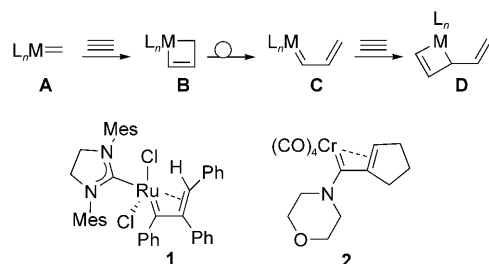


η^3 -Diphosphavinylcarbene: A P_2 Analogue of the Dötz Intermediate**

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Olefin metathesis^[1] constitutes a powerful tool for the construction of a plethora of unsaturated building blocks, pharmaceuticals, and advanced materials. The principle steps involve a transition-metal carbene complex (**A**) that under-

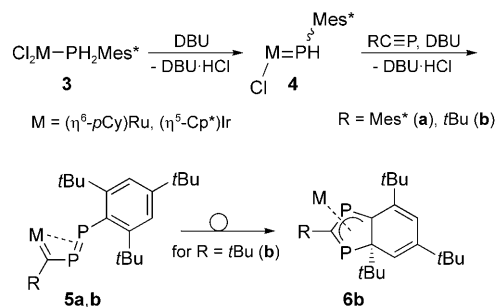


goes a [2+2] cycloaddition/cycloreversion protocol with alkenes according to the Chauvin mechanism.^[2] For the widely used Grubbs catalysts, however, support for the key intermediate of this process, the four-membered metallacyclobutane, relies on theoretical studies^[3] and low-temperature NMR spectroscopy.^[4,5] The unsaturated analogues provide more insight. For example, reaction of alkynes with the second-generation Grubbs catalyst gives stable η^3 -vinylcarbene complexes (**1**, Mes = 2,4,6-Me₃C₆H₂) that form after rearrangement of the initial ruthenium cyclobutenes (**B**).^[6,7] These puckered metal η^3 -vinylcarbene complexes^[8] (**C**) are highly potent and represent the key intermediate in enyne metathesis,^[9] alkyne polymerization (via **D**),^[10] and the versatile Fischer carbene mediated Dötz (benzannulation) reaction (which involves complexes such as **2**).^[11,12]

In our quest for novel reactivity patterns and in light of the diagonal relationship between carbon and phosphorus,^[13] we

herein report on a diphosphorus analogue of η^3 -vinylcarbene complex **C** (P_2 -**C**).^[14] Our approach involves the reaction of in situ generated phosphinidene [$M=PMes^*$] ($Mes^* = 2,4,6-tBu_3C_6H_2$;^[15] $M = (\eta^6-pCy)Ru$ ($pCy = para$ -cymene), $(\eta^5-Cp^*)Ir$ ($Cp^* = C_5Me_5$)), the phosphorus analogues of carbenes, with phosphalkynes ($RC\equiv P$; $R = Mes^*, tBu$).

Treatment of primary phosphine complexes [$Cl_2M-PH_2Mes^*$] (**3**) with two equivalents 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of one equivalent $Mes^*C\equiv P$ afforded η^3 -diphosphavinylcarbenes **5a** (P_2 -**C**) as the sole products in 89% (Ru) and 76% (Ir) yield after crystallization (Scheme 1). The synthesis of **5a** is remarkably



Scheme 1. Synthesis and reactivity of η^3 -diphosphavinylcarbene **5**.

selective, as evidenced by the single AB spin system in the ³¹P NMR spectrum (Ru-**5a**: $\delta = 52.1$ and -4.8 ppm, $^1J_{P,P} = 431.4$ Hz; Ir-**5a**: $\delta = 55.7$ and -21.1 ppm, $^1J_{P,P} = 394.0$ Hz); the large P,P coupling indicates the presence of a P–P bond. The highly deshielded resonances in the ¹³C NMR spectrum at $\delta = 306.9$ (Ru-**5a**) and 260.3 ppm (Ir-**5a**) are diagnostic for metal alkylidenes.^[6,16] They unambiguously support the carbenoid nature of the ring carbon atom and exclude the diphosphametallacyclobutene (P_2 -**B**) conformation.

X-ray crystal structure determination^[17] of dark green Ru-**5a** (Figure 1) and deep red crystals of Ir-**5a** revealed unequivocally the puckered structure of the unique η^3 -diphosphavinylcarbene ligand. Complex Ru-**5a** displays short metal–alkylidene and P2–C19 bonds (1.928(2) and 1.759(2) Å, respectively) and typical Ru–P (2.4339(5) and 2.4478(6) Å) and P–P bonds (2.1771(8) Å).

Whereas no intermediates could be detected by variable-temperature NMR spectroscopy during the formation of Ru-**5a**, selective monodehydrohalogenation of iridium precursor **3** occurred at -80°C to give *syn/anti*-Ir-**4** (³¹P NMR $\delta = 119.5$ ($^1J_{P,H} = 398.9$ Hz) and 128.3 ppm ($^1J_{P,H} = 369.6$ Hz)) in a 5:1 ratio. At this temperature, Ir-**4** is unreactive towards $Mes^*C\equiv P$, suggesting that the second dehydrohalogenation to afford

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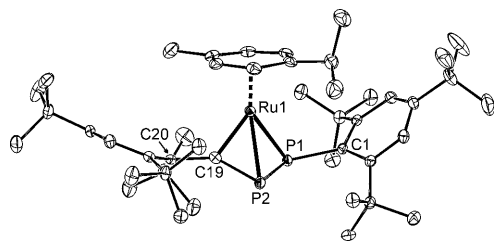


Figure 1. Displacement ellipsoid plot of Ru-**5a** with ellipsoids drawn at the 50% probability level. Hydrogen atoms and toluene solvent are omitted for clarity. Selected bond lengths [Å], angles [°], and torsion angle [°]: Ru1–P1 2.4339(5), Ru1–P2 2.4478(6), Ru1–C19 1.928(2), Ru1–pCy(cg) 1.7473(7), P1–C1 1.879(2), P1–P2 2.1771(8), P2–C19 1.759(2), C19–C20 1.480(3); P2–P1–Ru1 63.84(2), P1–P2–C19 88.26(7), Ru1–C19–P2 83.06(8); P1–P2–Ru1–C19 111.06(9).

the transient $[M=PMes^*]$ species takes place prior to phosphaaalkyne addition. At -60°C , the gradual formation of Ir-**5a** was observed.

Surprisingly, reaction of **3** with the less sterically congested phosphaaalkyne $t\text{BuC}\equiv\text{P}$ using two equivalents DBU resulted, at room temperature, in yellow crystalline **6b** (80% (Ru), 87% (Ir); Scheme 1) instead of the expected carbene **5b**, as indicated by a different set of signals in the ^{31}P NMR spectrum. The smaller P,P couplings are characteristic (Ru-**6b**: $\delta = -1.5$ and -92.1 ppm, $^2J_{\text{PP}} = 20.7$ Hz; Ir-**6b**: $\delta = -32.7$ and -113.0 ppm, $^2J_{\text{PP}} = 24.5$ Hz), as is the absence of a carbenoid resonance in the ^{13}C NMR spectrum. The molecular structure of Ru-**6b**, established by single-crystal X-ray structure determination,^[17] exhibits a number of fascinating features. First and foremost, **6b** contains an unprecedented 1,3-diphospha-3*H*-indene moiety^[18] bearing a dearomatized Mes* substituent (Figure 2). The striking resemblance of this stable P₂ entity with the benzannulation (Wheland) intermediate of the Dötz reaction is evident.^[12c] Secondly, η^4 coordination of the P₂C₂ moiety to the ruthenium center is favored over coordination of the all-carbon butadiene frag-

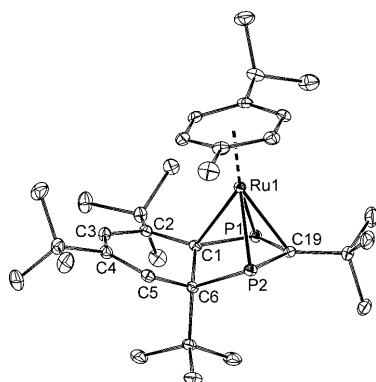


Figure 2. Displacement ellipsoid plot of Ru-**6b** with ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and torsion angle [°]: Ru1–P1 2.3664(4), Ru1–P2 2.3863(4), Ru1–C1 2.2624(14), Ru1–C19 2.2055(14), Ru1–pCy(cg) 1.7473(7), P1–C1 1.7926(15), P1–C19 1.7802(15), P2–C6 1.8777(15), P2–C19 1.7787(16), C1–C2 1.486(2), C1–C6 1.547(2), C2–C3 1.351(2), C3–C4 1.461(2), C4–C5 1.341(2), C5–C6 1.518(2); C1–P1–C19–P2 2.11(9).

ment.^[19] As a result, the P₂C₂ unit displays π delocalization, as evidenced by the similar P–C bond lengths (1.7787(16)–1.7926(15) Å) and an alternating bond pattern for the dearomatized Mes* ring.

Monitoring the reaction of ruthenium precursor **3** with $t\text{BuC}\equiv\text{P}$ by variable-temperature NMR spectroscopy showed full conversion at -80°C to dark green Ru-**5b** (^{31}P NMR: $\delta = -2.0$ and -35.7 ppm, $^1J_{\text{PP}} = 400.3$ Hz) and above -40°C its subsequent rearrangement to yellow Ru-**6b**. Monitoring the corresponding reaction of the iridium congener of **3** at -80°C showed, besides the monodehydrohalogenation to *syn/anti*-Ir-**4** (ca. 3:1 ratio), the formation of two new P₂ species (10:1 ratio) with sizable P,P and P,H couplings (major isomer, ^{31}P NMR $\delta = 358.7$ and -138.9 ppm, $^1J_{\text{PP}} = 164.0$ Hz, $^1J_{\text{PH}} = 387.8$ Hz). We ascribe these products to the *syn* and *anti* adducts of Ir-**7b** (Figure 3), which suggests that in this case the

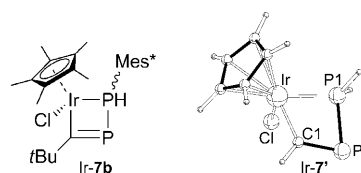


Figure 3. Intermediate Ir-**7b** and model structure Ir-**7'**, calculated at the B3PW91/6-31G(d,p) (LANL2DZ for Ir) level of theory. Selected bond lengths [Å] and a torsion angle [°] of Ir-**7'**: Ir–P1 2.304, Ir–C1 1.992, P1–P2 2.214, P2–C1 1.707; P1–P2–C1–Ir 4.86.

addition of the less congested phosphaaalkyne $t\text{BuC}\equiv\text{P}$ to Ir-**4** is plausible. The intermediacy of Ir-**7b** is supported by the calculated NMR spectral parameters^[20] of the unsubstituted model structure Ir-**7'** (^{31}P NMR $\delta = 352.6$ and -110.8 ppm, $^1J_{\text{PP}} = 256.9$ Hz; Figure 3). At -40°C , Ir-**7b** underwent the second base-induced dehydrohalogenation to yield Ir-**5b** (^{31}P NMR $\delta = -3.2$ and -24.4 ppm, $^1J_{\text{PP}} = 371.6$ Hz), which upon warming to room temperature rearranged into Wheland product Ir-**6b**, as was evident by the color change from red to yellow.

The remarkable conversion of **5b** into **6b** was examined by B3PW91/6-31G(d,p) calculations on model structures containing H instead of $t\text{Bu}$ substituents (labeled **5'**, **6'**, etc.; Figure 4). No simple direct pathway was found, but instead one that involves phosphinidene complex **8'** and η^3 -phosphaaalkenyl phosphinidene **9'**, the 1,3-isomer of **5**. Interestingly, the planar diphosphetametalacyclobutene conformer (P₂-**B**) is not an energy minimum but corresponds to the transition-state structure for inversion of puckered **5'** ($\Delta E^\ddagger = 24.4$ (Ru), 22.1 (Ir) kcal mol⁻¹). Isomerization of carbene **5'** to the less stable phosphinidene **8'** proceeds by P–P bond cleavage (Ru: $\Delta E = 19.8$, $\Delta E^\ddagger = 20.6$ kcal mol⁻¹). This step is then followed by facile rotation of the η^2 -coordinated phosphaaalkyne ligand and P–C bond formation to give regioisomer **9'** (Ru: $\Delta E = -22.5$, $\Delta E^\ddagger = 4.8$ kcal mol⁻¹). Finally, the subsequent electrophilic attack of P2 affords the unique Wheland product **6'** (Ru: $\Delta E = -0.6$, $\Delta E^\ddagger = 17.7$ kcal mol⁻¹), of which the experimental analogues, Ru-**6b** and Ir-**6b**, can be isolated.

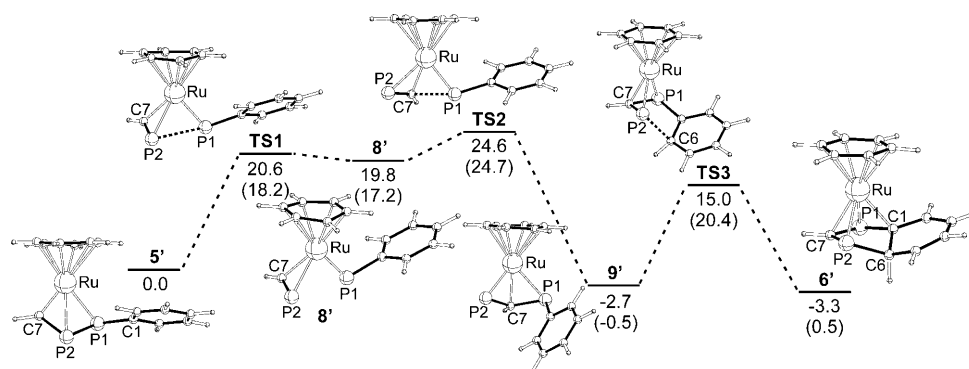
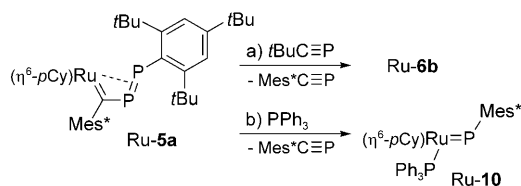


Figure 4. Relative B3PW91/6-31G(d,p) (LANL2DZ for Ru and Ir) energies (ZPE corrected, in kcal mol⁻¹) for the rearrangement of 5' into 6'. The relative energies for the η^5 -Cplr derivatives are given in parentheses. Selected bond lengths [Å] for Ru-5': Ru-P1 2.443, Ru-P2 2.571, Ru-C7 1.894, P1-P2 2.180, P2-C7 1.752; **TS1**: P1-P2 2.876, P2-C7 1.631; Ru-8': Ru-P1 2.177, Ru-P2 2.509, Ru-C7 2.105, P2-C7 1.617; **TS2**: P1-C7 2.439, P2-C7 1.630; Ru-9': Ru-P1 2.432, Ru-P2 2.194, Ru-C7 2.244, P1-C7 1.784, P2-C7 1.772; **TS3**: Ru-P1 2.404, P2-C6 2.106; Ru-6': Ru-P1 2.398, Ru-P2 2.437, Ru-C1 2.214, Ru-C7 2.199, P1-C1 1.804, P1-C7 1.787, P2-C6 1.887, P2-C7 1.783.

For an initial assessment of the reactivity of the novel η^3 -diphosphavinylcarbenes **5**, we treated the ruthenacycle Ru-**5a** with one equivalent *t*BuC≡P and observed the fast and selective formation of bicyclic Ru-**6b** (*t*_{1/2} = 18 min at 0°C; 93% yield according to ³¹P NMR spectroscopy) together with elimination of Mes**C*≡P (Scheme 2). Addition of PPh₃



Scheme 2. Reactivity of Ru-**5a** towards phosphines.

afforded instead the terminal phosphinidene complex [(η^6 -*p*Cy)(Ph₃P)Ru=PMe^{*}] (Ru-**10**)^[14a] (*t*_{1/2} = 100 min at 0°C; quantitative yield). Both conversions follow an unprecedented pathway for η^3 -vinylcarbenes for which an associative ligand exchange at the phosphinidene stage (**8**) is proposed, as the dissociative pathway (Ru-**8'** → [C₆H₆Ru=PPh] + HC≡P) corresponds to an uphill process (ΔE = 28.8 kcal mol⁻¹).

In conclusion, phosphorus substitution of metal-bound η^3 -vinylcarbenes has a marked influence on their reactivity. Depending on the substituent pattern, the readily obtained η^3 -diphosphavinylcarbene complexes **5** show facile ligand exchange reactions or undergo an unprecedented rearrangement to the stable Wheland product **6**.

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