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Synthesis and Crystal Structure of $[RuCl_2(PPh_3)\{N(SiMe_3)C(Ph)NH(PPh_2)\}]$

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The interaction of $(Ph_2P)NC(Ph)[N(SiMe_3)_2]$ with 1 equivalent of $[RuCl_2(PPh_3)_3]$ in tetrahydrofuran gave $[RuCl_2(PPh_3)\{N(SiMe_3)C(Ph)NH(PPh_2)\}]$ whose structure established by X-ray crystallography suggests the presence of a γ-agostic interaction between ruthenium and one of the methyl groups of the $N(SiMe_3)$ imino group.

Phosphorus–nitrogen compounds are π-electron-rich compounds and potential precursors for inorganic polymers with unusual properties.[1,2] This has led to considerable interest in the syntheses of phosphorus–nitrogen compounds[3] and their co-ordination chemistry toward transition metals.[4] The co-ordination chemistry of $(Ph_2P)NC(Ph)[N(SiMe_3)_2]$ has been briefly examined recently.[5,6] In this communication, we report the result of the interaction of $[RuCl_2(PPh_3)_3]$ with $(Ph_2P)NC(Ph)[N(SiMe_3)_2]$.

When $[RuCl_2(PPh_3)_3]$ was allowed to react with 1 equivalent of $(Ph_2P)NC(Ph)[N(SiMe_3)_2]$ in tetrahydrofuran for 1 week at room temperature, work-up gave dark green crystals of stoichiometry $C_{40}H_{40}Cl_2N_2P_2RuSi{\cdot}C_4H_{10}O$ **1**,† in low yield (30%) after recrystallization from diethyl ether solution.

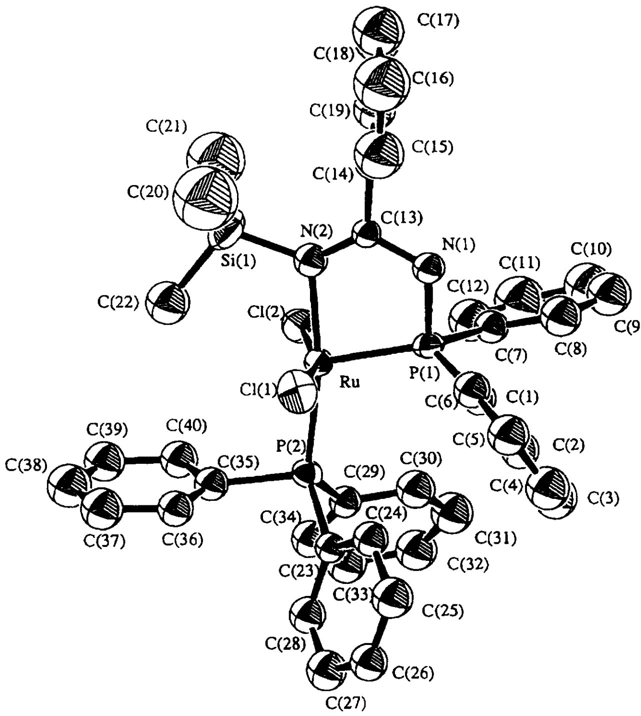

Fig. 1 A perspective drawing of compound **1**. Selected bond lengths (Å) and angles (°): Ru–Cl(1) 2.381(3), Ru–Cl(2) 2.382(3), Ru–P(1) 2.162(3), Ru–P(2) 2.304(3), Ru–N(2) 2.123(9), P(1)–N(1) 1.727(9), N(1)–C(13) 1.35(1), N(2)–C(13) 1.30(1), Ru ··· C(22) 3.16; Cl(1)–Ru–Cl(2) 160.4(1), Cl(1)–Ru–P(1) 95.4(1), Cl(2)–Ru–P(1) 102.9(1), P(1)–Ru–P(2) 106.8(1), Cl(1)–Ru–P(2) 92.9(1), Cl(2)–Ru–P(2) 88.8(1), N(2)–Ru–P(1) 83.0(2), N(2)–Ru–P(2) 170.2(3), C(13)–N(1)–P(1) 118.4(7), C(13)–N(2)–Ru, 116.7(7), Ru–N(2)–Si(1) 113.9(5), Ru–P(1)–N(1) 100.7(3), N(2)–Si(1)–C(20) 111.5(8), N(2)–Si(1)–C(21) 108.9(8), N(2)–Si(1)–C(22) 106.8(5)

Crystals of $[RuCl_2(PPh_3)\{N(SiMe_3)C(Ph)NH(PPh_2)\}]{\cdot}Et_2O$ **1** suitable for X-ray diffraction study ‡ were grown from a solution of diethyl ether and the structure established by X-ray crystallography (Fig. 1). The $N(SiMe_3)C(Ph)NH(PPh_2)$ moiety acts as a chelating ligand with the imino [N(2)] and phosphino [P(1)] groups co-ordinated to the ruthenium to form a five-

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† Crystals of $[RuCl_2(PPh_3)\{N(SiMe_3)C(Ph)NH(PPh_2)\}]{\cdot}Et_2O$ were obtained by the reaction of $[RuCl_2(PPh_3)_3]$ (1.08 g, 1.12 mmol) with an equimolar amount of $(Ph_2P)NC(Ph)[N(SiMe_3)_2]$ (0.50 g, 1.12 mmol) in tetrahydrofuran (50 cm^3) for 1 week at room temperature. Green crystals, m.p. 193–195 °C (decomp.) (Found: C, 59.5; H, 5.6; Cl, 8.1; N, 3.2. Calc. for $C_{44}H_{50}Cl_2N_2OP_2RuSi$: C, 59.7; H, 5.7, Cl, 8.0; N, 3.2%). IR (cm^{-1}, in KBr): 3424m, 2968m, 1584m, 1480w, 1432m, 1260s, 1092vs, 1018s, 946w, 800vs, 742w, 690s, 582w, 516m. $^{31}P\text{-}\{^1H\}$ NMR (C_6D_6): PPh_3, δ 47.3 (d, J_{P-P} = 32.5); Ph_2PN, δ 134.0 (d, J_{P-P} = 32.5 Hz). $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$): phenyl and phenylene carbons, δ 135.6, 134.7 (d, J_{P-C} =9.8), 134.4, 133.8, 132.7 (d, J_{P-C} = 11.0), 132.1 (d, J_{P-C} = 9.8), 130.4, 129.2, 128.6, 128.3, 127.7, 127.6 (d, J_{P-C} = 9.8 Hz); $SiMe_3$ carbons, δ 1.8; Et_2O carbons, δ 65.9 and 15.3. ^1H NMR (C_6D_6): phenyl protons, δ 7.89 (6 H, m), 7.69 (2 H, m), 7.48 (4 H, m), 6.80–7.10 (18 H, m); NH proton, δ 5.60 (1 H, d, J_{P-NH} = 3.0); $SiMe_3$ protons, δ 0.26 (9 H, s); Et_2O: CH_2 protons, δ 3.26 (4 H, q, J = 7.0); CH_3 protons, δ 1.11 (6 H, t, J = 7.0 Hz).

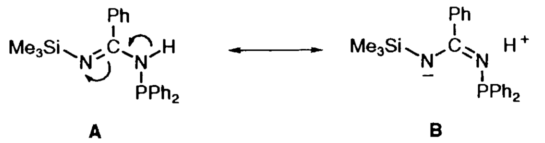
‡ Crystal data: $C_{40}H_{40}Cl_2N_2P_2RuSi{\cdot}C_4H_{10}O$, $M = 810.78$ (884.90 with solvent), monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), $a = 12.814(2)$, $b = 14.133(2)$, $c = 25.372(4)$ Å, $\beta = 104.03(2)°$, $U = 4458(1)$ Å^3, $Z = 4$, $D_c = 1.318$ g cm^{-3}, $F(000) = 1832$, Mo-Kα radiation, $\lambda = 0.710\,73$ Å, μ(Mo-Kα) = 6.04 cm^{-1}, ψ-scan absorption correction, crystal dimensions 0.22 × 0.24 × 0.30 mm, 2706 observed diffractometer data [$I > 3\sigma(I)$]. Structure solved by Patterson method and refined by full-matrix least-squares analysis using the TEXAN package[7] (Ru, Cl, P, Si anisotropic, and hydrogen atoms placed in their ideal positions, C–H 0.95, N–H 0.90 Å) to $R = 0.055$, $R' = 0.066$, $w = 4F^2/[\sigma^2(F^2) + 0.016F^2]^2$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

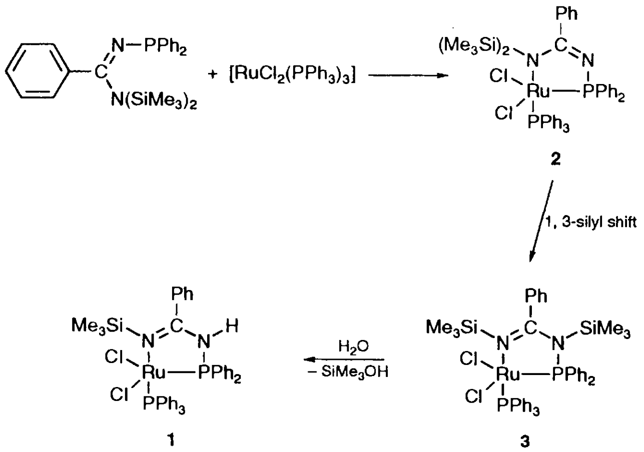
membered ring. The ruthenium adopts a pseudo-trigonal-bipyramidal geometry with the PPh_3 ligand and the $N(SiMe_3)$ imino group of the bidentate iminophosphine ligand occupying the axial positions. The Cl(1)–Ru–Cl(2) bond angle of 160.4(1)° deviates significantly from that expected for a trigonal-bipyramidal geometry and is closer to octahedral. The Ru ••• C(22) distance of 3.16 Å is rather short for non-interacting ruthenium and carbon atoms. There are two possible scenarios for the bonding of the $N(SiMe_3)$ imino group. One is the presence of a γ-agostic M⇠H–C interaction between ruthenium and one of the methyl groups. If this is the case, the idealized H atom will be placed coplanar with atoms C(22), Si(1), N(2) and Ru and the Ru–H distance will be 2.43 Å which is within a bonding interaction. The other scenario is the presence of weak hydrogen bonds between two of the H atoms of the methyl group with the two Cl atoms. If this is the case, then the idealized H atoms of the methyl group will be placed staggered with respect to bonds about Si(1), and the two H–Cl distances will be > 2.87 Å which are too long for any bonding interaction. The facts that the C(22)–Si(1)–N(2) bond angle of 106.8(5)° is smaller than the expected sp^3 silicon and is bent toward the ruthenium metal and that the C(22), Si(1), N(2) and Ru atoms are almost coplanar (±0.03 Å) suggest that there may be a γ-agostic M⇠H–C interaction between ruthenium and one of the methyl groups. Compound **1** will be an 18-electron species if one assumes an agostic interaction is present. This further supports the possibility of having a γ-agostic interaction between the metal and the $N(SiMe_3)$ group. However, the IR spectrum of **1** in KBr did not exhibit any low ν(C–H) in the region of 2250–2800 cm^{-1} assignable to the γ-agostic interaction. Attempts to verify the presence of the γ-agostic interaction with variable-temperature ^1H NMR spectroscopy were unsuccessful. In $[^2H_8]$toluene, the singlet for the $SiMe_3$ protons shifted from δ 0.26 at ambient temperature to δ 0.32 at −80 °C, and the resonance broadened only slightly but remained a singlet at −80 °C.

Within the bidentate iminophosphine ligand, the P(1)–N(1) bond length of 1.727(9) Å is in the normal range for a phosphorus–nitrogen single bond. The C(13)–N(1) and C(13)–N(2) distances of 1.35(1) and 1.30(1) Å, respectively, are intermediate between those expected for single (1.46 Å) and double (1.26 Å) bonds indicating some delocalization about the N–C–N framework. The delocalization is also reflected in the P(1)–N(1)–C(13) bond angle of 118.4(7)° which deviates significantly from that expected for a tetrahedral sp^3 nitrogen atom and is closer to a sp^2 nitrogen atom. Similar observations have been reported for related rhodium[5] and chromium[6] complexes. There are two possible resonance structures for the iminophosphine ligand as shown in Scheme 1 and the above structural data suggest that both resonance forms are important contributors to the structure of **1**. The contribution of the ionic resonance form **B** is further supported by the fact that the N–H amino proton of **1** underwent facile deuterium exchange with D_2O at ambient temperature.

The spectroscopic data of **1** are consistent with its solid-state structure. The $^{31}P\text{-}\{^1H\}$ NMR spectrum in C_6D_6 exhibited two doublets (J_{P-P} = 32.5 Hz) at δ 47.3 and 134.0 for the phosphorus of the PPh_3 and the $N(PPh_2)$ groups, respectively. The positive increase in chemical shift for the latter (from δ 37.4 to 134.0) is characteristic of chelate ring formation.[8] In addition to the resonances expected for the phenyl protons, the ^1H NMR spectrum of **1** exhibited a doublet (J_{P-NH} = 3.0 Hz) and a singlet of relative intensity 1:9 at δ 5.60 and 0.26 for the NH and $SiMe_3$ protons, respectively.



Scheme 1



Scheme 2

A possible mechanism for the formation of **1** is shown in Scheme 2. The compound $[RuCl_2(PPh_3)_3]$ reacted with the ligand to produce the intermediate **2**, which underwent a rapid 1,3-silyl shift to give intermediate **3**. The latter was then hydrolysed to produce the final product. A similar mechanism has been proposed for related complexes.[5,6]

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