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Dimeric complexes of trimethylplatinum(IV) with ethylacetoacetate, methylacetoacetate, dimethylmalonate and diethylmalonate, and their pyridine and 2,2′-bipyridyl adducts

Kenneth Kite and Alexander F. Psaila
Department of Chemistry, University of Exeter, Exeter EX4 4QD (UK)

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Abstract

An ^{1}H NMR study of the complexes $[PtMe_3(R^1COCHCOR^2)]_2$ ($R^1 = CH_3$, $R^2 = OCH_3$ (**1**) and $R^1 = CH_3$, $R^2 = OC_2H_5$ (**2**), $R^1 = R^2 = OCH_3$ (**3**) and $R^1 = R^2 = OC_2H_5$ (**4**)) shows that in solution **1–4** are non-fluxional at ambient temperature, in contrast to the complexes with $R^1 = R^2 =$ alkyl. Incorporation of alkoxy groups into the β-dicarbonyl ligand strengthens the Pt–C bridge bond. The 1:1 adducts of **1–4** with pyridine and 2,2′-bipyridyl contain bidentate (O,O′-bonded) and monodentate (C-bonded) dicarbonyl ligands, respectively. A correlation between $^2J(Pt–CH_3)$ and $^2J(Pt–CH)$ for compounds with a *trans* (CH_3)–Pt–(CH) feature is demonstrated.

Introduction

Extensive studies of complexes of Pd^{II} and Pt^{II} have shown that β-ketoesters are as versatile as β-diketones in the variety of ligand bonding modes that they display [1]. This is also illustrated by the trimethylplatinum(IV) complexes $[PtMe_3(R^1COCHCOR^2)]_2$ for which X-ray diffraction studies [2,3] have established the same structure (Fig. 1) for the compounds with $R^1 = R^2 = C_3H_7$ and $R^1 = CH_3$, $R^2 = OC_2H_5$. Molar mass measurements on a series of diketonates [4,5] show that the dimeric structure is preserved in solution. ^{1}H NMR studies reveal that the dimers undergo a rapid intramolecular fluxional process in solution at room temperature [5,6] which makes the three platinum methyl groups equivalent. The dissociation mechanism established for the acetylacetonate [7] is responsible for the observed stereochemical non-rigidity in other 1,3-dicarbonyl complexes of $Pt^{IV}Me_3$. The diketone dimers react with monodentate Lewis bases to give 1:1 adducts containing a bidentate β-diketone, while reaction with 2,2′-

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Correspondence to: Dr. K. Kite.

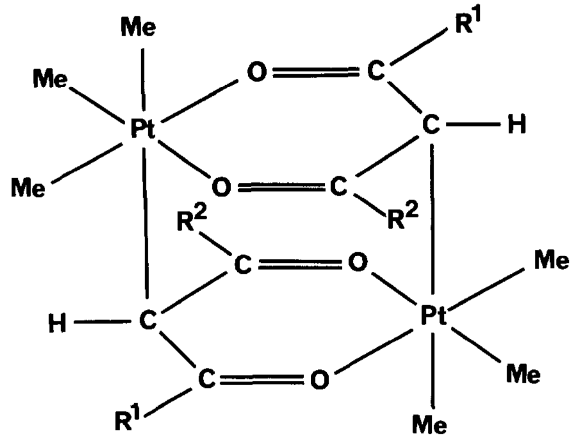

Fig. 1 Dimeric structure of the ketoester and diester complexes of trimethylplatinum(IV). For $R^1 \neq R^2$, the centrosymmetric structure with *trans* substituents is shown, formed from two enantiomeric monomer units (a + b). Two enantiomeric forms of the *cis* isomer (a + a) and (b + b) are also possible, the dimer now having a C_2 axis of rotation.

bipyridyl and 1,10-phenanthroline also gives 1 : 1 adducts, but here the diketone is monodentate through the γ-carbon atom [8,9].

We report here a study of the dimeric $Pt^{IV}Me_3$ β-ketoester complexes with $R^1 = CH_3$, $R^2 = OCH_3$ (**1**) and $R^1 = CH_3$, $R^2 = OC_2H_5$ (**2**), the diester complexes $R^1 = R^2 = OCH_3$ (**3**) and $R^1 = R^2 = OC_2H_5$ (**4**), and their 1 : 1 adducts with pyridine (**5–8**) and 2,2′-bipyridyl (**9–12**), which shows interesting points of similarity and difference when alkoxy groups are incorporated. A preliminary report on this work has been published [10].

Results and discussion

Analytical and spectroscopic data (Table 1) confirm that compounds **1–4** and their pyridine and bipyridyl adducts are exactly analogous to the corresponding acetylacetonate complexes, and contain tridentate (C,O,O′), bidentate (O,O′) and monodentate (C-bonded) ligands, respectively. Compounds **1–4** were readily prepared in high yield by Menzies' method [11] using TlOEt, $PtMe_3I$ and the ligand in benzene solution. Complex **2** was also made in good yield from the trimethylplatinum aquo ion and the ligand in aqueous solution containing sodium acetate as buffer, a hitherto unreported method for this type of platinum complex. The compounds are white crystalline solids, which sublime on heating, then decompose without melting. They are freely soluble in organic solvents, and are markedly more soluble than the complexes with $R^1 = R^2 =$ alkyl. Molar mass measurements in benzene at 30°C show that even at low concentrations (~ 0.05 *M*) the compounds are dimeric in solution. The diester compounds **3** and **4** were sufficiently volatile and stable for a dimeric molecular ion peak to be observed in the mass spectrum, while the ketoester compounds **1** and **2** gave several high intensity fragments at mass numbers intermediate between monomer and dimer.

The dimers are readily cleaved in benzene solution at room temperature by pyridine and 2,2′-bipyridyl to form 1 : 1 adducts. The pyridine derivatives **5–8** are

Table 1

Analytical and IR data

Complex [a]	Yield (%)	M.p. [b] (°C)	Anal. Found (calc.) %			ν(C=O) (cm^{-1})	ν(C–H) (cm^{-1})
			C	H	N		
1 $[PtMe_3(MAA)]_2$ [c]	47	165	27.0	4.50		1632	839
			(27.0)	(4.45)			
2 $[PtMe_3(EAA)]_2$ [c]	91	145	28.9	4.79		1640	850
			(29.3)	(4.91)			
3 $[PtMe_3(DMM)]_2$ [c]	90	160	25.5	4.34		1640	790
			(25.9)	(4.34)			
4 $[PtMe_3(DEM)]_2$ [c]	50	170	29.9	5.03		1638	795
			(30.1)	(5.05)			
5 $[PtMe_3(MAA)py]$	80	100	35.3	4.68	2.81	1612	778
			(35.9)	(4.87)	(3.22)		
6 $[PtMe_3(EAA)py]$	75	69–70	37.4	5.17	3.10	1605	780
			(37.5)	(5.17)	(3.12)		
7 $[PtMe_3(DMM)py]$	80	98–99	34.1	4.65	2.99	1612	778
			(34.7)	(4.70)	(3.11)		
8 $[PtMe_3(DEM)py]$	70	78–80	36.9	5.22	2.87	1613	776
			(37.6)	(5.27)	(2.93)		
9 $[PtMe_3(MAA)bipy]$	70	150	41.8	4.70	5.32	1700	
			(42.3)	(4.73)	(5.48)		
10 $[PtMe_3(EAA)bipy]$	84	140	43.2	5.00	5.27	1674	
			(43.4)	(4.99)	(5.33)		
11 $[PtMe_3(DMM)bipy]$	60	145	40.9	4.53	5.00	1720	
			(41.0)	(4.59)	(5.31)		
12 $[PtMe_3(DEM)bipy]$	75	178	43.2	5.01	5.00	1710	
			(43.4)	(4.74)	(5.06)		
13 $[PtMe_3(DBM)]_2$	25	200	47.5	4.46		1598	836
			(46.7)	(4.35)			
14 $[PtMe_3(DBM)py]$	90	145–146	50.5	4.64	2.55	1590	778
			(50.9)	(4.64)	(2.58)		
15 $[Al(MAA)_3]$	43	134–135	48.5	5.67		1612	788
			(48.4)	(5.68)			
16 $[Al(EAA)_3]$	43	78–80	52.1	6.54		1610	788
			(52.3)	(6.57)			

[a] Ligand abbreviations; MAA, R^1 = Me, R^2 = OMe; EAA, R^1 = Me, R^2 = OEt; DMM, $R^1 = R^2$ = OMe, DEM, $R^1 = R^2$ = OEt; DBM, $R^1 = R^2$ = Ph [b] Decomposes without melting unless a range is given. [c] Molar mass in benzene, found (calc.); (**1**) 702 (710), (**2**) 732 (738), (**3**) 720 (724), (**4**) 767 (798).

white, low-melting crystalline solids, while the bipyridyl adducts are pale yellow and melt with decomposition on heating. Both sets of adducts are readily soluble in chloroform and benzene, and were recrystallized from benzene/light petroleum.

Infrared spectra

The vibrational spectra of the complexes are consistent with their formulation as analogues of the acetylacetonates [8,9]. Two significant modes are a strong C=O stretch above 1590 cm^{-1} and a bending mode of the methine C–H bond in the range 760–850 cm^{-1} (Table 1). The former provides a clear discrimination between the three configurations of the dicarbonyl ligand, *i.e.* monodentate (C-bonded) 1720–1674 cm^{-1} > tridentate (C,O,O′) 1640–1632 cm^{-1} > bidentate (O,O′) 1612–1605 cm^{-1}, the ketonic character of the bond decreasing in this order

Table 2

^{1}H NMR data [a] for the Pt–Me$_3$ complexes

Complex [b]		Pt–Me signals {δ, ^2J (Hz)} for *trans* atoms [c]								Ligand C–H signal	
		O(ester)		O(carbonyl)		C(methyne)		N(py or bipy)		δ	^2J (Hz) [c]
1 [PtMe$_3$(MAA)]$_2$	(A)	1.09	77.9	0.98	75.9	0.91	71.2			4.14	44.2
	(B)	1.14	78.9	0.94	75.8	0.90	70 8			4.12	44.4
2 [PtMe$_3$(EAA)]$_2$	(A)	1.09	77.9	0.94	75 9	0.87	70.5			4.07	44.3
	(B)	1.11	78.7	0.93	75.6	0.86	70.5			4 06	44.7
3 [PtMe$_3$(DMM)]$_2$		1.00 [d]	78.8			0.76	67.3			3.48	47.0
	(C)	1.00 [d]	79.0			0 75	67.5			3.45	
4 [PtMe$_3$(DEM)]$_2$		1.00 [d]	79 0			0.72	66.7			3.44	46.1
	(C)	1.00 [d]	78.8			0 76	66.3			3.38	46.3
5 [PtMe$_3$(MAA)py]		1.06	77.2	0.94	72.8			0.88	71.2	4.57	
6 [PtMe$_3$(EAA)py]		1.08	76 8	0 96	72 7			0.91	70.7	4.64	
7 [PtMe$_3$(DMM)py]		1.02 [d]	75 8					0.91	69.8	4.08	
8 [PtMe$_3$(DEM)py]		1 00 [d]	76.0					0.91	70.5	4 08	
9 [PtMe$_3$(MAA)bipy]						0.16	62.9	1.02	69.3	3.32	53.3
								0.97	69 4		
10 [PtMe$_3$(EAA)bipy]						0.17	62.8	1 04	69.2	3.32	53.3
								1.00	69 4		
11 [PtMe$_3$(DMM)bipy]						0.98	61.2	1.01 [d]	70.0	2.96	53.2
12 [PtMe$_3$(DEM)bipy]						0.97	60.9	1.04 [d]	70.3	3.00	53.5
13 [PtMe$_3$(DBM)]$_2$	(C)			1.14 [d]	74.1			0.88	82.4 [e]	6.77	
17 [PtMe$_3$(AA)]$_2$	(C)			0 86 [d]	73.3			0.67	82.6 [e]	5.02	

[a] Spectra in CDCl$_3$ except for (C) which were run in acetone-d_6 [b] Ligand abbreviations as Table 1; AA, R^1 = R^2 = Me. [c] $^2J(^{195}\text{Pt}-^1\text{H})$. [d] Indicates the more intense signal in a 2:1 spectrum. [e] *trans* to solvent (acetone).

as expected. The values for the tris aluminium(III) chelates **15** and **16** confirm the range for bidentate ligands. In **2**, the C–O bond length is somewhat shorter [3] than it is in the diketone [2] complex R^1 = R^2 = C$_3$H$_7$ (120 pm compared to 126 pm), and it is therefore not surprising to find a higher C=O stretching mode in **2**–**4** (1640–1632 cm^{-1}) than in the corresponding diketonates (1600–1580 cm^{-1}). The high C=O stretch in the bipyridyl adducts **9**–**12** shows the presence of free carbonyl groups [1,8]. With the exception of complex **4**, the change from ketoester to diester increases the ketonic character of the C=O bond irrespective of how the ligand is bonded. The out-of-plane C–H bend also permits discrimination between the tridentate and bidentate alternatives, but cannot be so certainly assigned.

^{1}H NMR spectra

Solution ^{1}H NMR data for the PtMe$_3$ complexes in CDCl$_3$ at room temperature are recorded in Table 2. Spectra run in benzene showed identical features. Unambiguous assignments may readily be made by comparison with the spectra of the 1,3-diketone complexes [9,12]. The expected number of platinum methyl signals is seen in every case, *i.e.* 1:1:1 signals where the carbonyl ligand is unsymmetrical or a 2:1 pattern where it is symmetrical. The presence of two sets of 1:1:1 resonances in the approximate ratio 2:1 (A:B) for the dimers **1** and **2** shows that isomers are present in solution. In contrast to the diketonate dimers, **1**–**4** were stereochemically rigid in solution. Coupling constants for the platinum methyl signals showed the usual dependence on the *trans* atom [6,9,12,13]. For the dimers, $^2J(^{195}\text{Pt}-^1\text{H})$ values for the methyls *trans* to O(ester) and O(carbonyl) were in similar ranges (77.9–79.0 Hz and 75.6–75.9 Hz, respectively), while for methyls *trans* to the bridging carbon atom, somewhat lower values were found for the diester complexes **3** and **4** (67.3 and 66.7 Hz) compared to the ketoester dimers **1** and **2** (71.2 and 70.8 Hz). The correlation between ^2J and the strength of the bond *trans* to the Pt–Me group [13] shows clearly that an alkoxy substituent on the chelate ring strengthens the bridge bond.

In the adducts, ^2J values are found in the expected ranges for methyl *trans* to pyridine (69.8–71.2 Hz) and bipyridyl (69.2–70.3 Hz) [6]. The presence of a bidentate (O,O′) dicarbonyl ligand in the pyridine complexes **5–8** is shown by ^2J values of 75.8–77.2 Hz *trans* to O(ester) and 72.7–72.8 Hz *trans* to O(carbonyl). These values indicate that a carbonyl with an α-alkyl group bonds more strongly to the metal than does one with an α-alkoxy group. In the bipyridyl complexes **9–12**, ^2J for methyls *trans* to the monodentate C-bonded ligand are in the expected range (60.9–62.9 Hz), and show that the Pt–CH bond is stronger in the diester than in the ketoester adducts, as it is in the parent dimers.

The signal for the unique methine proton is particularly useful in assigning the dicarbonyl ligand configuration. The bidentate (O,O′) form is shown in **5–8** by a singlet in the range δ 4.08–4.64, with no coupling to ^{195}Pt (for the EAA complexes of Pd^{II} a range of δ 3.44–4.57 was found [1]). In the tridentate (C,O,O′) form the C–H signal is shifted to higher field (δ 3.44–4.12) with clear ^{195}Pt–^{1}H coupling, the ^2J values (44.2–44.7 Hz) being slightly higher than those reported [9] for some β-diketonate dimers (42.0–42.5 Hz). In the bipyridyl adducts, the C-bonded form has the C–H signal at an even higher field (δ 2.96–3.32), the clear coupling to ^{195}Pt ($^2J = 53.2$–53.5 Hz) showing that the Pt–C bond is intact.

In $[PtMe_3DEM]_2$, the NMR spectrum of the CH_2CH_3 group gave an ABX_3 pattern, the two the CH_2 protons showing a small chemical shift non-equivalence, but an equal coupling to the CH_3 protons. A similar feature was noted in all other compounds with R^1 and/or $R^2 = OC_2H_5$ with the exception of [PtMe$_3$(EAA)py], and the same observation has been reported [14] for the complexes [(C$_5$Me$_5$)Rh(EAA)Cl] and [(C$_5$Me$_5$)Rh(EAA)]$_2$(PF$_6$)$_2$]. The non-equivalence of the $-CH_2$ protons is possibly a consequence of hindered rotation. In the pyridine adducts, three multiplets (δ 8.7–7.2) and in the bipyridyl adducts four multiplets (δ 8.8–7.5) integrating for 5H and 8H, respectively, are attributable to the Lewis base. The lowest field multiplet in both series shows coupling to the metal, and is attributable to the α-protons of the Lewis base.

Variable temperature ^{1}H NMR spectra were run on the dimers **1–4** in an attempt to induce fluxional behaviour similar to that shown by the β-diketonates at above ambient temperatures. The spectra of the complexes **3** and **4** with the diester ligands showed no change over the range 25–100°C in C_6H_6 solution, indicating that the dimers are stereochemically rigid. For complex **1**, however, three changes in the Pt–Me signals occurred as the temperature was raised, the original six signals changing to three (ratio 1 : 1 : 1) at 63°C, then to two (ratio 2 : 1) at 76°C, and finally to one at 86°C. The final coalescence was accompanied by loss of Pt–H coupling to the methine carbon proton and a change in the number of C–CH_3 signals of the carbonyl ligand from two to one as the dimer is broken. Complex **2** showed very similar behaviour. The changes are reversed on cooling. They indicate an initial change to one dimeric isomer, followed by bridge bond breaking.

General discussion

As expected the ketoester and diester ligands behave in a very similar manner to the β-diketones, and can adopt the same monodentate (C-bonded), bidentate (O,O′) and tridentate (C,O,O′) configurations which are readily distinguishable by IR and NMR spectroscopy. The observation of isomers in solutions of **1** and **2** but not in **3** and **4** implies that the isomerism arises from the relative positions of the R^1 and R^2 substituents in the dimer. For the unsymmetrical ligands, two enantiomeric monomer units (a) and (b) are possible for the complexes, and Fig. 1 shows the combination of one of each to form an (a + b) mesomeric dimer (the centrosymmetric solid state structure). Combinations of (a + a) and (b + b) give two enantiomeric dimers (with a C_2 axis) which are indistinguishable by NMR. The observation of two sets of signals in the ratio 2 : 1 may be interpreted in terms of an equal mixture of all three possibilities. The proportions of the isomers remained the same at room temperature on changing from $CDCl_3$ to C_6D_6, and after prolonged refluxing in benzene, showing that the isomers are of comparable stability.

The striking absence of stereochemical non-rigidity in **1–4** compared with the 1,3-diketonates is almost certainly a consequence of a strengthened Pt–C bridge bond when alkoxy groups are incorporated into the dimer, as shown in the vapour phase by the mass spectra, and in solution by the ^2J(Pt–CH) coupling constants.

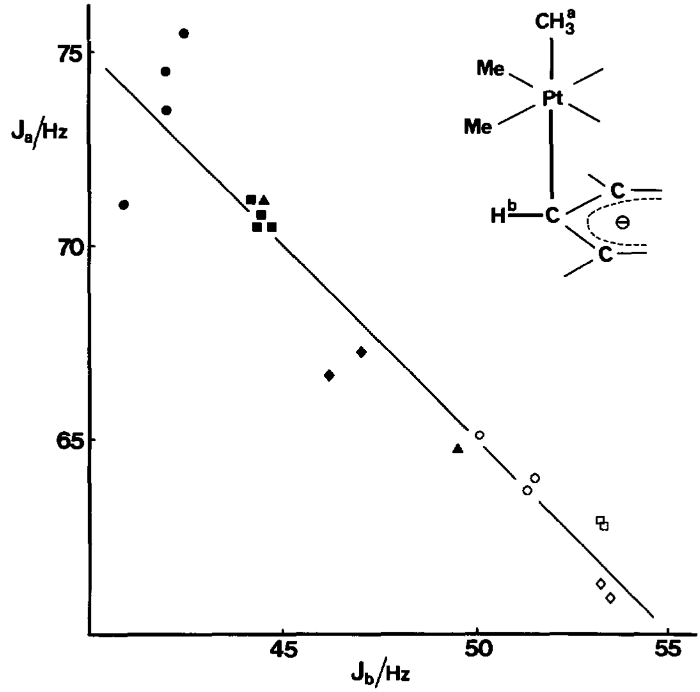

Fig. 2. Plot of values of ^2J(Pt–CH_3) against ^2J(Pt–CH) for compounds with the structural feature shown (data from this work and [5] and [9], and for the complex [$PtMe_3(C_4H_3SCOCHCOCH_3)$bipy] [19] for which $J_a = 65.1$ Hz and $J_b = 50.1$ Hz) Symbols refer as follows: ●, β-diketones [5], ■, β-ketoesterates; ◆, β-diesterates; ▲, β-iminoketonates [9] Closed symbols refer to the dimers, open symbols to the adducts with the bidentate bases 2,2′-bipyridyl or 1,10-phenanthroline.

Support for this conclusion is provided by the demonstration that the fluxional process in the dimeric diketonates does involve Pt–C bridge bond breaking [7], and it is further substantiated by the clear demonstration of the stability of **3** and **4** in acetone solution. The spectra of the dicarbonyl dimers with $R^1 = R^2 = CH_3$ (**17**) and C_6H_5 (**13**) at −50°C and −60°C, respectively, in acetone-d_6 show 2:1 platinum methyl resonances with ^2J values of 73.3 and 74.1 Hz for the more intense signal, *i.e.* methyls *trans* to O(diketone). The less intense signals with ^2J values of 82.6 and 82.4 Hz in **17** and **13**, respectively, correspond to methyl groups *trans* to O(solvent), and the presence of solvated monomer in the two solutions was confirmed by a methine proton signal showing no coupling to ^{195}Pt. At room temperature in acetone-d_6, **3** and **4** also show a 2:1 pattern of methylplatinum resonances, but the ^2J values are very similar to those in $CDCl_3$ and C_6H_6 solution, the spectra being virtually solvent independent, and consistent with the presence of strongly bonded dimers.

There is now substantial evidence that the magnitude of the ^2J(Pt–H) coupling constants for the platinum methyl groups in trimethylplatinum(IV) compounds is determined almost exclusively by the ligands in the *trans* position, and is virtually independent of the *cis* ligands [6,13,15]. The presence in the bipyridyl adducts of a Pt–Me group *trans* to a C–H group gives evidence for this very specific *trans* influence. In Fig. 2, values of ^2J(Pt–CH_3) are plotted against ^2J(Pt–CH) for a series of nineteen compounds. While a few compounds do deviate markedly, it is clear that the majority show an almost linear correlation between the two values. The factors that determine the magnitude of two bond couplings to platinum are not understood, and there is no *a priori* reason to expect the observed correlation. If the amount of *s*-orbital character is one determining factor, as it is in the Fermi contact mechanism, the result may reflect a practically constant amount of metal-orbital *s*-character along the *trans* bonds.

Experimental

$[PtMe_3I]_4$ and $[(PtMe_3)_2SO_4 \cdot 4H_2O)$ were made by published methods [16,17]. The ligands were commercial samples, and were distilled before use. The dimeric complexes **1**–**4** were made by Menzies' method [11]. In an alternative preparation of **2**, the sulphate was used as starting material.

Preparation of $[PtMe_3(EAA)]_2$ (**2**)

Ethylacetoacetate (0.5 cm^3, an excess) was added dropwise with stirring to a solution of $[(PtMe_3)_2SO_4 \cdot 4H_2O]$ (64.8 mg, 0.1 mmol) in water (10 cm^3) containing sodium acetate (0.3 g). A few drops of ethanol were added to aid dissolution of the ketoester. A dense white precipitate of $[PtMe_3(EAA)]_2$ formed. It was filtered off, washed with water, dried *in vacuo* and recrystallized from diethyl ether.

Preparation of $[PtMe_3(EAA)py]$ (**6**)

A solution of $[PtMe_3(EAA)]_2$ (73.8 mg, 0.2 mmol) in benzene (10 cm^3) was stirred with a few drops of pyridine for 1 h at room temperature. The clear solution was evaporated to dryness under reduced pressure. The glassy gum remaining crystallized on addition of light petroleum. Recrystallization from hot light petroleum gave clear prismatic crystals which became opaque on drying *in vacuo* (67 mg, 75%).

Compounds **5**, **7** and **8** were prepared by a similar method.

Preparation of [PtMe$_3$(EAA)bipyl] (**10**)

A solution of [PtMe$_3$(EAA)]$_2$ (123 mg, 0.33 mmol) and 2,2′-bipyridyl (52 mg, 0.33 mmol) in benzene (15 cm^3) was stirred for 1 h at room temperature. The yellow solution deposited pale yellow crystalline needles on addition of light petroleum (5 cm^3). The product was recrystallized from benzene/light petroleum (145 mg, 84%).

Compounds **9**, **11** and **12** were prepared similarly.

Preparation of [Tl(C$_6$H$_5$COCHCOC$_6$H$_5$)] [TlDBM)

Thallous carbonate (1.2 g) and dibenzoylmethane (1.1 g) in ethanol (20 cm^3) were refluxed with vigorous stirring for 4 h. The hot solution was filtered through a small glass wool plug to remove traces of unchanged carbonate. Cooling the filtrate yielded yellow crystals of TlDBM (1.7 g, 80%). Anal. Found: C, 41.8; H, 2.66; Tl, 47.4. $C_{15}H_{11}O_2Tl$ calc.: C, 42.1; H, 2.59; Tl, 47.8%.

Preparation of [PtMe$_3$(DBM)]$_2$ (**13**)

A solution of [PtMe$_3$I]$_4$ (370 mg, 0.25 mmol) and TlDBM (440 mg, 1.0 mmol) in benzene (80 cm^3) was refluxed for 4 h. The filtered solution was reduced in volume to 30 cm^3, and cooled to 10°C. Attempts to purify the white powder which separated (108 mg, 25%) were unsuccessful. The pyridine adduct was made to characterize the compound further.

Preparation of [PtMe$_3$(DBM)py] (**14**)

[PtMe$_3$(DBM)]$_2$ (180 mg) and excess pyridine (2 cm^3) were refluxed in benzene (10 cm^3) for 3 h. The clear yellow solution was evaporated to dryness, and the product recrystallized from ether/light petroleum as large pale yellow crystals (175 mg, 90%).

Preparation of [Al(MAA)$_3$] (**15**)

A solution of sodium hydroxide (2*M*) was added to an aqueous solution of $Al_2(SO_4)_3 \cdot 16H_2O$ (5.0 g) until the gelatinous precipitate redissolved. An excess of methylacetoacetate was added gradually. The dense white precipitate formed was filtered off, washed well with water, and dried. The solid was extracted with hot benzene (30 cm^3), the filtered solution evaporated to dryness, and the product recrystallized from benzene/light petroleum (1.5 g, 25%).

The aluminium complex Al(EAA)$_3$ (**16**) was made from aluminium ethoxide and the ligand by the literature method [18] (m.p. 78–80°C, lit. 78–79°C).

Molar mass measurements on **1–4** were carried out in benzene using a Mechrolab 301A vapour pressure osmometer operating at 37°C. The instrument was calibrated with benzil. Mass spectra were recorded on a Hitachi Perkin–Elmer RMU-6D mass spectrometer using an ionization chamber temperature of 200°C and an ionization potential of 70 V. Infrared spectra were recorded in KBr discs using a Perkin–Elmer model 357 spectrometer. All proton NMR spectra were run on a JEOL MH100 instrument, in $CDCl_3$ or C_6H_6 solution for **1–12**, and in acetone-d_6 for **3**, **4**, **13** and **17**.

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