

Supplementary material

Chromium-Templated Benzannulation of (η^5 -Cyclohexadienyl)Mn(CO)₃-Methoxy-Cr(CO)₅ Carbenes.

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Table 1. Crystal data and structure refinement parameters for complexes **5** and **12**, T=200(2) K, Diffractometer Kappa – CCD.

	Complex 7	Complex 12
Empirical formula	C ₂₃ H ₁₅ CrMnO ₁₀	C ₃₁ H ₄₀ CrO ₆ Si
Formula weight	558.29	588.72
Wavelength [Å]	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	P-1	P 21/c
<i>a</i> [Å]	10.0825(8)	17.8357(11)
<i>b</i> [Å]	10.5366(7)	10.3808(9)
<i>c</i> [Å]	12.9606(11)	17.0142(12)
α [°]	104.421(6)	90.00
β [°]	91.244(7)	91.700(6)
γ [°]	118.443(7)	90.00
<i>V</i> [Å ³]	1156.50(18)	3148.8(3)
<i>Z</i>	2	4
<i>D</i> _{calculated} [mg/m ³]	1603	1242
μ [mm ⁻¹]	1.072	0.440
<i>F</i> (000)	564	1248
Crystal size [mm]	0.2X0.2 X0.1	0.4X0.3 X0.05
θ range [°]	2.40 to 32.00	3 to 76
Limiting indices	-12 $\leq h \leq$ 12 -14 $\leq k \leq$ 14 -16 $\leq l \leq$ 16	-25 $\leq h \leq$ 25 -14 $\leq k \leq$ 14 -23 $\leq l \leq$ 23
Reflections coll.	24354	40905
Independent reflections	7989[R(int)=0.0389]	9098[R(int)=0.0509]
Refinement method	Least-square	on F ²
Data/restraints/parameters	7989/0/318	9098/0/361
Goodness-of-fit on <i>F</i> ²	1.025	1.014
Final <i>R</i> indices	<i>R</i> ¹ =0.0383	<i>R</i> ¹ =0.0911
[<i>I</i> >2 σ (<i>I</i>)]	w <i>R</i> ² =0.0891	w <i>R</i> ² =0.1209
<i>R</i> indices (all data)	<i>R</i> ¹ =0.0634	<i>R</i> ¹ =0.0444
	w <i>R</i> ² =0.0975	w <i>R</i> ² =0.1036
Largest diff. peak/hole [e.Å ⁻³]	0.392 and -0.551	0.340 and -0.425
CCDC depos. N°	846334	846633

Synthesis of 6. ^1H NMR (400 MHz, CDCl_3) δ 7.22-7.09 (m, 3H, Ph), 6.79 (d, J 7 Hz, 2H, Ph), 6.33 (dd, J = 7 and 2 Hz, 1H, H2), 5.89 (dd, J 7 and 2 Hz, 1H, H3), 5.12 (m, 2H, H7), 4.74 (d, J 7 Hz, 1H, H6), 3.74 (dd, J 7 and 2 Hz, 1H, H5), 3.61 (s, 3H, OMe), 3.51 (t, J 6 Hz, 2H, H10), 3.37 (s, 3H, OMe alkyl chain), 2.22 (m, 2H, H8), 1.87 (m, 2H, H9). ^{13}C NMR (100 MHz, CDCl_3) δ 338.33 (C=Cr), 222.63, 216.61 (CO), 144.62 (C4), 145.77, 128.61, 127.14, 125.22 (Ph), 100.32 (C2), 81.12 (C1), 80.68 (C7), 72.46 (C3), 72.18 (C10), 58.82 (OMe butyl chain), 55.20 (OMe), 44.57 (C5), 41.05 (C6), 26.85 (C8), 26.45 (C9). HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{23}\text{O}_7\text{MnNa}$ ($[\text{M}+\text{O}-\text{Cr}(\text{CO})_5+\text{Na}]^+$, oxidative demetalation product): 477.0710; found: 477.0717.

Synthesis of 7. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.19 (m, 3H, Ph), 6.81 (d, J 7 Hz, 2H, Ph), 5.66 (d, J 7.6 Hz, 1H, H2), 4.93 (s, 3H, OMe carbene), 3.98 (t, J 6 Hz, 1H, H5), 3.77 (s, 3H, OMe), 3.65 (m, 2H, H1,6), 3.51 (m, 2H, H10), 3.37 (s, 3H, OMe butyl chain), 2.28 (m, 2H, H8), 1.88 (m, 2H, H9). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 333.60 (C=Cr), 232.01, 230.39, 213.78, 212.74 (CO), 145.92 (C2, Ph), 147.08, 129.04, 127.86, 125.53 (Ph), 88.33, (C3), 86.71 (C4), 68.40 (OMe carbene), 64.72 (C5), 63.38, (OMe), 45.11 (C6), 43.11 (C1). HRMS (ESI): calculated for $\text{C}_{18}\text{H}_{15}\text{O}_6\text{MnNa}$ ($[\text{M}+\text{O}-\text{Cr}(\text{CO})_5+\text{Na}]^+$, oxidative demetalation product): 405.0141; found: 405.0143. Elem. Anal. calcd for $\text{C}_{23}\text{H}_{15}\text{CrMnO}_{10}$ C 49.48, H 2.71, found C 49.34, H 2.54.

Synthesis of 8. ^1H NMR (400 MHz, CDCl_3) δ 7.21 (m, 3H, Ph), 6.82 (m, 2H, Ph), 5.65 (d, J 7 Hz, 1H, H4), 5.22 (t, J 7 Hz, 2H, H7), 3.99 (t, J 6 Hz, 1H, H5), 3.78 (s, 3H, OMe), 3.64 (m, 2H, H1,6), 3.51 (m, 2H, H10), 3.37 (s, 3H, OMe butyl chain), 2.28 (m, 2H, H8), 1.88 (m, 2H, H9). ^{13}C NMR (75 MHz, CDCl_3) δ 231.84, 230.41, 213.02 (CO), 145.93 (C2), 129.05, 127.87, 125.53 (CPh), 88.37 (C3), 86.84 (C4), 82.01 (C7), 72.16 (C9), 64.80 (C5), 63.34, 58.76 (C10, OMe butyl chain), 45.01 (C6), 43.17 (C1), 26.72, 26.35 (C8,C9).). HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{23}\text{O}_7\text{MnNa}$ ($[\text{M}+\text{O}-\text{Cr}(\text{CO})_5+\text{Na}]^+$, oxidative demetalation product): 477.0710; found: 477.0714.