

SUPPLEMENTARY INFORMATION

Synthesis, reactivity and catalytic activity in transfer hydrogenation of ketones of ruthenium(II) and ruthenium(IV) complexes containing the novel *N*-thiophosphorylated iminophosphorane-phosphine ligands $\text{Ph}_2\text{PCH}_2\text{P}\{\text{=NP(=S)(OR)}_2\}\text{Ph}_2$ (R = Et, Ph)

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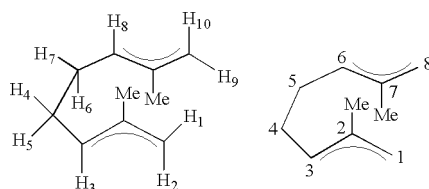
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Analytical and Spectroscopic Data

General comments

Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The conductivities were measured at room temperature, in *ca.* 10^{-3} mol dm⁻³ acetone solutions, with a Jenway PCM3 conductimeter. The C, H and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Melting points were determined on a Büchi CH-9230 oil-based apparatus and are uncorrected. Mass spectra (MALDI-TOF) were recorded using a VOYAGER-DE STR spectrometer; α -cyano-4-hydroxycinnamic acid was used as the matrix. NMR spectra were recorded on a Bruker DPX-300 instrument operating at 300 MHz (¹H), 121.5 MHz (³¹P) or 75.4 MHz (¹³C) using SiMe₄ or 85% H₃PO₄ as standards. DEPT experiments have been carried out for all the compounds reported. The numbering for protons and carbons of the 2,7-dimethylocta-2,6-diene-1,8-diyl skeleton is as follows:



Compound 1a: Found: C, 63.28; H, 5.79; N, 2.62. C₂₉H₃₂P₃O₂NS requires C, 63.15; H, 5.85; N, 2.54%; mp 118-120 °C; $\nu_{\max}/\text{cm}^{-1}$ (KBr) 3055, 2980, 2888, 1484, 1435, 1389, 1233, 1116, 1037, 999, 957, 837, 793, 732, 693, 529, 494; δ_{P} (CDCl₃) -27.18 (d, ²J(PP) = 62.7 Hz, Ph₂P), 15.66 (dd, ²J(PP) = 62.7 and 32.1 Hz, Ph₂P=N), 60.63 (d, ²J(PP) = 32.1 Hz, (EtO)₂P=S); δ_{H} (CDCl₃) 1.21 (t, 6H, ³J(HH) = 7.1 Hz, OCH₂CH₃), 3.74 (d, 2H, ²J(HP) = 13.9 Hz, PCH₂P), 4.01 (m, 4H, OCH₂), 7.17-7.47 (m, 16H, Ph), 7.68-7.75 (m, 4H, Ph); δ_{C} (CDCl₃) 16.06 (d, ³J(CP) = 8.1 Hz, OCH₂CH₃), 27.99 (dd, ¹J(CP) = 64.1 and 34.4 Hz, PCH₂P), 61.85 (d, ²J(CP) = 5.8 Hz, OCH₂), 128.17-132.91 (m, Ph), 137.49 (dd, ¹J(CP) = 14.6 Hz, ³J(CP) = 7.6 Hz, C_{ipso} of Ph); MS (MALDI-TOF) *m/z*: 552 [M + 1]⁺.

Compound 1b: Found: C, 68.55; H, 4.86; N, 2.24. C₃₇H₃₂P₃O₂NS requires C, 68.62; H, 4.98; N, 2.16%; mp 120-122 °C; $\nu_{\max}/\text{cm}^{-1}$ (KBr) 3066, 2972, 2885, 1485, 1435, 1270, 1178, 1164, 1115, 1024, 909, 883, 778, 734, 691, 531, 481; δ_{P} (CDCl₃) -27.58 (d, ²J(PP) = 63.4 Hz, Ph₂P), 17.15 (dd, ²J(PP) = 63.4 and 33.6 Hz, Ph₂P=N), 52.93 (d, ²J(PP) = 33.6 Hz, (PhO)₂P=S); δ_{H} (CDCl₃) 3.60 (d, 2H, ²J(HP) = 14.0 Hz, PCH₂P), 7.11-7.24 (m, 20H, Ph), 7.42-7.65 (m, 10H, Ph); δ_{C} (CDCl₃) 27.98 (dd, ¹J(CP) = 63.5 and 35.0 Hz, PCH₂P), 121.24-137.30 (m, Ph), 137.95 (dd, ¹J(CP) = 14.8 Hz, ³J(CP) = 7.7 Hz, C_{ipso} of Ph), 152.06 (d, ²J(CP) = 8.7 Hz, C_{ipso} of OPh); MS (MALDI-TOF) *m/z*: 648 [M + 1]⁺.

Compound 2a: Found: C, 54.55; H, 5.37; N, 1.63. $\text{RuC}_{39}\text{H}_{46}\text{P}_3\text{Cl}_2\text{O}_2\text{NS}$ requires C, 54.61; H, 5.40; N, 1.63%; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3042, 2969, 2901, 1589, 1483, 1437, 1385, 1253, 1167, 1035, 948, 799, 740, 690, 655, 504; δ_{P} (CD_2Cl_2) 11.81 (dd, $^2J(\text{PP}) = 38.7$ and 25.3 Hz, $\text{Ph}_2\text{P}=\text{N}$), 22.75 (d, $^2J(\text{PP}) = 38.7$ Hz, Ph_2P), 59.50 (d, $^2J(\text{PP}) = 25.3$ Hz, $(\text{EtO})_2\text{P}=\text{S}$); δ_{H} (CD_2Cl_2) 0.78 (d, 6H, $^3J(\text{HH}) = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.03 (t, 6H, $^3J(\text{HH}) = 7.0$ Hz, OCH_2CH_3), 1.74 (s, 3H, CH_3), 2.34 (sept, 1H, $^3J(\text{HH}) = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 3.45 (m, 4H, OCH_2), 3.87 (dd, 2H, $^2J(\text{HP}) = 9.4$ and 9.4 Hz, PCH_2P), 5.07 and 5.19 (d, 2H each, $^3J(\text{HH}) = 5.6$ Hz, CH of *p*-cymene), 7.23-8.02 (m, 20H, Ph); δ_{C} (CD_2Cl_2) 16.27 (d, $^3J(\text{CP}) = 6.4$ Hz, OCH_2CH_3), 17.47 (s, CH_3), 21.45 (s, $\text{CH}(\text{CH}_3)_2$), 21.75 (ddd, $^1J(\text{CP}) = 75.5$ and 18.6 Hz, $^3J(\text{CP}) = 6.4$ Hz, PCH_2P), 30.41 (s, $\text{CH}(\text{CH}_3)_2$), 61.58 (d, $^2J(\text{CP}) = 5.8$ Hz, OCH_2), 86.10 (d, $^2J(\text{CP}) = 5.8$ Hz, CH of *p*-cymene), 90.67 (d, $^2J(\text{CP}) = 4.1$ Hz, CH of *p*-cymene), 94.63 and 108.23 (s, C of *p*-cymene), 128.23-134.51 (m, Ph).

Compound 2b: Found: C, 58.90; H, 4.57; N, 1.45. $\text{RuC}_{47}\text{H}_{46}\text{P}_3\text{Cl}_2\text{O}_2\text{NS}$ requires C, 59.18; H, 4.86; N, 1.47%; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3038, 2963, 2899, 1488, 1438, 1429, 1303, 1198, 1107, 1026, 909, 823, 767, 692, 616, 546, 492; δ_{P} (CD_2Cl_2) 13.53 (dd, $^2J(\text{PP}) = 39.3$ and 23.4 Hz, $\text{Ph}_2\text{P}=\text{N}$), 23.94 (d, $^2J(\text{PP}) = 39.3$ Hz, Ph_2P), 51.69 (d, $^2J(\text{PP}) = 23.4$ Hz, $(\text{PhO})_2\text{P}=\text{S}$); δ_{H} (CD_2Cl_2) 0.77 (d, 6H, $^3J(\text{HH}) = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.78 (s, 3H, CH_3), 2.38 (sept, 1H, $^3J(\text{HH}) = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 4.02 (dd, 2H, $^2J(\text{HP}) = 9.8$ and 9.8 Hz, PCH_2P), 5.06 and 5.21 (d, 2H each, $^3J(\text{HH}) = 5.1$ Hz, CH of *p*-cymene), 7.22-8.05 (m, 30H, Ph); δ_{C} (CD_2Cl_2) 17.51 (s, CH_3), 20.30 (ddd, $^1J(\text{CP}) = 75.4$ and 18.9 Hz, $^3J(\text{CP}) = 6.2$ Hz, PCH_2P), 21.38 (s, $\text{CH}(\text{CH}_3)_2$), 30.43 (s, $\text{CH}(\text{CH}_3)_2$), 86.11 (d, $^2J(\text{CP}) = 5.8$ Hz, CH of *p*-cymene), 90.69 (d, $^2J(\text{CP}) = 4.6$ Hz, CH of *p*-cymene), 94.57 and 108.27 (s, C of *p*-cymene), 121.64-134.52 (m, Ph), 152.54 (d, $^2J(\text{CP}) = 8.7$ Hz, C_{ipso} of OPh).

Compound 3a: Found: C, 43.54; H, 4.37; N, 1.31. $\text{RuC}_{39}\text{H}_{46}\text{F}_6\text{P}_3\text{O}_2\text{ClINSSb}\cdot 1/4\text{CH}_2\text{Cl}_2$ requires C, 43.68; H, 4.34; N, 1.30%; conductivity (acetone, 20°C) $129 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3053, 2972, 1437, 1260, 1118, 1061, 1036, 849, 776, 738, 695, 624, 534; δ_{P} (CD_2Cl_2) 14.48 (dd, $^2J(\text{PP}) = 26.4$ and 3.8 Hz, $\text{Ph}_2\text{P}=\text{N}$), 25.91 (dd, $^3J(\text{PP}) = 10.7$ Hz, $^2J(\text{PP}) = 3.8$ Hz, Ph_2P), 54.92 (dd, $^2J(\text{PP}) = 26.4$ Hz, $^3J(\text{PP}) = 10.7$ Hz, $(\text{EtO})_2\text{P}=\text{S}$); δ_{H} (CD_2Cl_2) 0.83 (d, 3H, $^3J(\text{HH}) = 6.5$ Hz, $\text{CH}(\text{CH}_3)_2$), 0.98 (d, 3H, $^3J(\text{HH}) = 6.1$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.08 (t, 3H, $^3J(\text{HH}) = 6.4$ Hz, OCH_2CH_3), 1.46 (t, 3H, $^3J(\text{HH}) = 6.6$ Hz, OCH_2CH_3), 2.04 (s, 3H, CH_3), 2.44 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.15 and 5.63 (m, 1H each, PCH_2P), 4.13 and 4.99 (m, 2H each, OCH_2), 4.95 and 5.30 (s, 1H each, CH of *p*-cymene), 5.55 and 5.71 (d, 1H each, $^3J(\text{HH}) = 4.8$ Hz, CH of *p*-cymene), 7.09-7.58 (m, 20H, Ph); δ_{C} (CD_2Cl_2) 15.78 and 16.37 (d, $^3J(\text{CP}) = 8.4$ Hz, OCH_2CH_3), 18.52 (s, CH_3), 21.76 and 21.98 (s, $\text{CH}(\text{CH}_3)_2$), 26.84 (dd, $^1J(\text{CP}) = 59.5$ and 16.9 Hz, PCH_2P), 30.92 (s, $\text{CH}(\text{CH}_3)_2$), 64.47 and 64.86 (d, $^2J(\text{CP}) = 8.4$ Hz, OCH_2), 87.96 and 88.09 (s, CH of *p*-cymene), 90.32 (d, $^2J(\text{CP}) = 9.9$ Hz, CH of *p*-cymene), 95.00 (d, $^2J(\text{CP}) = 9.0$ Hz, CH of *p*-cymene), 102.00 and 113.12 (s, C of *p*-cymene), 126.95-138.97 (m, Ph).

Compound 3b: Found: C, 49.18; H, 4.10; N, 1.25. RuC₄₇H₄₆F₆P₃O₂Cl₂NSb requires C, 48.91; H, 4.02; N, 1.21%; conductivity (acetone, 20°C) 118 Ω⁻¹ cm² mol⁻¹; ν_{max}/cm⁻¹ (KBr) 3060, 2965, 1486, 1437, 1363, 1187, 1157, 1057, 942, 903, 830, 769, 740, 692, 533, 503; δ_p (CD₂Cl₂) 13.12 (dd, ²J(PP) = 28.3 and 3.8 Hz, Ph₂P=N), 26.36 (dd, ³J(PP) = 4.9 Hz, ²J(PP) = 3.8 Hz, Ph₂P), 46.61 (dd, ²J(PP) = 28.3 Hz, ³J(PP) = 4.9 Hz, (PhO)₂P=S); δ_H (CD₂Cl₂) 0.95 and 1.02 (d, 3H each, ³J(HH) = 6.8 Hz, CH(CH₃)₂), 1.95 (s, 3H, CH₃), 2.52 (m, 1H, CH(CH₃)₂), 3.17 and 5.26 (m, 1H each, PCH₂P), 4.76 and 5.09 (d, 1H each, ³J(HH) = 5.7 Hz, CH of *p*-cymene), 5.27 and 5.56 (d, 1H each, ³J(HH) = 6.3 Hz, CH of *p*-cymene), 6.81-7.62 (m, 30H, Ph); δ_C (CD₂Cl₂) 18.30 (s, CH₃), 21.84 and 22.04 (s, CH(CH₃)₂), 26.75 (dd, ¹J(CP) = 64.0 and 16.3 Hz, PCH₂P), 30.98 (s, CH(CH₃)₂), 88.72 (d, ²J(CP) = 1.8 Hz, CH of *p*-cymene), 89.77 (d, ²J(CP) = 3.0 Hz, CH of *p*-cymene), 94.49 and 94.55 (s, CH of *p*-cymene), 100.80 and 114.44 (s, C of *p*-cymene), 121.12-139.00 (m, Ph), 151.18 (d, ²J(CP) = 9.9 Hz, C_{ipso} of OPh), 151.54 (d, ²J(CP) = 11.1 Hz, C_{ipso} of OPh).

Compound 4a: Found: C, 37.56; H, 3.54; N, 1.30. RuC₃₉H₄₆F₁₂P₃O₂Sb₂NS requires C, 37.23; H, 3.68; N, 1.11%; conductivity (acetone, 20°C) 190 Ω⁻¹ cm² mol⁻¹; ν_{max}/cm⁻¹ (KBr) 3059, 2970, 1437, 1391, 1284, 1165, 1149, 1060, 997, 776, 738, 695, 622, 510, 487; δ_p (CD₂Cl₂) 43.38 (dd, ²J(PP) = 12.3 Hz, ³J(PP) = 5.7 Hz, Ph₂P), 46.00 (dd, ²J(PP) = 32.5 and 12.3 Hz, Ph₂P=N), 54.67 (dd, ²J(PP) = 32.5 Hz, ³J(PP) = 5.7 Hz, (EtO)₂P=S); δ_H (CD₂Cl₂) 0.55 and 1.55 (t, 3H each, ³J(HH) = 6.8 Hz, OCH₂CH₃), 0.88 and 1.13 (d, 3H each, ³J(HH) = 6.8 Hz, CH(CH₃)₂), 1.18 (s, 3H, CH₃), 2.12 (m, 1H, CH(CH₃)₂), 3.44 and 3.90 (m, 2H each, OCH₂), 4.72 and 4.94 (m, 1H each, PCH₂P), 5.73 and 6.20 (d, 1H each, ³J(HH) = 5.3 Hz, CH of *p*-cymene), 5.88 and 6.27 (d, 1H each, ³J(HH) = 5.7 Hz, CH of *p*-cymene), 7.14-8.30 (m, 20H, Ph); δ_C (CD₂Cl₂) 14.92 (d, ³J(CP) = 8.2 Hz, OCH₂CH₃), 16.10 (d, ³J(CP) = 9.3 Hz, OCH₂CH₃), 16.83 (s, CH₃), 21.35 and 22.28 (s, CH(CH₃)₂), 25.58 (dd, ¹J(CP) = 68.1 and 19.3 Hz, PCH₂P), 30.92 (s, CH(CH₃)₂), 65.62 (d, ²J(CP) = 7.6 Hz, OCH₂), 67.79 (d, ²J(CP) = 9.9 Hz, OCH₂), 79.51, 91.90 and 94.61 (s, CH of *p*-cymene), 89.50 (d, ²J(CP) = 7.6 Hz, CH of *p*-cymene), 106.08 (s, C of *p*-cymene), 121.93-135.90 (m, Ph and C of *p*-cymene).

Compound 4b: Found: C, 41.36; H, 3.61; N, 1.19. RuC₄₇H₄₆F₁₂P₃O₂Sb₂NS requires C, 41.68; H, 3.42; N, 1.03%; conductivity (acetone, 20°C) 197 Ω⁻¹ cm² mol⁻¹; ν_{max}/cm⁻¹ (KBr) 3063, 2969, 1586, 1485, 1438, 1378, 1191, 1152, 1063, 944, 772, 743, 691, 631, 509, 485; δ_p (CD₂Cl₂) 39.85 (dd, ²J(PP) = 9.8 Hz, ³J(PP) = 9.8 Hz, Ph₂P), 44.47 (dd, ²J(PP) = 32.6 and 9.8 Hz, Ph₂P=N), 56.95 (dd, ²J(PP) = 32.6 Hz, ³J(PP) = 9.8 Hz, (PhO)₂P=S); δ_H (CD₂Cl₂) 0.91 (s, 3H, CH₃), 0.93 and 1.02 (d, 3H each, ³J(HH) = 6.8 Hz, CH(CH₃)₂), 2.05 (m, 1H, CH(CH₃)₂), 3.98 and 5.17 (m, 1H each, PCH₂P), 5.57 and 5.87 (d, 1H each, ³J(HH) = 4.7 Hz, CH of *p*-cymene), 6.18 and 6.35 (d, 1H each, ³J(HH) = 6.3 Hz, CH of *p*-cymene), 6.95-8.37 (m, 30H, Ph); δ_C (CD₂Cl₂) 16.44 (s, CH₃), 21.19 and 22.10 (s, CH(CH₃)₂), 25.10 (dd, ¹J(CP) = 67.3 and 19.0 Hz, PCH₂P), 31.21 (s, CH(CH₃)₂), 77.45, 92.69 and 94.99 (s, CH of *p*-cymene), 89.56 (d,

$^2J(\text{CP}) = 8.2$ Hz, CH of *p*-cymene), 104.87 (s, C of *p*-cymene), 119.23-135.09 (m, Ph and C of *p*-cymene), 148.37 (d, $^2J(\text{CP}) = 10.5$ Hz, C_{ipso} of OPh), 149.50 (d, $^2J(\text{CP}) = 12.3$ Hz, C_{ipso} of OPh).

Compound 5a: Found: C, 54.12; H, 5.42; N, 1.61. $\text{RuC}_{39}\text{H}_{48}\text{P}_3\text{Cl}_2\text{O}_2\text{NS}$ requires C, 54.48; H, 5.63; N, 1.63%; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3051, 2974, 2898, 1435, 1385, 1277, 1247, 1167, 1106, 1029, 947, 795, 761, 743, 688, 655, 542, 506, 476; δ_{p} (CD_2Cl_2) 11.58 (dd, $^2J(\text{PP}) = 37.4$ and 27.9 Hz, $\text{Ph}_2\text{P}=\text{N}$), 20.30 (d, $^2J(\text{PP}) = 37.4$ Hz, Ph_2P), 59.68 (d, $^2J(\text{PP}) = 27.9$ Hz, $(\text{EtO})_2\text{P}=\text{S}$); δ_{H} (CD_2Cl_2) 1.10 (t, 6H, $^3J(\text{HH}) = 6.9$ Hz, OCH_2CH_3), 2.10 (s, 6H, CH_3), 2.61 (m, 2H, H_4 and H_6), 3.17 (d, 2H, $^3J(\text{HP}) = 3.1$ Hz, H_2 and H_{10}), 3.39 (m, 2H, H_5 and H_7), 3.64 (m, 4H, OCH_2), 4.08 and 4.35 (m, 1H each, PCH_2P), 4.17 (d, 2H, $^3J(\text{HP}) = 9.7$ Hz, H_1 and H_9), 5.13 (m, 2H, H_3 and H_8), 7.00-7.90 (m, 20H, Ph); δ_{C} (CD_2Cl_2) 16.28 (d, $^3J(\text{CP}) = 9.3$ Hz, OCH_2CH_3), 20.90 (s, CH_3), 25.02 (ddd, $^1J(\text{CP}) = 71.9$ and 16.0 Hz, $^3J(\text{CP}) = 4.9$ Hz, PCH_2P), 36.88 (s, C_4 and C_5), 61.90 (d, $^2J(\text{CP}) = 5.8$ Hz, OCH_2), 68.68 (d, $^2J(\text{CP}) = 5.2$ Hz, C_1 and C_8), 107.80 (d, $^2J(\text{CP}) = 10.5$ Hz, C_3 and C_6), 126.04 (s, C_2 and C_7), 127.20-134.60 (m, Ph).

Compound 5b: Found: C, 59.05; H, 4.90; N, 1.33. $\text{RuC}_{47}\text{H}_{48}\text{P}_3\text{Cl}_2\text{O}_2\text{NS}$ requires C, 59.06; H, 5.06; N, 1.46%; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3052, 2911, 2871, 1486, 1433, 1384, 1263, 1189, 1106, 1071, 1025, 899, 856, 802, 732, 688, 655, 621, 601, 539, 501, 464; δ_{p} (CD_2Cl_2) 13.49 (dd, $^2J(\text{PP}) = 38.1$ and 25.5 Hz, $\text{Ph}_2\text{P}=\text{N}$), 20.74 (d, $^2J(\text{PP}) = 38.1$ Hz, Ph_2P), 51.84 (d, $^2J(\text{PP}) = 25.5$ Hz, $(\text{PhO})_2\text{P}=\text{S}$); δ_{H} (CD_2Cl_2) 2.13 (s, 6H, CH_3), 2.63 (m, 2H, H_4 and H_6), 3.21 (br, 2H, H_2 and H_{10}), 3.42 (m, 2H, H_5 and H_7), 4.14 and 4.43 (m, 1H each, PCH_2P), 4.22 (d, 2H, $^3J(\text{HP}) = 9.7$ Hz, H_1 and H_9), 5.18 (m, 2H, H_3 and H_8), 6.90-7.75 (m, 30H, Ph); δ_{C} (CD_2Cl_2) 20.93 (s, CH_3), 24.71 (ddd, $^1J(\text{CP}) = 71.6$ and 15.1 Hz, $^3J(\text{CP}) = 4.7$ Hz, PCH_2P), 36.94 (s, C_4 and C_5), 68.59 (d, $^2J(\text{CP}) = 5.2$ Hz, C_1 and C_8), 108.02 (d, $^2J(\text{CP}) = 10.5$ Hz, C_3 and C_6), 126.02 (s, C_2 and C_7), 121.50-134.89 (m, Ph), 152.60 (d, $^2J(\text{CP}) = 8.7$ Hz, C_{ipso} of OPh).

Compound 6a: Found: C, 43.98; H, 4.54; N, 1.31. $\text{RuC}_{39}\text{H}_{48}\text{F}_6\text{P}_3\text{O}_2\text{ClNSsb}$ requires C, 44.19; H, 4.56; N, 1.32%; conductivity (acetone, 20°C) $119 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3059, 2982, 2905, 1437, 1386, 1249, 1160, 1114, 1024, 968, 844, 790, 744, 718, 692, 658, 589, 535, 506, 486; δ_{p} (CD_2Cl_2) 8.33 (s, Ph_2P), 15.36 (d, $^2J(\text{PP}) = 24.9$ Hz, $\text{Ph}_2\text{P}=\text{N}$), 54.30 (d, $^2J(\text{PP}) = 24.9$ Hz, $(\text{EtO})_2\text{P}=\text{S}$); δ_{H} (CD_2Cl_2) 1.08 and 1.26 (t, 3H each, $^3J(\text{HH}) = 6.8$ Hz, OCH_2CH_3), 2.11 and 2.42 (s, 3H each, CH_3), 2.47 and 3.77 (d, 1H each, $^3J(\text{HP}) = 6.4$ Hz, H_2 and H_{10}), 2.78 (m, 2H, H_4 and H_6), 3.10 and 3.28 (m, 1H each, H_5 and H_7), 3.94 (m, 4H, OCH_2), 4.02 and 4.75 (m, 1H each, PCH_2P), 4.09 and 4.87 (d, 1H each, $^3J(\text{HP}) = 9.4$ Hz, H_1 and H_9), 4.95 and 5.39 (m, 1H each, H_3 and H_8), 7.00-7.70 (m, 20H, Ph); δ_{C} (CD_2Cl_2) 15.86 (d, $^3J(\text{CP}) = 8.2$ Hz, OCH_2CH_3), 16.28 (d, $^3J(\text{CP}) = 7.0$ Hz, OCH_2CH_3), 19.66 (d, $^3J(\text{CP}) = 5.2$ Hz, CH_3), 20.83 (s, CH_3), 27.49 (dd, $^1J(\text{CP}) = 56.2$ and 8.7 Hz, PCH_2P), 35.95 and 36.11 (s, C_4 and C_5), 56.88 (d, $^2J(\text{CP}) = 5.2$ Hz, C_1 or C_8), 64.96 (d, $^2J(\text{CP}) = 9.9$ Hz, OCH_2), 65.14 (d, $^2J(\text{CP}) = 8.2$ Hz, OCH_2), 72.62 (s, C_1 or C_8), 106.28 and 110.70 (d, $^2J(\text{CP}) = 10.5$ Hz, C_3 and C_6), 121.57 and 124.90 (s, C_2 and C_7), 128.00-139.50 (m, Ph).

Compound 6b: Found: C, 47.50; H, 3.95; N, 1.22. $\text{RuC}_{47}\text{H}_{48}\text{F}_6\text{P}_3\text{O}_2\text{ClNSsb-1/2CH}_2\text{Cl}_2$ requires C, 47.60; H, 4.12; N, 1.17%; conductivity (acetone, 20°C) $135 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3058, 2969, 2916, 2857, 1486, 1436, 1382, 1356, 1282, 1185, 1161, 1110, 1023, 998, 931, 835, 770, 743, 690, 534, 503, 487; δ_{P} (CD_2Cl_2) 14.42 (s, Ph_2P), 15.52 (d, $^2J(\text{PP}) = 27.9 \text{ Hz}$, $\text{Ph}_2\text{P}=\text{N}$), 46.38 (d, $^2J(\text{PP}) = 27.9 \text{ Hz}$, $(\text{PhO})_2\text{P}=\text{S}$); δ_{H} (CD_2Cl_2) 2.14 and 2.34 (s, 3H each, CH_3), 2.60 (m, 2H, H_4 and H_6), 2.72 (d, 1H, $^3J(\text{HP}) = 5.4 \text{ Hz}$, H_2 or H_{10}), 3.27 (m, 2H, H_5 and H_7), 4.05 (d, 1H, $^3J(\text{HP}) = 4.8 \text{ Hz}$, H_2 or H_{10}), 4.11 (d, 1H, $^3J(\text{HP}) = 8.3 \text{ Hz}$, H_1 or H_9), 4.23 and 4.53 (m, 1H each, PCH_2P), 4.70 (d, 1H, $^3J(\text{HP}) = 8.0 \text{ Hz}$, H_1 or H_9), 5.12 and 5.50 (m, 1H each, H_3 and H_8), 7.00-7.60 (m, 30H, Ph); δ_{C} (CD_2Cl_2) 19.74 (d, $^3J(\text{CP}) = 5.8 \text{ Hz}$, CH_3), 21.40 (s, CH_3), 29.31 (dd, $^1J(\text{CP}) = 57.1$ and 7.6 Hz , PCH_2P), 36.24 and 37.25 (s, C_4 and C_5), 55.66 (d, $^2J(\text{CP}) = 4.1 \text{ Hz}$, C_1 or C_8), 71.62 (s, C_1 or C_8), 108.32 and 110.92 (d, $^2J(\text{CP}) = 9.9 \text{ Hz}$, C_3 and C_6), 124.71 and 126.40 (s, C_2 and C_7), 120.50-134.89 (m, Ph), 150.67 (d, $^2J(\text{CP}) = 10.5 \text{ Hz}$, C_{ipso} of OPh), 150.99 (d, $^2J(\text{CP}) = 12.8 \text{ Hz}$, C_{ipso} of OPh).

Compound 7a: Found: C, 36.89; H, 3.93; N, 1.30. $\text{RuC}_{39}\text{H}_{48}\text{F}_{12}\text{P}_3\text{O}_2\text{Sb}_2\text{NS}$ requires C, 37.17; H, 3.84; N, 1.11%; conductivity (acetone, 20°C) $195 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3066, 2999, 2938, 1588, 1486, 1475, 1456, 1388, 1339, 1317, 1291, 1159, 1139, 1117, 1040, 1012, 975, 817, 800, 749, 695, 657, 623, 565, 524, 504, 481; δ_{P} (CD_2Cl_2) 33.28 (dd, $^2J(\text{PP}) = 28.3 \text{ Hz}$, $^3J(\text{PP}) = 4.9 \text{ Hz}$, Ph_2P), 53.55 (dd, $^2J(\text{PP}) = 21.9 \text{ Hz}$, $^3J(\text{PP}) = 4.9 \text{ Hz}$, $(\text{EtO})_2\text{P}=\text{S}$), 55.31 (dd, $^2J(\text{PP}) = 28.3$ and 21.9 Hz , $\text{Ph}_2\text{P}=\text{N}$); δ_{H} (CD_2Cl_2) 1.04 and 1.25 (t, 3H each, $^3J(\text{HH}) = 6.9 \text{ Hz}$, OCH_2CH_3), 1.88 (d, 3H, $^4J(\text{HP}) = 2.0 \text{ Hz}$, CH_3), 2.43 (m, 1H, H_4 or H_6), 2.59 (s, 3H, CH_3), 2.74 (m, 2H, H_4 or H_6 and H_5 or H_7), 3.65 (m, 1H, H_5 or H_7), 3.76 (d, 1H, $^3J(\text{HP}) = 3.1 \text{ Hz}$, H_2 or H_{10}), 3.79 (br, 1H, H_1 or H_9), 4.02 (m, 7H, OCH_2 , PCH_2P and H_1 or H_9), 4.27 and 5.09 (m, 1H each, H_3 and H_8), 5.13 (d, 1H, $^3J(\text{HP}) = 3.1 \text{ Hz}$, H_2 or H_{10}), 7.20-8.15 (m, 20H, Ph); δ_{C} (CD_2Cl_2) 15.72 and 15.89 (d, $^3J(\text{CP}) = 5.7 \text{ Hz}$, OCH_2CH_3), 18.69 (d, $^3J(\text{CP}) = 2.5 \text{ Hz}$, CH_3), 21.39 (s, CH_3), 32.12 and 35.48 (s, C_4 and C_5), 34.26 (ddd, $^1J(\text{CP}) = 78.7$ and 17.8 Hz , $^3J(\text{CP}) = 8.3 \text{ Hz}$, PCH_2P), 67.59 and 67.78 (d, $^2J(\text{CP}) = 7.6 \text{ Hz}$, OCH_2), 73.75 and 75.42 (s, C_1 and C_8), 92.26 (s, C_3 or C_6), 97.65 (d, $^2J(\text{CP}) = 6.3 \text{ Hz}$, C_3 or C_6), 122.19 and 128.27 (s, C_2 and C_7), 121.10-136.65 (m, Ph).

Compound 7b: Found: C, 41.33; H, 3.68; N, 1.14. $\text{RuC}_{47}\text{H}_{48}\text{F}_{12}\text{P}_3\text{O}_2\text{Sb}_2\text{NS}$ requires C, 41.62; H, 3.57; N, 1.03%; conductivity (acetone, 20°C) $184 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3065, 2976, 2924, 1587, 1486, 1456, 1438, 1385, 1338, 1316, 1197, 1156, 1142, 1118, 1073, 1023, 999, 947, 793, 774, 746, 690, 659, 642, 578, 519, 502, 483; δ_{P} (CD_2Cl_2) 30.90 (dd, $^2J(\text{PP}) = 27.1 \text{ Hz}$, $^3J(\text{PP}) = 4.5 \text{ Hz}$, Ph_2P), 46.46 (dd, $^2J(\text{PP}) = 24.8 \text{ Hz}$, $^3J(\text{PP}) = 4.5 \text{ Hz}$, $(\text{PhO})_2\text{P}=\text{S}$), 55.69 (dd, $^2J(\text{PP}) = 27.1$ and 24.8 Hz , $\text{Ph}_2\text{P}=\text{N}$); δ_{H} (CD_2Cl_2) 1.91 (d, 3H, $^4J(\text{HP}) = 1.8 \text{ Hz}$, CH_3), 2.42 (s, 3H, CH_3), 2.71 (m, 4H, H_4 , H_5 , H_6 and H_7), 3.83 (d, 1H, $^3J(\text{HP}) = 2.3 \text{ Hz}$, H_2 or H_{10}), 4.03 (d, 1H, $^3J(\text{HP}) = 4.7 \text{ Hz}$, H_1 or H_9), 4.11 and 4.53 (m, 1H each, PCH_2P), 4.18 (m, 1H, H_1 or H_9), 4.53 and 5.12 (m, 1H each, H_3 and H_8), 5.28

(d, 1H, $^3J(\text{HP}) = 2.8$ Hz, H₂ or H₁₀), 6.60-8.15 (m, 30H, Ph); δ_{C} (CD₂Cl₂) 17.86 (d, $^3J(\text{CP}) = 2.1$ Hz, CH₃), 20.31 (s, CH₃), 31.48 (ddd, $^1J(\text{CP}) = 93.7$ and 18.3 Hz, $^3J(\text{CP}) = 7.4$ Hz, PCH₂P), 31.64 and 34.78 (s, C₄ and C₅), 73.02 and 75.16 (s, C₁ and C₈), 92.28 (s, C₃ or C₆), 97.52 (d, $^2J(\text{CP}) = 6.9$ Hz, C₃ or C₆), 122.40 and 127.14 (s, C₂ and C₇), 120.20-136.20 (m, Ph), 147.81 (d, $^2J(\text{CP}) = 9.5$ Hz, C_{ipso} of OPh), 148.28 (d, $^2J(\text{CP}) = 10.1$ Hz, C_{ipso} of OPh).

Compound 8: Found: C, 37.12; H, 3.63; N, 1.99. RuC₄₁H₄₉F₁₂P₃N₂O₂Sb₂S·1/2CH₂Cl₂ requires C, 37.14; H, 3.75; N, 2.08%; conductivity (acetone, 20°C) 191 Ω⁻¹ cm² mol⁻¹; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3076, 2980, 2291, 1482, 1439, 1392, 1262, 1162, 1113, 1036, 1025, 970, 845, 789, 742, 694, 658, 589, 537, 502, 488; δ_{P} (CD₂Cl₂) 13.48 (dd, $^2J(\text{PP}) = 30.1$ and 5.0 Hz, Ph₂P=N), 27.79 (d, $^2J(\text{PP}) = 5.0$ Hz, Ph₂P), 50.58 (d, $^2J(\text{PP}) = 30.1$ Hz, (EtO)₂P=S); δ_{H} (CD₂Cl₂) 0.98 and 1.10 (d, 3H each, $^3J(\text{HH}) = 5.4$ Hz, CH(CH₃)₂), 1.34 (t, 6H, $^3J(\text{HH}) = 8.1$ Hz, OCH₂CH₃), 2.10 (s, 3H, CH₃), 2.38 (s, 3H, CH₃C≡N), 2.52 (m, 1H, CH(CH₃)₂), 3.95 (m, 2H, PCH₂P), 4.13 (m, 4H, OCH₂), 5.51 (br, 2H, CH of *p*-cymene), 5.58 and 5.65 (br, 1H each, CH of *p*-cymene), 7.29-7.55 (m, 20H, Ph); δ_{C} (CD₂Cl₂) 4.13 (s, CH₃C≡N), 15.27 (d, $^3J(\text{CP}) = 8.5$ Hz, OCH₂CH₃), 15.87 (d, $^3J(\text{CP}) = 8.0$ Hz, OCH₂CH₃), 17.98 (s, CH₃), 20.71 and 21.84 (s, CH(CH₃)₂), 26.48 (dd, $^1J(\text{CP}) = 58.3$ and 16.5 Hz, PCH₂P), 30.46 (s, CH(CH₃)₂), 64.84 (d, $^2J(\text{CP}) = 3.2$ Hz, OCH₂), 64.90 (d, $^2J(\text{CP}) = 5.3$ Hz, OCH₂), 89.67 and 90.50 (s, CH of *p*-cymene), 93.01 (d, $^2J(\text{CP}) = 3.2$ Hz, CH of *p*-cymene), 95.29 (d, $^2J(\text{CP}) = 4.8$ Hz, CH of *p*-cymene), 108.07 and 116.05 (s, C of *p*-cymene), 120.86-136.28 (m, Ph and C≡N).

Compound 9: Found: C, 35.87; H, 4.14; N, 1.01. RuC₄₂H₅₅F₁₂P₄O₂Sb₂NS·3/2CH₂Cl₂ requires C, 35.74; H, 4.00; N, 0.96%; conductivity (acetone, 20°C) 191 Ω⁻¹ cm² mol⁻¹; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3062, 2982, 2930, 1484, 1436, 1392, 1288, 1262, 1162, 1109, 1090, 1026, 953, 851, 739, 695, 658, 585, 535, 490; δ_{P} (CD₂Cl₂) 1.30 (dd, $^2J(\text{PP}) = 49.5$ Hz, $^3J(\text{PP}) = 37.1$ Hz, PMe₃), 20.64 (dd, $^2J(\text{PP}) = 27.6$ and 9.6 Hz, Ph₂P=N), 33.63 (ddd, $^2J(\text{PP}) = 49.5$ and 9.6 Hz, $^3J(\text{PP}) = 8.6$ Hz, Ph₂P), 51.11 (ddd, $^3J(\text{PP}) = 37.1$ and 8.6 Hz, $^2J(\text{PP}) = 27.6$ Hz, (EtO)₂P=S); δ_{H} (CD₂Cl₂) 1.31 (br, 6H, CH(CH₃)₂), 1.45 (d, 9H, $^2J(\text{HP}) = 10.0$ Hz, PCH₃), 1.70 (s, 3H, CH₃), 1.80 (t, 6H, $^3J(\text{HH}) = 6.7$ Hz, OCH₂CH₃), 3.00 (m, 1H, CH(CH₃)₂), 3.96 (m, 2H, PCH₂P), 4.20 and 4.69 (m, 2H each, OCH₂), 5.99 and 6.79 (d, 1H each, $^3J(\text{HH}) = 5.2$ Hz, CH of *p*-cymene), 6.28 and 6.32 (br, 1H each, CH of *p*-cymene), 7.26-7.76 (m, 20H, Ph); δ_{C} (CD₂Cl₂) 13.74 (d, $^3J(\text{CP}) = 7.0$ Hz, OCH₂CH₃), 16.00 (d, $^3J(\text{CP}) = 8.2$ Hz, OCH₂CH₃), 18.24 (d, $^1J(\text{CP}) = 34.9$ Hz, PCH₃), 18.63 (s, CH₃), 22.16 and 22.67 (s, CH(CH₃)₂), 25.27 (dd, $^1J(\text{CP}) = 57.7$ and 15.1 Hz, PCH₂P), 31.31 (s, CH(CH₃)₂), 66.05 (d, $^2J(\text{CP}) = 7.0$ Hz, OCH₂), 66.52 (d, $^2J(\text{CP}) = 10.1$ Hz, OCH₂), 93.67 (s, CH of *p*-cymene), 95.75 and 100.69 (d, $^2J(\text{CP}) = 4.7$ Hz, CH of *p*-cymene), 96.20 (d, $^2J(\text{CP}) = 5.2$ Hz, CH of *p*-cymene), 111.92 (s, C of *p*-cymene), 123.58-133.83 (m, Ph and C of *p*-cymene).

Compound 10: Found: C, 39.71; H, 4.17; N, 0.97. RuC₄₇H₅₇F₁₂P₄O₂Sb₂NS·1/2CH₂Cl₂ requires C, 39.65; H, 4.06; N, 0.97%; conductivity (acetone, 20°C) 208 Ω⁻¹ cm² mol⁻¹; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3062, 2981, 2914, 1483, 1437, 1392, 1265,

1263, 1110, 1090, 1025, 967, 945, 909, 845, 738, 696, 657, 585, 535, 491, 451; δ_{P} (CD_2Cl_2) 0.78 (dd, $^2J(\text{PP}) = 49.7$ Hz, $^3J(\text{PP}) = 33.4$ Hz, PMe_2Ph), 20.48 (dd, $^2J(\text{PP}) = 30.7$ and 12.7 Hz, $\text{Ph}_2\text{P}=\text{N}$), 34.80 (ddd, $^2J(\text{PP}) = 49.7$ and 12.7 Hz, $^3J(\text{PP}) = 9.0$ Hz, Ph_2P), 49.66 (ddd, $^3J(\text{PP}) = 33.4$ and 9.0 Hz, $^2J(\text{PP}) = 30.7$ Hz, $(\text{EtO})_2\text{P}=\text{S}$); δ_{H} (CD_2Cl_2) 1.09, 1.31, 1.79 and 1.97 (br, 3H each, $\text{CH}(\text{CH}_3)_2$ and OCH_2CH_3), 1.41 (d, 6H, $^2J(\text{HP}) = 17.9$ Hz, PCH_3), 1.99 (s, 3H, CH_3), 2.56 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.45 (m, 2H, PCH_2P), 4.37 and 4.75 (m, 2H each, OCH_2), 5.34, 5.82, 6.09 and 6.30 (br, 1H each, CH of *p*-cymene), 6.79-7.89 (m, 25H, Ph); δ_{C} (CD_2Cl_2) 16.11 (d, $^3J(\text{CP}) = 6.7$ Hz, OCH_2CH_3), 16.59 (s, CH_3), 16.78 (d, $^3J(\text{CP}) = 4.5$ Hz, OCH_2CH_3), 18.34 (d, $^1J(\text{CP}) = 20.8$ Hz, PCH_3), 18.70 (d, $^1J(\text{CP}) = 18.7$ Hz, PCH_3), 21.70 and 22.94 (s, $\text{CH}(\text{CH}_3)_2$), 23.54 (dd, $^1J(\text{CP}) = 45.0$ and 15.6 Hz, PCH_2P), 30.70 (s, $\text{CH}(\text{CH}_3)_2$), 66.22 (d, $^2J(\text{CP}) = 7.1$ Hz, OCH_2), 66.52 (d, $^2J(\text{CP}) = 10.8$ Hz, OCH_2), 92.39, 96.92 and 98.01 (s, CH of *p*-cymene), 101.73 (d, $^2J(\text{CP}) = 5.2$ Hz, CH of *p*-cymene), 112.68 (s, C of *p*-cymene), 121.33-134.98 (m, Ph and C of *p*-cymene).

Compound 11: Found: C, 41.12; H, 4.08; N, 0.92. $\text{RuC}_{52}\text{H}_{59}\text{F}_{12}\text{P}_4\text{O}_2\text{Sb}_2\text{NS}\cdot\text{CH}_2\text{Cl}_2$ requires C, 41.24; H, 3.98; N, 0.91%; conductivity (acetone, 20°C) $207 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3061, 2978, 1484, 1437, 1391, 1266, 1163, 1110, 1095, 1026, 967, 886, 850, 739, 695, 655, 587, 515, 498; δ_{P} (CD_2Cl_2) 4.39 (dd, $^2J(\text{PP}) = 41.5$ Hz, $^3J(\text{PP}) = 33.4$ Hz, PMePh_2), 19.89 (dd, $^2J(\text{PP}) = 30.7$ and 12.7 Hz, $\text{Ph}_2\text{P}=\text{N}$), 28.80 (ddd, $^2J(\text{PP}) = 41.5$ and 12.7 Hz, $^3J(\text{PP}) = 10.8$ Hz, Ph_2P), 51.11 (ddd, $^3J(\text{PP}) = 33.4$ and 10.8 Hz, $^2J(\text{PP}) = 30.7$ Hz, $(\text{EtO})_2\text{P}=\text{S}$); δ_{H} (CD_2Cl_2) 1.09 (d, 3H, $^3J(\text{HH}) = 5.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.38 (d, 3H, $^3J(\text{HH}) = 6.7$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.48 (t, 3H, $^3J(\text{HH}) = 6.8$ Hz, OCH_2CH_3), 1.83 (t, 3H, $^3J(\text{HH}) = 7.0$ Hz, OCH_2CH_3), 1.88 (s, 3H, CH_3), 2.15 (d, 3H, $^2J(\text{HP}) = 8.9$ Hz, PCH_3), 2.81 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.20 (m, 2H, PCH_2P), 4.35 and 4.68 (m, 2H each, OCH_2), 5.46 and 5.86 (br, 1H each, CH of *p*-cymene), 6.17 and 6.68 (d, 1H each, $^3J(\text{HH}) = 5.7$ Hz, CH of *p*-cymene), 7.20-7.65 (m, 30H, Ph); δ_{C} (CD_2Cl_2) 13.57 (d, $^1J(\text{CP}) = 11.8$ Hz, PCH_3), 16.11 (d, $^3J(\text{CP}) = 8.1$ Hz, OCH_2CH_3), 16.60 (d, $^3J(\text{CP}) = 7.0$ Hz, OCH_2CH_3), 18.62 (s, CH_3), 20.27 and 23.18 (s, $\text{CH}(\text{CH}_3)_2$), 26.27 (dd, $^1J(\text{CP}) = 55.1$ and 16.9 Hz, PCH_2P), 31.23 (s, $\text{CH}(\text{CH}_3)_2$), 66.25 (d, $^2J(\text{CP}) = 7.5$ Hz, OCH_2), 66.60 (d, $^2J(\text{CP}) = 10.8$ Hz, OCH_2), 92.78 (d, $^2J(\text{CP}) = 6.4$ Hz, CH of *p*-cymene), 94.26 and 97.02 (s, CH of *p*-cymene), 100.96 (d, $^2J(\text{CP}) = 5.4$ Hz, CH of *p*-cymene), 109.34 (s, C of *p*-cymene), 124.51-133.78 (m, Ph and C of *p*-cymene).

Compound 12: Found: C, 40.49; H, 4.18; N, 1.18. $\text{RuC}_{39}\text{H}_{46}\text{F}_6\text{P}_3\text{O}_2\text{BrNSSb}\cdot\text{CH}_2\text{Cl}_2$ requires C, 40.46; H, 4.07; N, 1.18%; conductivity (acetone, 20°C) $113 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3056, 2964, 2902, 1475, 1439, 1389, 1365, 1236, 1155, 1110, 1007, 953, 850, 776, 742, 657, 585, 535; δ_{P} (CD_2Cl_2) 15.37 (dd, $^2J(\text{PP}) = 26.3$ and 4.5 Hz, $\text{Ph}_2\text{P}=\text{N}$), 23.99 (dd, $^3J(\text{PP}) = 11.7$ Hz, $^2J(\text{PP}) = 4.5$ Hz, Ph_2P), 55.39 (dd, $^2J(\text{PP}) = 26.3$ Hz, $^3J(\text{PP}) = 11.7$ Hz, $(\text{EtO})_2\text{P}=\text{S}$); δ_{H} (CD_2Cl_2) 0.81 and 0.93 (d, 3H each, $^3J(\text{HH}) = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.06 and 1.49 (t, 3H each, $^3J(\text{HH}) = 6.7$ Hz, OCH_2CH_3), 2.06 (s, 3H, CH_3), 2.53 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.20 and 5.15 (m, 1H each, PCH_2P), 3.92 and 4.15 (m, 2H each, OCH_2), 5.04 and 5.38 (d, 1H each, $^3J(\text{HH}) = 4.9$ Hz, CH of *p*-cymene), 5.57 and 5.78 (d, 1H each,

$^3J(\text{HH}) = 5.8$ Hz, CH of *p*-cymene), 7.03-7.64 (m, 20H, Ph); δ_{C} (CD_2Cl_2) 15.77 and 16.37 (d, $^3J(\text{CP}) = 8.1$ Hz, OCH_2CH_3), 18.65 (s, CH_3), 21.88 and 22.08 (s, $\text{CH}(\text{CH}_3)_2$), 28.53 (dd, $^1J(\text{CP}) = 58.9$ and 17.4 Hz, PCH_2P), 31.21 (s, $\text{CH}(\text{CH}_3)_2$), 64.63 and 64.79 (d, $^2J(\text{CP}) = 8.7$ Hz, OCH_2), 87.68 (s, CH of *p*-cymene), 88.04 (d, $^2J(\text{CP}) = 1.3$ Hz, CH of *p*-cymene), 90.45 (d, $^2J(\text{CP}) = 6.0$ Hz, CH of *p*-cymene), 94.26 (d, $^2J(\text{CP}) = 7.2$ Hz, CH of *p*-cymene), 104.09 and 112.72 (s, C of *p*-cymene), 125.52-139.08 (m, Ph).

Compound 13: Found: C, 39.45; H, 3.87; N, 1.17. $\text{RuC}_{39}\text{H}_{46}\text{F}_6\text{P}_3\text{O}_2\text{INSSb}\cdot 2/3\text{CH}_2\text{Cl}_2$ requires C, 39.50; H, 3.95; N, 1.16%; conductivity (acetone, 20°C) $109 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3055, 2965, 2899, 1476, 1439, 1389, 1364, 1237, 1157, 1109, 954, 859, 774, 736, 711, 657, 584, 535, 495; δ_{P} (CD_2Cl_2) 17.22 (dd, $^2J(\text{PP}) = 27.2$ and 5.5 Hz, $\text{Ph}_2\text{P}=\text{N}$), 23.48 (dd, $^3J(\text{PP}) = 12.5$ Hz, $^2J(\text{PP}) = 5.5$ Hz, Ph_2P), 56.21 (dd, $^2J(\text{PP}) = 27.2$ Hz, $^3J(\text{PP}) = 12.5$ Hz, $(\text{EtO})_2\text{P}=\text{S}$); δ_{H} (CD_2Cl_2) 0.82 and 0.84 (d, 3H each, $^3J(\text{HH}) = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.07 (t, 3H, $^3J(\text{HH}) = 6.9$ Hz, OCH_2CH_3), 1.55 (t, 3H, $^3J(\text{HH}) = 7.0$ Hz, OCH_2CH_3), 2.08 (s, 3H, CH_3), 2.58 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.35 and 5.20 (m, 1H each, PCH_2P), 3.91 and 4.20 (m, 2H each, OCH_2), 5.24 and 5.61 (d, 1H each, $^3J(\text{HH}) = 6.2$ Hz, CH of *p*-cymene), 5.69 and 6.01 (d, 1H each, $^3J(\text{HH}) = 5.6$ Hz, CH of *p*-cymene), 7.05-7.62 (m, 20H, Ph); δ_{C} (CD_2Cl_2) 15.83 and 16.45 (d, $^3J(\text{CP}) = 7.8$ Hz, OCH_2CH_3), 18.95 (s, CH_3), 22.08 and 22.58 (s, $\text{CH}(\text{CH}_3)_2$), 30.82 (dd, $^1J(\text{CP}) = 58.0$ and 18.3 Hz, PCH_2P), 31.56 (s, $\text{CH}(\text{CH}_3)_2$), 64.71 and 64.81 (d, $^2J(\text{CP}) = 7.5$ Hz, OCH_2), 88.12 (s, CH of *p*-cymene), 88.30 (d, $^2J(\text{CP}) = 2.4$ Hz, CH of *p*-cymene), 90.05 (d, $^2J(\text{CP}) = 4.2$ Hz, CH of *p*-cymene), 92.54 (d, $^2J(\text{CP}) = 7.2$ Hz, CH of *p*-cymene), 107.66 and 112.01 (s, C of *p*-cymene), 125.45-139.04 (m, Ph).

Compound 14: Found: C, 43.82; H, 4.51; N, 5.09. $\text{RuC}_{39}\text{H}_{46}\text{F}_6\text{N}_4\text{P}_3\text{O}_2\text{SSb}$ requires C, 44.00; H, 4.36; N, 5.26%; conductivity (acetone, 20°C) $117 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr) 3060, 2978, 2043, 1489, 1437, 1276, 1091, 1027, 965, 848, 783, 738, 691, 643, 585, 486; δ_{P} (CD_2Cl_2) 13.41 (dd, $^2J(\text{PP}) = 29.3$ and 7.3 Hz, $\text{Ph}_2\text{P}=\text{N}$), 30.40 (dd, $^3J(\text{PP}) = 7.3$ Hz, $^2J(\text{PP}) = 7.3$ Hz, Ph_2P), 52.87 (dd, $^2J(\text{PP}) = 29.3$ Hz, $^3J(\text{PP}) = 7.3$ Hz, $(\text{EtO})_2\text{P}=\text{S}$); δ_{H} (CD_2Cl_2) 1.02 (d, 3H, $^3J(\text{HH}) = 7.0$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.07 (d, 3H, $^3J(\text{HH}) = 6.7$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.22 (t, 3H, $^3J(\text{HH}) = 7.2$ Hz, OCH_2CH_3), 1.43 (t, 3H, $^3J(\text{HH}) = 7.0$ Hz, OCH_2CH_3), 2.08 (s, 3H, CH_3), 2.53 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.42 and 4.25 (m, 1H each, PCH_2P), 4.10 (m, 4H, OCH_2), 5.13 and 5.38 (d, 1H each, $^3J(\text{HH}) = 5.9$ Hz, CH of *p*-cymene), 5.30 and 5.45 (d, 1H each, $^3J(\text{HH}) = 6.3$ Hz, CH of *p*-cymene), 7.25-7.63 (m, 20H, Ph); δ_{C} (CD_2Cl_2) 15.96 (d, $^3J(\text{CP}) = 8.4$ Hz, OCH_2CH_3), 16.29 (d, $^3J(\text{CP}) = 7.8$ Hz, OCH_2CH_3), 18.30 (s, CH_3), 22.00 and 22.31 (s, $\text{CH}(\text{CH}_3)_2$), 26.35 (dd, $^1J(\text{CP}) = 58.9$ and 15.0 Hz, PCH_2P), 30.68 (s, $\text{CH}(\text{CH}_3)_2$), 64.42 (d, $^2J(\text{CP}) = 8.4$ Hz, OCH_2), 64.98 (d, $^2J(\text{CP}) = 7.2$ Hz, OCH_2), 89.13 (s, CH of *p*-cymene), 89.55 (d, $^2J(\text{CP}) = 4.2$ Hz, CH of *p*-cymene), 89.92 (d, $^2J(\text{CP}) = 3.6$ Hz, CH of *p*-cymene), 93.18 (d, $^2J(\text{CP}) = 4.8$ Hz, CH of *p*-cymene), 102.43 and 112.33 (s, C of *p*-cymene), 126.96-136.57 (m, Ph).