward the binding pocket. The P₁ atom has a slightly reduced C−P−C angle sum for P₁ in comparison to the other P atoms (P₁, 298.36(14); P₂, 306.15(16); P₃,

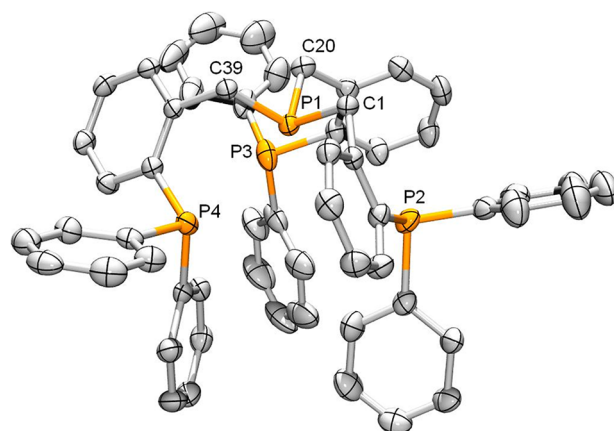


Figure 1. ORTEP plot (50% probability displacement ellipsoids) of PP₃ ligand **1**, tris(2-(diphenylphosphino)benzyl)phosphine. Hydrogen atoms and the toluene solvent molecule have been omitted for clarity. Selected bond lengths (Å) and angles (deg): P₁−C₁, 1.8582(18); P₁−P₂, 3.5299(7); P₁−P₃, 3.5043(6); P₂−P₄, 5.2926(7); C₁−P₁−C₂₀, 99.80(8); C₁−P₁−C₃₉, 99.27(8); C₂₀−P₁−C₃₉, 99.29(8).

305.74(14); P₄, 306.50(14)°), likely related to the difference in substitution (benzyl vs phenyl groups).

Coordination Behavior of Ligand 1 toward a Cationic Ir Precursor. Reaction of ligand **1** with 1 equiv of the cationic Ir precursor [Ir(COE)₂(acetone)₂]PF₆ in THF resulted in an immediate color change from orange to pale yellow, and extractive workup gave an off-white solid in 90% isolated yield. ³¹P{¹H} NMR spectroscopic analysis of this complex in CD₂Cl₂ indicated strong deviation from the ideal C₃ geometry observed for the free ligand, as four multiplet signals were observed in a 1:1:1:1 ratio at δ 33.6 (q, *J* = 20 Hz), 1.5 (ddd, *J* = 292, 20, 12 Hz), −3.6 (dd, *J* = 20, 12 Hz), and −73.7 (dt, *J* = 292, 20 Hz) ppm. ³¹P NMR spectroscopy in THF-*d*₈ at 60 °C did not result in a higher order symmetry spectrum.

Furthermore, the corresponding ¹H NMR spectrum did not show any indication of coordinated cyclooctene or acetone, suggestive of an additional substitution process after introduction of the Ir precursor to the PP₃ ligand. A complex hydride signal was discernible at δ −5.9 ppm, which resolved as a pseudo doublet of quartets with one large *trans* P−H coupling (²*J*_{P−H} = 115.4 Hz) and a much smaller *cis* coupling (²*J*_{P−H} = 10.8 Hz), presumably resulting from a C−H bond activation process (Figure 2). A selective ¹H{³¹P} NMR experiment at δ 33.6 ppm showed the disappearance of the large *trans* coupling of the hydride signal, which means that this phosphorus signal can be attributed to the pivotal P atom *trans* to the hydride. The ¹³C NMR spectrum revealed a doublet at 120.6 ppm, with a ²*J*_{P−C} value of 41.6 Hz, indicative of a direct Ir−carbon bond. The corresponding FAB-MS spectrum displayed a strong signal at *m/z* 1049.23, which agreed very favorably with the fragment [Ir(**1**)]⁺. On the basis of these observations, we concluded that the ortho-metalated Ir^{III} complex depicted in Scheme 2 is formed, with the hydride ligand *trans* to the phosphorus bridgehead of the PP₃ scaffold.

We were able to obtain single crystals, suitable for X-ray crystallographic analysis, by slow diffusion of pentane into a solution of **2** in dichloromethane. The resulting molecular structure is depicted in Figure 2, and bond distances, bond angles, and torsion angles are given in Table 1. Strikingly, reaction of **1** with the analogous Rh precursor failed to give any distinctive reactivity according to ³¹P NMR spectroscopy. We

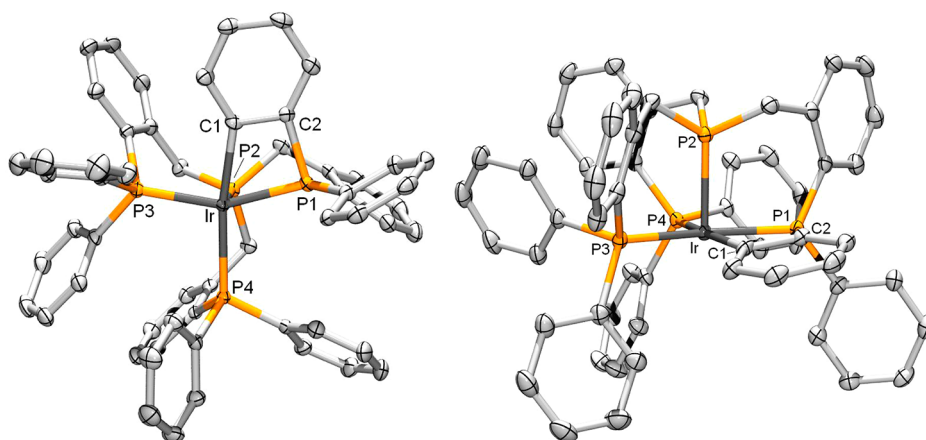


Figure 2. ORTEP plots (50% probability displacement ellipsoids) for the cationic portion of $[\text{Ir}(\text{H})(\kappa^5\text{P},\text{P},\text{P},\text{P},\text{C}-1)]\text{PF}_6$ (**2**) in bottom (left) and side-on (right) perspectives. Hydrogen atoms, the PF_6 anion, and solvent have been omitted for clarity.

Scheme 2. Preparation of Novel Ir^{III} Species **2, with $\kappa^5\text{P},\text{P},\text{P},\text{P},\text{C}$ Coordination of Ligand **1****

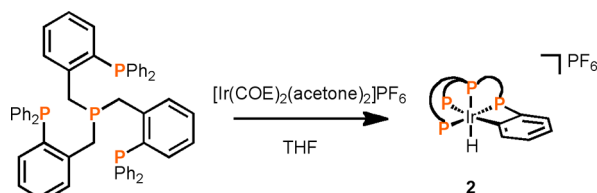


Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for **2**

Ir–P ₁	2.3279(7)	Ir–C ₁	2.133(3)
Ir–P ₂	2.3018(7)	P ₁ –C ₂	1.806(3)
Ir–P ₃	2.3305(7)	C ₁ –C ₂	1.408(4)
Ir–P ₄	2.3566(7)	Ir–H ₁ ^a	1.52(4)
P ₂ –P ₁	3.2153(11)	P ₂ –P ₃	3.3152(10)
P ₂ –P ₄	3.2912(11)	P ₁ –P ₃	4.5674(11)
P ₁ –Ir–P ₂	87.97(2)	P ₁ –Ir–C ₁	67.35(8)
P ₁ –Ir–P ₃	157.32(2)	P ₂ –Ir–C ₁	92.71(7)
P ₁ –Ir–P ₄	103.33(2)	P ₃ –Ir–C ₁	90.05(8)
P ₂ –Ir–P ₃	91.39(2)	P ₄ –Ir–C ₁	170.20(8)
P ₂ –Ir–P ₄	89.90(2)	Ir–P ₁ –C ₂	86.19(9)
P ₃ –Ir–P ₄	99.34(2)	P ₂ –Ir–H ₁	171.1(14)
C ₁ –Ir–P ₁ –C ₂	–5.53(12)	P ₂ –Ir–C ₁ –C ₂	–79.34(17)

^aHydride H₁ was refined with an isotropic displacement parameter.

are currently investigating details of this different behavior for the second-row congener.

Mononuclear Ir hydrido species with a four-membered ortho-metalated phosphine ligand that have been structurally characterized are rare.⁹ The structure in Figure 3 exhibits a phosphine *trans* to the phenyl ring and a phosphine *trans* to the hydride, which was refined freely with an isotropic displacement parameter and resolved at an Ir–H bond distance of 1.52(4) Å, with a P₂–Ir–H₁ angle of 171.1(14)°. The Ir–P distances are all similar at around 2.30–2.35 Å. The Ir–C₁ bond length is within the expected range for a cyclometalated phenyl ring. The P₁–Ir–C₁ angle is very acute at 67.35(8)°, typical for cyclometalated phenylphosphine fragments.⁸ The maximum intramolecular P–P distance is approximately 4.5 Å (P₁–P₃), which is significantly shorter than in free ligand **1**. The C–P–C angle sums (P₁, 321.7(2); P₂, 310.3(2); P₃,

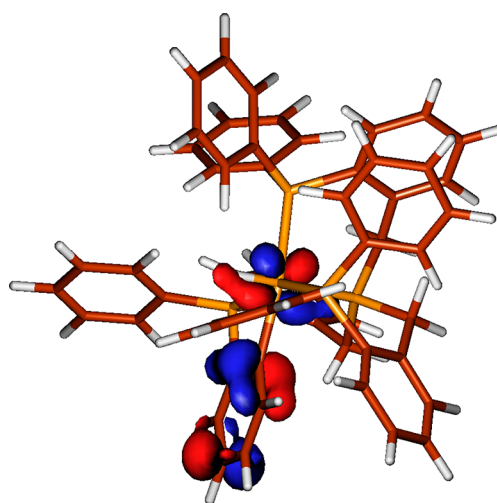


Figure 3. HOMO of complex **2**, as calculated by DFT (Turbomole, BP86, SV(P)).

306.9(2); P₄, 309.6(2)°) differ significantly, as a result of the varying coordination environments of the four phosphines in complex **2**.

In an effort to intercept the supposed Ir^I intermediate formed upon ligand exchange at the cationic Ir precursor, presumably giving rise to a species such as $\text{Ir}(\kappa^4\text{P},\text{P},\text{P},\text{P})(\text{L})\text{PF}_6$ (L = cyclooctene, acetone), we investigated the reaction between **1** and $[\text{Ir}(\mu\text{-Cl})(\text{COE})_2]_2$. When monitored by ³¹P NMR spectroscopy, this reaction did not proceed as cleanly as for the cationic Ir precursor, but the corresponding species **2Cl** was observed as the major species in solution. This was further corroborated by the presence of an identical hydride signal in the ¹H NMR spectrum, suggesting a favorable pathway for intramolecular C–H activation.

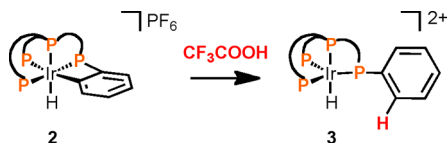
Reactivity of Complex **2.** To date, only four reports mention the formation of an ortho-metalated tripodal phosphine ligand, to the best of our knowledge.¹⁰ Two iridium-containing complexes are known, but in both cases a tridentate ligand with a noncoordinating pivot atom (either C^{10b} or B^{9e}) was employed. Hence, complex **2** is the only Ir species known that bears an all-phosphorus tetradentate ligand structure. Strikingly, no details of the potential reversible character of the M–C bond formation have been disclosed for any of these systems, but such behavior may become relevant in

the context of cooperative catalysis and metal–ligand bifunctional bond activation of small molecules.^{11,12} In order to determine the nature of the “hydride” ligand—the cationic character of the Ir^{III} center could give rise to more “protic” behavior—the reactivity of **2** to various electrophilic and nucleophilic reagents was explored. Addition of a base such as KHDMS or LiCH₂SiMe₃ or a hydride donor such as NaBH₄ did not result in any discernible reactivity of the Ir–H fragment, indicating a very poorly electrophilic Ir–H system, perhaps induced by shielding of the ligand scaffold. Weak acids such as NH₄PF₆ did not induce any conversion of this species either, and subjecting a solution of the Ir^{III} complex to 5 bar of H₂ also did not give any reaction. No reaction was observed when complex **2** was treated with an equimolar amount of methyl iodide.

The addition of ~20 mol equiv of DCl in THF at 60 °C led to complete conversion overnight, with disappearance of the high-field doublet at $\delta \sim -75$ ppm in the ³¹P NMR spectrum for the ortho-metalated phenylphosphino group in **2**. However, the reaction was not selective, giving a number of unidentified signals in the ³¹P NMR spectrum. Notably, Bianchini has reported on a somewhat related Rh(H)(Cl)(PP₃) species (PP₃ = P(CH₂CH₂PPh₂)₃), but with a *trans* relation between Cl and the pivotal P rather than the expected peripheral P in our case, upon substitution of the coordinated phenyl fragment for a chloride ligand.¹³

To induce cleaner conversion, we turned to trifluoroacetic acid (CF₃COOH, TFA) as the protonating agent. While an equimolar amount did not give appreciable conversion of **2** at room temperature, the use of 10 molar equiv of CF₃COOH (Scheme 3) resulted in bleaching of the pale yellow solution,

Scheme 3. Chemoselective Protonation of the Ir–C Bond in Ir^{III} Species **2, Resulting in Formation of the Dicationic Ir Hydrido Complex **3****



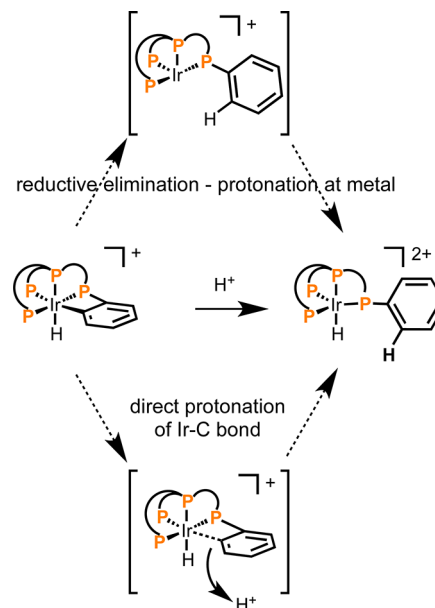
concomitant with formation of a new hydride signal at $\delta -9.75$ ppm (chemical shift $\Delta\delta$ of -3.85 ppm relative to **2**) in the ¹H NMR spectrum, with coupling constants J_{P-H} of 133.8 and 16.0 Hz. The corresponding ³¹P{¹H} NMR spectrum displayed two signals at δ 16.31 (pivotal phosphine) and -4.24 ppm (peripheral phosphines), both with a J_{P-P} value of 19 Hz. These data imply a *trans* disposition of a phosphine and a hydride ligand similar to that seen for species **2**, suggesting overall “protonation” of the Ir–C₁ bond rather than protonation of the hydride ligand.

In an attempt to rationalize the observed chemoselective protonation of the ortho-metalated fragment rather than the “hydride” ligand, we first investigated the electronic structure of species **2** with DFT (BP86). As is depicted in Figure 3, the HOMO of the ortho-metalated complex shows pronounced electron density being located in the antibonding Ir–C bond (π character). Hence, we argued that direct protonation of the ortho-metalated aryl fragment might be one possible pathway for the observed conversion of **2** with acids.

Alternatively, the reaction of **2** with H⁺ to form **3** might proceed via reductive elimination of a C_{Ar}–H bond involving

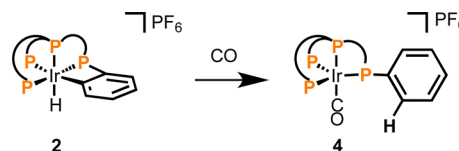
the Ir hydride and Ir–C bond in **2**, followed by protonation of the resulting (non-ortho-metalated) (κ^4 -P)₃Ir complex **2'** at iridium (see Scheme 4 for both pathways).

Scheme 4. Two Distinct Mechanisms for the Conversion of Ortho-Metalated Ir Hydride **2 into Hydride **3** by Reaction with Acid**



In an attempt to elaborate on the prevalent mechanism by which the conversion from **2** to **3** proceeds, we employed trifluoroacetic acid-*d*, which led to a signal at $\delta -9.75$ ppm in the ²H NMR spectrum for the corresponding Ir–D species, with no indication for the installment of any C_{Ph}–D bonds. This observation strongly supports the aforementioned reductive elimination pathway, as direct protonation of the Ir–C_{Ph} bond would result in a C_{Ph}–D fragment. TFA may favorably affect the overall process by transient protonation of the ortho-metalated ring, thereby enhancing intramolecular reductive elimination. Further support for the reductive elimination reaction path was obtained from submitting a solution of complex **2** in CD₂Cl₂ to an atmosphere of CO (5 bar) (Scheme 5). This slow reaction (80% conversion after 2

Scheme 5. Chemoselective Reduction of **2 to the Corresponding Ir^I Derivative **4** under a CO Atmosphere via Reductive Elimination–CO Coordination**



weeks at room temperature) resulted in clean formation of the new, highly symmetric species [Ir(**1**)(CO)]PF₆ (**4**). The (in situ) ³¹P{¹H} NMR spectrum displayed only two signals (δ 43.28 (broad) 1P; -11.69 ppm (d), 3P, $^2J_{P-P} = 37.7$ Hz). This species was further characterized by IR spectroscopy, showing the presence of a single carbonyl ligand bound to an electron-poor iridium center (ν_{CO} 2006 cm⁻¹).¹⁴

The energy profile for the reductive elimination process from **2** to **2'** according to DFT calculations is shown in Figure 4.

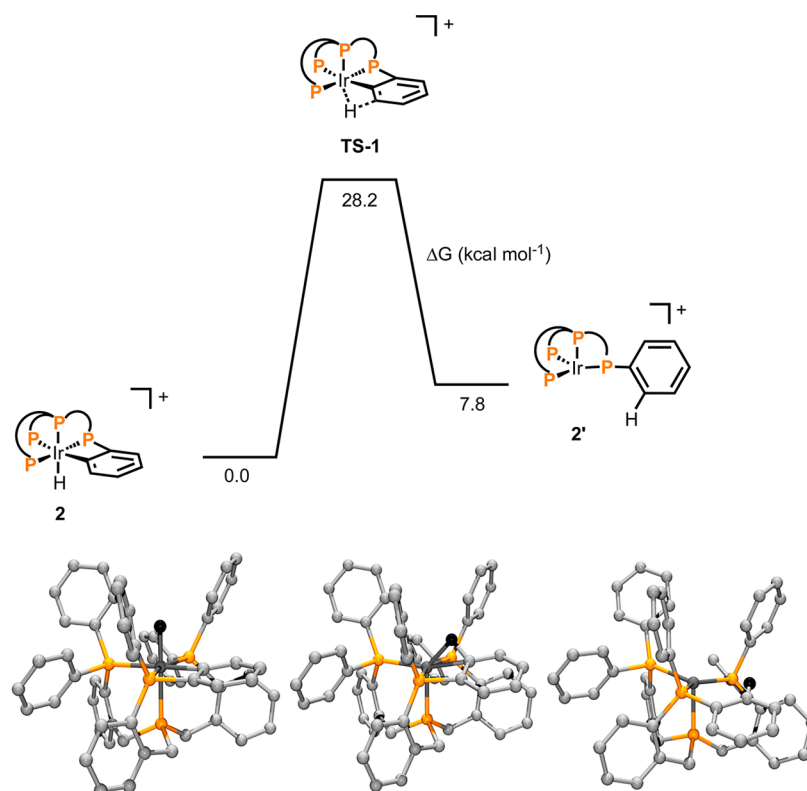


Figure 4. (top) Reaction profile for reductive elimination of Ph–H from ortho-metalated species **2** as calculated by DFT (Turbomole, BP86, SV(P)) with free energies in kcal mol^{−1}. (bottom) DFT optimized geometries for species **2** (left), TS-1 (middle), and **2'** (right).

These calculations suggest that the pathway involving initial reductive elimination is accessible, proceeding via transition state TS-1 with a barrier of 28.2 kcal mol^{−1}. The reductive elimination is endergonic, and protonation of the resulting iridium(I) species must therefore provide the thermodynamic driving force for the overall process. These data agree well with the experimentally observed oxidative addition of the aromatic C–H bond of the PP₃ ligand upon binding to iridium(I) precursors. This process has a substantially lower barrier (20.4 kcal mol^{−1}) and is exergonic.

In summary, we have reported the synthesis of a novel tripodal tetradentate all-phosphorus donor ligand **1** bearing a flexible benzylic backbone and diphenylphosphine side groups and its coordination behavior to a cationic Ir^I precursor. Facile ortho metalation of one of the phenyl groups gives rise to formation of the highly encapsulated, cationic octahedral Ir^{III}(hydrido) species **2**⁺. This complex is unreactive toward hydride sources, but it reacts smoothly with strong acid, generating the corresponding dicationic monohydrido species **3**.¹⁵ DFT calculations reveal a high-barrier reductive elimination process of the cyclometalated Ar–H moiety. Subsequent protonation of the thus formed cationic Ir^I species provides a viable pathway for the formation of **3**. Further support for this pathway was obtained by using a deuterium-labeled acid and from the slow but selective formation of [Ir(1)(CO)]PF₆ (**4**) by subjecting **2** to an atmosphere of CO (5 bar for 2 weeks). We are currently exploring the reactivity of PP₃ scaffold **1** with other metals and the possibility of utilizing the reductive elimination pathway for interesting reactivity with other substrates. In addition, the effect of ligand-induced encapsulation on the reactivity displayed by the shielded metal center is under investigation.

EXPERIMENTAL SECTION

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Reagents were purchased from commercial suppliers and used without further purification. [Ir(COE)₂(acetone)₂]PF₆ was prepared following a literature procedure.¹⁶ THF, pentane, hexane, and Et₂O were distilled from sodium benzophenone ketyl. CH₂Cl₂ was distilled from CaH₂ and toluene from sodium under nitrogen. NMR spectra (¹H, ¹H{³¹P}, ³¹P{¹H}, and ¹³C{¹H}) were measured on a Varian INOVA 500 MHz, a Bruker AV400, or a Varian MERCURY 300 MHz spectrometer. High-resolution mass spectra were recorded on a JEOL JMS SX/SX102A four-sector mass spectrometer; for FAB-MS, 3-nitrobenzyl alcohol was used as a matrix. IR spectra (ATR) were recorded with a Bruker Alpha-p FT-IR spectrometer.

Preparation of Tris((2-diphenylphosphino)benzyl)phosphine (1). A red solution of (diphenyl-*o*-tolylphosphino)-lithium¹⁷ (896.4 mg, 3.18 mmol) in diethyl ether (15 mL) was added to a PCl₃ solution (0.09 mL, 0.62 mmol) in diethyl ether (5 mL) via a Teflon cannula. The resulting off-white milky suspension was stirred for 4 h, during which time a dark orange suspension was formed that was subsequently concentrated in vacuo. The orange foam was dissolved in diethyl ether (20 mL) and added to a solution of LiAlH₄ (162.7 mg, 4.29 mmol) in diethyl ether (15 mL) at −35 °C (to reduce undesired side products, allowing for easier purification), and the mixture was stirred for 2.5 h. The solvent was evaporated, and toluene (30 mL) was added to the residue, followed by filtration (dual-layer silica–Celite) and washing with toluene (4 × 5 mL). The solvent was removed under reduced pressure. After this, the ligand was recrystallized in toluene at −20 °C to give pure **1** in 25% yield. Mp: 144 °C. ¹H NMR (400 MHz, 298 K, C₆D₆): δ (ppm) 7.46–7.42 (m, 9H, ArH), 7.31 (t, *J*_{HH} = 7.6, *J*_{PH} = 6.2 Hz, 3H, ArH), 7.21 (dd, *J*_{HH} = 7.1, *J*_{PH} = 3.5 Hz, 3H, ArH) 7.18–7.12 (m, 18H, ArH), 7.09 (t, *J*_{HH} = 7.0 Hz, 3H, ArH) 6.98 (t, *J*_{HH} = 7.4 Hz, 3H, ArH), 3.54 (s, 6H, CH₂). ¹³C NMR (100 MHz, 298 K, C₆D₆): δ (ppm) 143.79 (dd, *J*_{PC} = 26.5 and 7.3 Hz, ArC), 137.50 (d, *J*_{PC} = 13.0 Hz, ArC), 136.30 (dd, *J*_{PC} = 13.3 and 2.6 Hz, ArC), 133.97 (d, *J*_{PC} = 19.9 Hz, ArC), 130.10 (dd, *J*_{PC}

= 9.3 and 5.4 Hz, ArC), 128.77 (s, ArC), 128.30 (d, J_{PC} = 7.0 Hz, ArC), 128.17 (s, ArC), 34.13 (pt, J_{PC} = 21.5 Hz, CH₂). ³¹P NMR (161 MHz, 298 K, C₆D₆): δ (ppm) –15.92 (d, J = 25.0 Hz, 3P), –3.99 (q, J = 25.0 Hz, 1P). HR-MS (FAB⁺): C₅₇H₄₉P₄ m/z calcd 857.2785, found 857.2760.

Preparation of [Ir(H)(κ^5 P,P,P,P,C-1)]PF₆ (2). Tris(2-(diphenylphosphino)phenyl)phosphine (1; 212 mg, 0.25 mmol) in THF (18 mL) was added to [Ir(cod)(acetone)₂]PF₆ in THF (168 mg, 0.25 mmol, 2 mL) via a Teflon cannula. An immediate color change from orange to pale yellow was observed. The reaction mixture was stirred overnight at room temperature and thereafter concentrated to approximately 4 mL. After the solution was cooled to –35 °C, pentane (15 mL) was added and a beige solid precipitated. The cooling was removed, and THF (10 mL) was added, whereafter the precipitate was filtered and washed with pentane (20 × 1 mL). The product 2 was obtained as an off-white powder in 90% yield. Mp: >250 °C dec. ¹H NMR (400 MHz, 298 K, CD₂Cl₂): δ (ppm) 8.37 (pt, J_{HH} = 8.0 Hz, 2H), 7.68–6.52 (m, 37H), 6.27 (pt, J_{PH} = 8.0 Hz, J_{HH} = 6.9 Hz, 1H), 6.02 (pd, J_{PH} = 4.0 Hz, J_{HH} = 6.6 Hz, 1H), 3.90 (pt, J_{PH} = 13.6 Hz, 1H), 3.60 (pt, J_{PH} = 13.7 Hz, J_{HH} = 13.6 Hz, 1H), 3.36 (pt, J_{PH} = 13.2 Hz, J_{HH} = 13.7 Hz, 1H), 3.23 (d, J_{PH} = 8.4 Hz, J_{HH} = 13.5 Hz, 1H), 3.00 (m, J_{HH} = 15.0 Hz, 1H), 2.27 (m, J_{HH} = 14.2 Hz, 1H), –5.90 (dpq, J_{PH} = 11.5 and 10.8 Hz, hydride); the J_{HH} coupling constants are determined from the corresponding ¹H{³¹P} NMR spectrum. ¹³C NMR (100 MHz, 298 K, CD₂Cl₂): δ (ppm) 138.6 (br d, J_{PC} = 13.0 Hz, C), 138.0 (dd, J_{PC} = 12.0 and 3.8 Hz), 136.4 (br d, J_{PC} = 12.2 Hz), 136.1 (dd, J_{PC} = 3.2 and 1.5 Hz), 134.2–133.9 (m), 133.8–133.7 (m), 133.1 (t, J_{PC} = 7.6 Hz), 133.0–132.6 (m), 132.6–132.4 (m), 131.9–131.8 (m), 131.8–131.3 (m), 131.2 (s), 130.2 (s), 130.1–129.9 (m), 129.8–129.6 (m), 129.5–129.3 (m), 129.0 (d, J_{PC} = 25.6 Hz), 128.6–128.1 (m), 128.0 (d, J_{PC} = 9.9 Hz), 127.8–127.6 (m), 126.9 (br dd, J_{PC} = 27.3 and 7.5 Hz), 123.8–123.3 (m), 120.6 (br d, J_{PC} = 41.6 Hz), 67.6 (s), 30.0–29.4 (m, CH₂), 28.6 (dd, J_{PC} = 30.2 and 9.9 Hz, CH₂), 24.7 (br d, J_{PC} = 25.6 Hz, CH₂). ³¹P NMR (161 MHz, 298 K, CD₂Cl₂): δ (ppm) 33.63 (q, J = 19.8 Hz, P2), 1.50 (ddd, J = 292.1, 21.9, 10.6 Hz, P3), –3.56 (q, J = 14.0 Hz, P4), –73.68 (dt, J = 291.8, 17.3 Hz, P1), –144.29 (hept, J = 711.4 Hz, PF₆). HR-MS (FAB⁺): C₅₇H₄₉IrP₄ m/z calcd 1049.2341, found 1049.2336.

Reactivity of 2 toward Trifluoroacetic Acid and CO. Addition of 10 molar equiv of CF₃COOH (TFA) to a solution of 2 (40 mg, 33.5 μ mol) in CD₂Cl₂ at room temperature led to clean formation of a new species within 1 h, as indicated by ¹H and ³¹P NMR spectroscopy. ¹H NMR (400 MHz, 298 K, CD₂Cl₂): δ (ppm) –9.75 (1H, $J_{\text{P-H}}$ = 133.8, $J_{\text{P-H}}$ = 16.0 Hz). ³¹P NMR (161 MHz, 298 K, CD₂Cl₂): δ (ppm) 16.31 (q, 1P, $J_{\text{P-P}}$ = 19.0 Hz), –4.24 (overlapping doublets, 3P, $J_{\text{P-P}}$ = 19.0 Hz). A solution of 2 in CD₂Cl₂ (20 mg, 16.7 μ mol) was stirred for 2 weeks while under a static pressure of CO (5 bar), giving rise to \pm 80% conversion of 2 into a highly symmetrical species, according to in situ ³¹P NMR spectroscopy: ³¹P NMR (161 MHz, 298 K, CD₂Cl₂): δ (ppm) 43.28 (1P, broad), –11.69 (3P, $J_{\text{P-P}}$ = 37.7 Hz). Identical spectroscopic features were present after depressurizing the solution. ATR-IR: ν_{CO} 2006 (s) cm^{–1}.

DFT Calculations. Geometry optimizations were carried out with the Turbomole program package¹⁸ coupled to the PQS Baker optimizer¹⁹ at the ri-DFT level using the BP86²⁰ functional and the resolution-of-identity (ri) method.²¹ We used the SV(P) basis set²² for the geometry optimizations of all stationary points. All minima (no imaginary frequencies) and transition states (one imaginary frequency) were characterized by numerically calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated.

X-ray Crystal Structure Determinations. Reflections were measured on a Bruker Kappa ApexII diffractometer with a sealed tube and Triumph monochromator (λ = 0.71073 Å). The reflections were integrated with the SAINT²³ (compound 1) or EVAL15²⁴ (2) software. Absorption corrections based on multiple measured reflections were performed with SADABS.²⁵ The structures were solved with direct methods using SIR-97²⁶ (1) or SHELXS-97²⁷ (2). Refinement was performed with SHELXL-97²⁷ against F^2 values of all reflections. Non-hydrogen atoms were refined freely with anisotropic

displacement parameters. Hydrogen atoms were introduced in calculated positions. The hydride H atom of 2 was refined freely with an isotropic displacement parameter. The PF₆ anion in 2 was disordered over two orientations and was refined with restraints for the F–P–F angles and to approximate isotropic behavior. Geometry calculations and checks for higher symmetry were performed with the PLATON program.²⁸

Details for 1: C₅₇H₄₈P₄·C₇H₈, fw = 948.97, colorless block, 0.40 × 0.34 × 0.12 mm³, triclinic, $P\bar{1}$ (No. 2), a = 11.3975(3) Å, b = 12.4827(3) Å, c = 19.9754(5) Å, α = 102.5504(10)°, β = 105.3070(10)°, γ = 98.8375(11)°, V = 2607.55(11) Å³, Z = 2, D_x = 1.209 g/cm³, μ = 0.185 mm^{–1}. 44492 reflections measured up to ($\sin \theta/\lambda$)_{max} = 0.61 Å^{–1}, 9710 unique reflections (R_{int} = 0.022), of which 8131 were observed ($I > 2\sigma(I)$), $R1/wR2$ ($I > 2\sigma(I)$) 0.0392/0.1039, $R1/wR2$ (all reflections) 0.0500/0.1128, S = 1.031, residual electron density between –0.31 and 0.65 e/Å³.

Details for 2: [C₅₇H₄₈IrP₄]PF₆·CH₂Cl₂, fw = 1278.93, yellow block, 0.34 × 0.25 × 0.12 mm³, triclinic, $P\bar{1}$ (No. 2), a = 12.7688(3) Å, b = 12.9030(3) Å, c = 17.9973(3) Å, α = 89.388(1)°, β = 71.597(1)°, γ = 68.159(1)°, V = 2592.31(10) Å³, Z = 2, D_x = 1.638 g/cm³, μ = 2.894 mm^{–1}. 65351 reflections measured up to ($\sin \theta/\lambda$)_{max} = 0.65 Å^{–1}, 11894 unique reflections (R_{int} = 0.023), of which 11038 were observed ($I > 2\sigma(I)$), $R1/wR2$ ($I > 2\sigma(I)$) 0.0210/0.0523, $R1/wR2$ (all reflections) 0.0243/0.0537, S = 1.070, residual electron density between –1.16 and 0.79 e/Å³.

■ ASSOCIATED CONTENT

● Supporting Information

NMR spectra of compounds 1–3, CIF files giving crystallographic data for 1 and 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Selected relevant contributions: (a) Otte, M.; Kuijpers, P. F.; Troeppner, O.; Iva nović-Burmazović, I.; Reek, J. N. H.; de Bruin, B. *Chem. Eur. J.* **2013**, DOI: 10.1002/chem.201301411. (b) Gadzikwa, T.; Bellini, R.; Dekker, H. L.; Reek, J. N. H. *J. Am. Chem. Soc.* **2012**, *134*, 2860. (c) Anxolabéhère-Mallart, E.; Costentin, C.; Fournier, M.; Nowak, S.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2012**, *134*, 6104. (d) Inokuma, Y.; Kawano, M.; Fujita, M. *Nature Chem.* **2011**, *3*, 349. (e) Wang, Z. J.; Brown, C. J.; Bergman, R. G.; Raymond, K. N.; Toste, F. D. *J. Am. Chem. Soc.* **2011**, *133*, 7358. (f) Wiester, M. J.; Ulmann, P. A.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 114. (g) van der Vlugt, J. I.; Koblenz, T. S.; Wassenaar, J.; Reek, J. N. H. In *Molecular Encapsulation: Reactions in Constrained Systems*; Miesusset, J.-L., Brinker, U. H., Eds.; Wiley: Hoboken, NJ, 2010; p 145. (h) Koblenz, T. S.; Wassenaar, J.; Reek, J. N. H. *Chem. Soc. Rev.* **2008**, *37*, 1700. (i) Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 349.
- (2) Selected relevant contributions: (a) Siegl, W. O.; Lapporte, S. J.; Collman, J. P. *Inorg. Chem.* **1971**, *10*, 2158. (b) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1987**,

1093. (c) Kläui, W. *Angew. Chem., Int. Ed.* **1990**, *29*, 627. (d) Barbaro, P.; Blanchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 2227. (e) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (f) Herberhold, M.; Bauer, K.; Milius, W. *J. Organomet. Chem.* **1995**, *502*, C1. (g) MacBeth, C. E.; Golombek, A. P.; Young, V. G., Jr.; Yang, C.; Kuczera, K.; Hendrich, M. P.; Borovik, A. S. *Science* **2000**, *289*, 938. (h) Castro-Rodriguez, I.; Nakai, H.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *Science* **2004**, *305*, 1757. (i) Turculet, L.; Feldman, J. D.; Tilley, T. D. *Organometallics* **2004**, *23*, 2488. (j) Han, H.; Elsmaili, M.; Johnson, S. A. *Inorg. Chem.* **2006**, *45*, 7435. (k) Friesen, D. M.; Bowles, O. J.; McDonald, R.; Rosenberg, L. *Dalton Trans.* **2006**, 2671. (l) Ciclosi, M.; Llort, J.; Estevan, F.; Lahuerta, P.; Sanaú, M.; Pérez-Prieto, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6741. (m) Whited, M. T.; Rivard, E.; Peters, J. C. *Chem. Commun.* **2006**, 1613. (n) Leung, W.-H.; Zhang, Q.-F.; Yi, X.-Y. *Coord. Chem. Rev.* **2007**, *251*, 2266. (o) Takeda, N.; Watanabe, D.; Nakamura, T.; Unno, M. *Organometallics* **2010**, *29*, 2839. (p) Bhadbhade, M. M.; Field, L. D.; Gilbert-Wilson, R.; Guest, R. W.; Jensen, P. *Inorg. Chem.* **2011**, *50*, 6220. (q) Moret, M.-E.; Peters, J. C. *J. Am. Chem. Soc.* **2011**, *133*, 18118. (r) Boddien, A.; Mellmann, D.; Gärtner, F.; Jackstell, R.; Junge, H.; Dyson, P. J.; Laurenczy, G.; Ludwig, R.; Beller, M. *Science* **2011**, *333*, 1733. (s) Tejel, C.; Geer, A. M.; Jiménez, S.; López, J. A.; Ciriano, M. A. *Organometallics* **2012**, *31*, 2895. (t) Fernández-Anca, D.; García-Seijo, M. I.; García-Fernández, M. E. *RSC Adv.* **2012**, *2*, 1404. (u) Moriuchi, T.; Mao, L.; Wu, H.-L.; Ohmura, S. D.; Watanabe, M.; Hirao, T. *Dalton Trans.* **2012**, *41*, 9519. (v) Kropp, H.; King, A. E.; Khushniyarov, M. M.; Heinemann, F. W.; Lancaster, K. M.; DeBeer, S.; Bill, E.; Meyer, K. *J. Am. Chem. Soc.* **2012**, *134*, 15538. (w) Ziebart, C.; Federsel, C.; Anbarasan, P.; Jackstell, R.; Baumann, W.; Spannenberg, A.; Beller, M. *J. Am. Chem. Soc.* **2012**, *134*, 20701. (x) Broda, H.; Hinrichsen, S.; Tuzcek, F. *Coord. Chem. Rev.* **2013**, *257*, 587. (y) Gilbert-Wilson, R.; Field, L. D.; Colbran, S. B.; Bhadbhade, M. M. *Inorg. Chem.* **2013**, *52*, 3043.
- (3) (a) Sacconi, L.; Bertini, I. *J. Am. Chem. Soc.* **1967**, *89*, 2235. (b) Di Vaira, M.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1977**, *16*, 1518.
- (4) (a) Gossage, R. A.; McLennan, G. D.; Stobart, S. R. *Inorg. Chem.* **1996**, *35*, 1729. (b) Mankad, N. P.; Whited, M. T.; Peters, J. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 5768.
- (5) (a) Bontemps, S.; Bouhadir, G.; Dyer, P. W.; Miqueu, K.; Bourissou, D. *Inorg. Chem.* **2007**, *46*, 5149. (b) Sircoglou, M.; Bontemps, S.; Bouhadir, G.; Saffon, N.; Miqueu, K.; Gu, W.; Mercy, M.; Chen, C.-H.; Foxman, B. M.; Maron, L.; Ozerov, O. V.; Bourissou, D. *J. Am. Chem. Soc.* **2008**, *130*, 16729. (c) Bontemps, S.; Bouhadir, G.; Gu, W.; Mercy, M.; Chen, C.-H.; Foxman, B. M.; Maron, L.; Ozerov, O. V.; Bourissou, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 1481. (d) Moret, M.-E.; Peters, J. C. *Angew. Chem., Int. Ed.* **2011**, *50*, 2063. (e) Kameo, H.; Hashimoto, Y.; Nakazawa, H. *Organometallics* **2012**, *31*, 3155. (f) Kameo, H.; Hashimoto, Y.; Nakazawa, H. *Organometallics* **2012**, *31*, 4251. (g) Moret, M.-E.; Zhang, L.; Peters, J. C. *J. Am. Chem. Soc.* **2013**, *135*, 3792.
- (6) (a) Wassenaar, J.; de Bruin, B.; Siegler, M. A.; Spek, A. L.; Reek, J. N. H.; van der Vlugt, J. I. *Chem. Commun.* **2010**, *49*, 1232–1234. (b) Wassenaar, J.; Siegler, M. A.; Spek, A. L.; de Bruin, B.; Reek, J. N. H.; van der Vlugt, J. I. *Inorg. Chem.* **2010**, *49*, 6495. See also: (c) Penno, D.; Koshevoy, I. O.; Estevan, F.; Sanaú, M.; Ubeda, M. A.; Pérez-Prieto, J. *Organometallics* **2010**, *29*, 703. For another recent elegant addition to the class of PP₃ ligands, see: (d) Ziebart, C.; Federsel, C.; Anbarasan, P.; Jackstell, R.; Baumann, W.; Spannenberg, A.; Beller, M. *J. Am. Chem. Soc.* **2012**, *134*, 20701.
- (7) Bauer, R. C.; Gloaguen, Y.; Lutz, M.; Reek, J. N. H.; de Bruin, B.; van der Vlugt, J. I. *Dalton Trans.* **2011**, *40*, 8822.
- (8) Gloaguen, Y.; Jacobs, W.; de Bruin, B.; Lutz, M.; van der Vlugt, J. I. *Inorg. Chem.* **2013**, *52*, 1682.
- (9) (a) Del Piero, G.; Perego, G.; Zazzetta, A.; Cesari, M. *Cryst. Struct. Commun.* **1974**, *3*, 725. (b) von Deuten, K.; Dahlenburg, L. *Cryst. Struct. Commun.* **1980**, *9*, 421. (c) Crabtree, R. H.; Quirk, J. M.; Felkin, H.; Fillebeen-Khan, T.; Pascard, C. *J. Organomet. Chem.* **1980**, *187*, C32. (d) Cooper, A. C.; Clot, E.; Huffman, J. C.; Streib, W. E.; Maseras, F.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1999**, *121*, 97. (e) Feldman, J. D.; Peters, J. C.; Tilley, T. D. *Organometallics* **2002**, *21*, 4050. (f) Brym, M.; Jones, C. *Transition Met. Chem.* **2003**, *28*, 595. (g) Fang, H.; Choe, Y.-K.; Li, Y.; Shimada, S. *Chem. Asian J.* **2011**, *6*, 2512.
- (10) (a) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 6411. (b) Stössel, P.; Heins, W.; Mayer, H. A.; Fawzi, R.; Steimann, M. *Organometallics* **1996**, *15*, 3393. (c) Takaoka, A.; Mendiratta, A.; Peters, J. C. *Organometallics* **2009**, *28*, 3744. See also ref 9e.
- (11) Recent reviews: (a) van der Vlugt, J. I.; Reek, J. N. H. *Angew. Chem., Int. Ed.* **2009**, *48*, 8832. (b) Gunanathan, C.; Milstein, D. *Acc. Chem. Res.* **2011**, *44*, 588. (c) van der Vlugt, J. I. *Eur. J. Inorg. Chem.* **2012**, 363. (d) Askevold, B.; Roesky, H. W.; Schneider, S. *ChemCatChem* **2012**, *4*, 307. For a theoretical view on reversible M–C reactivity, see: (e) Ghatak, K.; Mane, M.; Vanka, K. *ACS Catal.* **2013**, *3*, 920.
- (12) Work from our group on cooperative bond activation: (a) van der Vlugt, J. I.; Pidko, E. A.; Vogt, D.; Lutz, M.; Spek, A. L.; Meetsma, A. *Inorg. Chem.* **2008**, *47*, 4442. (b) van der Vlugt, J. I.; Lutz, M.; Pidko, E. A.; Vogt, D.; Spek, A. L. *Dalton Trans.* **2009**, 1016. (c) van der Vlugt, J. I.; Pidko, E. A.; Vogt, D.; Lutz, M.; Spek, A. L. *Inorg. Chem.* **2009**, *48*, 7513. (d) van der Vlugt, J. I.; Siegler, M. A.; Janssen, M.; Vogt, D.; Spek, A. L. *Organometallics* **2009**, *29*, 7025. (e) van der Vlugt, J. I.; Pidko, E. A.; Bauer, R. C.; Gloaguen, Y.; Rong, M. K.; Lutz, M. *Chem. Eur. J.* **2011**, *17*, 3850. (f) Lindner, R.; van den Bosch, B.; Lutz, M.; Reek, J. N. H.; van der Vlugt, J. I. *Organometallics* **2011**, *30*, 499. (g) de Boer, S. Y.; Gloaguen, Y.; Lutz, M.; van der Vlugt, J. I. *Inorg. Chim. Acta* **2012**, *380*, 336. (h) de Boer, S. Y.; Gloaguen, Y.; Reek, J. N. H.; Lutz, M.; van der Vlugt, J. I. *Dalton Trans.* **2012**, *41*, 11276. Oldenhof, S.; de Bruin, B.; Lutz, M.; Siegler, M. A.; Patureau, F. W.; van der Vlugt, J. I.; Reek, J. N. H. *Chem. Eur. J.* **2013**, DOI: 10.1002/chem.201302230.
- (13) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 6411–6423.
- (14) (a) Dzik, W. I.; Smits, J. M. M.; Reek, J. N. H.; de Bruin, B. *Organometallics* **2009**, *28*, 1631. (b) Kerfoot, D. G. E.; Mawby, R. J.; Sgamelloiti, A.; Venanzi, L. M. *Inorg. Chim. Acta* **1974**, *8*, 195.
- (15) This transformation is different from the reported protonation of an ortho-metalated Ir^{III}(phosphino)aryl species by Bergman and co-workers, due to the rigid octahedral geometry and the presence of a hydride fragment in complex 3: (a) Luecke, H. F.; Bergman, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 11538. Our case bears some similarity to the reported reversible cyclometalation of silyl ligands; see: (b) Aizenberg, M.; Milstein, D. *Organometallics* **1996**, *15*, 3317. It is also related to a report by Caulton, describing similar behavior for a nonencapsulated iridium hydride species bearing an ortho-metalated phenylphosphine, which reacts with acetylene via reductive elimination rather than σ -bond metathesis: (c) Cooper, A. C.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1997**, *16*, 1974.
- (16) (a) Canepa, G.; Sola, E.; Martin, M.; Lahoz, F. J.; Oro, L. A.; Werner, H. *Organometallics* **2003**, *22*, 2151. (b) Dorta, R.; Goikhman, R.; Milstein, D. *Organometallics* **2003**, *22*, 2806.
- (17) (Diphenyl-*o*-tolylphosphino)lithium is generated by equimolar addition of *s*-BuLi to commercially available (diphenyl-*o*-tolylphosphine in the presence of TMEDA; see: (a) Longoni, G.; Chini, P.; Canziani, F.; Fantucci, P. *Chem. Commun.* **1971**, 470. (b) Koh, J. J.; Rieger, P. H.; Shim, I. W.; Risen, W. M., Jr. *Inorg. Chem.* **1985**, *24*, 2312. (c) Byrne, L. T.; Engelhardt, L. M.; Jacobsen, G. E.; Leung, W.-P.; Papasergio, R. I.; Raston, C. L.; Skelton, B. W.; Twiss, P.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1989**, 105. (d) Braunschweig, H.; Dirk, R.; Englert, U. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1093.
- (18) Ahlrichs, R. *Turbomole Version 5*; Theoretical Chemistry Group, University of Karlsruhe, Karlsruhe, Germany, 2002.
- (19) PQS version 2.4; Parallel Quantum Solutions, Fayetteville, AR, 2001. The Baker optimizer is available separately from PQS upon request; see: Baker, J. *J. Comput. Chem.* **1986**, *7*, 385.
- (20) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

- (21) Sierka, M.; Hoge Kamp, A.; Ahlrichs, R. *J. Chem. Phys.* **2003**, *118*, 9136.
- (22) Schaefer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.
- (23) *SAINT-Plus*; Bruker AXS Inc., Madison, WI, 2001.
- (24) Schreurs, A. M. M.; Xian, X.; Kroon-Batenburg, L. M. J. *J. Appl. Crystallogr.* **2010**, *43*, 70.
- (25) Sheldrick, G. M. *SADABS: Area-Detector Absorption Correction*, Universität Göttingen, Göttingen, Germany, 1999.
- (26) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.
- (27) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.
- (28) Spek, A. L. *Acta Crystallogr., Sect. D* **2009**, *65*, 148.