ORGANOMETALLICS
Organometallics, 1998, 17(6), 1002-1003, DOI:10.1021/om971033z

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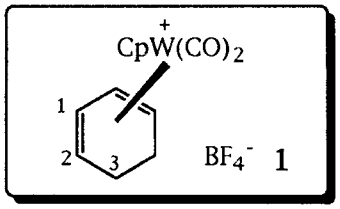
(I) General Procedure for the Synthesis of Tungsten-η(1,2,4)-σ,π–Species. Synthesis of **3** and **5**. To **1** (472 mg, 1.00 mmol) in a THF solution (20 mL) was added a THF solution of PhMgBr (2.0 M, 2.5 mL, 5.00 mmol) at -78^{0}C; and the solution was stirred for 2 h before slow addition of water (5 mL). The solution was concentrated to ca. 10 mL and the organic layer was extracted with diethyl ether (3 x 10 mL). The ether extract was concentrated and chromatographed through a silica column (diethyl ether/hexane=1/1) to yield two yellow band that yielded **3** (R_f = 0.90, 32 mg, 0.07 mmol, 7%) and **5** (R_f = 0.15, 264 mg, 0.54 mmol, 54%) respectively.

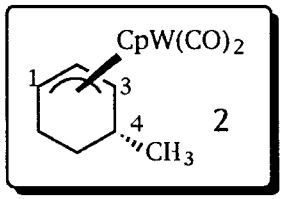
(II) Spectral Data for Compounds 1-11.

(1) Spectral data for $CpW(CO)_2(\eta^4$-Cyclohexadiene)BF_4 **1**



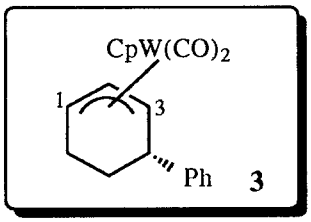
IR (CD_2Cl_2): $\upsilon_{W\text{-}CO}$ 2013 (s), 1972 (s) cm^{-1}; ^{1}H NMR (CD_3CN, 300 MHz): δ 5.72 (5H, s, Cp), 5.63 (2H, m, =CH^2), 3.95 (2H, m, 2H, =CH^1), 2.50 (2H, d, J = 6.8 Hz, CH^3), 1.98 (2H, d, J = 6.8 Hz, CH$^{3'}$); ^{13}C NMR (CD_3CN, 75 MHz): δ 203.7 (2 W-CO), 91.5 (Cp), 78.0 and 69.9 (C^1+C^2), 24.9. Anal. Calcd. for $C_{13}H_{13}WO_2BF_4$: C, 33.09; H, 2.79. Found: C, 33.15 ; H, 2.67.

(2) Spectral data for **2**



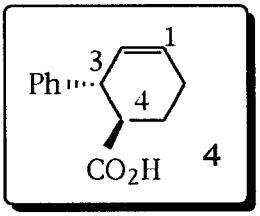
IR (CH_2Cl_2) $\upsilon_{W\text{-}CO}$ = 1929 (vs); 1843 (vs) cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) 5.37 (s, 5H, Cp), 3.81 (t, J = 7.1Hz, 1H, C_2H), 3.52 (dd, J = 7.1, 2.4 Hz, 1H, C_3H), 3.40 (m, 1H, C_1H), 2.07 (m, 1H, C_6H'), 1.87 (m, 1H, C_4H), 1.50 (ddd, J =14,4, 6.3, 2.9 Hz, 1H, C_6H), 1.16 (d, J = 6.9 Hz, 3H, Me), 0.70 (dd, J = 12.3, 6.0 Hz, 1H, C_5H'), 0.53 (m, 1H, C_5H); ^{13}C NMR ($CDCl_3$, 75 MHz): 224.1; 223.2 (2 W-CO), 90.8 (Cp), 51.2 (C_2), 49.6 (C_1), 46.3 (C_3), 26.5, 26.2 (C_4), 24.6 (Me), 17.8; Mass (EI^+; 75eV/m) : 400 (M^+); Anal. Calcd. $C_{14}H_{16}WO_2$: C, 42.03; H, 4.03. Found: C, 42.56; H, 3.85.

(3) Spectral Data for compound **3**



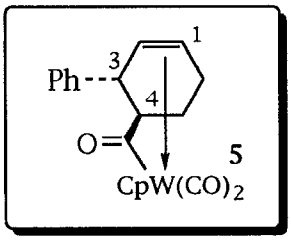
IR (CH_2Cl_2): $\upsilon_{W\text{-}CO}$ = 1932 (vs); 1845 (vs) cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) 7.44-7.16 (m, 5H, Ph), 5.41 (s, 5H, Cp), 4.12 (t, J = 6.9Hz, 1H, C_2H), 3.70 (dd, J = 6.6, 2.0 Hz, 1H, C_3H), 3.46 (m, 1H, C_1H), 3.01 (dd, J_{34} = 6.6, 2.0 Hz, 1H, C_4H), 2.22 (m, 1H, C_6H'), 1.67 (m, 1H, C_6H), 0.99 (dd, J = 14.1, 6.0 Hz, 1H, C_5H'), 0.86 (m, 1H, C_5H); ^{13}C NMR ($CDCl_3$, 75 MHz): 224.5, 222.9 (2 W-CO), 143.6, 128.8, 126.6 and 125.4, (Ph), 91.1 (Cp), 51.2 (C_2), 46.6 (C_1), 45.1 (C_3), 32.1 (C_4), 26.0 + 18.7 (C_5+C_6); Mass (EI; 75 ev): 462 (M^+). Anal. Calcd for $C_{19}H_{18}WO_2$: C, 49.37; H, 3.93. Found: C, 49.10; H, 3.88.

(4) Synthesis of Compound **4**



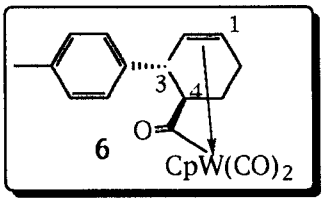
IR (CH_2Cl_2): $\upsilon_{C=O}$: 1707 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.31 - 7.19 (5H, Ph), 5.87 (ddd, J=10.0, 3.6, 2.4 Hz, 1H, C^1H), 5.65 (ddd, J =10.0, 2.5, 1.9 Hz, C^2H), 3.74 (ddd, J= 10.0, 2.7, 2.5 Hz, 1H, C^3H), 2.62 (ddd, J= 10.4, 10.0, 3.0 Hz, C^4H), 2.19 (m, 2H, C_5HH'), 2.04 (m, 1H, C_6H), 1.88 (m, 1H, C_6H'); ^{13}C NMR ($CDCl_3$, 75 MHz): 180.7 (CO), 143.7; 128.4; 128.1; 126.7 (Ph), 129.2 (C_2), 126.9 (C_1), 47.9 , 43.6 (C_4+C_3), 25.1 and 24.0 (C_6+C_5). HRMS Calcd. for $C_{13}H_{14}O_2$: 202.0994 Found : 202.1006

(5) Spectral Data for Compound **5**.



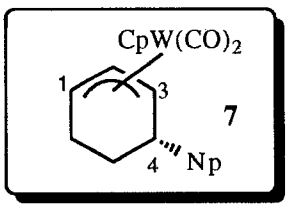
Spectral data for **5:** IR (CH_2Cl_2): $\upsilon_{W\text{-}CO}$ 1983 (s); 1845 (s), 1620 (m); ^1H NMR ($CDCl_3$, 300 MHz): δ 7.41-7.19 (5H, m, Ph), 5.22 (5H, s, Cp), 4.78 (1H, dd, J = 8.4, 2.7 Hz, CH^2), 4.45 (1H, ddd, J= 8.4, 3.0, 1.2 Hz, CH^1), 3.93 (1H, dd, J= 6.6, 2.7 Hz, CH^3) , 3.15 (1H, m, C^6H), 2.63 (1H, m, C^6H), 2.20 (1H, m, C^4H), 1.22 (2H, C^5H_2); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 273.4 (μ-CO), 224.5, 218.4 (2 W-CO), 142.8, 128.3, 128.0 and 126.3 (Ph) 90.8 (Cp), 77.8, 60.4 (C^1+C^2), 47.0, 44.1 (C^3+C^4), 24.6, 18.9. Mass (EI; 75 ev): 490 (M^+). Anal. Calcd. for $C_{20}H_{18}WO_3$: C, 49.99; H, 3.00 . Found: C, 49.44; H, 3.09.

6) Spectral data for Compound **6.**



IR (CH_2Cl_2): $\upsilon_{W\text{-}CO}$ 1986 (s), 1845 (s), 1645 (m); ^1H NMR ($CDCl_3$, 300MHz) 7.28 - 7.07 (4H, Ph), 5.22 (s, 5H, Cp), 4.78 (1H, dd, J= 8.4, 2.5 Hz, C^2H), 4.45 (1 H, ddd, $J_{45'}$= 8.4, 2.8, 1.2 Hz, C^1H), 3.89 (1H, dd, J = 3.0, 2.5 Hz, C^3H), 3.15 (1H, m, C^6H'), 2.33 (3H, s, CH_3), 2.28 (1H, m, C^6H), 2.16 (1H, m, C^6H), 1.20 (2H, m, C_5HH'); ^{13}C NMR ($CDCl_3$, 75 MHz): 274 (μ-CO), 224.7, 218.6 (2 W-CO), 139.7; 135.8; 129; 127.9 (Ph), 90.8 (5C, Cp), 78.3, 60.4 (C^1+C^2), 47.2 and 43.7 (C^4+C^3), 24.7 and 18.9 (C^5+C^6), 21.0 (Me),18.9 (C_6); Mass (EI^+; 75eV/m) 504 (M^+). Anal. Calcd. for $C_{21}H_{20}WO_3$: C, 50.02 ; H, 3.00. Found: C, 49.88; H, 50.10.

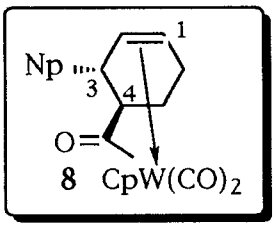
(7) Synthesis of Compound **7**



IR (CH_2Cl_2) $u_{W\text{-}CO}$ = 1931 (vs); 1844 (vs) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 8.10-7.43 (7H, m, Np), 5.46 (5H, s, Cp), 4.24 (1H, t, J = 6.9 Hz, C^2H), 3.97 (1H, dd, J= 6.9, 2.4 Hz, C^3H), 3.70 (1H, m, C^1H), 3.57 (1H, m, C^4H), 2.16 (1H, m, C^6H'), 1.70 (1H, m, C^6H), 1.19 (1H, dd, J = 14.1, 6.0 Hz C^5H'), 1.02 (1H, m, C^5H); ^{13}C NMR ($CDCl_3$, 75 MHz): 224.5; 222.9 (2 W-CO), 143.6, 134.0, 131.4, 128.8, 126.6, 125.9, 125.4, 123.7 and 123.4 (Np), 91.1 (Cp), 51.2 (C^2), 46.6

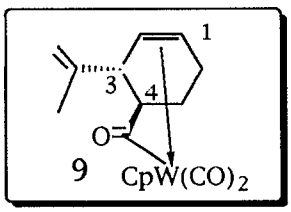
(C^1), 45.1 (C^3), 32.1 (C^4), 26.0 and 18.7 (C^6+C^5); Mass (EI^+; 75 eV/m): 512 (M^+). Anal. Calcd. for $C_{23}H_{20}WO_2$: C, 53.92 ; H, 3.94. Found: C, 53.88; H, 3.88.

(8) Spectral data for compound **8**.



IR (CH_2Cl_2): $\upsilon_{W\text{-}CO}$ 1986 (s), 1845 (s), 1625 (m); ^1H NMR ($CDCl_3$, 300 MHz): 7.90-7.39 (7H, m, Np), 5.27 (5H, s, Cp), 4.89 (1H, d, J=7.4 Hz, C^2H), 4.66 (1H, br s, 4.57 (1H, dd, J=7.2, 3.1 Hz, C^1H), 3.23 (1H, m, C^6H), 2.50 (m, 1H, C^6H), 2.33 (1H, m, C^4H'), 1.14 (2H, m, C^5HH'); ^{13}C NMR ($CDCl_3$, 75 MHz): 273.9 (μ-CO), 224.4; 218.5 (2 W-CO), 138.9; 133.8; 131.9; 128.7; 127.3; 126.2; 125.6; 125.4; 125.1; 124.8; 123.5 (Np), 90.9 (Cp), 78.7 and 58.3 (C^1+C^2), 47.2 and 40.8 (C^3+C^4), 24.6, 19.5 (C^5+C^6); Mass (EI^+; 75 eV): 540 (M^+). Anal. Calcd. for $C_{25}H_{22}WO_3$: C, 54.14; H, 4.00. Found: C, 54.09; H, 4.08.

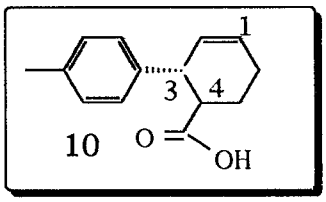
Spectral data for Compound **9**



IR (CH_2Cl_2): $\upsilon_{W\text{-}CO}$ 1985 (s), 1844 (s) and 1620 (m); ^1H NMR ($CDCl_3$, 300 MHz): 5.18 (5H, s, Cp), 5.11 (1H, s, =CH*H'*), 4.98 (1H, s, =C*H*H')), 4.65 (1H, d, J= 8.6 Hz, C^2H), 4.29 (d, J_{34}= 8.6 Hz, 1H, C^1H), 3.10 (m, 1H, C^3H'), 3.04 (m, 1H, C^6H), 1.76 (s, 3H, Me), 2.15 (m, 2H, C^6H + C^4H), 1.48 (m, 1H, C^5H), 1.20 (m, 1H,

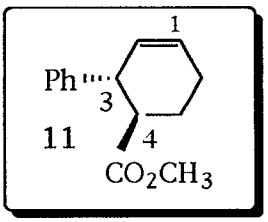
C^5H'); ^{13}C NMR ($CDCl_3$, 75 MHz): 273.6 (μ-CO), 225.0, 218.8 (2 W-CO), 147.3 (=C), 111.8 (=CH_2), 90.7 (Cp), 78.9 and 56.9 (C_1+C_2), 47.1, 45.3 (C_3+C_4), 24.0 , 23.5, 23.5 and 19.6; Mass (EI^+; 75 eV) 454 (M^+). Anal. Calcd. for $C_{17}H_{18}WO_3$: C, 44.93 ; H, 3.00. Found: C, 44.88; H, 2.88.

Spectral data for compound **10**.



IR (CH_2Cl_2): $\upsilon_{C=O}$: 1728 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.09 (s, 4H, tol), 5.85 (m, 1H, C^1H), 5.62 (m, 1H, C^2H), 3.72 (m, 1H, C^3H), 2.59 (ddd, $J_{16'}$= 11.2, 9.9, 3.2 Hz, 1H, C^4H), 2.31 (s, 3H, CH_3), 2.19 (m, 2H, C^6HH'), 2.04 (m, 1H, C^5H), 1.88 (m, 1H, C^5H'): ^{13}C NMR ($CDCl_3$, 75 MHz): 180.6 (C=O), 140.7, 136.1, 129.1 and 127.9 (Ph), 129.5, 126.7 (C^3+C^4), 48.1 (C^4), 43.2 (C^3), 25.2 and 24.0 (C^6+C^5), 21.0 (Me). Mass (EI^+; m/z) 216 (m^+). HRMS Calcd. for $C_{14}H_{16}O_2$: 216.1150 Found : 216.1146.

Spectral data for Compound **11**



IR (CH_2Cl_2): $\upsilon_{C=O}$: 1732 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.31-7.18 (5H, Ph), 5.87 (1H, ddd, J= 10.0, 3.6, 2.2 Hz, C^1H), 5.65 (1 H, ddd, J_{35}= 10.0, 2.2, 2.0 Hz, 1H, C^2H), 3.74 (1H, m, C^3H), 3.56 (3H, s, OCH_3), 2.59 (1H, ddd, J_1= 11.0, 9.8, 3.2 Hz, C^4H), 2.19 (m, 2H, C^6HH'), 1.96 (m, 1H, C^5H), 1.88 (m, 1H, C^5H'); ^{13}C

NMR ($CDCl_3$, 75 MHz): 175.6 (C=O), 144, 128.4, 128, 126.6 (Ph), 129.5, 126.9 (C^1+C^2), 51.5 (OMe), 48.5, 44.2 (C^3+C^4), 25.4, 24.2 (C^5+C^6); Mass (EI^+; m/z) 216 (M^+); HRMS Calcd. for $C_{14}H_{16}O_2$: 216.1150. Found : 216.1143