Synthesis and Crystal Structure of the Trimetal Compound $[Pt_3(C_2H_4)(C_8H_8)_2(1,5\text{-}C_8H_{12})_2]$*: a Complex of Platinum(0) and Platinum(II)

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Bis(cyclo-octa-1,5-diene)platinum, dissolved in ethylene-saturated diethyl ether, reacts with cyclo-octatetraene to give the triplatinum complex $[Pt_3(C_2H_4)(C_8H_8)_2(1,5\text{-}C_8H_{12})_2]$, which has been characterised by a single-crystal *X*-ray diffraction study. Crystals of the triplatinum compound are monoclinic, space group *C*2/*c*, with *Z* = 4 in a unit cell of dimensions *a* = 16.370(17), *b* = 7.465(5), *c* = 24.603(37) Å, β = 102.55(10)°. The structure has been solved by heavy-atom methods and refined by least squares to *R* 0.062 (*R*′ 0.062) for 3 341 independent diffracted intensities measured at 200 K. The molecule lies astride a crystallographic two-fold axis, with the trimetal system being significantly non-linear [Pt(2)–Pt(1)–Pt(2′) 158°]. The Pt–Pt separations of 3.166(1) Å indicate little or no direct metal–metal bonding. Two cyclo-octa-1,5-diene ligands, in their usual tub-like configuration, are η^4-co-ordinated to Pt(2) and Pt(2′). The Pt(1)–Pt(2) and Pt(1)–Pt(2′) vectors are bridged by two C_8H_8 ligands which employ four adjacent carbon atoms for bonding to the metal atoms. Of these carbon atoms, the central pair form a C=C bond η^2-co-ordinated to Pt(1) while the outer two are attached to Pt(2) [or Pt(2′)] by σ bonds. The central metal atom Pt(1) is also bonded to an ethylene molecule so that it is in a distorted trigonal configuration, in contrast to Pt(2) and Pt(2′) which have an essentially square-planar environment comprising the two σ bonds from one C_8H_8 ligand and the C=C bonds of a C_8H_{12} ring. Hence Pt(1) can be regarded as platinum(0), and the Pt(2) and Pt(2′) atoms as being in a Pt^{II} oxidation state. From variable-temperature ^1H n.m.r. studies it was shown that the compound undergoes dynamic behaviour in solution. The mechanism is discussed, and the spectrum analysed by spin-decoupling experiments. The ^{13}C n.m.r. spectrum is also reported.

A VERSATILE reagent for the synthesis of organoplatinum compounds is bis(cyclo-octa-1,5-diene)platinum,[1] and its extensive use in this respect followed the discovery that it could be prepared by reducing $[PtCl_2(cod)]$ (cod = cyclo-octa-1,5-diene) with $Li_2[cot]$ (cot = cyclo-octatetraene) in the presence of excess of cod.[2] This reaction might have yielded the compound [Pt(cod)(cot)] in which both cod and cot ligands are η^4-co-ordinated to platinum(0). However, if this species is an intermediate, then in the presence of excess of cyclo-octa-1,5-diene the cot group is displaced. In the presence of excess of C_2H_4 the complex $[Pt(cod)_2]$ affords $[Pt(C_2H_4)_3]$, although this reaction may be reversed by adding cod. This suggested that reaction of $[Pt(cod)_2]$ with excess of cot might give a cyclo-octatetraene complex of platinum(0). In the case of nickel, it has been shown that both $[Ni(cod)_2]$ and [Ni(cdt)] (cdt = *trans,trans,trans*,-cyclododeca-1,5,9-triene) react with cot to form the novel dinickel compound $[Ni_2(cot)_2]$.[3,4] In organoplatinum(II) chemistry several Pt–cot compounds are known in which the cot adopts an η^4 tub-like bonding mode.[5]

RESULTS AND DISCUSSION

Reaction of $[Pt(cod)_2]$ with cot gave a black intractable solid, and neither a platinum analogue of $[Ni_2(cot)_2]$ nor a complex [Pt(cod)(cot)] were isolated. Treatment of $[Pt(C_2H_4)_3]$ with cot yielded a very insoluble orange solid of indeterminate composition. It is possible that this product is $[Pt(cot)_2]$. Reaction of [Ni(cdt)] with cot at −78 °C gives a yellow insoluble compound which is probably $[Ni(cot)_2]$.[3] However, the latter on warming to room temperature produces $[Ni_2(cot)_2]$, in which the ligand molecules are η^3 bonded to the metal atoms so that the compound can be regarded as a ' bis(η^3-allyl)nickel ' complex.[4] In the case of platinum, a complex $[Pt(cot)_2]$ once formed might not convert to $[Pt_2(cot)_2]$ because of this metal's strong preference for an η^4 bonding mode with cyclic chelating dienes.[5]

In view of our inability to isolate characterisable cyclo-octatetraene–platinum complexes by treating cot with $[Pt(cod)_2]$ or $[Pt(C_2H_4)_3]$, we next investigated the effect of adding cot to the latter compound in the presence of cod. At −20 °C in diethyl ether, this reaction produced orange plate-like crystals which microanalysis indicated to be a trinuclear platinum complex. Since such a species would be expected to have a novel structure, a single-crystal *X*-ray diffraction study was carried out. This study, the results of which are summarised in Tables 1—3, established not only the molecular structure

TABLE 1

Final positional parameters (fractional co-ordinates) for the complex $[Pt_3(C_2H_4)(\mu\text{-}C_8H_8)_2(C_8H_{12})_2]$

Atom	*x*	*y*	*z*
Pt(1)	0.0 *	0.027 7(1)	0.25 *
Pt(2)	0.129 51(4)	0.109 27(8)	0.367 64(3)
C(1)	0.032(1)	0.247(2)	0.198 0(6)
C(2)	0.054(1)	0.326(2)	0.337 1(7)
C(3)	0.043(1)	0.444(2)	0.383 7(7)
C(4)	0.009(1)	0.405(2)	0.426 6(7)
C(5)	−0.017(1)	0.236(2)	0.465 9(7)
C(6)	−0.011(1)	0.068(2)	0.427 6(7)
C(7)	0.013(1)	0.007(2)	0.376 7(7)
C(8)	−0.050(1)	0.076(2)	0.322 9(7)
C(9)	0.208(1)	−0.078(2)	0.428 7(9)
C(10)	0.276(1)	0.018(3)	0.463 8(9)
C(11)	0.320(1)	0.163(3)	0.432 2(10)
C(12)	0.255(1)	0.250(3)	0.383 9(8)
C(13)	0.231(1)	0.192(2)	0.329 3(9)
C(14)	0.265(1)	0.023(3)	0.307 5(9)
C(15)	0.270(1)	−0.139(3)	0.346 4(9)
C(16)	0.201(1)	−0.145(2)	0.375 5(8)
C(101)	0.031(1)	−0.251(3)	0.235 2(9)

* Atom in special position, parameter not refined.

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* *ae*-Bis(1,2:5,6-η-cyclo-octa-1,5-diene)-*bd*-di-[μ-(1′,4′-σ; 2′-3′-η-cyclo-octatrien-1′,4′-ylene-$C^{2'}C^{3'}(Pt^2)$)]-*c*-ethylenetriplatinum.

but also the composition of the compound as $[Pt_3(C_2H_4)(cod)_2(cot)_2]$.

The molecule (Figure 1) lies astride a crystallographic two-fold axis with the trimetal system significantly non-linear [Pt(2)-Pt(1)-Pt(2′) 158°]. The two cod ligands are attached to Pt(2) and Pt(2′) and are in their usual tub-like configuration. The two cot ligands bridge the Pt-Pt vectors of 3.166(1) Å. These distances imply that there is no direct metal-metal bonding along the chain. Based on covalent radii, an estimated length for a Pt-Pt bond would be 2.6 Å. In the cluster complexes $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$ and $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$ in which the metal atoms adopt ‘ butterfly ’ configurations, the Pt-Pt separations are 2.998(2) and 3.206(1) Å respectively, and are considered not to involve direct bonding interactions.[6]

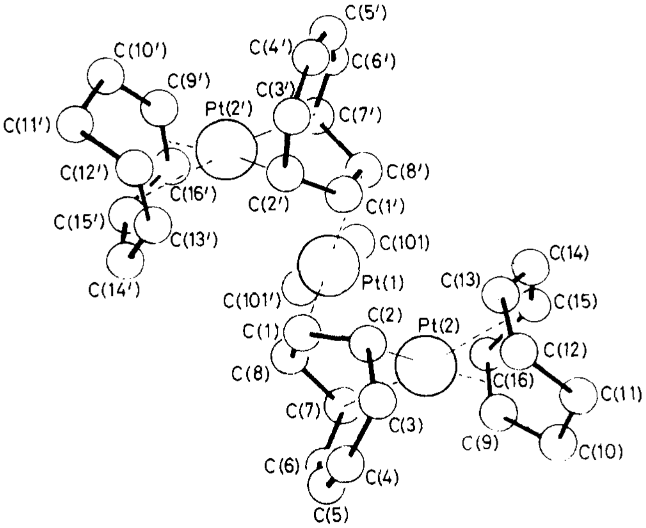


FIGURE 1 The molecule $[Pt_3(C_2H_4)(cod)_2(cot)_2]$ viewed down the crystallographic two-fold axis and showing the atomic numbering scheme

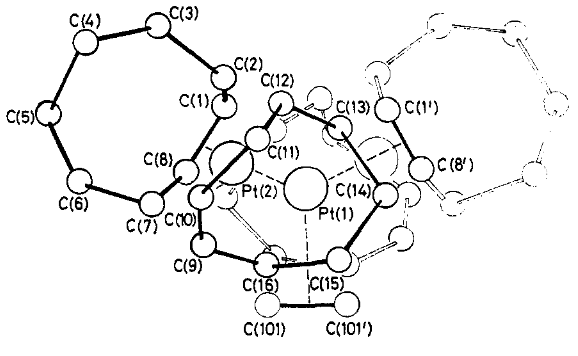


FIGURE 2 The molecule $[Pt_3(C_2H_4)(cod)_2(cot)_2]$ viewed onto the ‘ trigonal plane ’ C(1), C(8), C(101), Pt(1) and symmetry related atoms

The central platinum atom Pt(1) is essentially trigonally co-ordinated (Figure 2) to an ethylene molecule, $H_2C(101)=C(101')H_2$, and to the two cot ligands *via* C=C double bonds [C(1)-C(8) and C(1′)-C(8′)]. The six ligated carbon atoms are not planar, the ethylene-carbon atoms lying 0.26 Å (Table 3) from this mean plane. Consequently, there is a dihedral angle of 22.8° between the plane Pt, C(101), C(101′), and either Pt, C(1), C(8) or its symmetry related plane Pt,C(1′),C(8′). The distortions from a more regular trigonal arrangement probably arise from the constraints imposed by the cot rings [C(101,-101′)-Pt(1)-C(1,8) 118°]. The Pt-C(101) and Pt-C(101′) distances [2.19(2) Å] are similar to those found previously in the compounds $[Pt(C_2H_4)_3]$, 2.176(8),[7] $[Pt(C_7H_{10})_3]$, 2.18(2),[2] and $[Pt(C_2H_4)_2(C_2F_4)]$, 2.229(6) Å.[7] Likewise, the C(101)-C(101′) bond length [1.39(4) Å] compares with those established, 1.39(2), 1.39(2), and 1.371(8) Å respectively, for the aforementioned compounds.

TABLE 2

Internuclear distances (Å) and angles (°) in the complex $[Pt_3(C_2H_4)(\mu\text{-}C_8H_8)_2(C_8H_{12})_2]$

Distances [a,b]		Angles [a,b]	
Pt(1)-Pt(2)	3.166(1)	Pt(2)-Pt(1)-Pt(2′)	157.82(4)
Pt(1)-Pt(2′)	3.166(1)		
Pt(1)-C(101)	2.19(2)	C(101)-Pt(1)-C(101′)	37.0(10)
C(101)-C(101′)	1.39(4)		
Pt(1)-C(1)	2.22(1)	C(1)-Pt(1)-C(8)	38.0(5)
Pt(1)-C(8)	2.19(2)		
Pt(1) · · · C(2)	3.06(2)		
Pt(1) · · · C(7)	3.07(2)		
Pt(2)-C(2)	2.06(2)	C(2)-Pt(2)-C(7)	81.4
Pt(2)-C(7)	2.12(2)		
Pt(2)-C(9)	2.20(2)	C(9)-Pt(2)-C(16)	36.3(7)
Pt(2)-C(16)	2.21(2)		
Pt(2)-C(12)	2.24(2)	C(12)-Pt(2)-C(13)	35.8(7)
Pt(2)-C(13)	2.20(2)		
Pt(2)-C(9,16)	2.09(2)	C(9,16)-Pt(2)-C(12,13)	85.7(5)
Pt(2)-C(12,13)	2.12(2)		
C(1)-C(2)	1.56(2)	C(1)-C(2)-C(3)	112(1)
C(2)-C(3)	1.49(2)	C(2)-C(3)-C(4)	130(1)
C(3)-C(4)	1.34(2)	C(3)-C(4)-C(5)	131(1)
C(4)-C(5)	1.46(2)	C(4)-C(5)-C(6)	130(2)
C(5)-C(6)	1.34(2)	C(5)-C(6)-C(7)	130(2)
C(6)-C(7)	1.48(2)	C(6)-C(7)-C(8)	111(1)
C(7)-C(8)	1.54(2)	C(7)-C(8)-C(1)	117(1)
C(8)-C(1)	1.44(2)	C(8)-C(1)-C(2)	112(1)
C(9)-C(10)	1.41(3)	C(9)-C(10)-C(11)	115(2)
C(10-C(11)	1.61(3)	C(10)-C(11)-C(12)	111(2)
C(11)-C(12)	1.52(3)	C(11)-C(12)-C(13)	126(2)
C(12)-C(13)	1.37(3)	C(12)-C(13)-C(14)	125(2)
C(13)-C(14)	1.53(3)	C(13)-C(14)-C(15)	113(2)
C(14)-C(15)	1.54(3)	C(14)-C(15)-C(16)	114(2)
C(15)-C(16)	1.48(3)	C(15)-C(16)-C(9)	124(2)
C(16)-C(9)	1.38(3)	C(16)-C(9)-C(10)	129(2)
		C(9,16)-Pt(2)-C(2)	177(1)
		C(12,13)-Pt(2)-C(7)	177(1)

[a] Primes denote atoms related to corresponding non-primed atoms by two-fold rotation. [b] C(*n*,*m*) designates the midpoint of the lines joining the atoms *n* and *m*.

The outer platinum atoms Pt(2) and Pt(2′) can be described as four-co-ordinate with an approximately square-planar configuration. These atoms are η^2 bonded to the double bonds of the terminal cod ligands and are also attached to the cot molecules at C(2), C(7), and C(2′), C(7′) respectively, by σ bonds [Pt-C(mean) 2.09(1) Å]. The latter distance is within the range generally found [1.99(3)—2.15(2) Å][8] for such bonds. There can be no other interaction between the cot rings and Pt(2) or Pt(2′) since all other Pt-C distances involving

TABLE 3

Selected least-squares planes for the complex [$Pt_3(C_2H_4)(\mu\text{-}C_8H_8)_2(C_8H_{12})_2$] in the form $Ax + By + Cz = D$, where x, y, and z are fractional crystal co-ordinates; distances (Å) from the planes are given in square brackets

Plane (i): Pt(1), C(101), C(101′)
$8.249x + 17.251z = 12.562$
[C(1) −0.63, C(8) −0.84]
Plane (ii): Pt(1), C(1), C(8)
$13.058x - 0.268y + 9.140z = 15.335$
[C(101) 0.34, C(101′) −0.19]
Plane (iii): Pt(1), C(1), C(8), C(101), C(1′), C(8′), C(101′)
$12.990x + 9.322z = 15.320$
[C(1) 0.07, C(8) 0.03, C(101) 0.26]
Plane (iv): Pt(2), C(2), C(7)
$-0.073x + 2.744y + 22.106z = 8.345$
Plane (v): * Pt(2), C(9,16), C(12,13)
$-0.918x + 3.106y - 21.909z = 10.462$
Plane (vi): Pt(2), C(9), C(16)
$14.126x + 3.757y - 6.635z = 17.684$
Plane (vii): Pt(2), C(12), C(13)
$6.762x - 6.464y + 4.032z = 1.950$
Plane (viii): C(1), C(2), C(7), C(8)
$10.927x + 3.551y - 17.912z = 8.589$
[C(1) 0.02, C(2) −0.01, C(7) 0.01, C(8) −0.02]
Plane (ix): C(2), C(3), C(4), C(5), C(6), C(7)
$13.428x + 0.907y + 7.970z = 14.249$
[C(2) 0.05, C(3) −0.06, C(4) 0.004, C(5) 0.06, C(6) −0.04, C(7) −0.008]
Plane (x): * Pt(2), C(9,16), C(12,13), C(2), C(7)
$-2.783x + 3.112y + 22.296z = 8.388$

Dihedral angles (°) between least-squares planes

(i)–(ii)	22.8	(ii)–(iii)	2.1
(i)–(iii)	22.3	(iv)–(v)	4.3
(vi)–(vii)	84.7	(viii)–(ix)	106.6

The line through Pt(1)–Pt(2) has direction cosines: 0.6462, 0.1923, 0.7385 and makes angles with the planes (i) 36.8, (ii) 29.9, (iii) 28.6, and (x) 37.4°.

* C(n,m) indicates the midpoint of the line joining atoms C(n) and C(m).

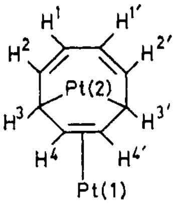
these ligands and these metal atoms are greater than 3 Å. Similarly, Pt(1) · · · C(2) and Pt(1) · · · C(7) are too long to involve a bonding interaction. In each cot ring there are two unco-ordinated C=C double bonds [C(3)–C(4) and C(5)–C(6); C(3′)–C(4′) and C(5′)–C(6′)] and six atoms [C(2)—C(7), and C(2′)—C(7′)] essentially coplanar (Table 3). The planes defined by the six carbon atoms make an angle of 107° with the planes containing the four carbon atoms [C(1), C(2), C(7), and C(8); and C(1′), C(2′), C(7′), and C(8′), respectively] bonded to the metal atoms.

The geometry of the cod ligands is as usual.[9] The angle of ' bite ' to the metal atoms is 84.7°, which compares with that of 85° in [Pt(cod)$_2$] [10] and 86° in the platinum–quinone complex [$Pt(C_6H_2O_2Bu^t{}_2\text{-}2,6)$(cod)].[11] Moreover, in [$Pt_3(C_2H_4)$(cod)$_2$(cot)$_2$] the Pt–C and C=C bonds involving the cod ligands, mean 2.21(2) and 1.37(3) Å respectively, compare closely with those found in [Pt(cod)$_2$], 2.211(6) and 1.398(9) Å,[10] and in [$Pt(C_6H_2O_2Bu^t{}_2\text{-}2,6)$(cod)], 2.182(4) and 1.396(6) Å.[11]

Having elucidated the molecular structure of [$Pt_3(C_2H_4)$(cod)$_2$(cot)$_2$] by the X-ray diffraction study, it was possible to interpret the n.m.r. data for this molecule. The variable-temperature ^{1}H n.m.r. spectra established that the molecule underwent dynamic behaviour in solution. At 0 °C (Figure 3), the ethylene protons were observed as a singlet at 3.11 p.p.m., flanked by ^{195}Pt satellites [^2J(PtH) 56 Hz]. The cod methine protons also appeared as a singlet [4.27 p.p.m., ^2J(PtH) 49 Hz], albeit broad (Table 4). This pattern indicated that at this temperature both the C_2H_4 ligand and the Pt(cod)(cot) moieties rotate around the axes through Pt(1) and the midpoints of the three co-ordinated C=C double bonds. Apart from these peaks, and a broad signal at 1.80 p.p.m. attributable to the cod methylene protons, the dominant feature of the spectrum [Figure 3(a)] was a pair of resonances at 5.95 and 6.54 p.p.m., a region associated with unco-ordinated olefinic protons. The latter can, therefore, be assigned as indicated in Table 4. Since the molecule is dynamic, H^1 and H$^{1'}$ and H^2 and H$^{2'}$ are chemically equivalent pairs and should give rise to an [AB]$_2$ sub-spectrum. The peak at δ 5.95 was well

TABLE 4

Hydrogen-1 n.m.r. data for the complex [$Pt_3(C_2H_4)$(cod)$_2$(cot)$_2$] *



Temperature θc/°C						cod	
	H^1,H$^{1'}$	H^2,H$^{2'}$	H^3,H$^{3'}$	H^4,H$^{4'}$	C_2H_4	CH	CH$_2$
0	5.95 m $J(\mathrm{H^1H^{1'}})$ 8.3 $J(\mathrm{H^1H^2})$ 11.1 $J(\mathrm{H^1H^{2'}})$ 0.6 ^4J[Pt(2)H] 25	6.54 m $J(\mathrm{H^2H^{2'}})$ 0 $J(\mathrm{H^2H^1})$ 11.1 $J(\mathrm{H^2H^{1'}})$ 0.6 $J(\mathrm{H^2H^3})$ 9.0 ^3J[Pt(2)H] 19	3.70 d $J(\mathrm{H^2H^3})$ 9.0 ^2J[Pt(2)H] 91 ^3J[Pt(1)H] 36	3.69 s ^2J[Pt(1)H] 56	3.11 s ^2J[Pt(1)H] 56	4.27 s,br ^2J[Pt(2)H] 49	1.80 s,br
−80	5.99 m	6.57 m $J(\mathrm{H^2H^3})$ 9.0	3.80 3.63 d d $J(\mathrm{H^3H^2})$ 9.0 $J(\mathrm{H^{3'}H^{2'}})$ 9.0	4.00 3.43 s s	3.15 3.06	4.36 4.21 s,br s,br	1.80 m

* Measured in [$^2H_2$]dichloromethane, chemical shifts (δ) in p.p.m. relative to SiMe$_4$ (0.0 p.p.m.), coupling constants in Hz.

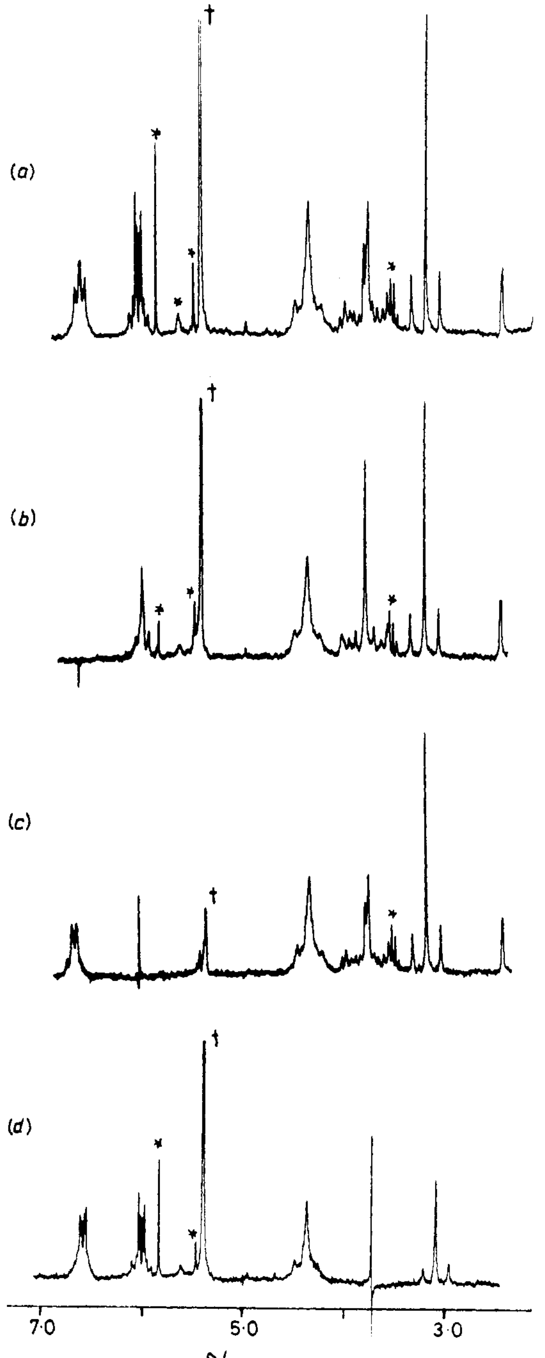


FIGURE 3 (a) Hydrogen-1 n.m.r. spectrum of [$Pt_3(C_2H_4)(cod)_2(cot)_2$] measured in CD_2Cl_2 at 0 °C, (b) {^1H}-decoupling at δ 6.54, (c) {^1H}-decoupling at δ 5.95, and (d) {^1H}-decoupling at δ 3.70. Impurity peaks indicated by asterisk, CD_2Cl_2 solvent by dagger

resolved, and analysis gave J(AA′) 8.3, J(AB) 11.1, J(AB′) 0.6, and J(BB′) 0 Hz. Platinum-195 satellites were also observed due to coupling with Pt(2) and Pt(2′). The peak at 6.54 p.p.m. was not as well resolved, appearing as a broad triplet with some fine structure. Irradiation of this resonance resulted in a collapse of the multiplet at 5.95 p.p.m. into a broad singlet and a change in the spectrum between 3.90 and 3.50 p.p.m. from a multiplet into a broad singlet, flanked by several sets of ^{195}Pt satellites [Figure 3(b)]. Previous integration of this region had indicated that the signals attributable to H^3, $H^{3'}$, H^4, and $H^{4'}$ occurred here. Decoupling of the resonance at 5.95 p.p.m. resulted in collapse of the signal at 6.54 p.p.m. to a broad doublet with ^{195}Pt satellites but had no effect on the region between δ 3.90 and 3.50 [Figure 3(c)]. Finally, irradiation at the centre of the multiplet at 3.70 p.p.m. caused sharpening of the signal at 6.54 p.p.m. into a pattern resembling the resonance at 5.95 p.p.m. [Figure 3(d)]. On the basis of this evidence, we assign the peaks at δ 5.95 to H^1 and $H^{1'}$, and the peaks at δ 6.54 to H^2 and $H^{2'}$ which are further split by coupling (9 Hz) to H^3 and $H^{3'}$. Assignment of the resonances due to H^3 and $H^{3'}$, and H^4 and $H^{4'}$, which we expected to involve a complex second-order sub-spectrum even though the molecule is dynamic, will be discussed below.

Cooling the solution containing the compound to −80 °C brought about a large change in the spectrum relative to that observed at 0 °C [Figures 4(a) and 3(a), respectively]. During cooling, the C_2H_4, cod, and cot proton resonances were observed to broaden simultaneously. The C_2H_4 resonance eventually collapsed to a broad $[AB]_2$ pattern, whilst the cod methine signal split into two peaks of equal intensity, and the resonances at δ 5.95 and 6.54 became broader and more complicated. This behaviour is expected if the rotations described previously have slowed down on the n.m.r. time scale, as seemingly equivalent protons have become inequivalent. Equally interesting was the observation of a pair of doublets (3.80 and 3.63 p.p.m.) and a pair of singlets (4.00 and 3.43 p.p.m.) in the region associated with H^3, $H^{3'}$, H^4, and $H^{4'}$ [Figure 4(a)]. Moreover, J(HH) of 9 Hz for each doublet was the same value as that previously found for $J(H^2H^3)$ and $J(H^{2'}H^{3'})$. Further irradiation of the resonance associated with H^2 and $H^{2'}$ at 6.54 p.p.m. resulted in the collapse of both doublets into singlets [Figure 4(b)]. Therefore, we attribute both these doublets to H^3 and $H^{3'}$ which in a limiting spectrum must appear inequivalent. Hence H^1 and $H^{1'}$ must produce the singlets observed at δ 3.43 and 4.00, although definitive assignment is not possible.

The observation of doublets for H^3 and H^3 and singlets for H^4 and $H^{4'}$ was surprising, since this implies there is little or no coupling between these sets of protons. However, when the conformation which these protons are forced to adopt by the metal co-ordination is considered, it seems likely that large vicinal coupling would be precluded. This realisation prompted a reappraisal of the spectrum recorded at 0 °C [Figure 3(a)], when the resonances between 3.50 and 3.90 p.p.m. were easily analysed as a doublet centred at δ 3.70 [$J(H^2H^3)$ 9, ^2J(PtH) 91, and ^3J(PtH) 36 Hz] due to H^3 and $H^{3'}$, overlapping a singlet at δ 3.69 [^2J(PtH) 56 Hz] due to H^4 and $H^{4'}$.

The observation of simultaneous collapse of the C_2H_4, cod, and cot resonances in the ^1H n.m.r. spectrum allowed calculation of the activation energy of the dynamic process. The coalescence temperature (T_c) was measured at -50 ± 5 °C and the activation parameters were obtained by application of the relation (1), which only strictly applies to a simple two-site exchange with no coupling,[12] to the cot protons H^3 and $H^{3'}$ (Table 4).

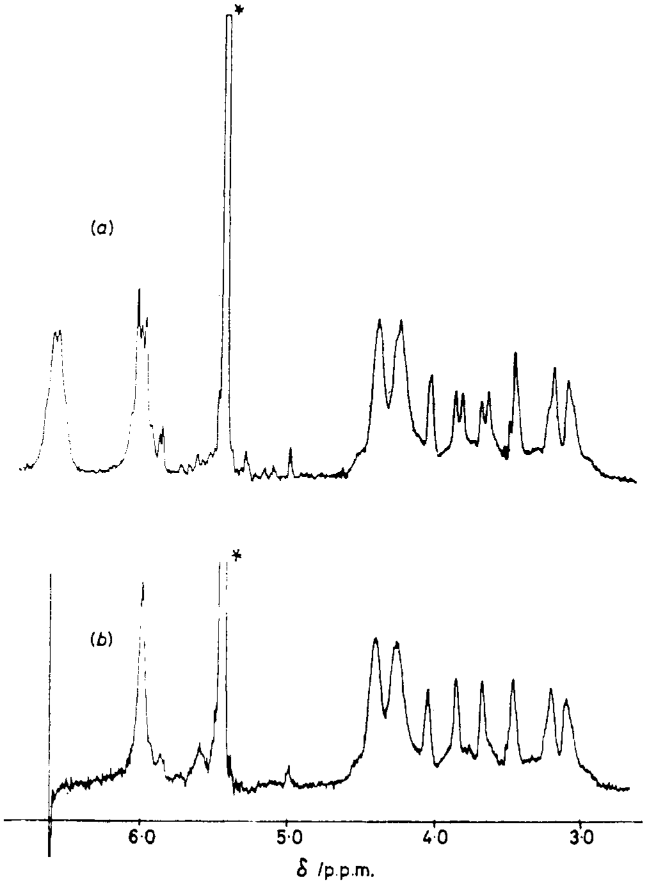


FIGURE 4 (*a*) Hydrogen-1 n.m.r. spectrum of $[Pt(C_2H_4)(cod)_2(cot)_2]$ measured in CD_2Cl_2 (*) at −80 °C, (*b*) $\{^1H\}$-decoupling at δ 6.57

$$\Delta G_{T_c}{}^{\ddagger} = -RT_c \ln(\pi \Delta \nu h / 2^{\frac{1}{2}} k T_c) \qquad (1)$$

This gave a value for the activation energy $\Delta G_{T_c}{}^{\ddagger}$ of 46.3 ± 2 kJ mol^{-1}.

The insolubility and instability in solution of $[Pt_3(C_2H_4)(cod)_2(cot)_2]$ made measurement of a good quality ^{13}C n.m.r. spectrum impossible. At −70 °C there were four resonances (δ 96.7, 96.3 95.2, and 91.6 p.p.m.) attributable to the cod ligand methine groups. At −15 °C these collapsed to two signals at 97.3 [^2J(PtC) 85 Hz] and 93.5 p.p.m., while the CH_2 group resonances were observed at 30.1 and 29.8 p.p.m. The behaviour of the CH signals supports the belief that the dynamic process involves rotation of the η^2 metal-bonded C=C groups of the cot ligands about an axis through the central platinum atom and the midpoints of the co-ordinated double bonds, the terminal Pt(cod)(cot) fragments remaining static, *viz.* no cod or cot rotation about Pt(2) and Pt(2′) (Figure 1).

At −70 °C, the carbon nuclei of the unco-ordinated diene fragments of the cot ligands have resonances at 143.3, 122.1, and 122.0 p.p.m. Signals for the other four carbon atoms occur at 81.1 and 74.1 p.p.m., and at 49.5 and 48.2 p.p.m. The inability to observe ^{195}Pt satellites precluded specific assignment of these peaks. At −15 °C, only two resonances are observed for the unco-ordinated diene fragment {143.1 and 122.5 p.p.m. [J(PtC) 28 Hz]}. Although the single resonance which should be formed by the coalescence of the peaks at 81.1 and 74.1 p.p.m. was not resolved at −15 °C, a single signal at 49.3 p.p.m. replaced the two resonances at 49.5 and 48.2 p.p.m. seen at −70 °C. The ^{13}C resonances for the C_2H_4 ligand were not visible and are thought to have been obscured by peaks due to the solvent (CH_2Cl_2).

EXPERIMENTAL

The n.m.r. studies were carried out with a JEOL FX 200 spectrometer at 199.50 (^1H) and 55.10 (^{13}C) MHz. Carbon-13 chemical shifts are relative to $SiMe_4$. All experiments were carried out under nitrogen using Schlenk-tube techniques, and dry oxygen-free solvents. Ethylene was CP grade and $[Pt(cod)_2]$ was prepared as described previously.[2]

Synthesis of $[Pt_3(C_2H_4)(cod)_2(cot)_2]$.—The compound $[Pt(cod)_2]$ (411 mg, 1 mmol) was dissolved in an ethylene-saturated solution of diethyl ether (20 cm^3) at −20 °C. Cyclo-octatetraene (104 mg, 0.096 cm^3, 1 mmol) was added, and the solution allowed to stand for 2 h, during which time flaky orange crystals deposited. The latter were removed by filtration, washed with light petroleum (2 × 10 cm^3), and dried *in vacuo* to afford orange *crystals* of the complex (310 mg, 90%), m.p. (*in vacuo*) 109—112 °C (decomp.) (Found: C, 39.5; H, 4.4. Calc. for $C_{34}H_{44}Pt_3$: C, 39.3; H, 4.3%), $\nu_{max.}$ (Nujol) at 1 534m, 1 499w, 1 475w, 1 432w, 1 423s, 1 333m, 1 305w, br, 1 293m, 1 246w, 1 241w, 1 229w, 1 223s, 1 192w, 1 176w, 1 157w, 1 135s, 1 074m, br, 1 062m, 1 002w, 991w, 963m, 943w, 918m, 875m, 861s, 830m, 816m, 775m, 754m, 739w, 723s, 683s, 522m, 458w, 448w, 415w, 393w cm^{-1}.

Crystal-structure Determination of $[Pt_3(C_2H_4)(cod)_2(cot)_2]$.—Crystals of the title compound grow as thin orange plates from diethyl ether and that used for data collection was of dimensions 0.175 × 0.032 × 0.145 mm. Diffracted intensities were recorded at 200 K on a Syntex $P2_1$ four-circle diffractometer by methods described previously.[13] Of the total 3 341 intensities measured in the range $2.9 \leqslant 2\theta \leqslant 55°$, 2 417 had $I \geqslant 3\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation in I based on counting statistics, and only these were used in the final refinement of the structure. Corrections were applied for Lorentz and polarisation effects and for X-ray absorption. Computations were carried out at the London Computing Centre on the CDC 7600 using the SHELX system of programs.[14]

Crystal data. $C_{34}H_{44}Pt_3$, $M = 1\,038$, Monoclinic, $a = 16.370(17)$, $b = 7.465(5)$, $c = 24.603(37)$ Å, $\beta = 102.55(10)°$, $U = 2\,127$ Å^3, $D_m = 2.35$, $Z = 4$, $D_c = 2.38$ g cm^{-3}, $F(000) = 2\,128$, Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 152 cm^{-1}, space group $C2/c$.

Structure solution and refinement. The platinum atoms were located from a Patterson synthesis, and all the carbon atoms by successive electron-density difference syntheses. Hydrogen atoms could not be readily located and so were incorporated at positions calculated for rigid-group atoms and only common temperature factors for chemically equivalent hydrogen atoms were refined. However, the hydrogen atoms attached to C(1), C(2), C(7), and C(8) were unstable, and together with the ethylene hydrogen atoms were omitted from the final refinements. The possibility of the molecule belonging to the acentric space group *Cc*, where the crystallographic restrictions of the two-fold rotation axis are removed, was tested, but this led to a less satisfactory refinement than when the internal symmetry of *C*2/*c* was invoked. The atoms C(101) and C(101′) proved to be the most difficult to refine in either space group, possibly due to a short range disorder which was unresolvable and hence the errors in the molecular parameters associated with them are consequently greater. The structure was refined by full-matrix least-squares methods with anisotropic thermal parameters for the metal atoms and all carbon atoms except those of the ethylene group, since anisotropic refinement of the latter resulted in physically meaningless parameters. Convergence was achieved at R 0.062 (R' 0.062) with the mean shift-to-error ratio in the final four cycles of refinement being 0.006 : 1 with a maximum of 0.03 : 1.

A weighting scheme of the form $w = 1.499[\sigma^2(F) + 0.0027|F|^2]^{-1}$, where $\sigma(F)$ is the estimated error in the observed structure factor based on counting statistics only, gave a satisfactory weight analysis. The final electron-density difference synthesis showed peaks of 3 e Å^{-3} in the immediate vicinity of platinum atoms but none elsewhere >0.9 or < -0.9 e Å^{-3}. Scattering factors were from ref. 15 for C, ref. 16 for hydrogen, and ref. 17 for Pt, including for the latter corrections for the effects of anomalous dispersion ($\Delta f'$ -2.352, $\Delta f''$ 8.388). The observed and calculated structure factors, thermal parameters, and positional parameters for hydrogen atoms are listed in Supplementary Publication No. SUP 23006 (14 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

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