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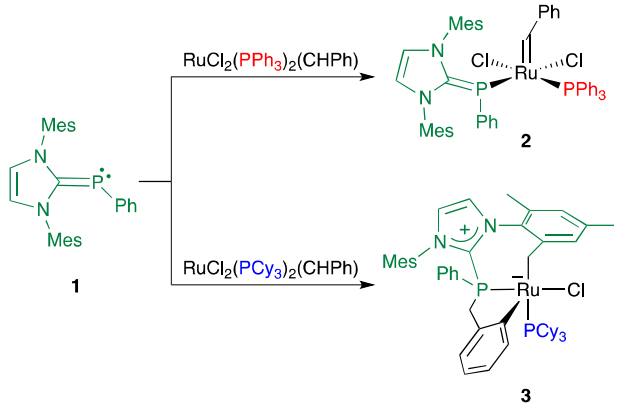
Graphical Abstract

Reaction of phosphaalkene IMes=PPh (**1**) with $RuCl_2L_2(CHPh)$ (L = PPh_3 and PCy_3) gives either the targeted ruthenium benzylidene complex (**2**) or the decomposition product (**3**).



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LETTER

Reactivity study of low-coordinate phosphaalkene IMes=PPh with Grubbs first-generation ruthenium benzylidene complexes

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Reaction of IMes=PPh with $RuCl_2L_2(CHPh)$ (L = PPh_3 and PCy_3) gave complexes with selectivity that is dependent on the metal precursor used. $RuCl_2(IMes=PPh)(PPh_3)(CHPh)$, which adopts the rare cis chloride configuration, was inactive in ring-opening metathesis of diallyl sulfide. In contrast, the PCy_3 analogue could not be isolated, and in fact led to an unusual decomposition product with two C–H activations.

Ruthenium alkylidene complexes have received much attention over the years due to their ability to effectively mediate metathesis of alkenes containing polar functional groups. Variations on the Grubbs first-generation $RuCl_2(PCy_3)_2(CHPh)$ complex have led to new catalysts with enhanced performance, with the most notable breakthrough achieved upon replacement of one of the phosphine ligands with a strong σ-donor N-heterocyclic carbene. As a result, complexes developed in the past years commonly comprise a substituted NHC ligand.[1] These systems can however undergo decomposition on the reaction timescale through several possible degradation pathways.[2-6] We thus became interested in preparing and studying the reactivity of a new class of ruthenium benzylidene complexes in which one of the trivalent phosphines in $RuCl_2(PR_3)_2(CHPh)$ is replaced by a low-coordinate phosphaalkene spectator ligand.

While a number of phosphaalkene ligands have been reported in the literature,[7] we were especially interested in the guanidine-like structure **B** (Fig. 1), which is formally an adduct of imidazol-2-ylidene and phosphinidene (structure **A**). The electron-donating capability of the imidazole ring allows the formation of the zwitterionic structure **C** similar to related imidazol-2-imines.[8] As a result, these phosphaalkenes are expected to be good σ-donors and poor π-acceptors, mimicking the electronics of NHCs used in Grubbs second-generation catalysts. Furthermore, they feature some unique combinations of sterics, with the phosphorus being low coordinate like

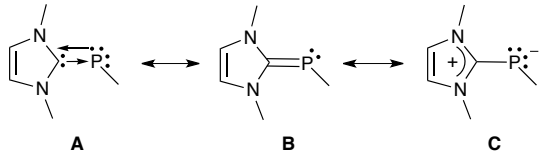

Fig. 1. Canonical forms of carbene–phosphinidene adducts.

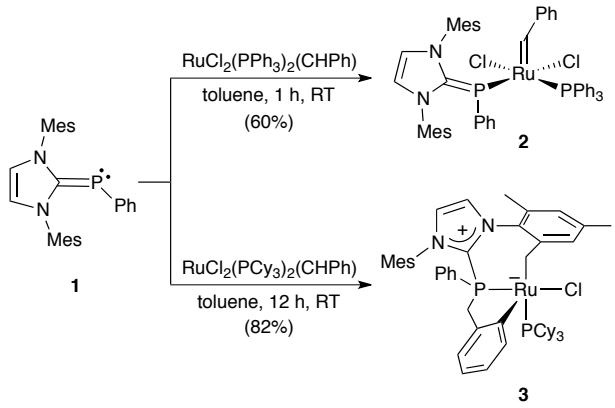

Fig. 2. Reaction of IMes=PPh (**1**) with Ru(II) benzylidene complexes.

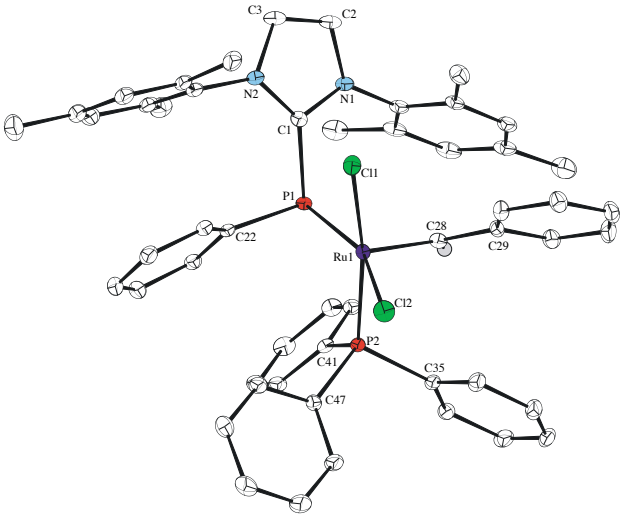

Fig. 3. ORTEP diagram of **2** (30% probability level). Most hydrogen atoms and one molecule of dichloromethane were omitted for clarity.

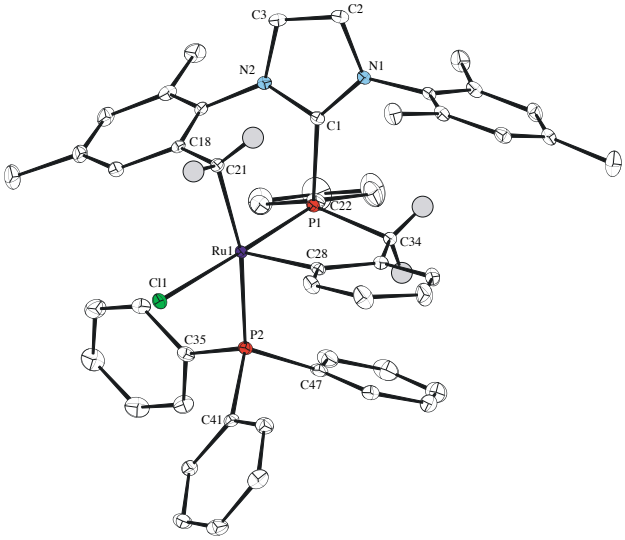

Fig. 4. ORTEP diagram of **4** (30% probability level). Most hydrogen atoms were omitted for clarity.

NHCs, with substituents protruding away from the metal centre as in tertiary phosphines. The study of new ruthenium alkylidene complexes with these phosphorus donors was thus undertaken.

Addition of a slight excess of phosphaalkene **1** to $RuCl_2(PCy_3)_2(CHPh)$ in toluene generated a light brown precipitate, with a solution ^1H NMR spectrum indicating the formation of one major species. Resonances in the aromatic regions were unexpectedly broad, indicative of fluxional behaviour that would not be expected for $RuCl_2$(**1**)$(PCy_3)(CHPh)$. Furthermore, the resonance for the benzylidene proton was not observed in the diagnostic δ 15–20 ppm region. In contrast, reaction of IMes=PPh (**1**) with $RuCl_2(PPh_3)_2(CHPh)$ resulted in a yellowish-brown solution with precipitation of a light brown powder. Compound **2** was isolated in moderate yield from the solution by recrystallisation from pentane and dichloromethane. The benzylidene proton of **2** resonates at δ = 15.48 ppm as a doublet of doublets, a result of coupling to two inequivalent phosphine nuclei observed at δ = 64.8 and 37.4 ppm in the $^{31}P\{^1H\}$ NMR spectrum for IMes=PPh and PPh_3. The benzylidene carbon resonates at δ = 299.7 ppm.

Crystals of **2** suitable for X-ray diffraction analysis were successfully isolated. The complex crystallised in the *C 2/c* space group and adopts a distorted square-pyramidal coordination (Fig. 3). The chlorides adopt a cis arrangement (∠ Cl1–Ru1–Cl2 86.46(2)°), a rare occurrence for complexes that do not have any other chelating ligands.[9-11] The benzylidene in **2** occupies the apical site with a Ru1–C28–C29 angle of 126.40(18)°. The phenyl ring is approximately orthogonal to the basal plane and *syn* to the chloride atoms, with the Ru1–C29 vector approximately bisecting the Cl1–Ru1–Cl2 angle. The Ru1–C28 bond measures 1.841(3) Å, comparable to that reported for Grubbs first- and second-generation catalysts.[12] The Ru1–P1 and Ru1–P2 bond lengths are 2.3643(7) and 2.3272(6) Å, respectively. More importantly, the P1–C1 bond length of 1.847(2) Å is comparable to the other four phosphorus–carbon bond lengths, which range from 1.824(2) to 1.842(3) Å, indicating single bond character. This results from significant π-electron donation from the imidazole ring to the phosphorus atom, further supported by the short C1–N1 and C1–N2 bond lengths (ca. 1.364 Å).

Attempts to grow X-ray quality crystals of the reaction product of **1** with $RuCl_2(PCy_3)_2(CHPh)$ were unsuccessful. Interestingly, when using a ruthenium precursor containing residual PPh_3, X-ray quality crystals of the aryl phosphine adduct **4** were isolated, with the complex crystallizing in the *P* $2_1/n$ space group (Fig. 4). The metal centre in **4** adopts a distorted square pyramidal geometry, with the basal plane formed by P1, P2, Cl1 and C21. The apical site is occupied by C28, which originates from the ortho carbon of the benzylidene ring in the ruthenium precursor. Similarly, the sp^3 carbon atom C34 in **4** corresponds to the original sp^2 alkylidene carbon atom. The hybridisation of C34 was further confirmed by the presence of two hydrogen atoms located on the density map. Both phosphine atoms retained their cis arrangement, with a slightly obtuse P1–Ru1–P2 angle of 95.21(2)°. The P1–C1 bond lengths of 1.883(2) Å shows greater single bond-character compared to that in **2**, possibly making the phosphorus atom a better σ-donor with a shorter Ru1–P1 bond (2.1844(6) Å). As expected, the Ru1–C21 (2.157(2) Å) and Ru1–C28 (2.035(2) Å) bond lengths in **4** are significantly longer than the Ru1–C28 carbene bond lengh in **2**. The formation of the five-membered metallacycle results in a P1–Ru1–C28 bite angle of 80.51(6)°. Finally, the Ru1–C21–C18 angle of 89.8(1)° is in line with other related stuctures.[13,14]

Spectroscopic data and microcombustion analysis of the reaction product of $RuCl_2(PCy_3)_2(CHPh)$ with **1** are consistent with the formation of compound **3** (Fig. 2), the PCy_3 analogue of **4**. Compound **3** presumably results from decomposition of

the $RuCl_2$(**1**)(PCy_3)(CHPh) short-lived intermediate. We believe that **4** may in fact be the minor product produced from the reaction of IMes=PPh with $RuCl_2(PPh_3)_2$(CHPh). We have however been unable to unambiguously confirm this by spectroscopic means.

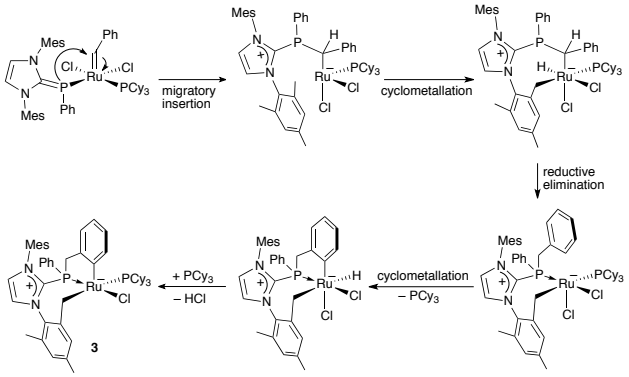

Fig. 5. Proposed mechanism for the formation of **3**.

As illustrated in Figure 5, we propose that upon formation of $RuCl_2$(**1**)(PCy_3)(CHPh), the electron-rich and low-valent phosphorus of the phosphaalkene inserts into the benzylidene group in a manner similar to that proposed for phosphines[3,13] and NHCs.[5,6] This results in a zwitterionic metal complex with a positive charge on the imidazole ring and a negative charge on the metal centre. The coordinatively-unsaturated and charged Ru(II) then easily undergoes C–H activation of a mesityl ring, as previously observed in other structurally-characterised NHC ruthenium complexes.[4,13-15] Reductive elimination, followed by sequential C–H activation of the former benzylidene phenyl ring and release of HCl, generates the observed product. The nucleophilic attack of the phosphaalkene on the benzylidene likely triggers all subsequent steps in the degradation of the complex.

Compound **2** was tested in ring-closing metathesis of diallyl sulfide, despite its unfavourable cis arrangement of the chloride ligand.[9,10,16] Performing the reaction at room temperature with 5 mol % catalyst in chloroform-*d* led to no observable conversion after 6 h with **2** remaining intact. In contrast, higher temperatures (70 °C) led to complete decomposition of **2**, possibly into **4**, within 1 h with no formation of the cyclic sulfide. We are currently further investigating these phosphaalkene ruthenium benzylidene complexes to determine the role of the ancillary ligands on their decomposition and to gain insight into other mechanistic details. Our work, which is related to lifetime issues of Grubbs-type catalysts, will be reported in due course.

Experimental Section

Reaction of $RuCl_2(PPh_3)_2$(CHPh) with IMes=PPh.

A toluene solution of IMes=PPh (**1**) (30.1 mg, 73.0 μmol) was added slowly over 1 min to a toluene solution (5 mL) of $RuCl_2(PPh_3)_2$(CHPh) (52.1 mg, 66.2 μmol). The solution was stirred for 1 h at room temperature, in a colour change from purple to yellowish brown and the formation of a light brown precipitate. The solution was filtered and dried under reduced pressure. Recrystallisation by slow liquid diffusion of pentane into a saturated dichloromethane solution at –35 °C to afford $RuCl_2$(IMes=PPh)(PPh_3)(CHPh) (**2**) as dark brown crystals (37.4 mg, 60%). Anal. Calcd. for $C_{52}H_{50}Cl_2N_2P_2Ru$ (%): C, 66.66; H, 5.38; N, 2.99. Found (%): C, 66.46; H, 5.60; N, 2.92.

Reaction of $RuCl_2(PCy_3)_2$(CHPh) with IMes=PPh.

A toluene solution of IMes=PPh (**1**) (67.1 mg, 158 μmol) was added slowly over 1 min to a toluene solution (5 mL) of $RuCl_2(PCy_3)_2$(CHPh) (92.7 mg, 113 μmol). The solution was stirred for 12 h at room temperature, resulting in a colour change from purple to brown and the formation of a light brown precipitate. The volatiles were removed under reduced pressure. The product was recrystallised from pentane and dichloromethane to yield **3** as a light brown powder (85.7 mg, 83%). Anal. Calcd. for $C_{52}H_{67}ClN_2P_2Ru$ (%): C, 67.99; H, 7.35; N, 3.05. Found (%): C, 68.28; H, 7.53; N, 2.77.

Ring-closing metathesis.

The ruthenium complex (0.006 mmol) was dissolved in $CDCl_3$ (0.5 mL). The solution was added to either an NMR tube fitted with a rubber septum or a scintillation vial fitted with a rubber septum. The neat substrate was added via syringe and the reaction stirred at either room temperature or at 70 °C. The reaction was monitored by ^{1}H NMR spectroscopy.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Full experimental details with spectroscopic data, and crystallographic data for **2** and **4** (CCDC reference numbers 945573 and 945574). See DOI: 10.1039/c000000x/

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