N-Heterocyclic Carbene Functionalized Iridium Phosphinidene Complex [Cp*(NHC)Ir=PMes*]: Comparison of Phosphinidene, Imido, and Carbene Complexes

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Abstract: The novel phosphinidene complex [Cp*(NHC)Ir=PMes*] (**3**; NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) was prepared in high yield from [Cp*(NHC)IrCl$_2$] (**2**) and [LiPHMes*]·3THF. It represents the first example of an NHC ligated transition metal phosphinidene complex. The X-ray crystal structure for **3** is also reported. DFT calculations on the N-heterocyclic carbene containing parent complexes [Cp(NHC)Ir=E] (E = PH, NH, CH$_2$) show that the NHC ligand acts as good σ-donor/weak π-acceptor ligand and forms strong Ir−C(NHC) single bonds. The Ir=E double bonds result from strong triplet–triplet interactions between [Cp(NHC)Ir] and E.

Keywords: carbenes · density functional calculations · iridium · P ligands

Introduction

In recent years, N-heterocyclic carbenes (NHC) have evolved towards highly valuable ligands in transition metal chemistry and homogeneous catalysis.[1, 2] Neutral imidazol-2-ylidenes, which are now readily available from established synthetic procedures,[1, 3] are thermally stable ligands that exhibit strong σ-donor and negligible π-acceptor capabilities.[1, 4, 5] They are often regarded as useful substitutes for tertiary phosphine ligands, due to their electronic and steric properties and low reactivity.[4, 6, 7] Phosphine substitution in the established Ru-based Grubbs catalysts [(PR$_3$)$_2$Cl$_2$Ru=CHR′] by imidazol-2-ylidenes, has already provided new catalytic systems with superior activities in olefin metathesis.[2, 6] Interestingly, these Ru complexes represent the only known examples of a new class of compounds that contain both an alkylidene moiety as well as an N-heterocyclic carbene ligand.[2] Similar complexes of other transition metals have not yet been reported, and neither have N-heterocyclic carbene complexes that bear reactive metal–ligand multiple bonds other than an alkylidene, such as imido (M=NR) and phosphinidene (M=PR) moieties.

Recently, our group reported on stable Group 8 and 9 phosphinidene complexes of the type [(η^6-Ar)(L)M=PAr] (M = Ru, Os)[8] and [(η^5-Cp^R)(L)M=PAr] (M = Co, Rh, Ir).[9, 10] A unique aspect of these novel complexes concerns the facile variation of stabilizing ligand L. So far, established ligands such as phosphines, arsines, phosphites, isocyanides and carbon monoxide have been introduced successfully, leading to stable, isolable complexes with strong metal−ligand bonds.[10] This encouraged us to investigate the availability of phosphinidene complexes that contain an N-heterocyclic carbene ligand, and to study their structural and electronic properties.

In this report, the synthesis and characterization of novel iridium complex [Cp*(NHC)Ir=PMes*] (NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) is described. Furthermore, structural and bonding properties for the iridium phosphinidene parent complex that contains the imidazol-2-ylidene ligand is evaluated theoretically, and comparisons are made with analogous alkylidene and imido complexes. The transition metal iridium is used because similar alkylidene,[11, 12] imido,[13] phosphinidene,[9] as well as N-heterocyclic carbene complexes[14] are known experimentally for iridium.

Results and Discussion

Synthesis of [Cp*(NHC)Ir=PMes*]: We explored the availability of NHC-ligated iridium phosphinidene complexes by

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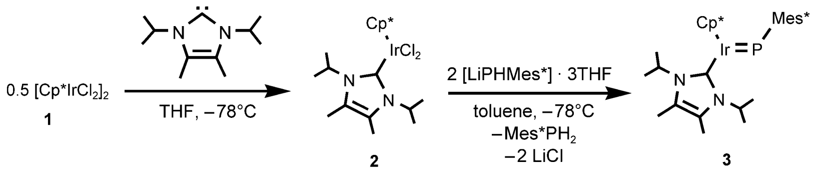
using a metathesis reaction with a lithiumphosphide. First, the NHC-ligated iridium complex **2** was prepared by a reaction of the commercially available dimer $[Cp^*IrCl_2]_2$ (**1**) with the readily available N-heterocyclic carbene ligand 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (Scheme 1). Novel complex **2** was obtained as an orange-yellow crystalline solid in 85 % isolated yield. The ^{13}C NMR resonance at δ 155.1 resembles that of a previously reported analogue $[Cp^*Cl_2Ir(1,3\text{-dicyclohexylimidazol-2-ylidene})]$,[14] and confirms the presence of the carbene moiety in **2**.



Scheme 1.

Treatment of **2** with two equivalents of $[LiPHMes^*]\cdot 3THF$ in toluene at −78 °C afforded terminal iridium phosphinidene complex **3** as dark red crystals in 78 % isolated yield. In the ^{31}P NMR spectrum, the presence of a single resonance at δ 560 confirms the presence of a bent phosphinidene moiety. Interestingly, the chemical shift of the phosphinidene is remarkably shielded with respect to analogous phosphinidene complexes such as $[Cp^*(PPh_3)Ir{=}PMes^*]$ (δ 687) and $[Cp^*(CO)Ir{=}PMes^*]$ (δ 805).[9] The ^{13}C NMR resonance of the carbene at δ 169.2 in **3** is deshielded with respect to **2**, due to charge donation to the metal moiety.

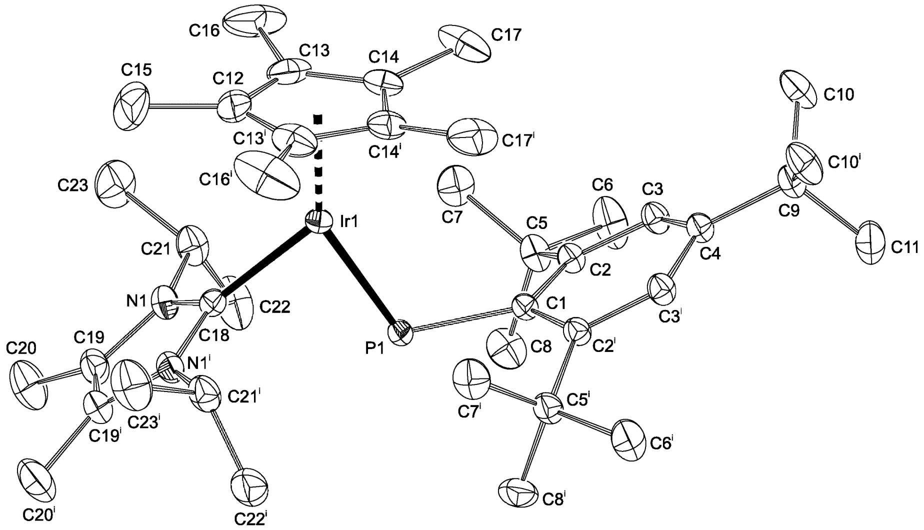


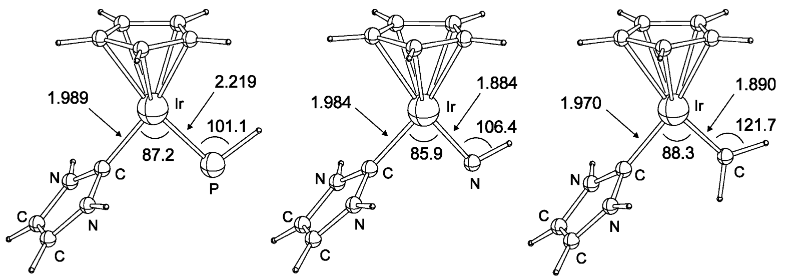
Figure 1. Displacement ellipsoid plot (50 % probability level) of $3\cdot C_7H_8$. Toluene and the hydrogen atoms are omitted for clarity (symmetry operation *i*: *x*, 0.5 − *y*, *z*). Selected bond lengths [Å], angles [°] and torsion angles [°]: Ir1−P1 2.1959(5), Ir1−C18 2.0278(19), Ir1−Cp(cg) 1.8919(8), P1−C1 1.8682(19), C18−N1 1.3693(16), N1−C19 1.3940(19), C19−C19^i 1.346(3), Ir1-P1-C1 110.76(6), P1-Ir1-Cp(cg) 147.74(3), P1-Ir1-C18 82.74(5), C18-Ir1-Cp(cg) 129.52(6), C2^i-C1-C2-C3 −15.6(2).

The structure of **3** was ascertained by X-ray crystallography (Figure 1) and strongly resembles that of the previously reported $[Cp^*(PPh_3)Ir{=}PMes^*]$.[9] This suggests that the observed shielding of the ^{31}P NMR resonance arises from the strong σ-donor and weak π-acceptor properties of the NHC ligand rather than from geometrical differences. The structure has a two-legged piano stool geometry with a crystallographic mirror plane through C15, C12, Ir1, C18, P1, C1, C4, C9, and C11. It exhibits an *E* configuration for the Ir=P bond and an acute P1-Ir1-C18 angle of 82.74(5)°. The 2.1959(5) Å Ir1−P1 bond illustrates the presence of an Ir=P double bond, whereas the Ir1−C18 bond is expectedly long at 2.0278(19) Å. The structure of **3** represents the first example of a transition-metal complex that contains both an N-heterocyclic carbene ligand as well as a metal–ligand multiple bond other than with an alkylidene.

Abstract in Dutch: *Het nieuwe fosfinideen complex $[Cp^*(NHC)Ir{=}PMes^*]$ (**3**; NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylideen) werd met hoge opbrengst uit $[Cp^*(NHC)IrCl_2]$ (**2**) en $[LiPHMes^*]\cdot 3THF$ gemaakt. Dit complex is het eerste voorbeeld van een NHC-gecoördineerd overgangsmetaal fosfinideen, waarvan in dit artikel de röntgen kristal structuur gepresenteerd wordt. DFT berekeningen aan het N-heterocyclische carbeen bevattende model complex [Cp(NHC)Ir=E] (E = PH, NH, CH$_2$) tonen aan dat het NHC ligand zich als een goede σ-donor en zwakke π-acceptor gedraagt en een sterke Ir−C(NHC) binding vormt. De Ir=E dubbele binding wordt veroorzaakt door een sterke triplet–triplet wisselwerking tussen Cp(NHC)Ir en E.*

Theoretical evaluation: To investigate the structural and electronic properties of iridium phosphinidene complexes that contain an N-heterocyclic carbene ligand and to compare these with similar alkylidene and imido complexes, we resorted to density functional theory (DFT) calculations. As model systems, we used the iridium parent complexes [Cp(NHC)Ir=E] (NHC = imidazol-2-ylidene; E = PH, NH, CH$_2$). The optimized structures (C_s symmetry) are depicted in Figure 2.

All three complexes (**4**–**6**) have similar two-legged piano stool geometries with acute E-Ir-C(NHC) angles that range from 85.9–88.3°. The calculated structure of phosphinidene **4** is in good agreement with the X-ray crystal structure of **3**, and has an Ir-P-H angle of 101.1° and an Ir=P distance of 2.219 Å. The imido complex **5** exhibits a short 1.884 Å Ir=N double bond which is elongated with respect to known Ir≡N triple bonds (1.71–1.75 Å).[13] A remarkable structural aspect of **5**



4 **5** **6**

Figure 2. DFT optimized structures (C_s symmetry) for [Cp(NHC)Ir=E]; E = PH (**4**), NH (**5**) and CH_2 (**6**).

concerns the sharp Ir-N-H angle of 106.4°. Whereas phosphinidene complexes are usually bent,[15, 16] the majority of known imido complexes have (nearly) linear M-N-R moieties with bond angles of 160–180°. This preference for linearity has already been established theoretically and is governed by subtle steric and electronic effects.[17] Experimental examples of strongly bent imido complexes are rare and are believed to exhibit high reactivity.[17a,b]

The Ir–C(NHC) bond lengths of **4**–**6** range from 1.970–1.989 Å, which is in good agreement with an experimentally reported Ir–C(NHC) bond length of 2.019 Å.[14] These distances are shortened with respect to normal Ir–C single bonds (~2.1 Å)[18] and longer than Ir=C double bonds.[12] The latter can be illustrated by the short Ir=C distance in **6** (1.890 Å) which agrees well with the experimentally known Ir alkylidene complex [Cp*(P*i*Pr$_3$)Ir=CPh$_2$] (1.904 Å).[12] The longer Ir–C(NHC) bond lengths in **4**–**6** mirror the different nature of the metal–carbene bonds with respect to alkylidene moieties. Interestingly, the difference between the Ir=C and Ir–C(NHC) distances of 0.08 Å in **6** is much less pronounced compared with NHC ligated Ru alkylidene complexes (0.23–0.30 Å).[2, 6] This suggests the NHC ligands to be tighter bound in the Ir complexes than in the Ru analogues.

The calculated atomic charges for Ir, E, and C(NHC) are collected for complexes **4**–**6** (Table 1). The nucleophilic character of the phosphinidene, imido, and alkylidene moieties is demonstrated by the high negative charges on E. The charges increase on going from P < C ≪ N which reflects the increase of the electonegativities of the elements ($\chi(P) = 2.1$, $\chi(C) = 2.5$, $\chi(N) = 3.0$).[19] The charges on Ir show only marginal differences, and these relate to some extent to those on E. Finally, the C(NHC) charges are hardly effected by the nature of E and they are slightly positive (+0.03) for all complexes. This is in sharp contrast with the free NHC ligand for which the C(NHC) charge was calculated to be −0.185, thereby illustrating its high nucleophilicity and good electron donating properties as a ligand.

Table 1. Calculated Hirshfeld charges for complexes **4**–**6**.[a]

Complex	Ir	E	C(NHC)
[Cp(NHC)Ir=PH] (**4**)	−0.026	−0.145	+0.029
[Cp(NHC)Ir=NH] (**5**)	+0.062	−0.329	+0.036
[Cp(NHC)Ir=CH$_2$] (**6**)	+0.017	−0.185	+0.034

[a] For a definition, see ref. [20].

To further elucidate the different nature of the Ir=E bonds in complexes **4**–**6**, we calculated the bond dissociation energies (BDEs) which are summarized in Table 2. All fragments have a preferred triplet ground state, 34.6 (PH), 53.7 (NH), 15.7 (CH_2) and 9.2 (Cp(NHC)Ir) kcal mol^{-1} more stable than their closed shell singlet states. The Ir=E bonds in all three complexes can be described as covalent double bonds resulting from the joint σ-interaction ($Ir(d_{z^2}) - E(p_z)$), the π-interaction ($Ir(d_{xz}) - E(p_x)$) and the electrostatic interaction between the fragments in their triplet state. This agrees with established bonding models for nucleophilic Schrock-type complexes that have been described previously.[15, 21, 22] Consequently, the Ir=E bonds are strong for all complexes, with the Ir=C bond in **6** being the strongest with a BDE of 117.2 kcal mol^{-1}. The BDE of the weaker Ir=P bond (92.3 kcal mol^{-1}) is in good agreement with previously reported theoretical values for the similar phosphinidene complexes [Cp(PH$_3$)Ir=PH] (92.4 kcal mol^{-1}) and [Cp(CO)Ir=PH] (90.7 kcal mol^{-1}).[21]

Table 2. Energy decomposition and bond dissociation energies (BDE) for the Ir=E bonds in complexes **4**–**6**.

Complex	ΔE_σ	ΔE_π	ΔE^{oi}	ΔE^{elst}	ΔE^{Pauli}	ΔE^{tot}	**BDE**
[Cp(NHC)Ir=PH] (**4**)	−114.3	−38.8	−153.1	−194.1	+250.1	−97.1	**+92.3**
[Cp(NHC)Ir=NH] (**5**)	−158.4	−50.9	−209.3	−174.4	+279.4	−104.3	**+98.4**
[Cp(NHC)Ir=CH$_2$] (**6**)	−140.7	−45.4	−186.0	−192.8	+250.6	−128.2	**+117.2**

The electrostatic interaction term (ΔE^{elst}) is very similar for both **4** and **6**, but is much lower for the Ir=N bond. This causes the Ir=N bond in **5** to be weaker (98.4 kcal mol^{-1}) as compared with the Ir=C bond in **6**, despite stronger orbital interactions (ΔE^{oi}). All complexes, however, exhibit similar σ-contributions to the total orbital interaction term (ΔE^{oi}) of 75%, whereas the π-contributions are smaller (25%).

The Ir–C(NHC) bonds of the complexes **4**–**6** were analyzed in a similar fashion (Table 3), but with respect to the fragments in their singlet ground states, which are highly preferred over the triplet states by as much as 90.1 (NHC), 25.8 (CpIrPH), 58.5 (CpIrNH), and 13.6 (CpIrCH$_2$) kcal mol^{-1}.[23] The results clearly demonstrate the fundamental difference between the Ir–C(NHC) bond and the Ir=CH$_2$ alkylidene bond. The dative Ir–C(NHC) single bond in **4**–**6** results from strong σ-donation ($C(p_y) \rightarrow Ir(d_{x^2-y^2})$), which amounts to ~80% of the total orbital interaction term (ΔE^{oi}). The contribution of π-backbonding ($Ir(d_{xy}) \rightarrow C(p_x)$) is much smaller (~20%). This leads to a mean σ/π ratio of 4.2, which is in good agreement with that

Table 3. Energy decomposition and bond dissociation energies (BDE) for the Ir–C(NHC) bonds in complexes **4**–**6**.[23]

Complex	ΔE_{σ}	ΔE_{π}	ΔE^{oi}	ΔE^{elst}	ΔE^{Pauli}	ΔE^{tot}	**BDE**
[Cp(NHC)Ir=PH] (**4**)	–80.5	–18.6	–99.1	–227.0	+248.5	–77.6	**+59.2**
[Cp(NHC)Ir=NH] (**5**)	–94.5	–20.4	–114.9	–246.2	+288.1	–73.0	**+25.9**
[Cp(NHC)Ir=CH_2] (**6**)	–76.9	–21.2	–98.1	–228.7	+252.6	–74.2	**+69.2**

obtained by Frenking et al. for the gold complex [ClAu(NHC)], calculated at the MP2 level of theory (4.35).[5]

The strong σ-donor/weak π-acceptor capabilities of the NHC ligand result in a significant charge transfer to the metal moiety upon bond formation, which was already expressed by the calculated atomic charges (Table 1). The resulting Ir–C(NHC) bonds are strong, especially for the phosphinidene **4** and the alkylidene **6**. The metal–ligand BDE for **4** strongly resembles that of previously reported Ir–CO bonds in similar phosphinidene complexes, [Cp(CO)Ir=PH].[10] However, the Ir–CO bond length is much shorter (1.85 Å) than the Ir–C(NHC) bond, thereby illustrating the different nature of these ligands. The orbital interaction term (ΔE^{oi}) of the imido complex **5** resembles those of **4** and **6**, but larger Pauli repulsion (ΔE^{Pauli}) as well as a larger preparation energy (ΔE^{prep}), due to unfavorable distortion from linearity of the Ir=N-H moiety in the CpIrNH fragment, result in a much weaker Ir–C(NHC) bond with a BDE of only 25.9 kcal mol^{-1}. Again, the diagonal C–P relationship[15] in the Periodic Table is stressed, whereas the vertical N–P relationship is much less pronounced. The high nucleophilicity involved with bent imido moieties, however, makes **5** an interesting synthetic target, which remains topic of future research.

Conclusion

Novel, stable phosphinidene complex [Cp*(NHC)Ir=PMes*] (**3**; NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) was synthesized (78%) by reaction of [Cp*(NHC)IrCl_2] (**2**) with [LiPHMes*]·3THF. The X-ray crystal structure of this first example of an NHC-ligated pnictidene complex is reported.

A theoretical evaluation (DFT) of structurally similar complexes [Cp(NHC)Ir=E] (E = PH, NH, CH_2) revealed intriguing trends in electronic properties. The M=E double bonds result from strong covalent bonding interactions between the triplet Cp(NHC)Ir and E fragments. The N-heterocyclic carbene behaves as a strong σ-donor and weak π-acceptor spectator ligand, which is accompanied by pronounced charge donation to the metal moiety. The Ir–C(NHC) single bonds are very strong for the phosphinidene and alkylidene complexes **4** (58.9 kcal mol^{-1}) and **6** (69.3 kcal mol^{-1}), and much weaker for the imido complex **5** (25.9 kcal mol^{-1}). The high nucleophilicity of the imido complex **5**, demonstrated by the high atomic charge on N and the bent geometry of the Ir=N–H moiety, makes it an attractive synthetic target.

Computational Section

All calculations were performed using the parallelized Amsterdam density functional (ADF) package (version 2002.01).[24] All atoms were described by a triple-ζ basis set with polarization functions, 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 iridium centers were described by a triple-ζ basis set for the outer *n*s, *n*p, *n*d and (*n*+1)s orbitals, whereas the shells of lower energy were treated by the frozen core approximation. 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 parametrization[25] with nonlocal corrections for exchange (Becke88)[26] and correlation (Perdew86).[27] All geometries were optimized using the analytical gradient method implemented by Versluis and Ziegler,[28] including relativistic effects by the zero-order regular approximation (ZORA).[29]

The metal–ligand bonds were analyzed with ADF's established energy decomposition[30] into an exchange (or Pauli) repulsion (ΔE^{Pauli}) plus electrostatic interaction energy part (ΔE^{elst}) and an orbital interaction energy (charge transfer, polarization) part (ΔE^{oi}). The energy necessary to convert fragments from their ground state equilibrium geometries to the geometry and electronic state they acquire in the complex is represented by a preparation energy term (ΔE^{prep}). The overall bond energy (ΔE^{tot}) is formulated as:

$$\Delta E^{\text{tot}} = \Delta E^{\text{Pauli}} + \Delta E^{\text{elst}} + \Delta E^{\text{oi}} + \Delta E^{\text{prep}} \tag{1}$$

Note that ΔE^{tot} is defined as the negative of the bond dissociation energy (BDE), i.e., $\Delta E^{\text{tot}} = E(\text{molecule}) - \Sigma E(\text{fragments})$, thereby giving negative values for stable bonds. The orbital interaction term ΔE^{oi} accounts for interactions between occupied orbitals on one fragment with unoccupied orbitals on the other fragment, including HOMO–LUMO interactions and polarization (empty/occupied orbital mixing on the same fragment). The charge transfer part is the result of both σ-donation from the ligand to the metal, and π-back-donation from the metal into the unoccupied orbitals of the ligand. Instead of separating the charge transfer and polarization parts, we used the extended transition state (ETS) method developed by Ziegler and Rauk to decompose ΔE^{oi} into contributions from each irreducible representation of the interacting system.[30] In systems with a clear σ,π-separation, this symmetry partitioning proves to be most informative.

Experimental Section

General data: All experiments were performed in flame-dried glassware and under an atmosphere of dry nitrogen or argon. Solvents were distilled (under N_2) from sodium (toluene), sodium benzophenone (THF) or lithium aluminum hydride (*n*-pentane). Deuterated solvents were dried over 4 Å molecular sieves ($CDCl_3$, C_6D_6). All solid starting materials were dried in vacuo. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 300 K on a Bruker Avance 250 spectrometer at 250.13, 62.90 and 101.25 MHz, respectively. ^{1}H NMR spectra were referenced to $CHCl_3$ (δ 7.27) or C_6D_5H (δ 7.17), ^{13}C NMR spectra to $CDCl_3$ (δ 77.16) or C_6D_6 (δ 128.06) and ^{31}P NMR spectra to external 85% H_3PO_4. High-resolution mass spectra (HRMS) were recorded on a Finnigan Mat 900 spectrometer. [Cp*IrCl_2]$_2$,[31] 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene,[3] and [LiPHMes*]·3THF[32] were prepared according to literature procedures.

[Cp*(NHC)IrCl_2] (2): A solution of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (198 mg, 1.10 mmol) was added to a stirred suspension of

$[\mathrm{Cp^*IrCl_2}]_2$ (0.40 g, 0.50 mmol) in THF (15 mL) at −78 °C. The mixture was slowly warmed to room temperature and stirred for 12 h and subsequently filtered to remove insoluble material. The solvent was removed in vacuo and the residue was washed with *n*-pentane (30 mL). Recrystallization from $\mathrm{CH_2Cl_2}$/*n*-pentane gave orange-yellow crystals of **2** (0.49 g, 0.85 mmol, 85 %). M.p. 231 – 232 °C; ^{1}H NMR (250.13 MHz, $\mathrm{CDCl_3}$, 300 K): $\delta = 1.43$ (d, $^3J(\mathrm{H,H}) = 7.2$ Hz, 6 H, $\mathrm{CH(C}H_3)_2$), 1.61 (s, 15 H, $\mathrm{C_5(C}H_3)_5$), 1.67 (d, $^3J(\mathrm{H,H}) = 6.8$ Hz, 6 H, $\mathrm{CH(C}H_3)_2$), 2.27 (s, 6 H, $\mathrm{C}H_3$), 5.43 (septet, $^3J(\mathrm{H,H}) = 7.0$ Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (62.90 MHz, $\mathrm{CDCl_3}$, 300 K): $\delta = 9.30$ (s, $\mathrm{C_5(}C\mathrm{H_3)_5}$), 10.6 (s, $C\mathrm{H_3}$), 23.8 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 24.0 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 53.0 (s, $C\mathrm{H(CH_3)_2}$), 88.7 (s, $C_5\mathrm{(CH_3)_5}$), 126.7 (s, *C-C*), 155.1 (s, $\mathrm{N_2}C$); HRMS: *m*/*z*: calcd for $\mathrm{C_{21}H_{35}Cl_2N_2Ir}$: 578.18066; found: 578.18459.

[Cp*(NHC)Ir=PMes*] (3): A freshly prepared solution of [LiPHMes*] · 3 THF (0.50 g, 1.00 mmol) in toluene (15 mL) was added slowly to an orange suspension of **2** (289 mg, 0.50 mmol) in toluene (10 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 2 h. After removal of the solvent, the orange-brown residue was extracted into *n*-pentane (50 mL) and filtered to remove LiCl. The solvents were removed in vacuo and the residue was washed with cold *n*-pentane (10 mL) to remove $\mathrm{Mes^*PH_2}$, and recrystallized from toluene at −20 °C to give large dark red crystals of **3** (306 mg, 0.39 mmol, 78 %). M.p. 192 – 194 °C; ^{1}H NMR (250.13 MHz, $\mathrm{C_6D_6}$, 300 K): $\delta = 1.36$ (d, $^3J(\mathrm{H,H}) = 7.3$ Hz, 6 H, $\mathrm{CH(C}H_3)_2$), 1.42 (d, $^3J(\mathrm{H,H}) = 7.0$ Hz, 6 H, $\mathrm{CH(C}H_3)_2$), 1.56 (s, 9 H, *p*-$\mathrm{C(C}H_3)_3$), 1.63 (s, 15 H, $\mathrm{C_5(C}H_3)_5$), 1.87 (s, 18 H, *o*-$\mathrm{C(C}H_3)_3$), 1.88 (s, 6 H, $\mathrm{C}H_3$), 5.89 (septet, $^3J(\mathrm{H,H}) = 7.2$ Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 7.54 (s, 2 H, *m*-Mes*); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (62.90 MHz, $\mathrm{C_6D_6}$, 300 K): $\delta = 10.4$ (s, $C\mathrm{H_3}$), 10.4 (s, $\mathrm{C_5(}C\mathrm{H_3)_5}$), 22.0 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 22.8 (s, $\mathrm{CH(}C\mathrm{H_3)_2}$), 32.2 d, $^4J(\mathrm{P,C}) = 8.4$ Hz, *o*-$\mathrm{C(}C\mathrm{H_3)_3}$), 32.3 (s, *p*-$\mathrm{C(}C\mathrm{H_3)_3}$), 34.6 (s, *p*-$C\mathrm{(CH_3)_3}$), 38.6 (s, *o*-$C\mathrm{(CH_3)_3}$), 54.9 (s, $C\mathrm{H(CH_3)_2}$), 89.4 (s, $C_5\mathrm{(CH_3)_5}$), 120.4 (s, *m*-Mes*), 124.3 (s, *C-C*), 144.2 (s, *p*-Mes*), 145.2 (s, *o*-Mes*), 169.2 (s, $\mathrm{N_2}C$), 172.7 (d, $^1J(\mathrm{P,C}) = 107.8$ Hz, *i*-Mes*); ^{31}P NMR (101.3 MHz, $\mathrm{C_6D_6}$, 300 K): $\delta = 560.0$ (s, Ir-*P*); HRMS: *m*/*z*: calcd for $\mathrm{C_{39}H_{64}N_2PIr}$: 784.44360; found: 784.43777.

Crystal structure determination of complex 3: $\mathrm{C_{39}H_{64}IrN_2P \cdot C_7H_8}$, $F_\mathrm{w} = 876.23$, dark red block, 0.24 × 0.15 × 0.15 $\mathrm{mm^3}$, monoclinic, $P2_1/m$ (no. 11), $a = 10.6694(1)$, $b = 14.5237(1)$, $c = 14.4093(1)$ Å; $\beta = 99.4693(4)^\circ$, $V = 2202.43(3)$ $\mathrm{Å^3}$, $Z = 2$, $\rho_\mathrm{calcd} = 1.321$ $\mathrm{g\,cm^{-3}}$, $\mu = 3.099$ $\mathrm{mm^{-1}}$. 51131 Reflections were measured on a Nonius KappaCCD diffractometer with rotating anode ($\lambda = 0.71073$ Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_\mathrm{max} = 0.81$ $\mathrm{Å^{-1}}$; 9951 reflections were unique ($R_\mathrm{int} = 0.049$). An analytical absorption correction was applied (0.40 – 0.54 transmission). The structure was solved with Patterson methods (DIRDIF-97)[33] and refined with SHELXL-97[34] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups. 260 refined parameters, no restraints. *R* values [$I > 2\sigma(I)$]: $R1 = 0.0233$, $wR2 = 0.0498$. *R* values [all refl.]: $R1 = 0.0299$, $wR2 = 0.0515$. GoF = 1.034. Residual electron density between −0.96 and 1.27 $\mathrm{e\,Å^{-3}}$. Molecular illustration, structure checking and calculations were performed with the PLATON package.[35] CCDC-201350 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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[22] Carbene complexes are usually classified in terms of electrophilic (Fischer-type) and nucleophilic (Schrock-type) complexes, depending on the carbene-substituent, the metal and its oxidation state, and the ancillary ligands. Whereas a σ-donor/π-acceptor model appropriately describes the M=C bond in Fischer-type complexes, the M=C bond in Schrock-type complexes should be discussed in terms of a covalent double bond between the triplet carbene and metal fragments. For a detailed discussion see: a) T. E. Taylor, M. B. Hall, *J. Am. Chem. Soc.* **1984**, *106*, 1576; b) E. A. Carter, W. A. Goddard III, *J. Am. Chem. Soc.* **1986**, *108*, 4746; c) S. F. Vyboishchikov, G. Frenking, *Chem. Eur. J.* **1998**, *4*, 1428.

[23] Due to the low symmetry (C_s) of the complexes, a 90° rotation of the NHC ligand was necessary to achieve symmetry partitioning between σ- and π-contributions. The π-contribution is then located perpendicular to the symmetry plane and is hence represented by a different irrep (a'') than the σ-conribution (a'). The optimized geometries were found to be only marginally higher in energy (0.01 – 0.35 $\mathrm{kcal\,mol^{-1}}$) with respect to **4** – **6**. For both the phosphinidene and the imido complex, the M=P bond was optimized in a *Z* configuration to avoid interactions between the lone pair and the NHC ligand. Both structural as well as electronic features of **4** – **6** are hardly effected by the rotation of the NHC ligand.

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