

Supplementary Materials

Syntheses, spectroscopic and analytical data for new complexes

Syntheses

Preparation of $\text{Pt}(\eta^1, \eta^2\text{-C}_5\text{Me}_5\text{O}_2)(\text{PR}_3)\text{I}$, **2**

The complex $\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)(\text{PR}_3)\text{I}$ (100 mg) was dissolved in 20 ml of distilled hexane/chloroform. The green solution was stirred at room temperature in the air until the green solution turned light yellow (approximately 2 to 3 hours) at which time a white precipitate of product had formed. The solution was stripped off to dryness, the residue dissolved in 2 ml of dichloromethane and hexane was added (10 to 15 ml). Pale yellow crystals were isolated upon refrigeration at -30°C . The crystals were washed with hexane and dried *in vacuo*. These crystals were stored in dark at -78°C .

Preparation of $\text{Pt}(\eta^1, \eta^2\text{-C}_5\text{Me}_5\text{dienophile})(\text{PPh}_3)\text{I}$, **3**

The mixture of hexane (20 ml) and an excess of dienophile was refluxed for 20 minutes under nitrogen gas to remove traces of oxygen. The resulting solution was brought to room temperature. The complex $\text{Pt}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)\text{I}$ (100 mg, 0.139 mmol) was added under flow of nitrogen gas. The resulting mixture was refluxed for 36 (methyl acrylate) to 48 (acrolein, ethyl vinyl ketone) hours. The resulting solution was kept overnight at -30°C , the supernatant liquid was decanted and the cream colour crystals dissolved in 2 ml of CH_2Cl_2 and hexane (10 to 15 ml) were added. upon refrigeration at -30°C . The crystals were washed with hexane and dried *in vacuo*. Yields 70% (acrolein), 85% (methyl acrylate, ethyl vinyl ketone).

Analytical and spectroscopic data for $\text{Pt}(\eta^1, \eta^2\text{-C}_5\text{Me}_5\text{O}_2)(\text{PR}_3)\text{I}$
($\text{PR}_3 = \text{PPh}_3$, **2a**; $\text{PR}_3 = \text{PPhCy}_2$, **2b**; $\text{PR}_3 = \text{PMe}^t\text{BuPh}$, **2c**)

Analyses

2a	calc. for $\text{C}_{28}\text{H}_{30}\text{IO}_2\text{PPt}$	C 44.75	H 4.02
	found:	C 44.68	H 4.09
2b	calc. for $\text{C}_{28}\text{H}_{42}\text{IO}_2\text{PPt}$:	C 44.04	H 5.54
	found:	C 44.03	H 5.55
2c	calc. for $\text{C}_{27}\text{H}_{32}\text{IO}_2\text{PPt}$:	C 37.68	H 4.81
	found:	C 37.95	H 4.88

NMR

	2a	2b^a	2c
	C_6D_6 RT	C_6D_6 RT	C_6D_6 RT
$^{195}\text{Pt}\{^1\text{H}\}^{\text{a}}$	420 [4585]	444 ^a [4461]	438 [4487]
$^{31}\text{P}\{^1\text{H}\}^{\text{a}}$	23.3 [4584]	28.3 ^b [4459]	22.6 [4487]

[] J_{PtP} ; a) 457 [4442] in CD_2Cl_2 ; b) 27.9 [4443] in CD_2Cl_2

$^{13}\text{C}\{^1\text{H}\}$	2a	2b	2c
	CDCl_3 250 K	CD_2Cl_2 RT	CDCl_3 230 K
C(1)	42.3 [477]	42.0 [503]	41.5 [500]
C(2)	95.1 [66]	95.9 [69] {4}	95.3 [66]
C(3)	113.5 [77] {14}	113.2 [78] {13}	114.0, 111.6 [72], [78] {12}, {13}
Me(1)	7.6 {5}	9.1 {4}	6.8 {3}
Me(2)	9.6 [16]	10.7 [17]	9.7, 9.9 [unobs], [unobs]
Me(3)	13.2 [unobs]	13.3 [11]	12.9, 12.7 [17], [16]
Ph	128.1 {11}	126.2 {47} [69]	127.8 {10}
	129.2 {58}	128.2 {10}	129.8 {50} [44]
	130.8	131.2	130.7
	133.8 {11}	134.0 {8} [34]	132.5 {11} [26]
Cy		26.5	
		26.7 {10}, 26.9 {10}	
		28.9 [15], 29.5 [15]	
		4.5 {28} [32]	
Bu ^t			26.0
			32.3 {31} [62]
Me			8.3 [43] {33}

{ } J_{PC}, [] J_{PtC}

¹ H	2a	2b	2c
	CDCl ₃ RT	CD ₂ Cl ₂ RT	CDCl ₃ RT
Me(1)	0.29 [59.3] {1.5}	0.39 [61.5] {0.9}	0.11 [60.5] {1.3}
Me(2)	1.32	1.34	1.20, 1.35
Me(3)	2.05 [29.4] {2.8}	1.97 [27.7] {3.0}	1.89, 1.94 [33.5], [25.0] {2.6}, {3.4}
Ph	7.32-7.81	7.40-7.50	7.37-7.64
Cy		1.00-2.80	
Bu ^t			1.29 {15.6}
Me			1.87 {9.1} [48.3]

{ } J_{PC}, [] J_{PtC}

Analytical and spectroscopic data for [Pt(η^1 , η^2 -C₅Me₅CH₂CHR)(PPh₃)I]
(R = CHO, **3a**; R = CO₂Me, **3b**; R = C(O)Et, **3c**)

Analyses

3a	calc. for C ₂₈ H ₃₄ IOPPt:	C 48.01	H 4.42
	found:	C 47.79	H 4.61
3b	calc. for C ₃₂ H ₃₆ IO ₂ PPt:	C 47.71	H 4.50
	found:	C 48.31	H 4.56
3c	calc. for C ₃₃ H ₃₈ IOPPt:	C 49.32	H 4.77
	found:	C 49.38	H 4.76

NMR Data	3a		3b		3c	
	major	minor	major	minor	major	minor
	85%	15%	>95%	<5%	>95%	<8%
¹⁹⁵ Pt{ ¹ H} (C ₆ D ₆)	730 [4619]	725 [4566]	719 [4587]		717 [4594]	742 [4578]
³¹ P{ ¹ H} (C ₆ D ₆)	18.8 [4617]	19.8 [4563]	19.9 [4588]	21.4 [4579]	18.8 [4594]	
¹ H (CDCl ₃)						
Me(1)	-0.17 (d) [63.5] {1.5}	-0.13 (d) [63.5] {1.9}	-0.19 (d) [64.0] {1.3}		-0.17 (d) [63.4] {1.4}	0.05 (d) [unobs] {~2}
Me(2)	1.36, 1.53	1.35, 1.41	1.33, 1.47		1.34, 1.49	
Me(3)	1.83 (d), 1.94 (d) [28.3], [~ 22] {3.3}, {3.3}	1.89 (×2) (d) [~33] {4.2}	1.81 (d), 1.98 (d) [36.6], [30.8] {3.2}, {3.3}		1.77 (d), 2.00 (d) [37.0], [29.6] {3.2}, {3.3}	
H(a)	2.53 (d of d of d)	-	2.46 (d of d)		2.74 (d of d)	

	$J(H_aH_b) = 4.9$ $J(H_aH_c) = 9.4$ $J(H_aH_{CHO}) = 3.1$		$J(H_aH_b) = 4.9$ $J(H_aH_c) = 9.7$		$J(H_aH_b) = 5.2$ $J(H_aH_c) = 9.5$	
H(b)	1.26 (d of d) $J(H_bH_c) = 13.3$	-	1.27 (d of d) $J(H_bH_c) = 12.9$		1.22 (d of d) $J(H_bH_c) = 12.7$	
H(c)	1.49 (d of d)	-	1.55 (d of d)		1.47 (d of d)	
HC(O)	9.53 (d)	9.42 (d) $J(H_aH_{CHO}) = 3.4$				
CH ₃ C(O)			3.61 (s)	3.56 (s)		
Ph	7.1-7.8 (m)		7.1-7.8 (m)		7.2-7.8 (m)	
CH ₂					2.32, 2.48 $J(AB) = 18.0$ $J(H_AH_{Me}) = 7.2$ $J(H_BH_{Me}) = 7.2$	
CH ₃					0.97 ("t")	

$^{13}\text{C}\{^1\text{H}\}$ (CDCl_3)						
C(1)	36.8 [unobs] {4}		36.6 [468] {4}		32.9 [unobs] {unobs}	
C(2)	63.8, 68.1 [88], [84]		63.2, 67.4 [88], [84]		63.6, 68.2 [90], [83]	
C(3)	109.5, 114.3 [unobs], [unobs] {17}, {14}		110.0, 113.8 [73], [68] {15}, {15}		111.5, 114.2 [69], [65] {15}, {16}	
Me(1)	9.2 {5}		8.9 {6}		9.4 {5}	
Me(2)	15.0, 15.5 [34], [35]		14.4, 15.2 [32], [34]		15.6, 15.7 [32], [35]	
Me(3)	13.7, 16.4 [15], [18]		13.5, 15.5 [17], [17] {3}, {2}		13.9, 16.5 [14], [16] {3}, {3}	
CH_2	37.2 [113]		39.9 [110]		40.8 [108]	
CH	62.0 [104]		52.6 [111]		60.2 [100]	
C(O)	202.2	202.0	173.4		211.7	
Me			51.2			
CH_2					38.0	

CH ₂ CH ₃					10.1	
Ph	128.0 {11}		127.1 {11}		128.0 {11}	
	130.4		130.1		130.3	
	131.7 [unob] {57}		131.5 [43] {57}		131.9 [42] {56}	
	134.5 {11}		134.2 {11}		134.5 {12}	