Preparation and Reactivity of 16-Electron 'Half-Sandwich' Ruthenium Complexes; *X*-Ray Crystal Structure of (η^5-C_5Me_5)Ru(PPr$^i_3$)Cl

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The new 16-electron ruthenium compounds (η^5-C_5Me_5)Ru(L)Cl [(**1**), L = PPr$^i_3$; (**2**), L = PCy$_3$] (Cy = cyclohexyl) were prepared from [(η^5-C_5Me_5)RuCl]$_4$ and PPr$^i_3$ or PCy$_3$, respectively, and the *X*-ray crystal structure of (**1**) has been determined; reactions of the title compounds with CO, C_2H_4, pyridine, and PhSiH$_3$ are described.

A plethora of mechanistic and synthetic information has been reported regarding compounds of the type (η^5-C_5H_5)FeL$_2$X, and related Ru and Os systems.[1] In many instances reactive 16-electron intermediates formed *via* thermal or photo-induced dissociation of L play an important role in the chemistry of these species.[2] Here we report the preparation, characterization, and initial reactivity studies of stable, co-ordinatively unsaturated 'half sandwich' compounds (η^5-C_5Me_5)Ru(PR$_3$)Cl.

Combination of methylene chloride solutions of PR$_3$ [4 equiv.; R = Pr^i or Cy, (Cy = cyclohexyl)] and [(η^5-C_5Me_5)-RuCl]$_4$[3] (1 equiv.) at room temperature produced an immediate colour change from dark orange to deep blue. The highly crystalline 16-electron complexes (η^5-C_5Me_5)Ru(L)Cl [(**1**), L = PPr$^i_3$; (**2**), L = PCy$_3$] were isolated as blue crystals from pentane in 92 and 82% yields, respectively (equation 1).

Both reactions are quantitative in [$^2H_6$]benzene by ^{1}H n.m.r. spectroscopy. Compounds (**1**) and (**2**) were characterized by n.m.r., i.r., and elemental analyses.† U.v.–visible spectra revealed two absorptions for (**1**) at 283 (ε 2662) and

$$[(\eta^5\text{-}C_5Me_5)RuCl]_4 + 4L \xrightarrow{CH_2Cl_2} 4(\eta^5\text{-}C_5Me_5)Ru(L)Cl \quad (1)$$
$$\begin{array}{l}(\mathbf{1}), L = PPr^i_3 \\ (\mathbf{2}), L = PCy_3\end{array}$$

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† *Selected data* for (**1**): Satisfactory elemental analysis was obtained for C, H and P; ^{1}H n.m.r. (300 MHz, [$^2H_6$]benzene, 20 °C): δ 1.07 (q, 18 H, P–C–CH$_3$), 1.43 (s, 15 H, C_5Me_5), 2.23 (m, 3 H, P–CH); $^{13}C\{^1H\}$ n.m.r. (75.5 MHz, [$^2H_6$]benzene, 20 °C): δ 11.2 (C_5*Me*$_5$), 20.4 (P–C–*C*H$_3$), 24.2 (d, J_{PC} 15.1 Hz, P–*C*H), 74.6 (*C*$_5$Me$_5$); $^{31}P\{^1H\}$ n.m.r. (121.5 Hz, [$^2H_6$]benzene, 20 °C): δ 51.7 p.p.m.

For (**2**): Satisfactory elemental analysis for C, H, and P; ^{1}H n.m.r. (300 MHz, [$^2H_6$] benzene, 20 °C): δ 1.15—2.26 (m, 33 H, P–Cy), 1.48 (s, 15 H, C_5Me_5); $^{13}C\{^1H\}$ n.m.r. (75.5 MHz, [$^2H_6$]benzene, 20 °C): δ 11.33 (C_5*Me*$_5$), 27.0 (s), 28.1 (d, J_{PC} 10.2 Hz, PCy$_3$), 30.7 (s), 34.2 (d, J_{PC} 17 Hz, PCy$_3$), 74.5 (*C*$_5$Me$_5$); $^{31}P\{^1H\}$ n.m.r. (121.5 Hz, [$^2H_6$]benzene, 20 °C): δ 40.4 p.p.m.

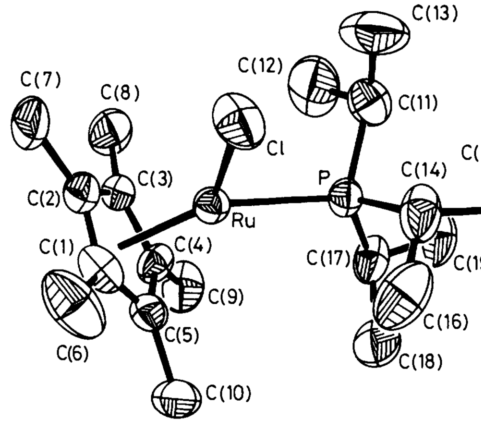

Figure 1. ORTEP view, based on 50% thermal ellipsoids, and labelling scheme for (**1**).

576 nm (ε 1692), and for (**2**) at 284 (ε 3027) and 580 nm (ε 1742). Addition of 4 equiv. of PEt_3 to $[(\eta^5\text{-}C_5Me_5)RuCl]_4$ in $[^2H_6]$benzene produced a 50:50 mixture of the previously described $(\eta^5\text{-}C_5Me_5)Ru(PEt_3)_2Cl$[4] and the $[(\eta^5\text{-}C_5Me_5)RuCl]_4$ starting material (by ^1H and ^{31}P n.m.r.). To our knowledge, (**1**) and (**2**) represent the first examples of isolable, 16-electron group VIII complexes of the type $(\eta^5\text{-}C_5R_5)M(L)X$.

An *X*-ray crystal structure of (**1**) was undertaken to determine the co-ordination geometry about ruthenium.‡ An ORTEP view of the molecule is presented in Figure 1. The environment about the Ru atom corresponds to that of a two-legged piano stool, with a Cl–Ru–P angle of 91.5 (1)°. The Cl, P, and Ru atoms and the centroid of the C_5Me_5 ligand are very nearly planar (mean deviation 0.003 Å; maximum deviation is by Ru, 0.007 Å), and this plane is perpendicular (90.2°) to the mean plane formed by all the carbon atoms of the C_5Me_5 ligand. The Ru–Cl bond length in (**1**), 2.365(2) Å, is significantly shorter than the corresponding distances in $(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl$ [2.453(2) Å] and $(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2Cl$ (average 2.44 Å),[5] reflecting the smaller co-ordination number in (**1**). Note that the Ru–Cl distance in $Ru(PPh_3)_3Cl_2$ is 2.387(7) Å.[6] The Ru–P distance in (**1**) [2.395(2) Å], however, is longer than the Ru–P distances in $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ (average 2.34 Å) and $(\eta^5\text{-}C_5H_5)Ru(PMe_3)_2Cl$ (average 2.28 Å), perhaps because of steric congestion about the donor atom of the PPr^i_3 ligand.

Preliminary investigations reveal the co-ordination of sterically undemanding 2-electron donor ligands to (**1**) and (**2**)

$$(\eta^5\text{-}C_5Me_5)Ru(L)Cl \xrightarrow[\text{pentane}]{L'} (\eta^5\text{-}C_5Me_5)Ru(L)(L')Cl \qquad (2)$$

$L = PCy_3$, $L' = CO$
$L = PPr^i_3$, L' = pyridine (pyr), C_2H_4

(equation 2). Complex (**2**) reacts with 1 equiv. of CO in pentane to give yellow crystals of $(\eta^5\text{-}C_5Me_5)Ru(PCy_3)(CO)Cl$ (**3**) in 76% isolated yield. The CO ligand in (**3**) appears as a doublet at δ 210.1 ($^2J_{PC}$ 22.5 Hz) in the ^{13}C n.m.r. spectrum, and the ν_{CO} stretching frequency occurs at 1908 cm^{-1} (Nujol mull). Attempts to form mixed phosphine complexes have met with little success. For example, reaction of (**1**) with 1 equiv. of PMe_3 in pentane at −78 °C gave only the known compound $(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2Cl$ and unreacted (**1**).[7] Upon addition of 1 equiv. of PPr^i_3 to compound (**1**) in $[^2H_6]$benzene, only free phosphine and (**1**) were observed by ^1H and ^{31}P n.m.r. spectroscopy. Evidently the steric properties of PPr^i_3 (cone angle 170°)[8] prevent formation of the bis-phosphine complex $(\eta^5\text{-}C_5Me_5)Ru(PPr^i_3)_2Cl$.

$(\eta^5\text{-}C_5Me_5)Ru(PCy_3)(CO)Cl$
(**3**)

$(\eta^5\text{-}C_5Me_5)Ru(PPr^i_3)(C_2H_4)Cl$
(**4**)

$(\eta^5\text{-}C_5Me_5)Ru(PPr^i_3)(pyr)Cl$
(**5**)

$(\eta^5\text{-}C_5Me_5)Ru(PPr^i_3)(SiH_2Ph)(H)Cl$
(**6**)

When a pentane solution of (**1**) was pressurized with ethylene (30 p.s.i.), the initial blue colour turned to red within 10 min. However, when the pressure was released during work-up, the blue colour returned and only (**1**) was isolated from solution. The labile product of ethylene addition to (**1**), $(\eta^5\text{-}C_5Me_5)Ru(PPr^i_3)(C_2H_4)Cl$ (**4**), was prepared *in situ* by addition of excess ethylene to (**1**) and was characterized utilizing variable temperature n.m.r. spectroscopy. At −65 °C in $[^2H_8]$toluene, the inequivalent protons of co-ordinated ethylene are clearly evident.§

Pyridine co-ordinates to (**1**) to give $(\eta^5\text{-}C_5Me_5)Ru(PPr^i_3)(pyr)Cl$ (**5**). Yellow-orange needles of (**5**) were isolated from hexane in 77% yield and characterized by n.m.r. and elemental analysis.¶ No reactions were observed between (**1**) and CO_2 (pentane, 50 p.s.i., 20 °C), H_2 (pentane, 100 p.s.i., 20 °C), or but-2-yne ($[^2H_6]$benzene, 2 equiv., 20 °C).

Reaction of (**1**) with the silane H_3SiPh proceeds by oxidative addition to give the Ru^{IV} silyl $(\eta^5\text{-}C_5Me_5)Ru(PPr^i_3)(SiH_2Ph)(H)Cl$ (**6**), isolated as analytically pure, golden yellow crystals from diethyl ether in 66% yield. In the ^1H n.m.r. spectrum, the Ru–H resonance for (**6**) appears as a

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‡ *Crystal data* for (**1**): $C_{19}H_{36}ClPRu$, orthorhombic, $P2_12_12_1$, a = 7.897(2), b = 15.216(4), c = 17.820(4) Å, U = 2141(1) Å^3, Z = 4, D_c = 1.34 g/cm^3, $F(000)$ = 904, μ = 9 cm^{-1}, Mo-K_α radiation (λ = 0.71073 Å). Data were collected at *ca.* 23 °C (296 K) on a Nicolet R3m/μ automated diffractometer using θ/2θ scans (variable scan speed, 1.5—15 deg. min^{-1}) and were corrected for absorption. Of 2201 reflections collected ($3° \leqslant 2\theta \leqslant 50°$), 2179 were independent. The space group was uniquely determined from systematic absences. The Ru atom was located by Patterson methods, and all remaining non-hydrogen atoms were located and refined anisotropically by difference Fourier and full-matrix least-squares methods (SHELXTL PLUS computer programs, Nicolet Instrument Corp., Madison, WI). The refinement was based on 1873 observed reflections [$F_o > 3\sigma(F_o)$]. Hydrogen atoms were calculated and fixed in ideal positions [d(C–H) = 0.96 Å, U = 60 Å^2 × 10^3]. The absolute configuration was tested by inverting the co-ordinates of all atoms and re-refining the structure. The results indicated that the original model was the correct enantiomorph. R_F = 2.97, R_{wF} = 3.61%, G.O.F. = 1.335, data/parameter ratio = 9.4, $\Delta(\rho)$ = 0.28 e/Å^3 (1.11 Å from Ru, 1.34 Å from Cl).

§ *Selected data* for (**4**): ^1H n.m.r. (300 MHz, $[^2H_8]$toluene, −65 °C): δ 1.67, 2.58, 2.71, 2.84 (m, 4H, C_2H_4); $^{31}P\{^1H\}$ n.m.r. (121.5 MHz, $[^2H_8]$toluene, 20 °C): δ 44.3 p.p.m. See ref. 2(b) for similar $Ru(\eta^2\text{-}C_2H_4)$ compounds.

¶ *Selected data* for (**5**): Satisfactory elemental analysis for C, H, Cl, N, and P, m.p. 117—118 °C; ^1H n.m.r. (300 MHz, $[^2H_6]$benzene, 20 °C): δ 1.15 (q, 18 H, P–C–CH_3), 1.40 (s, 15 H, C_5Me_5), 2.43 (m, 3H, P–CH), 6.54, 6.87, 9.00 (m, 5 H, C_5H_5N); $^{13}C\{^1H\}$ n.m.r. (75.5 MHz, $[^2H_6]$benzene, 20 °C): δ 10.3 ($C_5\mathit{Me}_5$), 20.34 (P–C–$\mathit{C}H_3$), 24.0 (d, J_{PC} 13.6 Hz, P–CH), 78.5 (d, J_{PC} 0.8 Hz, C_5Me_5), 123.4, 134.5, 154.3 (C_5H_5N); $^{31}P\{^1H\}$ n.m.r. (121.5 MHz, $[^2H_6]$benzene, 20 °C): δ 45.3 p.p.m.

doublet at δ −10.33, and the $^2J_{PH}$ coupling constant (30.6 Hz) indicates a *cis*-arrangement of the phosphine and hydride ligands.[7] The inequivalent $-SiH_2Ph$ protons are observed at δ 4.97 and 5.41. The ν_{RuH} and ν_{SiH} i.r. stretches overlap in the region 2000—2050 cm^{-1}; however, the strong Si–H deformation frequency is observed at 831 cm^{-1} (Nujol mull).

These results show that compounds (**1**) and (**2**) may serve as useful reagents for the preparation of compounds of the types $(\eta^5\text{-}C_5Me_5)Ru(L)(L')Cl$[9] and $(\eta^5\text{-}C_5Me_5)Ru(L)(X)(Y)Cl$ ($L = PPr^i_3$ or PCy_3). We have also observed that under some reaction conditions the bulky phosphine ligands of (**1**) and (**2**) are readily displaced. Further reports will address additional aspects of the reactivity of (**1**) and (**2**).

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References

1 (a) J. P. Collman and L. S. Hegedus, 'Principles and Applications of Organotransition Metal Chemistry,' University Science, Mill Valley, CA, 1980; (b) C. M. Lukehart, 'Fundamental Transition Metal Organometallic Chemistry,' Brooks/Cole, Monterey, CA, 1985; (c) M. Rosenblum, *J. Organomet. Chem.*, 1986, **300**, 191; (d) M. O. Albers, D. J. Robinson, and E. Singleton, *Coord. Chem. Rev.*, 1987, **79**, 1.

2 See for example: (a) D. B. Pourreau and G. L. Geoffroy, *Adv. Organomet. Chem.*, 1985, **24**, 280; (b) H. Lehmkuhl, J. Grundke, and R. Mynott, *Chem. Ber.*, 1983, **116**, 159; (c) R. J. Kazlauskas and M. S. Wrighton, *Organometallics*, 1982, **1**, 602.

3 P. J. Fagen, M. D. Ward, J. C. Calabrese, J. Caspar, and P. J. Krusic, *J. Am. Chem. Soc.*, submitted for publication.

4 R. A. Paciello, Ph.D. Thesis, California Institute of Technology, 1987.

5 M. I. Bruce, F. S. Wong, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 1398.

6 S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778.

7 T. D. Tilley, R. H. Grubbs, and J. E. Bercaw, *Organometallics*, 1984, **3**, 274.

8 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.

9 F. M. Conroy-Lewis and S. J. Simpson, *J. Organomet. Chem.*, 1987, **322**, 221.