Supporting Information

Synthesis and characterisation of tetramethylfulvene complexes of ruthenium

Andrea Rodríguez-Bárzano, A. John Blacker and Patrick C. McGowan

Synthesis of [RuCl(η^6-$C_5Me_4CH_2$)(PhCOCCOPh)] (1): $[RuCp^*Cl_2]_2$ (0.2 g, 0.65 mmol) was dissolved in dry dichloromethane (50 ml) and dibenzoylmethane (0.15 g, 0.65 mmol) and triethylamine (0.18 ml, 1.3 mmol) were added. The mixture was stirred at room temperature overnight, the solvent evaporated and the brown residue treated with dichloromethane and diethyl ether. Triethylamine hydrochloride precipitated. After filtration, the filtrate was evaporated and the residue washed with pentane and recrystallised in a mixture of dichloromethane and hexane at -20ºC (0.142 g, 0.29 mmol, 44%). **^{1}H NMR** ($CDCl_3$, 300.13 MHz, 299.9 K): δ (ppm) 7.96 [m, 5H, $CH(COC_6\underline{H}_5)_2$], 7.42 [m, 5H, $CH(COC_6\underline{H}_5)_2$], 6.62 [s, 1H, $C\underline{H}(COC_6H_5)_2$], 5.42 [s, 1H, $C_5(CH_3)_4C\underline{H}_2$], 5.01 [s, 1H, $C_5(CH_3)_4C\underline{H}_2$], 1.98 [s, 3H, $C_5(C\underline{H}_3)_4CH_2$], 1.78 [s, 3H, $C_5(C\underline{H}_3)_4CH_2$], 1.70 [s, 3H, $C_5(C\underline{H}_3)_4CH_2$], 1.54 [s, 3H, $C_5(C\underline{H}_3)_4CH_2$]; **^{13}C{^{1}H} NMR** ($CDCl_3$, 125.88 MHz, 300.0 K): δ (ppm) 181.8 [$CH(\underline{C}OC_6H_5)_2$], 180.5 [$CH(\underline{C}OC_6H_5)_2$], 139.5 [Quaternary C of $CH(CO\underline{C}_6H_5)_2$], 139.0 [Quaternary C of $CH(CO\underline{C}_6H_5)_2$], 130.9 [$CH(CO\underline{C}_6H_5)_2$], 130.8 [$CH(CO\underline{C}_6H_5)_2$], 128.2 [$CH(CO\underline{C}_6H_5)_2$], 128.1 [$CH(CO\underline{C}_6H_5)_2$], 127.2 [$CH(CO\underline{C}_6H_5)_2$], 127.1 [$CH(CO\underline{C}_6H_5)_2$], 103.0 [$\underline{C}_5(CH_3)_4CH_2$], 101.5 [$\underline{C}_5(CH_3)_4CH_2$], 100.3 [$\underline{C}_5(CH_3)_4CH_2$], 97.0 [$\underline{C}_5(CH_3)_4CH_2$], 95.0 [$\underline{C}_5(CH_3)_4CH_2$], 93.8 [$\underline{C}H(COC_6H_5)_2$], 80.5 [$C_5(CH_3)_4\underline{C}H_2$], 8.8 [$C_5(\underline{C}H_3)_4CH_2$], 8.3 [$C_5(\underline{C}H_3)_4CH_2$], 8.2 [$C_5(\underline{C}H_3)_4CH_2$], 7.6 [$C_5(\underline{C}H_3)_4CH_2$]; **ES MS (+):** m/z 459.09 $[M\text{-}Cl]^+$; **Elemental Analysis Calculated (%) for $C_{25}H_{25}ClO_2Ru$ (493.77 g mol^{-1}):** C 60.8; H 5.1; Cl 7.2%. **Found:** C 60.3; H 5.2; Cl 6.7%.

Synthesis of [$RuCl_3$(η^6-$C_5Me_4CH_2$)][RuCp*($C_6H_5CH_3$)] (2): $[RuCp^*Cl_2]_2$ (0.15 g, 0.5 mmol) was dissolved in dry toluene (50 ml) and dibenzoylmethane (0.11 g, 0.5 mmol) and triethylamine (70 µl, 0.5 mmol) were added. The mixture was stirred at reflux for two hours, filtered, the solvent evaporated and the orange residue treated with dichloromethane and diethyl ether, from where dark orange crystals formed at -20ºC in low yield. **^{1}H NMR** ($CDCl_3$, 500.23 MHz, 300.1 K): δ (ppm) 6.55 [br. s, 2H, $C_6\underline{H}_5CH_3$], 6.45 [br. s, 1H, $C_6\underline{H}_5CH_3$], 6.16 [br. s, 2H, $C_6\underline{H}_5CH_3$], 5.30 [s, 1H, $C_5(CH_3)_4C\underline{H}_2$], 5.13 [s, 1H, $C_5(CH_3)_4C\underline{H}_2$], 2.35 [s, 3H, $C_6H_5C\underline{H}_3$], 2.11 [s, 15H, $C_5(C\underline{H}_3)_5$], 1.86 [s, 6H, $C_5(C\underline{H}_3)_4CH_2$], 1.56 [s, 6H, $C_5(C\underline{H}_3)_4CH_2$]; **ES MS (+):** m/z 329.1 $[C_{17}H_{23}Ru]^+$. **Elemental Analysis Calculated (%) for $C_{27}H_{37}Cl_3Ru_2$ (669.93 g mol^{-1}):** C 48.4; H 5.6; Cl 15.9%. **Found:** C 48.2; H 5.6; Cl 16.0%.

Table S1 Crystallographic data for compounds **1** and **2**.

Compound	**1**	**2**
formula	$C_{25}H_{25}ClO_2Ru$	$C_{27}H_{37}Cl_3Ru_2$
formula weight [g mol^{-1}]	493.97	670.06
crystal system	Orthorhombic	Monoclinic
space group	$P2_12_12_1$	$P2_1/c$
a [Å]	7.432(6)	8.7750(14)
b [Å]	11.285(2)	24.948(4)
c [Å]	25.701(12)	14.7032(18)
α [°]	90	90
β [°]	90	124.722(7)
γ [°]	90	90
V [Å^3]	2155(2)	2645.6(7)
Z	4	4
T [K]	150(2)	150(2)
ρ_{calcd} [mg m^{-3}]	1.522	1.682
μ [mm^{-1}]	0.87	1.459
transmission factors [max/min]	1 and 0.93834	0.8799 and 0.7792
crystal size [mm]	0.18 x 0.15 x 0.09	0.18 x 0.15 x 0.09
θ_{max} [°]	25.03	33.23
total reflns	31477	34450
unique reflns, R_{int}	3808, 0.148	9748, 0.1168
reflns with $F^2 > 2\sigma(F^2)$	3668	5806
no. of parameters	266	299
R_1, wR_2 [$F^2 > 2\sigma(F^2)$]	0.0843, 0.1642	0.069, 0.1434
R_1, wR_2 (all data)	0.0888, 0.1667	0.1191, 0.1706
GOF (S)	1.21	1.019
largest difference peak and hole [e Å^{-3}]	0.881 and -1.064	1.511 and -1.727