

Iridium Phosphinidene Complexes: A Comparison with Iridium Imido Complexes in Their Reaction with Isocyanides

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Abstract: 18-Electron nucleophilic, Schrock-type phosphinidene complexes **3** [$\text{Cp}^*(\text{Xy}-\text{N}\equiv\text{C})\text{Ir}=\text{PAR}$] ($\text{R} = \text{Mes}^*, \text{Dmp}, \text{Mes}$) are capable of unprecedented $[1 + 2]$ -cycloadditions with 1 equiv of isocyanide RNC ($\text{R} = \text{Xy}, \text{Ph}$) to give novel iridaphosphirane complexes $[\text{Cp}^*(\text{Xy}-\text{N}\equiv\text{C})\text{IrPARC}=\text{NR}]$. Their structures were ascertained by X-ray diffraction. Density functional theory investigations on model structures revealed that the iridaphosphirane complexes are formed from the addition of the isocyanide to 16-electron species $[\text{Cp}^*\text{Ir}=\text{PAR}]$ forming first complex **3** that subsequently reacts with another isocyanide to give the products following a different pathway than its nitrogen analogue $[\text{Cp}^*\text{Ir}=\text{Nt-Bu}]$ **1**.

Introduction

Ever since stable nucleophilic phosphinidenes were discovered by Lappert et al. in 1987,¹ the structural properties and intriguing reactivity of these Schrock-type species continue to fascinate.² Exemplary valuable transfer reactions are those with oxo- and halophilic transition metal complexes,³ such as the phospho-Wittig reaction with carbonyl compounds that yields phosphalkenes^{4,5} and the P/O-exchange with epoxides that gives the three-membered phosphiranes.⁴ Phosphalkenes also result on reaction with geminal dihalides,^{4,6,7} while other dihalides give phosphorus heterocycles.⁴ Four-membered phosphametalloacycles are accessible by $[2 + 2]$ -cycloadditions with

alkenes⁸ and alkynes,⁹ thereby mimicking the behavior of Schrock-type carbenes.¹⁰ In the present study we compare the behavior of phosphinidene and imido complexes.

Inspired by the reported reaction of stable, linear, 18-electron imido complex $[(\eta^5\text{-Cp}^*)\text{Ir}=\text{Nt-Bu}]$ **1** with isocyanides that gives η^2 -coordinated carbodiimide complex **2**,¹¹ we targeted this reaction for the corresponding phosphinidenes.¹³ At the outset there is an intriguing difference between imido complex **1** and its phosphorus analogue, namely bent 16-electron complex $[(\eta^5\text{-Cp}^*)\text{Ir}=\text{P}-\text{R}]$ is not a stable species.¹² Also whereas many 18-electron $[(\eta^5\text{-Cp}^*)(\text{L})\text{Ir}=\text{P}-\text{Mes}^*]$ ($\text{L} = \text{PR}_3, \text{AsR}_3, \text{dppe}, \text{RN}\equiv\text{C}, \text{CO}, \text{NHC}$) have been reported,^{6,14} it is not known to be capable of $[1 + 2]$ -cycloadditions like its well-established Fischer-type electrophilic counterpart.¹⁵

Isocyanide-stabilized 18-electron $[(\eta^5\text{-Cp}^*)(\text{Xy}-\text{N}\equiv\text{C})\text{Ir}=\text{PMes}^*]$ **3a** ($\text{Mes}^* = 2,4,6\text{-tri-}t\text{-butylphenyl}$),⁶ generated by double dehydrohalogenation^{6,16} of $[(\eta^5\text{-Cp}^*)\text{IrCl}_2(\text{PH}_2\text{Mes}^*)]$ and concomitant ligation with 2,6-xylyl isocyanide, is an ideal

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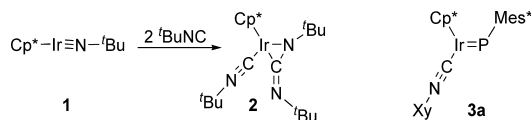
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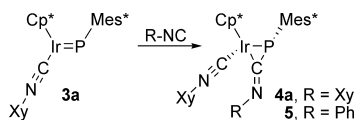
starting point for the present study in which we examine the Ir=P reactivity toward isocyanides and explore the scope of reaction for the transient, in situ generated 16-electron complex $[(\eta^5\text{-Cp}^*)\text{Ir}=\text{P}-\text{R}]$. We use DFT calculations to address differences between the imido and phosphinidene complexes.



Results and Discussion

Reaction of deep pink iridium phosphinidene $[(\eta^5\text{-Cp}^*)(\text{Xy}-\text{N}=\text{C})\text{Ir}=\text{P}(\text{Mes})^*]$ **3a** ($\delta^{31}\text{P}$ 757.1)⁶ with a 10-fold excess of phenyl or 2,6-xylyl isocyanide at room temperature resulted in the formation of yellow crystalline [1 + 2]-adducts **4a** and **5** ($\text{R} = \text{4a, Xy}$; **5, Ph**) as sole products in respectively 77% and 87% yield after crystallization (Scheme 1). The highly shielded resonances in the ^{31}P NMR spectrum at $\delta = -190.4$ (**4a**) and -190.2 ppm (**5**) are diagnostic for three-membered P-rings and indicate the formation of the desired iridaphosphiranes in analogy to iridaaziridine **2**. Single-crystal X-ray analysis of **4a** and **5** established unequivocally the $\eta^2\text{-(P,C)}$ -phosphaazaallene moiety¹⁷ and the linear 2,6-xylyl isocyanide, both coordinated to iridium (Figure 1). The ca. 2.41 Å Ir–P bond of the IrPC ring is elongated from the reported 2.17–2.21 Å Ir=P double bond of phosphinidene complexes like **3a** (carrying PPh_3 , CO, and NHC ligands instead of an isocyanide),^{6,14} whereas the ca. 2.03 Å Ir–C bond compares well with the 2.017(9) Å reported for the IrNC ring in carbodiimide complex **2**,^{11c} the ca. 1.80 Å P–C bond length is normal for three-membered P-rings.

Scheme 1. Synthesis of Iridaphosphiranes **4a** and **5**



The described reaction illustrates that *different* isocyanides can be embedded in the product, something that appears not feasible for the imido complexes.¹¹ The question is then whether the reaction mechanisms are the same for the two systems. Does the distinction lie in the stability of the 16-electron intermediate or the lack thereof? By reducing the stability of the 18-electron phosphinidene complex and attempting to synthesize iridaphosphiranes directly via in situ generated 16-electron iridium phosphinidene complexes, we examined whether the reaction with isocyanides would mimic more closely that of imido complex **1**. The first step was to reproduce the formation of **4a**. Double dehydrohalogenation^{6,16} of orange colored primary phosphine complex $[(\eta^5\text{-Cp}^*)\text{IrCl}_2(\text{PH}_2\text{Mes}^*)]$ (**6a**) with 2 equiv

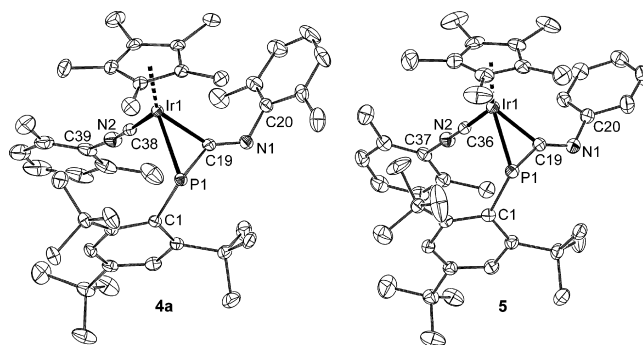
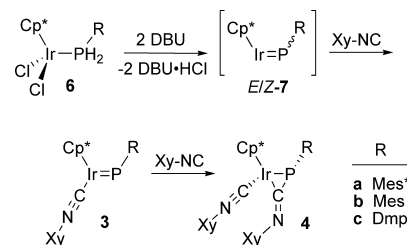


Figure 1. Displacement ellipsoid plot (50% probability) of **4a** and **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg] for **4a** and **5** (in square brackets): Ir1–P1 2.4147(5) [2.4082(6)], Ir1–C19 2.036(2) [2.029(2)], Ir1–C38[C36] 1.900(2) [1.895(2)], P1–C19 1.8766(19) [1.877(2)], P1–C19 1.805(2) [1.799(2)], N1–C19 1.267(2) [1.265(3)], N1–C20 1.424(3) [1.424(3)], N2–C38[C36] 1.169(3) [1.168(3)], N2–C39[C37] 1.402(3) [1.396(3)], Ir1–P1–C19 55.46(6) [55.40(7)], P1–Ir1–C19 46.91(6) [46.89(7)], Ir1–C38[C36]–N2 177.27(19) [178.3(2)], C19–N1–C20 125.99(18) [123.2(2)], C38[C36]–N2–C39[C37] 171.7(2) [175.9(2)].

Scheme 2. Synthesis of Iridaphosphiranes **4** via in situ generated Phosphinidenes **3**



of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) at -78°C in the presence of 10 equiv of 2,6-xylyl isocyanide resulted in an immediate color change to deep purple, indicative of the formation of 18-electron **3a**, and upon warming to room temperature to yellow to give after crystallization indeed iridaphosphirane **4a** in 86% isolated yield (Scheme 2). This protocol was extended to other phosphine complexes as illustrated in Scheme 2 for $[(\eta^5\text{-Cp}^*)\text{IrCl}_2(\text{PH}_2\text{R})]$ **6b** ($\text{R} = \text{Mes}$) and **6c** ($\text{R} = \text{Dmp} = 2,6\text{-dimesitylphenyl}$).¹⁸ Mesityl-substituted **6b** undergoes a facile double dehydrohalogenation–ligation with 2 equiv of DBU and an excess of 2,6-xylyl isocyanide to afford iridacycle **4b** ($\delta^{31}\text{P}$ -218.7) as the sole product, which was isolated by crystallization (60%; Scheme 2) and structurally characterized by a single-crystal X-ray structure determination (Figure 2). In this case, the sterically less shielded phosphinidene intermediate $[(\eta^5\text{-Cp}^*)(\text{Xy}-\text{N}=\text{C})\text{Ir}=\text{P}(\text{Mes})^*]$ **3b** could not be detected by ^{31}P NMR spectroscopy under the reaction conditions; the accordingly obtained more encumbered Dmp derivative **3c** (deep purple) was observed ($\delta^{31}\text{P}$ 768.1) and converted at room temperature to yellow complex **4c** (64%; $\delta^{31}\text{P}$ -216.7).

Is the suggested 16-electron $[(\eta^5\text{-Cp}^*)\text{Ir}=\text{P}(\text{R})]$ indeed formed on double dehydrohalogenation of **6** in the *absence* of isocyanides (**7**; Scheme 2)? So far, only 16-electron zirconium phosphinidenes have been observed in arene solvents by ^{31}P NMR spectroscopy ($\delta^{31}\text{P}$ 438–526 ppm)¹⁹ and as an unstable $\text{Cp}^*_2\text{Zr}=\text{P}(\text{Mes})^*-\text{LiCl}$ adduct in dimethoxyethane ($\delta^{31}\text{P}$ 537

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(18) Base-induced double dehydrohalogenation of $[(\eta^5\text{-Cp}^*)\text{IrCl}_2(\text{PH}_2\text{Ph})]$ (**6d**) in the presence of 10 equiv of 2,6-xylyl isocyanide gave a mixture of unidentifiable products.

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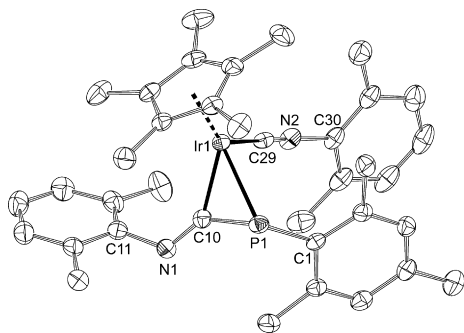


Figure 2. Displacement ellipsoid plot (50% probability) of **4b**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg] for **4b**: Ir1–P1 2.3952(6), Ir1–C10 2.039(2), Ir1–C29 1.888(2), P1–C1 1.837(2), P1–C10 1.799(3), N1–C10 1.267(3), N1–C11 1.429(3), N2–C29 1.172(3), N2–C30 1.398(3); Ir1–P1–C10 56.04(8), P1–Ir1–C10 47.02(7), Ir1–C10–P1 76.94(9), Ir1–C29–N2 179.4(3), C10–N1–C11 123.8(2), C29–N2–C30 161.9(2).

ppm).²⁰ In contrast to imido analogue **1**, attempted access to Mes- and Mes*-substituted 16-electron $[(\eta^5\text{-Cp}^*)\text{Ir}=\text{PR}]$ (**7a,b**) only led to dimers.¹² DFT calculations have shown the imido and phosphinidene complexes to differ with the first having a linear IrNH arrangement with an Ir≡N triple bond²¹ and $[(\eta^5\text{-Cp})\text{Ir}=\text{PH}]$ having a bent conformation ($\angle\text{IrPH } 126.4^\circ$) with an Ir=P double bond,¹² a difference with consequences for their reactivity. By introducing the sterically demanding Dmp substituent on phosphorus, we envisioned stabilizing the 16-electron species by shielding the Ir=P double bond. Double dehydrohalogenation of primary phosphine complex $[(\eta^5\text{-Cp}^*)\text{IrCl}_2(\text{PH}_2\text{Dmp})]$ (**6c**) with 2 equiv of DBU in CD_2Cl_2 at -10°C showed after warmup to room temperature a low-field ^{31}P NMR resonance at 672 ppm, suggesting indeed the formation of a bent phosphinidene. To confirm its identity the ^{31}P NMR chemical shifts were calculated for the *E* and *Z* conformers of $[(\eta^5\text{-Cp}^*)\text{Ir}=\text{PDmp}]$ **7c** and their solvent adducts. Those for “solvent-free” *E*-**7c** and *Z*-**7c** (178.9 and 418.2, respectively) are significantly shielded from the experimental one, but those for the solvent adducts are in the expected range (*E*-[**7c**(CH_2Cl_2)] 457.2, *Z*-[**7c**(CH_2Cl_2)] 683.6; Figure 3) with an excellent match for the more stable *Z*-conformer ($\Delta E = 0.3 \text{ kcal}\cdot\text{mol}^{-1}$). Therefore, we conclude that the *Z*-conformer is also a likely intermediate when applying smaller donor ligands.^{6,16a,22}

The experimental work leads us to conclude that the in situ formed 16-electron phosphinidene coordinates with an isocyanide to the observable and isolable 18-electron complex **3**, which gives a [1 + 2]-cycloaddition with another isocyanide molecule to form iridaphosphirane **4**. The reaction with imido complex **1** is different in that this species is stable and that there are no indications for an observable isocyanide coordinated 18-electron imido complex. The question then arises whether this distinction is due to the relative stabilities of the reactants, thus whether the first or second isocyanide addition is rate-determining, or to different mechanistic pathways. To answer this question we used density functional theory at BP86/TZP to compare the reaction of the imido and phosphinidene complexes **1'** and **7'** with isocyanide $\text{HN}=\text{C}$ using model structures incorporating

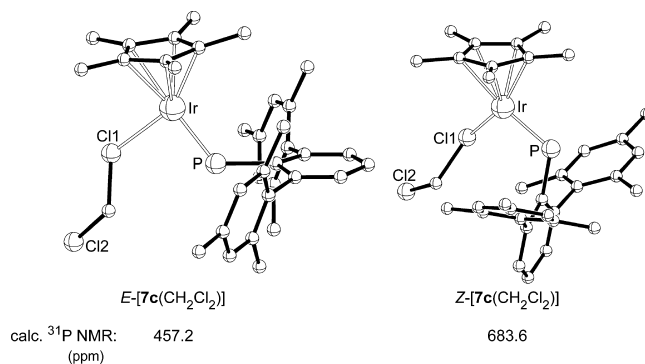


Figure 3. Intermediate *E*- and *Z*-[**7c**(CH_2Cl_2)] calculated at the BP86/TZP level of theory. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg] for *E*-[**7c**(CH_2Cl_2)] and *Z*-[**7c**(CH_2Cl_2)] (in square brackets): Ir–P 2.192 [2.206], Ir–C11 2.567 [2.368]; Ir–P–Dmp 125.2 [114.6], P–Ir–C11 87.5 [102.9].

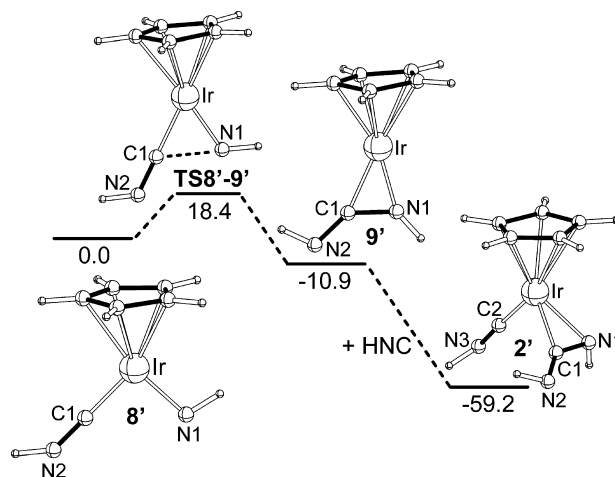


Figure 4. Relative BP86/TZP energies (in $\text{kcal}\cdot\text{mol}^{-1}$) for the reaction of $[(\eta^5\text{-Cp})\text{Ir}=\text{NH}]$ **1'** with HNC. Selected bond lengths [Å] and angles [deg] for **8'**: Ir1–N1 1.876, Ir1–C1 1.859, C1–N2 1.210, Ir1–N1–H 105.5; **TS8'–9'**: Ir1–N1 1.883, Ir1–C1 1.926, C1–N1 1.900, C1–N2 1.216, Ir1–N1–H 120.1; **9'**: Ir1–N1 1.913, Ir1–C1 2.040, C1–N1 1.352, C1–N2 1.275, Ir1–N1–H 153.1; **2'**: Ir1–N1 2.124, Ir1–C1 2.076, C1–N1 1.337, C1–N2 1.264, Ir1–C2 1.843, C2–N3 1.218, Ir1–N1–H 115.5.

only H substituents. We begin with the imido complex, $[(\eta^5\text{-Cp})\text{Ir}=\text{NH}]$ **1'**. The reaction starts with the addition of the isocyanide to give bent 18-electron imido complex **8'** ($\Delta E = -26.1 \text{ kcal}\cdot\text{mol}^{-1}$; Figure 4),²³ followed by ring closure to 16-electron η^2 -carbodiimide complex **9'**, requiring $18.4 \text{ kcal}\cdot\text{mol}^{-1}$ ($\Delta E = -10.9 \text{ kcal}\cdot\text{mol}^{-1}$), and subsequent addition of a second isocyanide to afford the $48.3 \text{ kcal}\cdot\text{mol}^{-1}$ more stable product **2'**.

The mechanism for formation of iridaphosphirane **4** is different. Namely, addition of $\text{HN}=\text{C}$ to $[(\eta^5\text{-Cp})\text{Ir}=\text{PH}]$ **7'** is far more exothermic in giving the bent 18-electron species $[(\eta^5\text{-Cp})(\text{HNC})\text{Ir}=\text{PH}]$ **3'** ($\Delta E = -58.2 \text{ kcal}\cdot\text{mol}^{-1}$; Figure 5) that, moreover, is energetically prohibited to undergo ring closure to **10'** ($\Delta E = 27.1 \text{ kcal}\cdot\text{mol}^{-1}$) and instead is susceptible to attack of a second isocyanide to the phosphorus center to give $\eta^1\text{-(P,C)}$ -phosphaazaallene complex **11'** ($\Delta E = -17.6 \text{ kcal}\cdot\text{mol}^{-1}$), which rearranges barrierless to the more favorable η^2 -coordinated product **4'** ($\Delta E = -20.3 \text{ kcal}\cdot\text{mol}^{-1}$).

(23) The alternative, direct [1 + 2]-cycloaddition of HNC to $[(\eta^5\text{-Cp})\text{Ir}=\text{NH}]$ **1'** to afford η^2 -carbodiimide complex **9'** was not investigated in detail.

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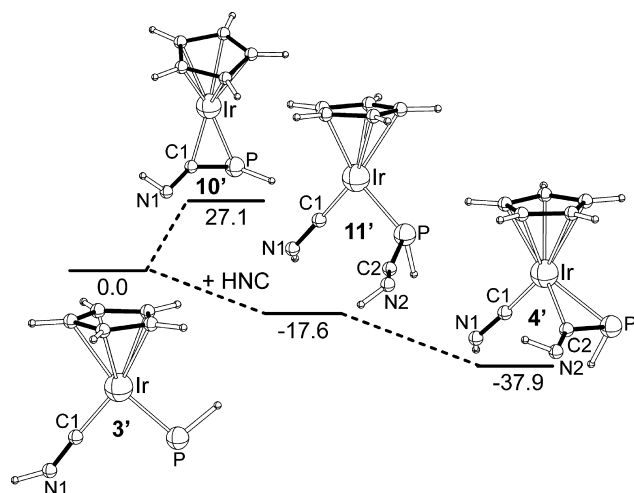


Figure 5. Relative BP86/TZP energies (in kcal·mol^{−1}) for the reaction of [(η^5 -Cp)Ir=PH] **7'** with HNC. Selected bond lengths [Å] and angles [deg] for **3'**: Ir1–P1 2.223, Ir1–C1 1.858, C1–N2 1.213, Ir1–P1–H 98.9; **10'**: Ir1–P1 2.307, Ir1–C1 2.025, P1–C1 1.818, C1–N2 1.268, Ir1–P1–H 110.7; **11'**: Ir1–P1 2.241, Ir1–C1 1.834, Ir1–C2 3.403, P1–C2 1.726, C1–N1 1.229, C2–N2 1.217, Ir1–P1–H 122.9; **4'**: Ir1–P1 2.439, Ir1–C1 1.850, Ir1–C2 2.066, P1–C2 1.813, C1–N1 1.216, C2–N2 1.258, Ir1–P1–H 101.2, C2–Ir1–P1 46.6.

The higher nucleophilicity of the imido complex originates from the lower energies of the ligand orbitals (NH -6.79 eV; PH -5.46 eV) and is reflected in the calculated charges (-0.27 on N in **8'**; -0.04 on P in **3'**).²⁴ Two differences that define the dissimilar chemistries of the phosphinidene and imido complexes are revealed by the calculated reaction pathways. First, as noted, the initial ligand addition to the 16-electron complex is far more exothermic for the phosphinidene than for imido complex **8'**, which suffers from distortion of the Ir=N–R unit from linearity. The second difference lies in the electronic structure of the ring-closed structures of **9'** and **10'**. An allenic, π -conjugated N–C–N moiety is formed in C_s -symmetric **9'** that binds in a bidentate κ^2 -fashion to the metal, but in phosphorus analogue **10'** π -conjugation is less favorable due to the smaller overlap between the C(2p) and P(3p) orbitals so that the allenic N–C–P unit binds instead to the metal in an η^2 -fashion, acting as a 2-electron and not a 4-electron donor as is the case for **9'**. Therefore, nucleophilic attack of the phosphorus of **3'** at the isocyanide is prohibited, while a modest barrier is observed for the corresponding nitrogen attack of **8'**. As a consequence, stable 18-electron phosphinidene complexes can be observed experimentally whereas the imido complexes are prone to rearrangements. Formation of the final product **4'** occurs by direct attack of a second isocyanide to the phosphorus, but this process can be hindered by steric congestion using bulky substituents, which explains why **3a** can be observed at low temperatures by NMR spectroscopy even in an excess of isocyanide.

Conclusions

Imido and phosphinidene iridium complexes differ in their properties and reactivities as established for the reaction with isocyanides. Both isolated and in situ generated 18-electron iridium phosphinidene [(η^5 -Cp*)(Xy–N≡C)Ir=PMes*] **3** afford iridaphosphirane **4** as the sole product. Despite this apparent resemblance with the stable imido complex **1** that gives

iridaazirane **2**, the course of events is entirely different for the two reactions as elucidated by DFT calculations. The imido complex uses the first isocyanide molecule to construct a 16-electron η^2 -carbodiimide complex, whereas for the phosphorus analogue it is the second isocyanide molecule that induces the ring closure, thereby giving the unique η^2 -phosphaazallene complex. It is further established that the sterically demanding dimesitylphenyl substituent enables the detection of the solvent-stabilized 16-electron phosphinidene intermediate [(η^5 -Cp*)Ir=PDmp] **7c**, generated by double dehydrogenation of phosphine precursor **6**, prior to the reaction with isocyanides.

Experimental Section

Computations. All density functional theory calculations have been performed with the parallelized Amsterdam density functional (ADF) package (version 2005.01b and 2006.01).²⁵ The Kohn–Sham MOs were expanded in a large, uncontracted basis set of Slater-type orbitals (STOs), of a triple- ζ basis set with polarization function quality, corresponding to basis set TZP in the ADF package. The 1s core shell of carbon and nitrogen and the 1s2s2p core shells of phosphorus were treated by the frozen core approximation. The transition metal centers were described by a triple- ζ basis set for the outer ns , np , nd , and $(n+1)s$ orbitals, whereas the shells of lower energy were treated by the frozen core approximation using a small core. All calculations were performed at the nonlocal exchange self-consistent field (NL-SCF) level, using the local density approximation (LDA) in the Vosko–Wilk–Nusair parametrization²⁶ with nonlocal corrections for exchange (Becke88)²⁷ and correlation (Perdew86).²⁸ All geometries were optimized using the analytical gradient method implemented by Versluis and Ziegler,²⁹ including relativistic effects by the Zeroth Order Regular Approximation (ZORA).³⁰ The ³¹P NMR chemical shift tensors were calculated with ADF's NMR program,³¹ using single-point calculations with an all-electron basis for P within the ZORA approximation on the optimized frozen core structures (vide supra), using the *E*-isomer of [Cp*(Me₃P)Ir=PMes*]⁶ as reference ($\sigma -455.2$ ppm) for the total isotropic shielding tensors ($\delta +629.3$ ppm with respect to 85% H₃PO₄). All model complexes were calculated without molecular symmetry.

General Procedures. All experiments and manipulations were performed under an atmosphere of dry nitrogen with rigorous exclusion of air and moisture using flame-dried glassware using Schlenk techniques. Solvents were distilled from sodium (toluene), CaCl₂ (CH₂Cl₂), or LiAlH₄ (pentanes, diethyl ether) and kept under an atmosphere of dry nitrogen. Deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves (CD₂Cl₂, CDCl₃, C₆D₆). All solid starting materials were dried in vacuo. NMR spectra were recorded on a Bruker Avance 250 (¹H, ¹³C, ³¹P; 85% H₃PO₄) or a Bruker Avance 400 (¹H, ¹³C, ³¹P; 85% H₃PO₄) and referenced internally to residual solvent resonances (CDCl₃: ¹H: δ 7.26, ¹³C{¹H}: δ 77.16; CD₂Cl₂: ¹H: δ 5.25, ¹³C{¹H}: δ 54.00; C₆D₆: ¹H: δ 7.16, ¹³C{¹H}: δ 128.06). IR spectra were recorded on a Mattson-6030 Galaxy FT-IR spectrophotometer, high-resolution

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mass spectra (HR-MS) were recorded on a Finnigan Mat 900 spectrometer operating at an ionization potential of 70 eV, and fast atom bombardment (FAB) mass spectrometry was carried out using a JEOL JMS SX/SX 102A four-sector mass spectrometer (70 eV). Melting points were measured on samples in sealed capillaries on a Stuart Scientific SMP3 melting point apparatus and are uncorrected. $[(\eta^5\text{-Cp}^*)\text{IrCl}_2(\text{PH}_2\text{Mes}^*)]$ (**6a**),⁶ $[(\eta^5\text{-Cp}^*)\text{IrCl}_2(\text{PH}_2\text{Mes})]$ (**6b**),⁶ $[(\eta^5\text{-Cp}^*)\text{Xy-N}\equiv\text{C}]\text{Ir}=\text{PMes}^*$ (**3a**),⁶ and Mes^*PH_2 ³² were prepared according to literature procedures. PhPH_2 , MesPH_2 , and DmpPH_2 ³³ were prepared analogously to IsPH_2 ,³⁴ by LiAlH_4 reduction of respectively PhPCl_2 , MesPCl_2 , and DmpPCl_2 .³⁵ $\text{Ph-N}\equiv\text{C}$ ³⁶ was prepared by dehydration of the corresponding formamide with phosphoryl chloride. 2,6-Xylylisocyanide ($\text{Xy-N}\equiv\text{C}$) was purchased from Fluka and used as received.

$[(\eta^5\text{-Cp}^*)\text{IrCl}_2(\text{PH}_2\text{Dmp})]$ (**6c**). A mixture of freshly prepared DmpPH_2 (1.00 g, 2.89 mmol) and $[(\eta^5\text{-Cp}^*)\text{IrCl}_2]_2$ (0.59 g, 0.74 mmol) in CH_2Cl_2 (50 mL) was stirred for 30 min at room temperature. Evaporation to dryness and chromatography of the residue over silica with CHCl_3 followed by $\text{CHCl}_3/\text{diethyl ether}$ 4:1 as eluent and subsequent crystallization from $\text{CH}_2\text{Cl}_2/\text{pentane}$ at -20°C yielded $[(\eta^5\text{-Cp}^*)\text{IrCl}_2(\text{PH}_2\text{Dmp})]$ (**6c**) (1.08 g, 1.45 mmol, 98%) as orange crystals. Mp: 258°C (dec). ^1H NMR (400.13 MHz, CDCl_3 , 300 K): δ 1.32 (d, $^4J(\text{H},\text{P}) = 3.3$ Hz, 15H; $\text{C}_5(\text{CH}_3)_5$), 2.15 (s, 12H; $o\text{-CH}_3$), 2.34 (s, 6H; $p\text{-CH}_3$), 5.49 (d, $^1J(\text{H},\text{P}) = 378.6$ Hz, 2H; PH_2), 6.95 (s, 4H; $m\text{-MesH}$), 7.05 (dd, $^3J(\text{H},\text{H}) = 7.5$ Hz, $^4J(\text{H},\text{P}) = 2.9$ Hz, 2H; $m\text{-PhH}$), 7.48 (t, $^3J(\text{H},\text{H}) = 7.5$ Hz, 1H; $p\text{-PhH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.64 MHz, CDCl_3 , 300 K): δ 7.9 (s; $\text{C}_5(\text{CH}_3)_5$), 21.2 (s; $p\text{-CH}_3$), 21.5 (s; $o\text{-CH}_3$), 92.1 (d, $^2J(\text{C},\text{P}) = 3.0$ Hz; $\text{C}_5(\text{CH}_3)_5$), 121.1 (d, $^1J(\text{C},\text{P}) = 52.0$ Hz; $ipso\text{-Ph}$), 128.9 (s; $m\text{-Mes}$), 129.7 (d, $^3J(\text{C},\text{P}) = 7.8$ Hz; $m\text{-Ph}$), 131.1 (d, $^4J(\text{C},\text{P}) = 2.1$ Hz; $p\text{-Ph}$), 136.7 (s; $p\text{-Mes}$), 137.3 (s; $o\text{-Mes}$), 138.0 (d, $^3J(\text{C},\text{P}) = 4.3$ Hz; $ipso\text{-Mes}$), 146.9 (d, $^2J(\text{C},\text{P}) = 8.8$ Hz; $o\text{-Ph}$). ^{31}P NMR (101.3 MHz, CDCl_3 , 300 K): δ -82.8 (t, $^1J(\text{P},\text{H}) = 378.6$ Hz, PH_2). IR (KBr): ν 3023.9 (w), 2988.2 (m), 2962.1 (m), 2915.9 (s), 2854.1 (w), 2383.6 (m, P-H), 2370.1 (m, P-H), 1610.3 (s), 1565.0 (s), 1448.3 (s), 1376.9 (s), 1027.9 (s), 921.8 (s), 845.6 (s), 806.1 (s), 745.4 (s), 460.9 cm^{-1} (s). HR FAB-MS: calcd for $\text{C}_{34}\text{H}_{42}\text{Cl}_2\text{P}^+\text{Ir}$: 744.2018, found 744.2024. m/z (%): 744 (5) $[\text{M}]^+$, 709 (100) $[\text{M} - \text{Cl}]^+$, 673 (12) $[\text{M} - \text{Cl} - \text{HCl}]^+$, 363 (95) $[\text{M} - \text{Cl} - \text{DmpPH}_2]^+$.

$[(\eta^5\text{-Cp}^*)\text{IrCl}_2(\text{PH}_2\text{Ph})]$ (**6d**). A freshly prepared solution of PhPH_2 (0.6 M in Et_2O , 1.05 mL, 0.63 mmol) was added to an orange solution of $[(\eta^5\text{-Cp}^*)\text{IrCl}_2]_2$ (0.250 g, 0.314 mmol) in CH_2Cl_2 (20 mL) at room temperature. After 30 min, the resulting mixture was filtered over a short silica column and eluted with CHCl_3 , after which the orange fractions were combined and evaporated to dryness. Subsequent crystallization from $\text{CH}_2\text{Cl}_2/\text{pentane}$ at -20°C yielded $[(\eta^5\text{-Cp}^*)\text{IrCl}_2(\text{PH}_2\text{Ph})]$ (**6d**) as yellow microcrystals, which were washed with pentane and dried in vacuo (0.268 g, 0.528 mmol, 84%). Mp: 222°C (dec). ^1H NMR (250.13 MHz, CDCl_3 , 300 K): δ 1.63 (s, 15H; $\text{C}_5(\text{CH}_3)_5$), 5.88 (d, $^1J(\text{H},\text{P}) = 394.1$ Hz, 2H; PH_2), 7.44–7.47 (m, 3H; $m\text{-}$ and $p\text{-PhH}$), 7.78–7.85 (m, 2H; $o\text{-PhH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.90 MHz, CDCl_3 , 300 K): δ 8.6 (s; $\text{C}_5(\text{CH}_3)_5$), 91.9 (d, $^2J(\text{C},\text{P}) = 3.3$ Hz; $\text{C}_5(\text{CH}_3)_5$), 122.6 (d, $^1J(\text{C},\text{P}) = 53.3$ Hz; $ipso\text{-Ph}$), 128.8 (d, $^2J(\text{C},\text{P}) = 10.7$ Hz; $o\text{-Ph}$), 131.5 (d, $^4J(\text{C},\text{P}) = 2.7$ Hz; $p\text{-Ph}$), 133.5 (d, $^3J(\text{C},\text{P}) = 8.8$ Hz; $m\text{-Ph}$). ^{31}P NMR (101.3 MHz, CDCl_3 , 300 K): δ -56.3 (t, $^1J(\text{P},\text{H}) = 394.1$ Hz, PH_2). IR (KBr): ν 3051.8 (s), 2973.7 (s), 2914.9 (s), 2870.5 (m), 2412.5 (w, P-H), 2389.4 (m, P-H), 1451.2 (s), 1435.8 (s), 1378.9 (s), 1156.1 (w), 1070.3 (m), 1031.7 (s), 899.6 (s), 745.4

(s), 697.1 cm^{-1} (s). HR FAB-MS: calcd for $\text{C}_{16}\text{H}_{22}\text{Cl}_2\text{P}^+\text{Ir}$: 508.0451, found 508.0459. m/z (%): 508 (8) $[\text{M}]^+$, 473 (29) $[\text{M} - \text{Cl}]^+$, 363 (20) $[\text{M} - \text{Cl} - \text{PhPH}_2]^+$.

$[(\text{Cp}^*)(\text{Xy-N}\equiv\text{C})\text{IrPMes}^*\text{C}\equiv\text{NXY}]$ (**4a**). An orange solution of $[(\eta^5\text{-Cp}^*)\text{IrCl}_2(\text{PH}_2\text{Mes}^*)]$ (**6a**; 0.135 g, 0.20 mmol) in CH_2Cl_2 (2 mL) was added to a mixture of DBU (59.8 μL , 0.40 mmol) and $\text{Xy-N}\equiv\text{C}$ (0.262 g, 2.0 mmol) in CH_2Cl_2 (3 mL) at -78°C , which resulted in a immediate color change to deep purple. After 1 h, the reaction mixture was allowed to warm up to room temperature and stirred for an additional hour. After evaporation to dryness, the yellow residue was washed with pentane (2×1 mL) and extracted into diethyl ether (4×15 mL), and the solution was filtered. After concentration of the solution to a few milliliters, **4a** (0.148 g, 0.171 mmol, 86%) was obtained as yellow crystals by crystallization at -20°C . Mp: 143°C (dec). ^1H NMR (400.13 MHz, C_6D_6 , 300 K): δ 1.11 (s, 9H; $p\text{-C}(\text{CH}_3)_3$), 1.60 (s, 15H; $\text{C}_5(\text{CH}_3)_5$), 1.92 (s, 9H; $o\text{-C}(\text{CH}_3)_3$), 1.93 (s, 6H; $o\text{-C}\equiv\text{NXyCH}_3$), 2.02 (s, 9H; $o\text{-C}(\text{CH}_3)_3$), 2.39 (s, 3H; $o\text{-C}\equiv\text{NXyCH}_3$), 2.45 (s, 3H; $o\text{-C}\equiv\text{NXyCH}_3$), 6.69 (d, $^3J(\text{H},\text{H}) = 7.5$ Hz, 2H; $m\text{-C}\equiv\text{NXy}$), 6.75 (m, $^3J(\text{H},\text{H}) = 7.5$ Hz, 1H; $p\text{-C}\equiv\text{NXy}$), 6.92 (m, $^3J(\text{H},\text{H}) = 7.0$ Hz, 1H; $m\text{-C}\equiv\text{NXy}$), 6.95 (m, $^3J(\text{H},\text{H}) = 7.0$ Hz, 1H; $p\text{-C}\equiv\text{NXy}$), 7.04 (m, $^3J(\text{H},\text{H}) = 7.0$ Hz, 1H; $m\text{-C}\equiv\text{NXy}$), 7.06 (s, 1H; $m\text{-Mes}^*$), 7.29 (s, 1H; $m\text{-Mes}^*$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.64 MHz, C_6D_6 , 300 K): δ 9.4 (s; $\text{C}_5(\text{CH}_3)_5$), 19.5 (s; $o\text{-C}\equiv\text{NXyCH}_3$), 20.0 and 22.1 (s; $o\text{-C}\equiv\text{NXyCH}_3$), 31.2 (s; $p\text{-C}(\text{CH}_3)_3$), 33.9 (d, $^4J(\text{C},\text{P}) = 11.2$ Hz; $o\text{-C}(\text{CH}_3)_3$), 34.3 (s; $p\text{-C}(\text{CH}_3)_3$), 34.6 (d, $^4J(\text{C},\text{P}) = 6.3$ Hz; $o\text{-C}(\text{CH}_3)_3$), 39.8 and 41.0 (s; $o\text{-C}(\text{CH}_3)_3$), 97.1 (s; $\text{C}_5(\text{CH}_3)_5$), 121.9 (s; $m\text{-Mes}^*$), 122.7 (s; $p\text{-C}\equiv\text{NXy}$), 123.8 (s; $m\text{-Mes}^*$), 125.9 (s; $p\text{-C}\equiv\text{NXy}$), 126.7 (s; $o\text{-C}\equiv\text{NXy}$), 127.8 (s; $m\text{-C}\equiv\text{NXy}$), 127.9 (s; $m\text{-C}\equiv\text{NXy}$), 128.8 (s; $m\text{-C}\equiv\text{NXy}$), 129.7 (s; $o\text{-C}\equiv\text{NXy}$), 130.3 (s; $o\text{-C}\equiv\text{NXy}$), 132.1 (d, $^1J(\text{C},\text{P}) = 92.1$ Hz; $\text{C}\equiv\text{NXy}$), 134.1 (s; $ipso\text{-C}\equiv\text{NXy}$), 141.5 (s; $\text{C}\equiv\text{NXy}$), 146.1 (s; $p\text{-Mes}^*$), 150.6 (d, $^4J(\text{C},\text{P}) = 12.9$ Hz; $ipso\text{-C}\equiv\text{NXy}$), 156.9 (d, $^2J(\text{C},\text{P}) = 8.4$ Hz; $o\text{-Mes}^*$), 158.4 (s; $o\text{-Mes}^*$), 180.6 (d, $^1J(\text{C},\text{P}) = 103.4$ Hz; $ipso\text{-Mes}^*$). ^{31}P NMR (101.3 MHz, C_6D_6 , 300 K): δ -190.4 (s; PMes^*). IR (KBr): ν = 3062.4 (w), 2960.2 (s), 2948.6 (s), 2903.3 (s), 2863.8 (s), 2272.7 (very broad w, $\text{PC}\equiv\text{N}$), 2072.2 and 2020.1 (s, $\text{C}\equiv\text{N}$), 1637.3 and 1586.2 (s, $\text{C}\equiv\text{N}$), 1463.7 (s, $\text{C}\equiv\text{C}$), 1390.4, 1381.8 and 1359.6 (s, P-Ar), 1240.0 (s), 1195.7 and 1185.1 (s, $\text{P} = \text{C}$), 1124.3 (w), 1090.6 (w), 1025.0 (m, P-Ar), 922.8 (w), 873.6 (w), 773.3 and 745.4 (s, P-C), 708.7 (w), 697.8 (m), 522.6 cm^{-1} (m). HR EI-MS: calcd for $\text{C}_{37}\text{H}_{53}\text{IrNP}$ ($\text{M} - \text{C}\equiv\text{NXy}$) 735.3548, found 735.3541. m/z (%): 866 (2) $[\text{M}]^+$, 735 (100) $[\text{M} - \text{C}\equiv\text{NXy}]^+$, 590 (16) $[\text{M} - \text{PMes}^*]^+$, 455 (24) $[\text{M} - \text{PMes}^* - \text{Cp}^*]^+$. Alternatively, **4a** can be prepared from **3a** as follows: $\text{Xy-N}\equiv\text{C}$ (0.197 g, 1.50 mmol) was added to a dark purple solution of **3a** (0.110 mg, 0.15 mmol) in pentanes (20 mL) at room temperature. After 15 h, the yellow reaction mixture was evaporated to dryness and the residue was washed with pentane (2×1 mL) and extracted into diethyl ether. After filtration and concentration to a few milliliters, yellow crystals of **4a** (0.113 g, 0.131 mmol, 87%) were obtained at -20°C .

$[(\text{Cp}^*)(\text{Xy-N}\equiv\text{C})\text{IrPMes}^*\text{C}\equiv\text{NPh}]$ (**5**). A freshly prepared solution of $\text{Ph-N}\equiv\text{C}$ (0.143 M, 10.5 mL, 1.50 mmol) in CH_2Cl_2 was added to a dark purple solution of **3a** (0.110 mg, 0.15 mmol) in pentane (10 mL) at room temperature. After 15 h, the yellow reaction mixture was evaporated to dryness and the residue was extracted into pentane. After removal of a black residue by filtration, all volatiles were removed in vacuo. The residual yellow solid was extracted into diethyl ether, and after concentration to a few milliliters, yellow crystals of **5** (0.097 g, 0.116 mmol, 77%) were obtained at -20°C . Mp: 159°C (dec). ^1H NMR (400.13 MHz, C_6D_6 , 300 K): δ 0.93 (s, 9H; $p\text{-C}(\text{CH}_3)_3$), 1.62 (s, 15H; $\text{C}_5(\text{CH}_3)_5$), 1.94 (s, 15H; $o\text{-C}(\text{CH}_3)_3$ and $o\text{-C}\equiv\text{NXyCH}_3$), 2.05 (s, 9H; $o\text{-C}(\text{CH}_3)_3$), 6.63 (d, $^3J(\text{H},\text{H}) = 7.4$ Hz, 2H; $m\text{-C}\equiv\text{NXy}$), 6.70 (t, $^3J(\text{H},\text{H}) = 7.4$ Hz, 1H; $p\text{-C}\equiv\text{NXy}$), 7.00 (t, $^3J(\text{H},\text{H}) = 7.3$ Hz, 1H; $p\text{-C}\equiv\text{NPh}$), 7.03 (d, $^4J(\text{C},\text{P}) = 7.8$ Hz, 1H; $m\text{-Mes}^*$), 7.18 (d, $^3J(\text{H},\text{H}) = 7.9$ Hz, 2H; $m\text{-C}\equiv\text{NPh}$), 7.45 (d, $^4J(\text{C},\text{P}) = 7.8$ Hz, 1H; $m\text{-Mes}^*$), 7.82 (d, $^3J(\text{H},\text{H}) = 7.9$ Hz, 2H; $o\text{-C}\equiv\text{NPh}$). $^{13}\text{C}\{^1\text{H}\}$

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NMR (100.64 MHz, C_6D_6 , 300 K): δ 9.4 (s; $C_5(CH_3)_5$), 19.0 (s; $o-C\equiv NXYCH_3$), 31.0 (s; $p-C(CH_3)_3$), 33.6 (d, $^4J(C,P) = 11.3$ Hz; $o-C(CH_3)_3$), 34.1 (s; $p-C(CH_3)_3$), 34.6 (d, $^4J(C,P) = 6.8$ Hz; $o-C(CH_3)_3$), 39.9 and 40.9 (s; $o-C(CH_3)_3$), 96.7 (s; $C_5(CH_3)_5$), 119.6 (s; $m-Mes^*$), 122.2 (s; $m-Mes^*$), 122.6 (s; $o-C\equiv NPh$), 123.8 (s; $p-C\equiv NPh$), 125.8 (s; $p-C\equiv NXY$), 127.9 (s; $m-C\equiv NXY$), 128.8 (s; $m-C\equiv NPh$), 129.9 (s; $ipso-C\equiv NXY$), 131.6 (d, $^1J(C,P) = 80.0$ Hz; $C\equiv NPh$), 133.9 (s; $o-C\equiv NXY$), 140.6 (bs, $C\equiv NXY$), 146.2 (s; $p-Mes^*$), 152.9 (d, $^3J(C,P) = 13.1$ Hz; $ipso-C\equiv NPh$), 156.9 (d, $^2J(C,P) = 8.2$ Hz; $o-Mes^*$), 157.7 (s; $o-Mes^*$), 187.6 (d, $^1J(C,P) = 101.4$ Hz; $ipso-Mes^*$). ^{31}P NMR (101.3 MHz, C_6D_6 , 300 K): δ -190.2 (s; $PMes^*$). IR (KBr): $\nu = 3069.2$ (m), 3047.0 (w), 2966.0 (m), 2945.6 (s), 2913.9 (m), 2898.5 (w), 2866.7 (w), 2851.3 (w), 2283.3 (very broad w, $PC\equiv N$), 2084.7 and 2037.4 (s, $C\equiv N$), 1677.8, 1644.0, 1583.3 and 1544.7 (s, $C\equiv N$), 1480.1, 1462.8 and 1441.5 (s, $C\equiv C$), 1390.4, 1375.0 and 1359.6 (m, $P-Ar$), 1315.2 (m), 1261.2 (m), 1198.5 (m, $P=C$), 1066.4 (m), 1026.0 (m, $P-Ar$), 898.7 (m), 875.5 (m), 789.7, 763.7, 747.3, and 735.7 (s, $P-C$), 692.3 and 683.6 (s), 523.6 (m), 496.6 cm^{-1} (w). HR EI-MS: calcd for $C_{37}H_{53}IrNP$ ($M - C\equiv NPh$) 735.3548, found 735.3517. m/z (%): 838 (2) $[M]^+$, 735 (5) $[M - C\equiv NPh]^+$, 707 (5) $[M - C\equiv NXY]^+$, 562 (6) $[M - PMes^*]^+$.

$[(\eta^5-Cp^*)(Xy-N\equiv C)IrPMesC\equiv NXY]$ (4b). DBU (59.8 μL , 0.40 mmol) was added to a yellow solution of $[(\eta^5-Cp^*)-IrCl_2(PH_2Mes)]$ (**6b**; 0.110 g, 0.20 mmol) and $Xy-N\equiv C$ (0.262 g, 2.0 mmol) in CH_2Cl_2 (6 mL) at $-78^\circ C$, and the mixture was allowed to warm up to room temperature. After evaporation to dryness, the residue was washed with pentane (3 mL) and extracted into diethyl ether (2×10 mL), and the solution was filtered. After concentration of the solution to a few milliliters, a yellow solid was obtained, which was recrystallized from diethyl ether at $-20^\circ C$ to yield **4b** (0.089 g, 0.120 mmol, 60%) as yellow crystals. Mp: $122^\circ C$ (dec). 1H NMR (400.13 MHz, C_6D_6 , 300 K): δ 1.74 (s, 15H; $C_5(CH_3)_5$), 1.81 (s, 6H; $o-C\equiv NXYCH_3$), 1.85 (s, 3H; $p-MesCH_3$), 2.46 (s, 6H; $o-MesCH_3$), 2.84 (s, 6H; $o-C\equiv NXYCH_3$), 6.44 (bs, 2H; $m-Mes$), 6.64 (d, $^3J(H,H) = 7.3$ Hz, 2H; $m-C\equiv NXY$), 6.71 (m, $^3J(H,H) = 7.3$ Hz, 1H; $p-C\equiv NXY$), 6.99 (m, $^3J(H,H) = 7.0$ Hz, 1H; $p-C\equiv NXY$), 7.06 (d, $^3J(H,H) = 7.0$ Hz, 2H; $m-C\equiv NXY$). $^{13}C\{^1H\}$ NMR (100.64 MHz, C_6D_6 , 300 K): δ 9.5 (s; $C_5(CH_3)_5$), 18.8 (s; $o-C\equiv NXYCH_3$), 20.6 (d, $^3J(C,P) = 16.5$ Hz, $o-MesCH_3$), 20.8 (s; $p-MesCH_3$), 23.8 and 23.9 (s; $o-C\equiv NXYCH_3$), 96.7 (s; $C_5(CH_3)_5$), 122.7 (s; $p-C\equiv NXY$), 125.9 (s; $p-C\equiv NXY$), 127.4 (s; $m-C\equiv NXY$), 127.5 (s; $o-C\equiv NXY$), 128.0 (s; $p-Mes$), 128.1 (s; $m-C\equiv NXY$), 128.7 (s; $m-Mes$), 130.2 (s; $ipso-C\equiv NXY$), 133.7 (s; $o-C\equiv NXY$), 135.4 (s; $o-Mes$), 143.5 (d, $^2J(C,P) = 9.7$ Hz, $C\equiv NXY$), 151.9 (d, $^1J(C,P) = 70$ Hz, $ipso-Mes$), $C\equiv NXY$ and $ipso-C\equiv NXY$ could not be detected. ^{31}P NMR (101.3 MHz, C_6D_6 , 300 K): δ -218.7 (s; $PMes$). IR (KBr): $\nu = 3034.6$ (w), 2972.8 (w), 2940.0 (w), 2911.0 (m), 2886.0 (m), 2871.5 (m), 2842.6 (w), 2281.4 (very broad w, $PC\equiv N$), 2057.7 and 2019.1 (s, $C\equiv N$), 1638.2 and 1587.1 (s, $C\equiv N$), 1459.9 and 1437.7 (s, $C\equiv C$), 1376.0 (s, $P-Ar$), 1240.0 (s), 1187.9 (m, $P=C$), 1025.0 (m, $P-Ar$), 984.5 (m), 840.8 (s), 774.3 and 761.7 (s, $P-C$), 678.8 (s), 517.8 cm^{-1} (s). HR EI-MS: calcd for $C_{37}H_{44}IrN_2P$ 740.2871, found 740.2896. m/z (%): 740 (<1) $[M]^+$, 609 (1) $[M - CNXY]^+$, 590 (20) $[M - PMes]^+$.

$[(Cp^*)(Xy-N\equiv C)IrPDmpC\equiv NXY]$ (4c). An orange solution of $[(\eta^5-Cp^*)-IrCl_2(PH_2Dmp)]$ (**6c**; 0.075 g, 0.10 mmol) in CH_2Cl_2 (1.5 mL) was added to a mixture of DBU (29.9 μL , 0.20 mmol) and $Xy-N\equiv C$ (0.131 g, 1.0 mmol) in CH_2Cl_2 (1 mL) at $-78^\circ C$, and the reaction mixture was allowed to warm up to room temperature. After evaporation to dryness, the residue was washed with pentane (2×1 mL) and extracted into diethyl ether (2×10 mL), and the solution was filtered. After concentration of the solution to a few milliliters, **4c** (0.060 g, 0.064 mmol, 64%) was obtained as yellow crystals by crystallization at $-20^\circ C$. Mp: $175^\circ C$ (dec). 1H NMR (400.13 MHz, C_6D_6 , 346 K): δ 1.41 (s, 15H; $C_5(CH_3)_5$), 1.97 (s, 6H; $o-C\equiv NXYCH_3$), 2.15 (s, 6H; $o-MesCH_3$), 2.20 (s, 6H; $o-MesCH_3$), 2.23 (s, 3H; $p-MesCH_3$), 2.50 (s, 3H;

$p-MesCH_3$), 2.58 (s, 6H; $o-C\equiv NXYCH_3$), 6.77 (m, 5H; $m-C\equiv NXY$, $m-Mes$, and $p-C\equiv NXY$), 6.84 (m, $^3J(H,H) = 7.4$ Hz, 3H; $m-PhP$ and $p-C\equiv NXY$), 6.96 (d, $^3J(H,H) = 7.4$ Hz, 2H; $m-C\equiv NXY$), 6.98 (s, 2H; $m-Mes$), 7.08 (t, $^3J(H,H) = 7.4$ Hz, 1H; $p-PhP$). $^{13}C\{^1H\}$ NMR (100.64 MHz, C_6D_6 , 300 K): δ 9.1 (d, $^3J(C,P) = 2.9$ Hz; $C_5(CH_3)_5$), 19.2 (s; $o-C\equiv NXYCH_3$), 19.8 (s; $p-MesCH_3$), 21.0 (s; $o-MesCH_3$), 22.0–22.2 (bs; $o-MesCH_3$, $o-C\equiv NXYCH_3$, $o-C\equiv NXYCH_3$, and $p-MesCH_3$), 96.9 (s; $C_5(CH_3)_5$), 122.4 (s; $p-C\equiv NXY$), 126.0 (s; $o-C\equiv NXY$), 126.1 (s; $o-C\equiv NXY$), 126.2 (s; $p-C\equiv NXY$), 127.1 (s; $m-C\equiv NXY$), 127.2 (s; $p-PhP$), 128.0 (s; $ipso-Mes$, and $m-Mes$), 128.5 (s; $m-C\equiv NXY$), 128.6 (s; $m-C\equiv NXY$), 129.0 (s; $m-Mes$), 129.8 (s; $p-Mes$), 129.9 (bs; $m-PhP$), 130.6 (s; $ipso-C\equiv NXY$), 134.5 (s; $o-C\equiv NXY$), 136.1 and 136.5 (s; $o-Mes$), 138.0 (d, $^1J(C,P) = 69.5$ Hz; $ipso-PhP$), 140.8 (s; $ipso-Mes$), 144.0 (s; $C\equiv NXY$), 148.0 (s; $ipso-C\equiv NXY$), 148.2 (d, $^2J(C,P) = 12.9$ Hz; $o-Ph$), 173.3 (d, $^1J(C,P) = 93.5$ Hz; $P-C\equiv NXY$). ^{31}P NMR (101.3 MHz, C_6D_6 , 300 K): δ -216.7 (s; $PDmp$). IR (KBr): $\nu = 3036.4$ (m), 2977.6 (m), 2949.6 (s), 2909.1 (m), 2851.3 (m), 2268.9 (very broad w, $PC\equiv N$), 2054.8 and 2012.4 (s, $C\equiv N$), 1645.0 and 1586.2 (s, $C\equiv N$), 1457.0 and 1443.5 (s, $C\equiv C$), 1377.0 (s, $P-Ar$), 1188.9 (m, $P=C$), 1088.6 (m), 1030.8 (m, $P-Ar$), 845.6 (m), 800.3 (m), 761.7 and 745.4 (s, $P-C$), 672.1 (s), 546.7 (w), 520.0 cm^{-1} (w). HR EI-MS: calcd for $C_{52}H_{58}IrN_2P$ 934.3967, found 934.3930. m/z (%): 934 (14) $[M]^+$, 803 (100) $[M - C\equiv NXY]^+$, 589 (60) $[M - DmpPH]^+$, 454 (16) $[M - DmpPH - Cp^*]^+$.

Double Dehydrohalogenation of $[(\eta^5-Cp^*)IrCl_2(PH_2Dmp)]$ (6c). DBU (2 equiv, 8.4 μL , 5.6 μmol) was added to an orange solution of $[(\eta^5-Cp^*)IrCl_2(PH_2Dmp)]$ (**6c**; 20.9 mg, 2.8 μmol) in CD_2Cl_2 (0.4 mL) at $-10^\circ C$. After 5 min at room temperature, the reaction mixture turned deep red of which ^{31}P NMR spectroscopy at 263 K showed unreacted $[(\eta^5-Cp^*)IrCl_2(PH_2Dmp)]$ at δ -81.5 (9.2%) together with phosphinidene $[(\eta^5-Cp^*)(CD_2Cl_2)Ir=PDmp]$ (**7c**(DCM)) at δ 672.1 (11.5%), the monodehydrohalogenated product $[(\eta^5-Cp^*)(Cl)Ir=PHDmp]$ at δ 105.8 (d, $^1J(P,H) = 369.6$ Hz, 50.7%), and two minor products at δ -17.4 (d, $^1J(P,H) = 185.3$ Hz, 19.3%) and -67.9 (d, $^1J(P,H) = 212.6$ Hz, 9.3%).

Attempted Synthesis of $[(\eta^5-Cp^*)(Xy-N'C)Ir=PDmp]$ (3c). An orange solution of $[(\eta^5-Cp^*)IrCl_2(PH_2Dmp)]$ (**6c**; 75 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) was added to a clear, colorless solution of $Xy-N\equiv C$ (13 mg, 0.10 mmol) and DBU (29.8 μL , 0.20 mmol) in toluene (2 mL) at room temperature. After 3 h, a color change to dark purple was observed and the phosphinidene $[(\eta^5-Cp^*)(Xy-N\equiv C)Ir=PDmp]$ (**3c**) could be detected by ^{31}P NMR spectroscopy at δ 768.1 (50%) together with another product at -88.6 (d, $^1J(P,H) = 202$ Hz, 50%).

X-ray Crystal Structure Determinations. Intensities were measured at 150(2) K on a Nonius KappaCCD diffractometer with a rotating anode (graphite monochromator, $\lambda = 0.71073$ Å) up to a resolution of $(\sin \theta/\lambda)_{\max} = 0.65$ Å $^{-1}$. Integration was performed with EvalCCD³⁷ (compounds **4a** and **4b**) or HKL2000³⁸ (compound **5**). The program SADABS³⁹ was used for absorption correction and scaling. The structures were solved with automated Patterson methods using the program DIRDIF-99⁴⁰ and refined with SHELXL-97⁴¹ against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. Geometry

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calculations and checking for higher symmetry were performed with the PLATON program.⁴² Further details are given in Table 1 in the Supporting Information.

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Supporting Information Available: Cartesian coordinates ($\text{\AA}$) and energies (au) of all stationary points. Cif files with crystallographic data and copies of the NMR spectra of all novel compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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