

DIASTEREOSELECTIVITY IN THE FORMATION OF QUATERNARY CENTERS WITH ARYLLEAD(IV) TRICARBOXYLATES

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SUPPORTING INFORMATION

Experimental Section

General Methods. All air and moisture sensitive reactions were carried out under argon or nitrogen using oven-dried glassware and standard syringe techniques. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl. Reaction solvents CHCl₃, pyridine, and toluene were used as received. *p*-Methoxyphenyllead triacetate was prepared according to the published procedure and used over a two week period. All β -ketoesters were distilled prior to use.

Flash chromatography was performed using 60 mesh EMI silica gel. Thin layer chromatography TLC was carried out on Merck silica gel plates with UV detection. Melting points are uncorrected. ¹H NMR spectra were recorded at 500 MHz and ¹³C NMR spectra were recorded either at 125 or 62.5 MHz, in CDCl₃ unless otherwise indicated. The following abbreviations were utilized to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet.

Compound **3b** has been described in the literature. See reference 6a in main paper.

General procedure for arylations:

Pyridine as base. β -Ketoester (1 mmol) is stirred in CHCl₃ (5 mL) at room temperature. To this solution, pyridine (3.3 mmol) is added and the solution allowed to stir for 10 min. A solution of aryllead tricarboxylate (1.1 mmol) in CHCl₃ (5 mL) is added. The resulting solution is allowed

to stir for 48 h at room temperature. The reaction is quenched with the addition of H₂SO₄ (2 M solution, 3 mL) and stirred for an additional 5 min. The reaction mixture is passed through Celite to remove solid material, the organic layer is separated and the aqueous layer is extracted with CHCl₃ (3 x 5 mL). The organic layer is dried over sodium sulfate, and concentrated *in vacuo*. Column chromatography affords the desired product.

Sodium salt. Sodium hydride (1 mmol, washed with hexanes [3 x 5 mL]) is stirred in dry THF (10 mL). To this solution is added β-ketoester (1 mmol, solution in THF), and the resulting mixture is allowed to react with stirring at room temperature for 15 min prior to concentration *in vacuo*. The resultant dry sodium salt of the β-ketoester is stirred in CHCl₃ (5 mL) and treated with a solution of *p*-methoxyphenyllead tricarboxylate (1.1 mmol in 5 mL CHCl₃). The resultant heterogeneous solution is allowed to stir for 48 h at room temperature. The reaction is quenched with 3 mL of 2 M H₂SO₄ and stirred for an additional 5 minutes. The reaction mixture is passed through Celite to remove solid material, the organic layer is separated and the aqueous layer is extracted with CHCl₃ (3 x 5 mL). The organic layer is dried over sodium sulfate, and concentrated *in vacuo*. Column chromatography affords the desired product.

***p*-Methoxyphenyllead tribenzoate.** *p*-Methoxyphenyllead triacetate (1.1 mmol) is stirred in toluene (5 mL). To this solution is added benzoic acid (3.3 mmol) and a small amount of AcOH to aid in the dissolution of the mixture. The resulting solution is allowed to stir at room temperature for 1 h, then is concentrated *in vacuo*. Toluene is added and removed *in vacuo* until the ¹H NMR resonance for free acetic acid is no longer present.

Methyl 5-Methyl-2-cyclohexanone-1-*p*-methoxyphenyl-1-carboxylate (Table 1, 3a): Yield: 74%. *Major isomer:* Crystallized from ether/hexane: mp 78-9 °C; ¹H NMR δ 7.157 (d, *J* = 9 Hz, 2H), 6.918 (d, *J* = 8.5 Hz, 2H), 3.822 (s, 3H), 3.690 (s, 3H), 2.682 (dt, *J* = 14.5, 3.5 Hz, 1H),

2.504 (dt, $J = 13.5, 6$ Hz, 1H), 2.99 (m, 2H), 1.964 (m, 1H), 1.883 (m, 1H), 1.504 (dq, $J = 4, 1$ Hz, 1H), 1.037 (d, $J = 6.5$ Hz, 3H); ^{13}C δ 208.6, 172.2, 159.1, 129.2, 128.3, 114.3, 65.7, 55.3, 52.7, 41.4, 38.9, 35.9, 27.1, 21.3; IR (thin film): 2928, 1728, 1460, 1252 cm^{-1} .

Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_4$: C, 69.55; H, 7.30. Found: C, 69.40; H, 7.21.

Methyl 5-*tert*-Butyl-2-cyclohexanone-1-*p*-methoxyphenyl-1-carboxylate (Table 1, 3b):

Yield: 66%. *Major isomer*: Crystallized from ether/hexane: mp 103-5 °C (dec); ^1H NMR δ 7.137 (d, $J = 9$ Hz, 2H), 6.929 (d, $J = 9$ Hz, 2H), 3.838 (s, 3H), 3.679 (s, 3H), 2.790 (ddd, $J = 14.5, 5.5, 1.5$ Hz, 1H), 2.498 (dt, $J = 14, 6.5$ Hz, 1H), 2.4-2.3 (m, 2H), 1.968 (m, 1H), 1.620-1.583 (m, 2H), 0.971 (s, 9H); ^{13}C δ 209, 172, 159, 129.2, 128.4, 114.3, 65.7, 55.3, 52.7, 41.6, 39.1, 34.7, 32.6, 28.8, 27.5; IR (thin film): 2955, 1735, 1710, 1531, 1249 cm^{-1} .

Methyl-5-(*tert*-butyldimethylsilyloxy)-2-cyclohexanone-1-*p*-methoxyphenyl-1-carboxylate

(Table 1, 3c): Yield: 74%. Clear oil. *Major isomer*: ^1H NMR δ 7.131 (d, $J = 9$ Hz, 2H), 6.908 (d, $J = 9.5$ Hz, 2H), 4.21-4.16 (m, 1H) 3.83 (s, 3H), 3.70 (s, 3H), 2.85-2.76 (m, 2H) 2.609 (dd, $J = 14.5, 3$ Hz, 1H) 2.52-2.46 (m, 1H) 1.96 (q, $J = 14, 7$ Hz, 2H); ^{13}C δ 206.7, 171.9, 159.1, 128.7, 114.1, 94.8, 65.9, 63.6, 55.3, 52.7, 41.8, 36.6, 35.6, 31.3, 25.9, 17.2; IR (thin film): 2950, 1723, 1610, 1513, 1251, 1033, 836 cm^{-1} .

Anal. Calcd. for $\text{C}_{21}\text{H}_{32}\text{O}_5\text{Si}$: C, 64.25; H, 8.22. Found: C, 64.03; H, 8.05.

(1 *R'*, 2*R'*, 2*RS*)-2-carbomethoxy-2-*p*-methoxyphenyl-4-(1',2'-diphenyl)ethylene dioxy-

cyclohexan-1-one (Table 1, 3d). Yield 73%. This material (white solid) was obtained as a 3:2 mixture of diastereomers, mp 66-98 °C; Minor isomer given in [] when known. ^1H NMR (500 MHz, CDCl_3) 7-7.3 (m) 7.27-7.25 (m) 7.19 (dd, $J = 7$ Hz, $J = 4$ Hz.) 7.159 (dd, $J = 9$ Hz, $J = 1.5$ Hz) 6.921 (dd $J = 8.5$ Hz., $J = 4.5$ Hz), 4.824 (dt $J = 29.5, 9$ Hz.) [3.830 (s, 2H), 3.825] (s, 3H) 3.630 (s, 3H), [3.522 (s, 2H)], 3.41-3.28 (m), 2.865 (d, $J = 13.5$) 2.783 (d, $J = 13.5$ Hz) 2.758-

2.68 (m) 2.475-2.435 (m) 2.38-2.34 (m); ^{13}C (125 MHz) 204.9, [204.7], 172.50, [172.45], 159.1, [136.3], 136.1, 135.6, 128.9-126.2, 114.3, [114.2], [113.6], 113.4, 107.9, [107.6], 87.0, 86.6, 82.3, 86.2, 86.1, 85.9, 85.9, 85.8, 85.75, 85.69, 85.43, 85.38, 85.29, [63.4], 62.8, 55.5, [55.2], 54.4, 53.6, 53.3, 52.6, 52.2, 38.1, 37.8, 36.8, 36.1. IR (thin film): 1723, 1513, 1252, 1120 cm^{-1} .

Anal. Calcd. for $\text{C}_{29}\text{H}_{28}\text{O}_6$: C, 73.71; H, 5.97. Found: C, 73.80; H, 6.10.

Methyl 3-methyl-2-cyclohexanone-1-*p*-methoxyphenyl-1-carboxylate (Table 3, 3e). Major diastereomer reported. (clear oil) ^1H NMR (500 MHz, CDCl_3) 7.14 (d, $J = 9$ Hz, 2H), 6.92 (d, $J = 8.5$ Hz, 2H), 3.83 (s, 3H), 3.68 (s, 3H), 2.794 (dd, $J = 15, 3$ Hz, 1H), 2.660-2.576 (m, 2H) 1.951 (dq, $J = 9, 6, 3$ Hz, 1H) 1.780-1.728 (m, 3H) 1.015 (d, $J = 5$ Hz, 3 H). ^{13}C (125 MHz) 209, 172, 159, 129, 128, 114, 66, 55.3, 52.6, 42.3, 37.3, 34.0, 21.1, 14.2. IR (thin film): cm^{-1} .

Methyl 4-methyl-2-cyclohexanone-1-*p*-methoxyphenyl-1-carboxylate (Table 3, 3f). Have not separated diastereomers. Data is reported for both diastereomers. (clear oil). ^1H NMR (500 MHz, CDCl_3) 7.178-7.144 (m) 6.924 (d, $J = 8$ Hz), 6.888 (d, $J = 8$ Hz) 3.833 (s), 3.809 (s), 3.778 (s) 3.692 (s), 2.855 (dt, $J = 13.5, 3.5$ Hz) 2.687 (dt $J = 13.5, 3.5$ Hz), 2.620-2.559 (m), 2.392 (ddd $J = 13.5, 4, 1.5$ Hz) 2.336 (dd, $J = 13, 12$ Hz), 2.183 (dd, $J = 13.5, 12$ Hz) 2.106-1.921 (m), 1.821-1.785 (m), 1.456-1.382 (m), 1.056 (d, $J = 6.5$ Hz) 0.925 (d, $J = 6.5$ Hz). ^{13}C (125 MHz) 207.7, 172.3, 159.1, 129.2, [128.9], 128.0, 114.2, [113.7], 65.3, 55.3, [52.8], 52.7, [49.3], 47.6, 35.4, [35.0], [34.7], 32.2, [31.3], 29.4, [22.0], 21.7. IR (thin film): 2953, 1711, 1512, 1251 cm^{-1} .
Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_4$: C, 69.55; H, 7.30. Found: C, 69.37; H, 7.14.

Methyl 6-methyl-2-cyclohexanone-1-*p*-methoxyphenyl-1-carboxylate (Table 3, 3g). Data is reported for both diastereomers. ^1H NMR (500 MHz, CDCl_3) [7.169] (d, $J = 9$ Hz.) 7.103 (d, $J = 9$ Hz, 2H), [6.922] (d, $J = 9$ Hz), 6.900 (d, $J = 9$ Hz, 2H) 3.816 (s, 3H), 3.790 (s, 3H), [3.778] (s), [3.743] (s), 3.075 (dd, $J = 11, 1$ Hz, 1H), 2.604-2.537 (m, 2H), [2.501-2.467] 2.400-2.262, (m)

2.090-2.037 (m), [1.958-1.923] (ddd, $J = 13.5, 4, 1.5$ Hz), 1.897-1.737 (m), 1.458-1.424 (dd $J = 17.5, 3$ Hz) 1.068-1.054 (d, $J = 7$ Hz, 3 H), [1.054-1.041] (d, $J = 6.5$ Hz). ^{13}C (125 MHz) 205.8, 171.1, 158.6, 129.4, 129.2, 113.7, 65.3, 55.3, 52.1, 43.0, 40.5, 30.0, 25.5, 17.0. IR (thin film): 2940, 1716, 1512, 1252 cm^{-1} .

Table 7. Crystal data and structure refinement for Compound 3a.

Identification code	mn932	
Empirical formula	C ₁₆ H ₂₀ O ₄	
Formula weight	276.32	
Temperature	297(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$\bar{P}1$	
Unit cell dimensions	a = 7.981(13) Å	$\alpha = 80.61(2)^\circ$.
	b = 8.737(15) Å	$\beta = 73.49(2)^\circ$.
	c = 12.26(2) Å	$\gamma = 66.55(2)^\circ$.
Volume	750(2) Å ³	
Z	2	
Density (calculated)	1.223 Mg/m ³	
Absorption coefficient	0.087 mm ⁻¹	
F(000)	296	
Crystal size	0.44 x 0.30 x 0.06 mm ³	
Crystal color and habit	colorless plate	
Diffractometer	Bruker SMART	
Theta range for data collection	1.74 to 26.00°.	
Index ranges	-9 ≤ h ≤ 8, -10 ≤ k ≤ 10, -15 ≤ l ≤ 14	
Reflections collected	4939	
Independent reflections	2897 [R(int) = 0.0687]	
Completeness to theta = 26.00°	98.5 %	
Absorption correction	None	
Max. and min. transmission	0.995 and 0.963	
Solution method	SHELXS-97 (Sheldrick, 1990)	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2897 / 0 / 182	
Goodness-of-fit on F ²	0.932	
Final R indices [I > 2σ(I)]	R1 = 0.0532, wR2 = 0.1023	
R indices (all data)	R1 = 0.1769, wR2 = 0.1452	
Extinction coefficient	0.014(4)	
Largest diff. peak and hole	0.264 and -0.163 e.Å ⁻³	

Table 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Compound 3a. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	3446(4)	7094(3)	5105(2)	64(1)
O(2)	7617(4)	6488(3)	3233(2)	71(1)
O(3)	5562(3)	9103(3)	3457(2)	65(1)
O(4)	-219(4)	12901(3)	795(2)	72(1)
C(1)	4438(4)	7157(4)	3040(2)	37(1)
C(2)	3245(5)	6789(4)	4221(3)	42(1)
C(3)	1840(5)	6042(4)	4214(3)	54(1)
C(4)	2725(5)	4512(4)	3489(3)	59(1)
C(5)	3811(5)	4872(4)	2302(3)	49(1)
C(6)	5279(4)	5512(4)	2404(3)	44(1)
C(7)	4731(6)	3323(4)	1584(3)	74(1)
C(8)	6069(5)	7513(4)	3252(3)	44(1)
C(9)	6983(6)	9532(5)	3723(4)	83(1)
C(10)	3191(4)	8666(4)	2419(3)	39(1)
C(11)	1717(5)	10007(4)	3010(3)	47(1)
C(12)	612(5)	11395(4)	2460(3)	52(1)
C(13)	955(5)	11474(4)	1278(3)	50(1)
C(14)	2394(5)	10192(4)	664(3)	52(1)
C(15)	3499(5)	8808(4)	1241(3)	50(1)
C(16)	55(6)	13041(5)	-409(4)	85(1)

Table 9. Bond lengths [Å] and angles [°] for Compound 3a.

O(1)-C(2)	1.224(4)	C(6)-H(6B)	0.9700
O(2)-C(8)	1.200(4)	C(7)-H(7A)	0.9600
O(3)-C(8)	1.328(4)	C(7)-H(7B)	0.9600
O(3)-C(9)	1.457(4)	C(7)-H(7C)	0.9600
O(4)-C(13)	1.388(4)	C(9)-H(9A)	0.9600
O(4)-C(16)	1.421(5)	C(9)-H(9B)	0.9600
C(1)-C(10)	1.539(4)	C(9)-H(9C)	0.9600
C(1)-C(8)	1.550(5)	C(10)-C(15)	1.388(5)
C(1)-C(2)	1.553(5)	C(10)-C(11)	1.406(4)
C(1)-C(6)	1.557(4)	C(11)-C(12)	1.387(5)
C(2)-C(3)	1.509(5)	C(11)-H(11A)	0.9300
C(3)-C(4)	1.534(5)	C(12)-C(13)	1.392(5)
C(3)-H(3A)	0.9700	C(12)-H(12A)	0.9300
C(3)-H(3B)	0.9700	C(13)-C(14)	1.378(5)
C(4)-C(5)	1.522(5)	C(14)-C(15)	1.402(5)
C(4)-H(4A)	0.9700	C(14)-H(14A)	0.9300
C(4)-H(4B)	0.9700	C(15)-H(15A)	0.9300
C(5)-C(6)	1.526(5)	C(16)-H(16A)	0.9600
C(5)-C(7)	1.541(5)	C(16)-H(16B)	0.9600
C(5)-H(5A)	0.9800	C(16)-H(16C)	0.9600
C(6)-H(6A)	0.9700		
C(8)-O(3)-C(9)	115.8(3)	C(2)-C(3)-C(4)	112.3(3)
C(13)-O(4)-C(16)	118.0(3)	C(2)-C(3)-H(3A)	109.1
C(10)-C(1)-C(8)	111.2(3)	C(4)-C(3)-H(3A)	109.1
C(10)-C(1)-C(2)	109.6(3)	C(2)-C(3)-H(3B)	109.1
C(8)-C(1)-C(2)	107.5(3)	C(4)-C(3)-H(3B)	109.1
C(10)-C(1)-C(6)	113.7(3)	H(3A)-C(3)-H(3B)	107.9
C(8)-C(1)-C(6)	108.8(3)	C(5)-C(4)-C(3)	111.9(3)
C(2)-C(1)-C(6)	105.8(3)	C(5)-C(4)-H(4A)	109.2
O(1)-C(2)-C(3)	122.3(3)	C(3)-C(4)-H(4A)	109.2
O(1)-C(2)-C(1)	121.3(3)	C(5)-C(4)-H(4B)	109.2
C(3)-C(2)-C(1)	116.4(3)	C(3)-C(4)-H(4B)	109.2

H(4A)-C(4)-H(4B)	107.9	C(13)-C(12)-H(12A)	120.4
C(4)-C(5)-C(6)	109.3(3)	C(14)-C(13)-O(4)	124.3(4)
C(4)-C(5)-C(7)	111.8(3)	C(14)-C(13)-C(12)	120.1(3)
C(6)-C(5)-C(7)	111.1(3)	O(4)-C(13)-C(12)	115.6(3)
C(4)-C(5)-H(5A)	108.2	C(13)-C(14)-C(15)	119.5(3)
C(6)-C(5)-H(5A)	108.2	C(13)-C(14)-H(14A)	120.3
C(7)-C(5)-H(5A)	108.2	C(15)-C(14)-H(14A)	120.3
C(5)-C(6)-C(1)	114.1(3)	C(10)-C(15)-C(14)	122.4(3)
C(5)-C(6)-H(6A)	108.7	C(10)-C(15)-H(15A)	118.8
C(1)-C(6)-H(6A)	108.7	C(14)-C(15)-H(15A)	118.8
C(5)-C(6)-H(6B)	108.7	O(4)-C(16)-H(16A)	109.5
C(1)-C(6)-H(6B)	108.7	O(4)-C(16)-H(16B)	109.5
H(6A)-C(6)-H(6B)	107.6	H(16A)-C(16)-H(16B)	109.5
C(5)-C(7)-H(7A)	109.5	O(4)-C(16)-H(16C)	109.5
C(5)-C(7)-H(7B)	109.5	H(16A)-C(16)-H(16C)	109.5
H(7A)-C(7)-H(7B)	109.5	H(16B)-C(16)-H(16C)	109.
C(5)-C(7)-H(7C)	109.5		
H(7A)-C(7)-H(7C)	109.5		
H(7B)-C(7)-H(7C)	109.5		
O(2)-C(8)-O(3)	123.3(3)		
O(2)-C(8)-C(1)	124.6(3)		
O(3)-C(8)-C(1)	112.1(3)		
O(3)-C(9)-H(9A)	109.5		
O(3)-C(9)-H(9B)	109.5		
H(9A)-C(9)-H(9B)	109.5		
O(3)-C(9)-H(9C)	109.5		
H(9A)-C(9)-H(9C)	109.5		
H(9B)-C(9)-H(9C)	109.5		
C(15)-C(10)-C(11)	116.2(3)		
C(15)-C(10)-C(1)	121.8(3)		
C(11)-C(10)-C(1)	121.9(3)		
C(12)-C(11)-C(10)	122.5(3)		
C(12)-C(11)-H(11A)	118.7		
C(10)-C(11)-H(11A)	118.7		
C(11)-C(12)-C(13)	119.3(3)		
C(11)-C(12)-H(12A)	120.4		

Table 10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Compound 3a. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
O(1)	84(2)	72(2)	47(2)	-7(1)	-13(1)	-40(2)
O(2)	49(2)	64(2)	104(2)	-15(2)	-33(2)	-11(2)
O(3)	51(2)	53(2)	108(2)	-12(2)	-38(2)	-20(1)
O(4)	71(2)	65(2)	72(2)	16(1)	-31(2)	-14(2)
C(1)	37(2)	40(2)	35(2)	-5(2)	-7(2)	-15(2)
C(2)	46(2)	37(2)	41(2)	-4(2)	-15(2)	-10(2)
C(3)	48(2)	67(2)	50(2)	3(2)	-7(2)	-29(2)
C(4)	63(3)	60(2)	67(3)	5(2)	-22(2)	-34(2)
C(5)	55(3)	48(2)	50(2)	-6(2)	-14(2)	-23(2)
C(6)	41(2)	49(2)	40(2)	-4(2)	-9(2)	-15(2)
C(7)	88(3)	67(3)	79(3)	-21(2)	-14(2)	-38(2)
C(8)	43(2)	46(2)	49(2)	-4(2)	-15(2)	-19(2)
C(9)	73(3)	67(3)	135(4)	-13(3)	-48(3)	-31(2)
C(10)	43(2)	41(2)	37(2)	-3(2)	-11(2)	-18(2)
C(11)	51(2)	53(2)	36(2)	-1(2)	-10(2)	-19(2)
C(12)	45(2)	52(2)	51(3)	-2(2)	-14(2)	-11(2)
C(13)	50(2)	45(2)	59(3)	10(2)	-26(2)	-21(2)
C(14)	64(3)	59(2)	37(2)	5(2)	-18(2)	-25(2)
C(15)	50(2)	50(2)	43(2)	-8(2)	-7(2)	-14(2)
C(16)	104(4)	80(3)	82(3)	24(3)	-53(3)	-35(3)

Table 11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Compound 3a.

	x	y	z	U(eq)
H(3A)	817	6881	3917	65
H(3B)	1314	5717	4989	65
H(4A)	3570	3594	3868	71
H(4B)	1741	4173	3423	71
H(5A)	2923	5757	1915	59
H(6A)	5994	5698	1645	52
H(6B)	6146	4653	2804	52
H(7A)	5392	3599	842	111
H(7B)	3775	2970	1511	111
H(7C)	5600	2436	1953	111
H(9A)	6487	10701	3853	125
H(9B)	8077	9285	3097	125
H(9C)	7322	8892	4396	125
H(11A)	1474	9961	3801	57
H(12A)	-347	12264	2877	62
H(14A)	2631	10245	-127	63
H(15A)	4473	7954	818	60
H(16A)	-850	14076	-627	128
H(16B)	-104	12125	-649	128
H(16C)	1303	13017	-764	128