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N-Heterocyclic Carbene-Functionalized Ruthenium Phosphinidenes: What a Difference a Twist Makes

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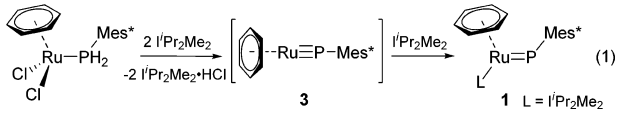
N-Heterocyclic carbenes (NHCs)[1] are ubiquitous ligands in transition-metal chemistry and homogeneous catalysis and serve increasingly often as a replacement for tertiary phosphines (R_3P). The two ligand classes exert often subtle but crucially different electronic influences on the properties of catalysts.[2] Exemplary is the enhanced activity of the second-generation Grubbs metathesis catalyst [$(Cy_3P)(L)Cl_2Ru{=}CHPh$] [L = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (H_2IMes)] relative to that of the first-generation catalyst (L = Cy_3P), which is caused by the differences in σ-donor/π-acceptor ability,[3] shape, and symmetry of the ligands.[4]

Does a similar sensitivity apply to the isolobal phosphinidene[5] complexes? We address here the ligand and conformational sensitivities for [$(\eta^6\text{-}C_6H_6)(L)Ru{=}PMes^*$] [Mes* = 2,4,6-^{t}Bu$_3C_6H_2$; L = $I^iPr_2Me_2$ (**1**), L = Ph_3P (**2**)[6]] by examining their solution-phase chemistry together with their structure−activity parameters modeled by density functional theory. We simultaneously demonstrate the applicability of phosphinidene complexes to the synthesis of phosphaalkenes (P=C),[5a] which are unique P-ligands[7] and attractive building blocks for P-functionalized polymers.[8]

The desired novel dark-green crystalline compound **1** (84%) was obtained by a double dehydrohalogenation−ligation sequence[9] of the phosphine complex [$(\eta^6\text{-}C_6H_6)RuCl_2(PH_2Mes^*)$][6] using 3 equiv of $I^iPr_2Me_2$ in toluene (eq 1):



In this reaction, two NHCs act as Brønsted bases, while the third carbene captures the putative 16-electron intermediate [$(\eta^6\text{-}C_6H_6)Ru{\equiv}PMes^*$] (**3**). The single ^{31}P NMR resonance of **1** at 751.7 ppm is highly shielded compared with that of the known triphenylphosphine analogue **2** (845.9 ppm),[6] which is attributed to the σ-donor capacity of $I^iPr_2Me_2$ (see below). The molecular structure of **1**, established unequivocally by single-crystal X-ray analysis (Figure 1), has an exact mirror symmetry and shows a two-legged "piano stool" shape with a characteristic acute C15−Ru1−P1 angle of 84.88(9)°, a bent phosphinidene complex with a Ru1−P1−C1 angle of 105.81(9)°, and an *E* configuration for the congested Ru1−P1 double bond [2.2222(8) Å]. This bond is longer than that of the "first-generation" phosphinidene **2** [2.1988(6) Å],[6] whereas its Ru1−Bz(cg) bond is correspondingly shorter [1.7390(12) Å in **1**; 1.7560(12) Å in **2**[6]]. Steric congestion is reflected in the 18.7(4)° distortion from planarity of the Mes* ring and in the restricted rotation of the isopropyl wingtip groups of the NHC fragment, indicated by the two ^{13}C resonances at 21.6 and 21.8 ppm. A striking feature is the orthogonal relationship between the NHC and Ru=P units, which contrasts with the in-plane arrangement of the NHC and Ru=C units in the second-generation Grubbs catalyst.[10]

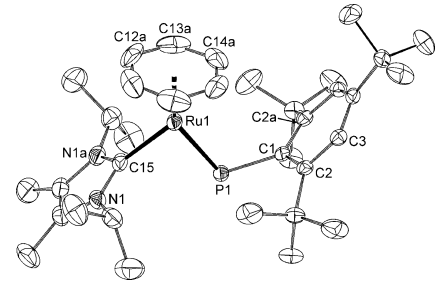
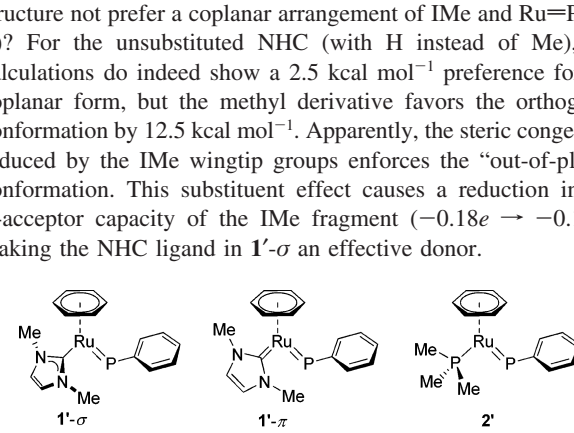


Figure 1. Displacement ellipsoid plot (50% probability level) for **1**. Only one conformation of the disordered *tert*-butyl group is shown. Hydrogen atoms have been omitted for clarity. Bz denotes the centroid position of the benzene ring. Symmetry operation a: x, 0.5 − y, z. Selected bond distances (Å) and bond and torsion angles (deg): Ru1−P1, 2.2222(8); Ru1−C15, 2.091(3); Ru1−Bz(cg), 1.7390(12); P1−C1, 1.876(3); Ru1−P1−C1, 105.81(9); P1−Ru1−C15, 84.88(9); N1−C15−N1a, 104.8(3); C2a−C1−C2−C3, −18.7(4).

To address the effect of the NHC ligand orientation in **1** and the impact of the stabilizing ligand (NHC vs R_3P) on the properties of **1** and **2**, we performed BP86/TZP calculations on model structures (labeled ′) bearing a *P*-phenyl group (instead of P−Mes*) and methyl groups on the NHC (IMe) and phosphine (PMe_3) ligands. The optimized geometries of **1′**-σ, in which the IMe ligand and the Ru=P bond are orthogonal, and **2′** compare well with the corresponding X-ray structures.[6] But why does the NHC-ligated structure not prefer a coplanar arrangement of IMe and Ru=P (**1′**-π)? For the unsubstituted NHC (with H instead of Me), the calculations do indeed show a 2.5 kcal mol^{-1} preference for the coplanar form, but the methyl derivative favors the orthogonal conformation by 12.5 kcal mol^{-1}. Apparently, the steric congestion induced by the IMe wingtip groups enforces the "out-of-plane" conformation. This substituent effect causes a reduction in the π-acceptor capacity of the IMe fragment ($-0.18e \rightarrow -0.10e$), making the NHC ligand in **1′**-σ an effective donor.



The Ru−L bond properties impact those of the Ru=P bond, which is evident from the energy decomposition scheme in ADF. Because the carbene provides less back-bonding than PMe_3, the frontier orbitals of the [$(\eta^6\text{-}C_6H_6)$(IMe)Ru] fragment [$E(d_{xz})$ =

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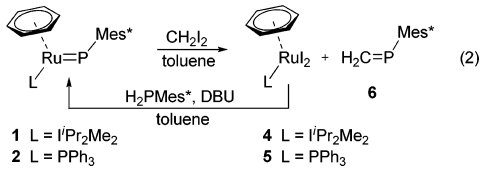
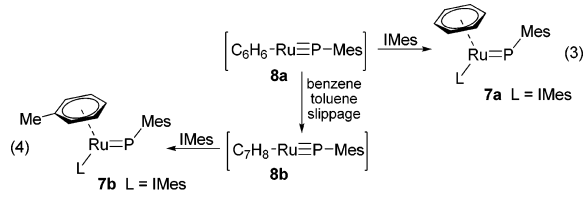
−2.27 eV, $E(d_{yz})$ = −2.49 eV] are higher in energy than those of the Ru−phosphine fragment [$E(d_{xz})$ = −2.61 eV, $E(d_{yz})$ = −2.86 eV]. Ru=P bond formation causes a transfer of charge from [(η^6-C_6H_6)(L)Ru] to the ^{3}PPh fragment [$E(p_x)$ = −4.59 eV, $E(p_y)$ = −4.86 eV], which is largest for **1′**-σ. Whereas the Ru=P bonds are of similar lengths (2.216 and 2.209 Å for **1′**-σ and **2′**, respectively), the polarity varies with the phosphorus atom, which carries more charge in **1′**-σ (−0.113e) than in **2′** (−0.086e).

The greater Ru=P bond polarity is reflected in the enhanced reactivity of the NHC-containing phosphinidene **1** (L = I^{i}Pr$_2$Me$_2$) over that of "first-generation" **2** (L = Ph_3P) toward diiodomethane (eq 2):[11]



^{31}P NMR monitoring of the reaction of complex **1** showed the quantitative formation of the phosphaalkene H_2C=PMes* (**6**, 94% isolated yield) within 1 min at 20 °C [$t_{1/2}$(0 °C, C_6D_6) = 22 min; 5 equiv of CH_2I_2]. In contrast, the reaction of phosphine-ligated complex **2** with CH_2I_2 is much slower [$t_{1/2}$(20 °C, toluene) = 60 min; $t_{1/2}$(0 °C, C_6D_6) = 925 min] and also less selective (**6**, 45%). This difference between **1** and **2** demonstrates that like the catalytic activity of the Grubbs catalysts, the reactivity of the isolobal nucleophilic 18-electron phosphinidene complexes can also be readily modified by changing the ancillary ligands. The applicability of the illustrated reaction is underscored by the quantitative regeneration of **1** from the transition-metal byproduct [(η^6-C_6H_6)(I^{i}Pr$_2$Me$_2$)RuI$_2$] (**4**) with DBU and H$_2$PMes*[12] as determined by ^{31}P NMR (63% isolated yield), thereby demonstrating that ruthenium phosphinidene complexes are viable reagents for the synthesis of phosphaalkenes.

A final aspect to address is the presumed 16-electron phosphinidene intermediate **3**, which could not be detected by ^{31}P NMR spectroscopy,[13,14] suggesting that if it is indeed formed, it is readily captured by I^{i}Pr$_2$Me$_2$ to yield **1**. Increasing the steric bulk by using 1,3-dimesitylimidazol-2-ylidene (IMes) to slow the NHC complexation enough for detection was unsuccessful, but monitoring its ligation with less crowded [(η^6-C_6H_6)RuCl$_2$(PH$_2$Mes)], which carries a Mes instead of a Mes* substituent, did have the anticipated effect. Besides dark-brown crystalline [(η^6-C_6H_6)(IMes)Ru=PMes] (**7a**; ^{31}P, 752.5 ppm; 65%), small amounts of the corresponding toluene adduct [(η^6-Tol)(IMes)Ru=PMes] (**7b**; ^{31}P, 736.8 ppm; 3%) were also observed (eqs 3 and 4):[15]



The apparent arene exchange is supported by detection of **7b**-d_3 when toluene-d_3 was used as the solvent. Since no ligand exchange was observed for the isolated products, it appears that the 16-electron intermediate is prone to arene exchange. BP86/TZP calculations support this view. Simplified 16-electron [(η^6-C_6H_6)Ru=PH], which has an energy minimum, reacts barrier-free with toluene to form the 5.6 kcal mol^{-1}-favored [(η^2-Tol)(η^6-C_6H_6)Ru=PH] as an initial adduct in the exchange of the two arene ligands. Associative ring slippage[16] via [(η^4-Tol)(η^4-C_6H_6)Ru=PH] then gives [(η^6-Tol)(η^2-C_6H_6)Ru=PH] (ΔE = 1.4 kcal mol^{-1}), which requires 4.2 kcal mol^{-1} to lose benzene and form the product. Implicitly, this process supports a 16-electron intermediate that undergoes ligand exchange of aromatic molecules (**8a** → **8b**) before being captured by the carbene ligand to give **7b**.

Catalyst tuning is generally sought via a change of ligands because their effect is considered to be constant for a given transition-metal complex. We have now demonstrated that the relative σ-donor/π-acceptor ability of NHC ligands can easily be influenced by a simple substituent-controlled conformational change. The sterically imposed ligand rotation of the NHC fragment in **1** enhances its reactivity and thereby facilitates the synthesis of phosphaalkene (P=C) building blocks.

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Supporting Information Available: Full experimental and computational details and crystallographic data for compound **1** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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