Cyclopropanation of Ru-diimino-pyridine ligand complexes†

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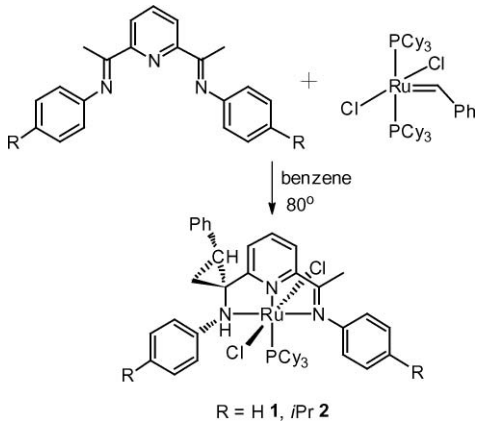
Reaction of 2,6-bis(imino)pyridines with $(Cy_3P)_2RuCl_2(CHPh)$ affords the complexes $C_6H_3N(CMeNC_6H_4R)(CCH_2CHPh)NHC_6H_5)RuCl_2(PCy_3)$ (R = H 1, *i*Pr 2) arising from the cyclopropanation of the ligand.

Since the breakthrough discoveries in the Brookhart[1] and Gibson[2] laboratories in the 1990s, late transition metal complexes bearing 2,6-bis(imino)pyridyl ligands [N3] have garnered much attention.[3] While much of the focus has been on the development of olefin polymerization catalysts, the chemistry of complexes of these ligands continues to be explored.[4] For example, while the complex $[N3]RuCl_2(NCMe)$ was shown to exhibit good activity for the epoxidation of cyclohexene with iodosobenzene.[5] The related complex $[N3]RuCl(NCMe)_3(SbF_6)_2$ has been shown to be inactive as a catalyst for the oxidation of cyclohexane by H_2O_2.[6] More recently, Chirik *et al.* have employed [N3]Fe complexes for catalytic hydrogenation, hydrosilylation, and cycloaddition reactions.[7] Bianchini and Lee[8] have described the use of [N3]Ru complexes in the catalytic cyclopropanation of styrene with ethyl diazoacetate. In these cases, the six-coordinate Ru(II) 2,6-bis(imino)pyridyl carbene complexes are thought to effect carbene transfer to the olefin *via* an intermolecular process, although the authors cautioned that this may not be true in the presence of halide scavengers. Our interest in [N3] complexes focused on the reactivity of [N3]Ru alkylidenes. In this report we describe the reaction of [N3] ligands with the Grubbs alkylidene species $(Cy_3P)_2RuCl_2(CHPh)$.[9] Herein, we demonstrate that [N3] is not an innocent ancillary ligand in these reactions but rather is cyclopropanated to give a dissymmetric amino-imino-pyridyl ligand.

In an effort to generate Ru-alkylidene complexes bearing bisiminopyridine ligands, reactions of $(Cy_3P)_2RuCl_2(CHPh)$ with the ligand $C_5H_3(C(Me{=}NPh)_2)N$ were undertaken. Combining these species in a 1 : 1 ratio in benzene, the reaction was heated to 80 °C and monitored by ^{31}P NMR spectroscopy over a 36 h period. The ^{31}P NMR spectral data for the reaction mixture revealed the liberation of Cy_3P and the generation of a new singlet resonance. Subsequent workup provided the new Ru containing product **1** in 71% isolated yield.‡ Spectroscopic examination of compound **1** confirmed the presence of a ^{31}P resonance at 12.81 ppm. The corresponding ^1H spectrum inferred dissymmetry in the ligand. A resonance at 1.89 ppm accounts for one ligand methyl backbone group. Signals at 2.50 and 1.41 ppm correspond to methine and methylene groups. Aromatic and pyridine resonances account for the ligand and alkylidene phenyl protons.

In a similar fashion the corresponding reaction of $(Cy_3P)_2RuCl_2(CHPh)$ with the ligand $C_5H_3(C(Me{=}NC_6H_4iPr)_2)N$ gave a similar product in 62% isolated yield which exhibited a ^{31}P resonance at 13.22 ppm and ^1H NMR signals at 2.51 and 1.96 ppm for the methine and methylene resonances. The spectral data for **1** and **2** suggests that the alkylidene-group has transferred to the ligand generating dissymmetry (Scheme 1).



R = H **1**, *i*Pr **2**

Scheme 1 Synthesis of **1** and **2**.

The precise nature of these products was confirmed *via* crystallographic study (Fig. 1). Crystallographic data for **1** confirmed the connectivity as $C_6H_3N(CMeNC_6H_4R)(CCH_2CHPh)NHC_6H_5)RuCl_2(PCy_3)$. The Ru center adopts a distorted octahedral geometry in which the two chlorides are disposed in *trans*-positions with a Cl–Ru–Cl angle of 169.97(6)°. The

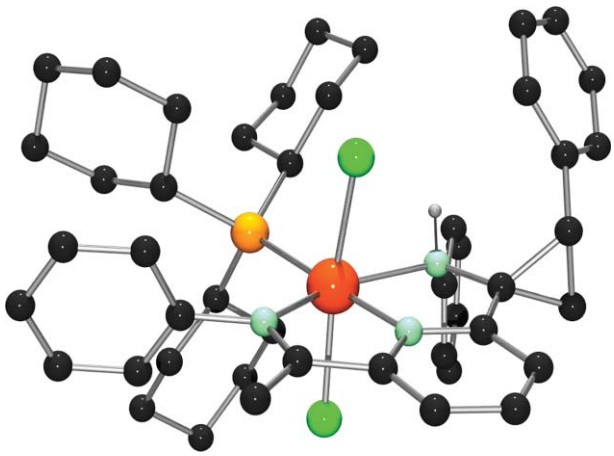


Fig. 1 POV-ray drawing of **1**, all H-atoms except the NH are omitted for clarity C: black, Cl: green, P: orange, N: blue–green, Ru red–orange.

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Ru–Cl distances were found to be 2.4099(18) Å and 2.4145(17) Å. The tridentate ligand is meridonally coordinated to Ru in the plane perpendicular to the Cl–Ru–Cl vector, with the pyridine N *trans* to a coordinated PCy_3. The corresponding Ru–N and Ru–P distances are 2.001(5) Å and 2.4480(17) Å, respectively. The tridentate ligand is dissymmetric as one imino-fragment is reduced to an amine with concurrent formation of a cyclopropane ring, derived from the alkylidene fragment and the carbons *alpha*- and *beta*- to N. The resulting Ru–N distances for the imino and amino-N atoms are 2.056(5) Å and 2.239(5) Å. This difference reflects the lower basicity of the amino-N in comparison to the imine N. The C–C bond distances within the cyclopropane ring are 1.515(9) Å, 1.539(9) Å and 1.485(9) Å,with C–C–C angles of 58.2(4)°, 60.1(4)° and 61.7(4)°, reflecting the ring strain. An analogous structure was confirmed by preliminary crystallographic study for **2**, although these data were not suitable for publication.

The mechanism of formation of **1** and **2** is the subject of speculation. We note that Bianchini and coworkers have prepared di-imino-pyridine-alkylidene Ru complexes of the form [N3]$RuCl_2(CHCO_2Et)$ and thus it is reasonable to suggest that an analogous species could be formed initially upon reaction of the ligand with the Ru-alkylidene precursor. However, it is also noteworthy that tautomerization of such ligands to an exocyclic enamine has been previously observed in several systems.[10] Transient generation of the enamine combined with the more reactive alkylidene fragment results in cyclopropanation accounting for the formation of **1** and **2**. While the formation of the cyclopropane ring generates two chiral carbon centers and thus a mixture of diastereomeric products, it is difficult to envision an intramolecular process. Thus, these reactions are thought to occur in a bimolecular fashion although this aspect could not be unambiguously confirmed. It is also reasonable to suggest that the lesser steric congestion favors cyclopropanation of the enamine over olefin metathesis.

To put this finding in context, we note that cyclopropanation of olefins using ethyl diazoacetate has been previously described using a variety of Ru precursors.[8,11] In addition, Dixneuf and coworkers[12] demonstrated catalytic formation of alkenylbicyclo[3.1.0]-hexanes from enynes and N_2CHCO_2Et or N_2CHPh using Cp*RuCl(COD) as the catalyst precursor. Suitably modified ligand set variants have been employed to effect catalytic asymmetric cyclopropanation.[13] Despite these previous developments, to our knowledge, cyclopropanation has not been reported using Grubbs-type alkylidene complexes and thus compounds **1** and **2** are the first examples that result from transfer of Ru-bound alkylidene to transient enamines. The stoichiometric nature of the present reactions may result from the "non-innocent" nature of the [N3]Ru complexes. The participation of the enamine tautomer in chemistry has been previously reported by Blackmore *et al.*[10] More recently, Berry and coworkers showed that low-valent [N3]Ru complexes delocalize electron density from the metal center further demonstrating the "non-innocent" electronic nature of these ligands.[14]

The present results suggest that strong donor ligand sets in an alkylidene complex encourage reactivity. The present products are unique examples of the cyclopropanation of the metal bound enamine fragment. This finding prompts us to probe the reactivity of other Ru-tridentate alkylidenes. The results of these on-going studies will be reported in due course.

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Notes and references

‡ [2] **Synthesis of $(C_6H_3N(CMe{=}NC_6H_4R)(C(CH_2CHPh)NHC_6H_4R)RuCl_2(PCy_3)$ (R = H 1, *i*Pr 2)** These compounds were prepared in a similar fashion and thus only one preparation is detailed. $(Cy_3P)_2RuCl_2(CHPh)$ (164 mg, 0.20 mmol) was dissolved in benzene (5 mL) before a benzene solution (5mL) of 2,6-bis(1-phenyliminoethyl)pyridine (65 mg, 0.20 mmol) was added. The reaction was sealed in a Teflon capped reaction tube and heated at 80 °C for 36 h. The reaction colour changes from purple to deep green. The reaction was cooled to 25 °C and the benzene was removed *in vacuo*. The solid was dissolved in a minimum amount of dichloromethane (2–3 mL) to which pentane (15 mL) was added. The solution was cooled to −35 °C overnight after which large green crystals formed. Subsequent removal of the supernatant, and recrystallization of the remaining crude product yielded more green crystals. (71%, 0.14 mmol, 121 mg) **1**: ^{1}H NMR (CD_2Cl_2): 8.12 (d, 1H, Ph), 7.75 (d, 1H, Ph), 7.53 (d, 2H, Ph), 7.12–6.7 (m, 11H, Ph), 6.07 (d, 1H, Ph), 5.88 (d, 1H, Ph), 5.67 (s, 1H, Ph), 3.16-2.86 (m, 3H, Cy), 2.50 (t, 1H, Ph(C*H*)py), 1.89 (s, 3H, CH_3), 1.8–1.5 (m, 14H, Cy), 1.41 (d, 1H, $CHCH_2$), 1.40 (d, 1H, $CHCH_2$), 1.4–1.0 (m, 13H, Cy), 0.8–0.7 (m, 3H, Cy) $^{31}P\{^1H\}$ NMR (CD_2Cl_2) : 12.81 ^{13}C NMR (CD_2Cl_2) (partial): 131.7 (Ph), 131.4 (Ph), 125 (Ph), 124.3 (Ph), 123 (Ph), 122.6 (Ph), 115.3 (Ph), 41.7 Ph(*C*H)py), 22.8 ($CHCH_2$). C,H,N analysis calc. for $C_{46}H_{58}Cl_2N_3PRu$ C, 64.55; H, 6.83; N, 4.91. Found: C, 64.54; H, 7.04; N, 4.76. **2**: (62%, 0.08 mmol, 116 mg) ^{1}H NMR (CD_2Cl_2) : 8.13 (d, 1H, Ph), 7.74 (d, 1H, Ph), 7.60 (d, 2H, Ph), 7.25–6.86 (m, 8H, Ph), 6.73 (d, 1H, Ph), 6.08 (d, 1H, Ph), 5.85 (d, 1H, Ph), 5.69(d, 1H, Ph), 3.25–2.9 (m, 3H, Cy), 2.66 (m, 2H, $CH(CH_3)_2$), 2.51(t, 1H, Ph(C*H*)py), 2.4–2.1 (m, 3H, Cy), 1.96 (s, 3H, CH_3), 1.9–1.5 (m, 18H, Cy), 1.3–1.2 (m, 6H, Cy), 0.9–0.8 (m, 3H, Cy), 1.13 (m, 12H, $CH(CH_3)_2$), 1.43 (m, 2H, $CHCH_2$), $^{31}P\{^1H\}$ NMR (CD_2Cl_2) : 13.22 ^{13}C NMR (CD_2Cl_2) (partial) : 131.8 (Ph), 131.2 (Ph), 123 (m, Ph), 115.6 (Ph), 41.9 Ph(*C*H)py), 22.4 ($CHCH_2$), 18.6 (CH_3). C,H,N analysis calc. for $C_{52}H_{69}Cl_2N_3PRu$ C, 66.44; H, 7.51; N, 4.47. Found: C, 66.54; H, 7.79; N, 4.60. Crystallographic data for **1**: $C_{46}H_{57}Cl_2N_3PRu(2\,CH_2Cl_2)(0.5\,H_2O)$, MW = 1034.75, T = −100° C, space group triclinic, $P\bar{1}$, a = 12.5917(8) Å, b = 12.8624(7) Å, c = 15.5806(10) Å, α = 91.817(3)°, β = 103.746(4)°, γ = 93.184(3) V = 2444.7(3) Å^3, Z = 2, μ = 0.719 mm^{-1}, measured reflections = 42719, independent reflections = 6702, parameters = 865, R_{int} = 0.0914, R = 0.0552, R_w = 0.1445, GOF = 1.012.

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