Supplementary Material (ESI) for Chemical Communications

ELECTRONIC SUPPLEMENTARY INFORMATION

$[Ru(\eta^3\text{-}2\text{-}C_3H_4Me)(CO)(dppf)][SbF_6]$: A mononuclear $16e^-$ ruthenium(II) catalyst for propargylic substitution and isomerization of $HC{\equiv}CCPh_2(OH)$

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Experimental Section

General methods. The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification with the exception of compound [RuCl(η^3-2-C_3H_4Me)(CO)(dppf)] (**1**) which was prepared by following the method reported in the literature.[1] Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C, H and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. The conductivities were measured at room temperature, in *ca.* 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. NMR spectra were recorded on a Bruker DPX300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds reported in this paper. GC measurements were made on a Hewlett-Packard HP6890 equipment using a HP-INNOWAX cross-linked polyethyleneglycol (30 m, 250 μm) or Supelco Beta-Dex^{TM} 120 (30 m, 250 μm) column. GC/MS measurements were performed on a Agilent 6890N equipment coupled to a 5973 mass detector (70eV electron impact ionization) using a HP-1MS column.

Synthesis of [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (2). A solution of complex [RuCl(η^3-2-C_3H_4Me)(CO)(dppf)] (**1**) (0.774 g, 1 mmol) in dichloromethane (50 cm^3) was treated with $AgSbF_6$ (351 mg, 1 mmol) and stirred for 15 min at room temperature in the absence of light. The AgCl formed was then filtered off (Kieselguhr) and the resulting solution evaporated to dryness to afford a yellow solid which was washed with diethyl ether (3 x 50 cm^3) and vacuum-dried. Yield: 0.945 g, 97% (Found: C, 47.92; H, 3.71. $RuFeC_{39}H_{35}F_6P_2OSb$ requires C, 48.08; H, 3.62%). Conductivity (acetone, 20°C) 113.4 Ω^{-1} cm^2 mol^{-1}. ν/cm^{-1} (CO) 1944s (KBr). δ_P (CD_2Cl_2) 39.79 (s); δ_H (CD_2Cl_2) 1.26 (s, 2 H, CH$H_{(anti)}$), 2.21 (s, 3 H, CH_3), 3.79 (s, 2 H, CH$H_{(syn)}$), 4.31, 4.51, 4.69 and 4.93 (br, 2 H each, C_5H_4), 7.10-7.70 (m, 20 H, Ph); δ_C (CD_2Cl_2) 26.07 (s, CH_3), 60.87 (m, CH_2), 72.96, 73.18, 75.16 and 75.47 (br, CH of C_5H_4), 81.24 (d, ^1J(C,P) = 48.8 Hz, C of C_5H_4), 121.72 (s, C), 127.80-135.50 (m, Ph), 205.01 (t, ^2J(C,P) = 16.8 Hz, CO); MS (FAB) *m/z* 739 [M^+], 655 [M^+ - CO - C_3H_4Me].

Synthesis of [Ru(η^3-2-C_3H_4Me)(CO)(NCMe)(dppf)][SbF_6] (3). A solution of complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**2**) (0.974 g, 1 mmol) in a dichloromethane/acetonitrile mixture (50 cm^3; 1:1 v/v) was stirred at room temperature for 4 h. The resulting solution was then evaporated to dryness to afford a yellow solid which was washed with diethyl ether (3 x 50 cm^3) and vacuum-dried. Yield: 0.924 g, 91% (Found: C, 48.31; H, 3.42; N, 1.31. $RuFeC_{41}H_{38}F_6P_2NOSb$ requires C, 48.50; H, 3.77; N, 1.38%). Conductivity (acetone, 20°C) 120.4 Ω^{-1} cm^2 mol^{-1}. ν/cm^{-1} (CO) 1959s, (CN) 2291w (KBr). δ_P (CD_2Cl_2) 39.30 (s); δ_H (CD_2Cl_2) 1.25 (s, 3 H, $NCCH_3$), 1.66 (s, 2 H, $CH\mathit{H}_{(anti)}$), 2.28 (s, 3 H, CH_3), 3.58 (s, 2 H, $CH\mathit{H}_{(syn)}$), 4.38, 4.55, 4.73 and 4.86 (br, 2 H each, C_5H_4), 7.40-7.70 (m, 20 H, Ph); δ_C (CD_2Cl_2) 2.19 (s, $NC\mathit{C}H_3$), 25.39 (s, CH_3), 55.58 (m, CH_2), 72.73, 72.92, 74.87 and 75.04 (br, CH of C_5H_4), 81.36 (d, ^1J(C,P) = 48.5 Hz, C of C_5H_4), 119.59 (s, C), 124.26 (s, $N\mathit{C}CH_3$), 128.65-135.95 (m, Ph), 205.02 (t, ^2J(C,P) = 16.2 Hz, CO).

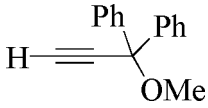
Synthesis of [Ru(η^3-2-C_3H_4Me)$(CO)_2$(dppf)][SbF_6] (4). Carbon monoxide was bubbled at room temperature through a solution of [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**2**) (0.974 g, 1 mmol) in dichloromethane (50 cm^3) for 1.5 h. The resulting solution was then evaporated to dryness to afford a yellow solid which was washed with diethyl ether (3 x 50 cm^3) and vacuum-dried. Yield: 0.952 g, 95% (Found: C, 47.57; H, 3.31. $RuFeC_{40}H_{35}F_6O_2P_2Sb$ requires C, 47.93; H, 3.52%). Conductivity (acetone, 20°C) 115.7 Ω^{-1} cm^2 mol^{-1}. ν/cm^{-1} (CO) 1998s and 2058s (KBr). δ_P (CD_2Cl_2) 33.82 (s); δ_H (CD_2Cl_2) 2.26 (s, 2 H, $CH\mathit{H}_{(anti)}$), 2.38 (s, 3 H, CH_3), 3.31 (s, 2 H, $CH\mathit{H}_{(syn)}$), 4.59, 4.79, 4.83 and 4.86 (br, 2 H each, C_5H_4), 7.25-7.70 (m, 20 H, Ph); δ_C (CD_2Cl_2) 24.36 (s, CH_3), 46.75 (m, CH_2), 73.67, 73.91, 75.15 and 75.43 (br, CH of C_5H_4), 79.83 (d, ^1J(C,P) = 53.0 Hz, C of C_5H_4), 118.83 (s, C), 129.00-136.50 (m, Ph), 196.91 (t, ^2J(C,P) = 14.2 Hz, CO), 201.13 (t, ^2J(C,P) = 16.1 Hz, CO).

Synthesis of [Ru(η^3-2-C_3H_4Me)(CO)(CNBz)(dppf)][SbF_6] (5). A solution of complex [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**2**) (0.974 g, 1 mmol) in dichloromethane (30 cm^3) was treated, at room temperature, with benzyl isocyanide (1.22 cm^3, 10 mmol) for 2 h. The resulting solution was then evaporated to dryness to afford a yellow solid which was washed with diethyl ether (3 x 50 cm^3) and vacuum-

dried. Yield: 0.993 g, 91% (Found: C, 51.47; H, 3.92; N, 1.31. $RuFeC_{47}H_{42}F_6P_2NOSb$ requires C, 51.72; H, 3.88; N, 1.28%). Conductivity (acetone, 20°C) 116.1 Ω^{-1} cm^2 mol^{-1}. ν/cm^{-1} (CO) 1982s, (CN) 2202s (KBr). δ_P (CD_2Cl_2) 37.31 (s); δ_H (CD_2Cl_2) 1.90 (s, 2 H, $CH_{(anti)}H$), 2.29 (s, 3 H, CH_3), 3.19 (s, 2 H, $CH_{(syn)}H$), 4.07, 4.53, 4.61, 4.67 and 4.70 (br, 2 H each, C_5H_4 and NCH_2), 7.00-7.60 (m, 25 H, Ph); δ_C (CD_2Cl_2) 25.53 (s, CH_3), 48.32 (m, CH_2), 48.91 (s, NCH_2), 72.88, 73.76, 75.68 and 77.99 (br, CH of C_5H_4), 81.34 (d, ^1J(C,P) = 50.2 Hz, C of C_5H_4), 116.95 (s, C), 127.15-138.30 (m, Ph and CN), 204.49 (t, ^2J(C,P) = 15.4 Hz, CO).

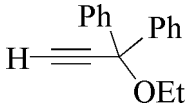
General procedure for the catalytic propargylic substitution reactions. In a Schlenk tube, [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**2**) (0.049 g, 0.05 mmol) and 1,1-diphenyl-2-propyn-1-ol (0.208 g, 1 mmol) were dissolved, under inert atmosphere, in the corresponding alcohol (1 cm^3) and the reaction mixture stirred at 75ºC for the indicated time. The course of the reaction was monitored by GC. Column chromatography (SiO_2) using a mixture EtOAc/hexane (1/30) as eluent afforded ethers **6** as pale yellow oils.

(1,1-diphenyl-2-propynyl)methylether (6a)[2]



Time = 4 h; Yield: 0.167 g, 75%; ν/cm^{-1} (C≡C) 2114w, (≡C-H) 3301m (Nujol); δ_H ($CDCl_3$) 3.02 (s, 1 H, ≡CH), 3.56 (s, 3 H, OCH_3), 7.41-7.81 (m, 10 H, Ph); δ_C ($CDCl_3$) 52.50 (s, OCH_3), 77.84 (s, ≡CH), 80.78 (s, ≡C), 83.08 (s, *C*Ph_2), 126.74, 127.81 and 128.26 (s, CH of Ph), 143.04 (s, C of Ph); MS (EI 70eV) *m/z* 222 [M^+], 207 [M^+ - Me], 191 [M^+ - OMe], 165 [M^+ - OMe - C≡CH], 145 [M^+ - Ph].

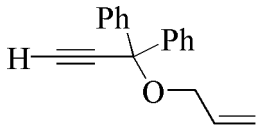
(1,1-diphenyl-2-propynyl)ethylether (6b)[3]



Time = 6 h; Yield: 0.170 g, 72%; ν/cm^{-1} (C≡C) 2109w, (≡C-H) 3286m (Nujol); δ_H ($CDCl_3$) 1.29 (t, 3 H, ^3J(H,H) = 7.1 Hz, CH_3), 2.95 (s, 1 H, ≡CH), 3.57 (q, 2 H, ^3J(H,H) = 7.1 Hz, OCH_2), 7.28-7.70 (m, 10 H, Ph); δ_C ($CDCl_3$) 15.37 (s, CH_3), 65.76 (s, OCH_2), 77.50 (s, ≡CH), 81.01 (s, ≡C), 83.15 (s, *C*Ph_2), 126.59, 127.89 and 128.31

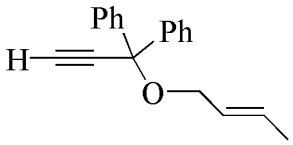
(s, CH of Ph), 143.51 (s, C of Ph); MS (EI 70eV) *m/z* 236 [M^+], 207 [M^+ - Et], 191 [M^+ - OEt], 159 [M^+ - Ph].

(1,1-diphenyl-2-propynyl)allylether (6c)[4]



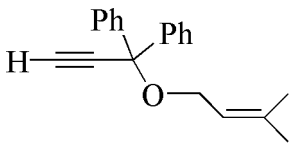
Time = 5 h; Yield: 0.216 g, 87%; ν/cm^{-1} (C=C) 1664m, (C≡C) 2111w, (≡C-H) 3307m (Nujol); δ_H ($CDCl_3$) 2.94 (s, 1 H, ≡CH), 4.11 (d, 2 H, ^3J(H,H) = 4.8 Hz, OCH_2), 5.23 (d, 1 H, ^3J(H,H) = 10.3 Hz, $=CH_2$), 5.43 (d, 1 H, ^3J(H,H) = 17.4 Hz, $=CH_2$), 6.05 (ddt, 1 H, ^3J(H,H) = 17.4, 10.3 and 4.8 Hz, =CH), 7.28-7.66 (m, 10 H, Ph); δ_C ($CDCl_3$) 65.91 (s, OCH_2), 77.59 (s, ≡CH), 80.03 (s, ≡C), 83.23 (s, *C*Ph_2), 116.12 (s, $=CH_2$), 126.56, 127.72 and 128.19 (s, CH of Ph), 134.73 (s, =CH), 143.11 (s, C of Ph); MS (EI 70eV) *m/z* 248 [M^+], 207 [M^+ - $CH_2CH=CH_2$], 191 [M^+ - $OCH_2CH=CH_2$], 165 [M^+ - $OCH_2CH=CH_2$ - C≡CH].

(*E*)-(1,1-diphenyl-2-propynyl)-2-butenylether (6d)[4]



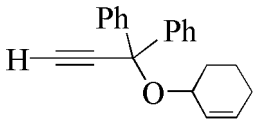
Time = 8 h; Yield: 0.210 g, 80%; ν/cm^{-1} (C=C) 1660m, (C≡C) 2112w, (≡C-H) 3306m (Nujol); δ_H ($CDCl_3$) 1.75 (d, 3 H, ^3J(H,H) = 5.8 Hz, CH_3), 2.91 (s, 1 H, ≡CH), 4.00 (d, 2 H, ^3J(H,H) = 5.1 Hz, OCH_2), 5.51 (dt, 1 H, ^3J(H,H) = 15.1 and 5.1 Hz, =C*H*CH_2), 5.72 (dq, 1 H, ^3J(H,H) = 15.1 and 5.8 Hz, =C*H*CH_3), 7.28-7.61 (m, 10 H, Ph); δ_C ($CDCl_3$) 18.31 (s, CH_3), 66.28 (s, OCH_2), 76.09 (s, ≡CH), 80.43 (s, ≡C), 83.87 (s, *C*Ph_2), 127.06, 128.09 and 128.60 (s, CH of Ph), 128.71 and 132.85 (s, =CH), 143.67 (s, C of Ph); MS (EI 70eV) *m/z* 262 [M^+], 207 [M^+ - $CH_2CH=CHMe$], 191 [M^+ - $OCH_2CH=CHMe$], 165 [M^+ - $OCH_2CH=CHMe$ - C≡CH].

(1,1-diphenyl-2-propynyl)-3-methyl-2-butenylether (6e)



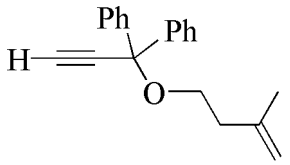
Time = 24 h; Yield: 0.188 g, 68%; ν/cm^{-1} (C=C) 1662m, (C≡C) 2107w, (≡C-H) 3286m (Nujol); δ_H ($CDCl_3$) 1.72 and 1.79 (s, 3 H each, CH_3), 2.93 (s, 1 H, ≡CH), 4.07 (d, 2 H, ^3J(H,H) = 6.8 Hz, OCH_2), 5.44 (t, 1 H, ^3J(H,H) = 6.8 Hz, =CH), 7.28-7.63 (m, 10 H, Ph); δ_C ($CDCl_3$) 18.09 and 25.81 (s, CH_3), 61.84 (s, OCH_2), 77.00 (s, ≡CH), 79.88 (s, ≡C), 83.51 (s, *C*Ph_2), 120.96 (s, =CH), 126.65, 127.68 and 128.23 (s, CH of Ph), 136.69 (s, =C), 143.24 (s, C of Ph); MS (EI 70eV) *m/z* 276 [M^+], 261 [M^+ - Me], 246 [M^+ - 2 Me], 199 [M^+ - Ph], 191 [M^+ - $OCH_2CH{=}CMe_2$], 165 [M^+ - $OCH_2CH{=}CMe_2$ - C≡CH].

(1,1-diphenyl-2-propynyl)-2-cyclohexenylether (6f)



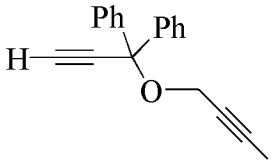
Time = 24 h; Yield: 0.161 g, 56%; ν/cm^{-1} (C=C) 1648m, (C≡C) 2129w, (≡C-H) 3284m (Nujol); δ_H ($CDCl_3$) 1.54-2.06 (m, 6 H, CH_2), 2.93 (s, 1 H, ≡CH), 4.04 (br, 1 H, OCH), 5.83 (m, 2 H, =CH), 7.29-7.65 (m, 10 H, Ph); δ_C ($CDCl_3$) 19.59, 25.19 and 30.21 (s, CH_2), 69.47 (s, OCH), 70.57 (s, ≡CH), 79.57 (s, ≡C), 84.52 (s, *C*Ph_2), 127.10, 127.59 and 127.92 (s, CH of Ph), 129.43 and 130.13 (s, =CH), 144.00 (s, C of Ph); MS (EI 70eV) *m/z* 288 [M^+], 207 [M^+ - C_6H_9], 191 [M^+ - OC_6H_9], 165 [M^+ - OC_6H_9 - C≡CH].

(1,1-diphenyl-2-propynyl)-3-methyl-3-butenylether (6g)



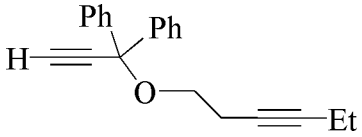
Time = 24 h; Yield: 0.246 g, 89%; ν/cm^{-1} (C=C) 1649m, (C≡C) 2110w, (≡C-H) 3286m (Nujol); δ_H ($CDCl_3$) 1.80 (s, 3 H, CH_3), 2.46 (t, 2 H, ^3J(H,H) = 6.8 Hz, CH_2), 2.93 (s, 1 H, ≡CH), 3.67 (t, 2 H, ^3J(H,H) = 6.8 Hz, OCH_2), 4.85 (br, 2 H, $=CH_2$), 7.28-7.70 (m, 10 H, Ph); δ_C ($CDCl_3$) 23.21 (s, CH_3), 38.52 (s, CH_2), 63.58 (s, OCH_2), 77.90 (s, ≡CH), 80.31 (s, ≡C), 83.91 (s, *C*Ph_2), 112.09 (s, $=CH_2$), 127.07, 128.11 and 128.62 (s, CH of Ph), 143.49 (s, =C), 143.87 (s, C of Ph); MS (EI 70eV) *m/z* 276 [M^+], 261 [M^+ - Me], 207 [M^+ - $CH_2CH_2CMe{=}CH_2$], 191 [M^+ - $OCH_2CH_2CMe{=}CH_2$], 165 [M^+ - $OCH_2CH_2CMe{=}CH_2$ - C≡CH].

(1,1-diphenyl-2-propynyl)-2-butynylether (6h)



Time = 11 h; Yield: 0.211 g, 81%; ν/cm^{-1} (C≡C) 2111w and 2241w, (≡C-H) 3280m (Nujol); δ_H ($CDCl_3$) 1.87 (t, 3 H, ^5J(H,H) = 2.3 Hz, CH_3), 2.94 (s, 1 H, ≡CH), 4.17 (q, 2 H, ^5J(H,H) = 2.3 Hz, OCH_2), 7.25-7.61 (m, 10 H, Ph); δ_C ($CDCl_3$) 4.25 (s, CH_3), 54.36 (s, OCH_2), 75.77, 77.11 and 82.51 (s, ≡C), 78.63 (s, ≡CH), 83.04 (s, *C*Ph_2), 127.15, 128.33 and 128.67 (s, CH of Ph), 142.86 (s, C of Ph); MS (EI 70eV) *m/z* 260 [M^+], 245 [M^+ - Me], 183 [M^+ - Ph], 165 [M^+ - $OCH_2C{\equiv}CMe$ - C≡CH].

(1,1-diphenyl-2-propynyl)-3-hexynylether (6i)



Time = 10 h; Yield: 0.259 g, 90%; ν/cm^{-1} (C≡C) 2135w and 2250w, (≡C-H) 3282m (Nujol); δ_H ($CDCl_3$) 1.15 (t, 3 H, ^3J(H,H) = 7.4 Hz, CH_3), 2.18 and 2.57 (m, 2 H each, CH_2), 2.92 (s, 1 H, ≡CH), 3.63 (t, 2 H, ^3J(H,H) = 7.3 Hz, OCH_2), 7.28-7.62 (m, 10 H, Ph); δ_C ($CDCl_3$) 12.68 and 20.66 (s, CH_2), 14.66 (s, CH_3), 64.13 (s, OCH_2), 76.50, 80.43 and 83.64 (s, ≡C), 78.05 (s, ≡CH), 83.13 (s, *C*Ph_2), 127.04, 128.17 and 128.62 (s, CH of Ph), 143.56 (s, C of Ph); MS (EI 70eV) *m/z* 288 [M^+], 273 [M^+ - Me], 191 [M^+ - $OCH_2CH_2C{\equiv}CEt$], 165 [M^+ - $OCH_2CH_2C{\equiv}CEt$ - C≡CH].

Procedure for the isomerization of 1,1-diphenyl-2-propyn-1-ol into 3,3-diphenyl-2-propen-1-al (7). In a Schlenk tube, [Ru(η^3-2-C_3H_4Me)(CO)(dppf)][SbF_6] (**2**) (0.049 g, 0.05 mmol) and 1,1-diphenyl-2-propyn-1-ol (0.208 g, 1 mmol) were dissolved, under inert atmosphere, in undistilled THF (1 cm^3) and the reaction mixture stirred at 75ºC for 1.5 h. The course of the reaction was monitored by GC. Column chromatography (SiO_2) using a mixture EtOAc/hexane (1/5) as eluent afforded **7** as pale yellow oil.[5] Yield: 0.198 g, 95%; ν/cm^{-1} (C=C) 1650m, (C=O) 1663s (Nujol); δ_H ($CDCl_3$) 6.63 (d, 1 H, ^3J(H,H) = 7.9 Hz, =CH), 7.28-7.66 (m, 10 H, Ph), 9.56 (d, 1 H, ^3J(H,H) = 7.9 Hz, CHO); δ_C ($CDCl_3$) 125.92, 127.24, 128.26, 128.31, 129.43, 130.47

and 130.72 (s, =CH and CH of Ph), 136.63 and 139.67 (s, C of Ph), 162.26 (s, =C), 193.54 (s, CHO); MS (EI 70eV) *m/z* 207 [M^+], 178 [M^+ - CHO], 165 [M^+ - CHCHO], 102 [M^+ - CHO - Ph], 89 [M^+ - CHCHO - Ph].

Crystal data for [Ru(η^3-2-C_3H_4Me)(CO)(CNBz)(dppf)][SbF_6] (5):

$RuFeC_{47}H_{42}F_6P_2NOSb$, M = 1091.43, yellow prism (0.297 x 0.132 x 0.132 mm), monoclinic, $P2_1/c$, a = 10.884(11) Å, b = 30.69(6) Å, c = 13.706(4) Å, α = 90º, β = 104.55(3)º, γ = 90º, V = 4431(10) Å^3, Z = 4, D_{calc} = 1.636 g cm^{-3}, μ(Mo-Kα) = 1.399 mm^{-1}, Enraf Nonius CAD4 diffractometer, Mo-Kα radiation (λ = 0.71073 Å). 9152 reflections collected, 8687 unique (R_{int} = 0.0610). R_1 = 0.0617; wR_2 = 0.1326 both for $I > 2\sigma(I)$. CCDC 245208.

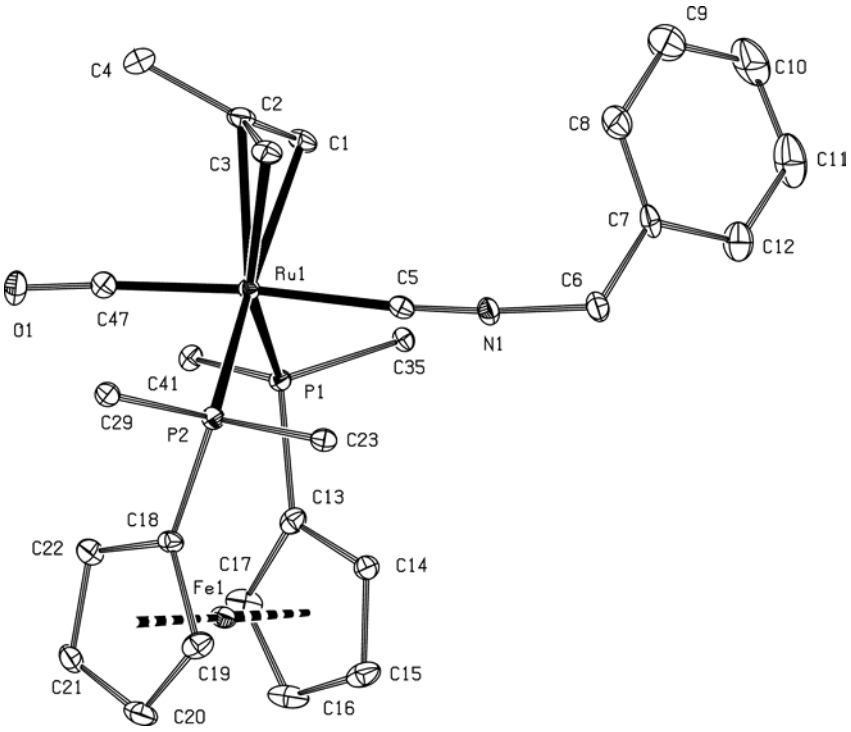


Fig.S1 Molecular structure of [Ru(η^3-2-C_3H_4Me)(CO)(CNBz)(dppf)][SbF_6] (**5**). SbF_6^- anion, hydrogen atoms and phenyl groups of the dppf ligand have been omitted. Selected bond distances (Å) and angles (°): Ru-C(1) 2.255(9); Ru-C(2) 2.229(9); Ru-C(3) 2.282(9); Ru-C(5) 2.022(9); Ru-C(47) 1.891(10); Ru-P(1) 2.381(3); Ru-P(2) 2.362(3); C(1)-C(2) 1.402(13); C(2)-C(3) 1.378(13); C(47)-O(1) 1.114(10); C(5)-N(1) 1.156(10); Ru-C(47)-O(1) 176.0(8); C(47)-Ru-C(5) 173.4(3); Ru-C(5)-N(1) 175.4(8); C(1)-C(2)-C(3) = 121.6(9).

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