Chemistry of Bis(cyclo-octa-1,5-diene)platinum: Reactions with Electrophiles

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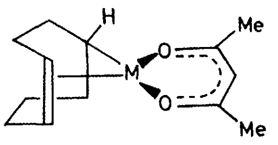
Bis(cyclo-octa-1,5-diene)platinum, $[Pt(cod)_2]$, reacts with the β-diketones acetyl-, hexafluoroacetyl-, and trifluoroacetyl-acetone to give (cyclo-oct-4-en-1-yl)platinum complexes $[Pt(1\text{-}\sigma,4\text{—}5\text{-}\eta\text{-}C_8H_{13})(L_2)]$ (L_2 = acac, hfacac, or tfacac). Protonation $[HBF_4$ or $HPF_6\text{–}(CF_3CO)_2O]$ of $[Pt(cod)_2]$ yields salts $[Pt(1\text{-}\sigma,4\text{—}5\text{-}\eta\text{-}C_8H_{13})(cod)][X]$ ($X = BF_4^-$ or PF_6^-); the same cationic species is formed from CF_3CO_2H. The electrophilic reagents $[C_7H_6R][BF_4]$ (R = H or Ph) react with $[Pt(cod)_2]$ to give fluxional complexes $[Pt(C_7H_6R)(cod)][BF_4]$. Treatment of $[MCl_2(cod)]$ (M = Pt or Pd) with $Ag[BF_4]$ in the presence of cod yields $[Pt(1\text{-}\sigma,4\text{—}5\text{-}\eta\text{-}C_8H_{13})(cod)][BF_4]$ and $[Pd(1\text{—}3\text{-}\eta\text{-}C_8H_{13})(cod)][BF_4]$, respectively. The former product reacts with $(PhO)_3P$ to give $[PtH\{(PhO)_3P\}_3][BF_4]$, and with $(MeO)_3P$ or $(EtO)_3P$ to form $[PtH\{(RO)_3P\}_4][BF_4]$. The five-co-ordinate hydridophosphite complexes undergo dynamic behaviour in solution.

ORGANONICKEL chemistry developed very rapidly following the discovery of 'ligand-free' olefin complexes such as $[Ni(cod)_2]$ (cod = $1,5\text{-}C_8H_{12}$).[1] A recently described [2] preparation of bis(cyclo-octa-1,5-diene)platinum allows this complex to be similarly used as a starting point for many new syntheses in organoplatinum chemistry. With this in mind we are engaged in a detailed investigation of the reactivity of $[Pt(cod)_2]$, and have already reported studies with bulky tertiary phosphines,[3] isocyanides,[4] hexafluorobut-2-yne,[5] hexafluoroacetone,[6] and fluoro-olefins.[7] The unsaturated fluorocarbons afford a variety of products, the nature of which is understandable in terms of attack of nucleophilic $[Pt(cod)_2]$ on these electrophilic species. For this reason a study of the reactions of the platinum complex with more conventional electrophiles, including β-diketones and protonic acids, was undertaken.

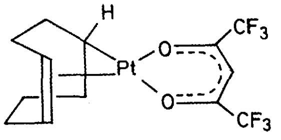
RESULTS AND DISCUSSION

Treatment of $[Pt(cod)_2]$ with acetylacetone (Hacac) afforded in low yield complex (1b), the analogue of the nickel complex (1a).[8] However, formation of (1b) was less ready than that of (1a) indicating that the platinum complex is less reactive than $[Ni(cod)_2]$, paralleling the greater relative stability of $[Pt(cod)_2]$.

With the stronger acid, hexafluoroacetylacetone (Hhfacac), reaction with $[Pt(cod)_2]$ occurred rapidly at 0 °C to give a mixture of two complexes. The major product (2) was separable on account of its solubility in light petroleum. The molecular structure may be inferred from the analytical data and from the ^{19}F and ^{13}C n.m.r. spectra. The ^{19}F spectrum showed two peaks of equal intensity at 73.9 and 75.1 p.p.m. (relative to CCl_3F, 0.0 p.p.m.) with $J(PtF)$ 14.6 and <5 Hz, respectively. The magnitudes of the couplings and the chemical shifts are similar to those observed [6] for related



(1a) M = Ni
(1b) M = Pt



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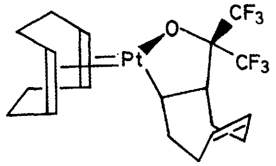

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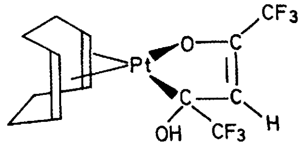

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[1] P. W. Jolly and G. Wilke, 'The Organic Chemistry of Nickel,' Academic Press, New York, 1974, vol. 1; 1975, vol. 2.

[2] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 271.

[3] J. Fornies, M. Green, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1006.

[4] M. Green, J. A. K. Howard, M. Murray, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1509.

[5] L. E. Smart, J. Browning, M. Green, A. Laguna, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1777.

[6] M. Green, J. A. K. Howard, A. Laguna, L. E. Smart, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 278.

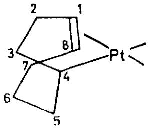
[7] M. Green, A. Laguna, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1010.

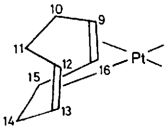
[8] B. Bogdanović, M. Kröner, and G. Wilke, *Annalen*, 1966, **699**, 1.

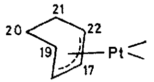
complexes such as (3) [J(PtF) 11.0 and 0 Hz, δ 71.0 and 76.7 p.p.m.]. The ^{13}C spectrum of (2) (Table 1) shows a signal at 27.6 p.p.m. [J(PtC) 711 Hz] characteristic of a platinum–carbon σ bond, and resonances indicative of η^2-olefinic carbon atoms at 77.7 and 80.5 p.p.m. The other signals can be assigned as shown in Table 1.

TABLE 1

Carbon-13 n.m.r. data for some platinum complexes [a]







	Complex (2) [b]			Complex (4)	
Carbon atom	δ	J(PtC)	Carbon atom	δ	J(PtC)
1, 8	77.7, 80.5	269, 266	9, 16	115.0, 114.8	33, 38
2, 7	35.6, 28.6	36.6, 36.6	12, 13	84.8, 79.7	203, 210
3	39.0	74	10, 11	34.4, 30.7	
4	27.6	711	14, 15	28.9, 25.8	
5	24.7	50.4			
6	28.2				
	(6a) [c]			(6a) [c]	
1, 8	110.7, 108.7	157.2, 154.3	9, 16	121.2, 116.3	16.6, 16.6
2, 7	37.4, 32.8	38, *ca.* 30	12, 13	126.9, 115.2	118.2, 108.4
3	41.2	56.6	10, 11	29.0, 27.1	*ca.* 15, *ca.* 15
4	46.1	543	14, 15	29.7, 33.4	*ca.* 20, *ca.* 20
5	24.2	43.9			
6	28.3	10			
	(9)			(9)	
9, 16	104.3	121	17	111.9	46.4
12, 13	102.3	103	18, 22	82.3	161
10, 11	30.3	*ca.* 16	19, 21	31.2	32
15, 14	29.7	<5	20	18.0	<5
	(10) [d]			(11) [e]	
9, 16 12, 13	109.3 (br)	112	9, 16 12, 13	109.2	113
10, 11 14, 15	30.5 (br)	10	10, 11 14, 15	30.9	*ca.* 9

[a] ^1H and ^{19}F decoupled, $CDCl_3$ solvent, chemical shifts relative to $SiMe_4$ (0.0 p.p.m.), coupling constants in Hz. [b] hfacac ligand: CH, 92.2 [J(PtC) 55; J(CH) 165 Hz]; 118.5, 157.9, and 172.2 p.p.m. [c] Complexes (6) and (7) had identical spectra for the C_8H_{13} and C_8H_{12} ligands. [d] For C_7-ring signal see text. [e] Signals due to C_7H_6Ph at 130.3, 129.9, 127.7, and 114.2 p.p.m.

The minor product (4) (*ca.* 15%) of the reaction of [Pt(cod)$_2$] with Hhfacac was a white solid which was only sparingly soluble in polar solvents. Elemental analysis was consistent with an empirical formula [Pt(cod)(Hhfacac)]. The ^{19}F spectrum showed two resonances [75.8 p.p.m., J(PtF) 58 Hz; 82.4 p.p.m., J(PtF) 14.9 Hz], the signal at lower field being indicative of a Pt·C(CF$_3$) group, as in the complex [$Pt\{C(CF_3)_2\cdot O\cdot C(CF_3)_2\cdot O\}(cod)$].[6] The ^{13}C n.m.r. spectrum showed eight peaks characteristic of a cod ligand attached to platinum which is part of an unsymmetrical ring system. Due to the insolubility of (4), leading to poor quality signals, further useful information from the ^{13}C spectrum could not be obtained. However, the i.r. spectrum showed a broad band at 3 400 cm^{-1} characteristic of an OH group. It is tentatively suggested that the complex results from 1,4-addition of [Pt(cod)$_2$] to the enol form of Hhfacac to give the structure shown (4). It is known that 1,4-addition of [Pt(cod)$_2$] to $CH_2{:}CMeCMe{:}CH_2$ occurs to give a five-membered ring system,[9] so that it is possible that the enol form $CF_3\cdot C(OH){:}CH\cdot C(CF_3){:}O$ of Hhfacac acts in the manner of a substituted 1,3-diene in a minor reaction path.

Reaction of trifluoroacetylacetone with [Pt(cod)$_2$], under the same conditions as those which gave complexes (2) and (4), yielded a product, the ^{19}F n.m.r. spectrum of which indicated the presence of two isomers (5a) and (5b). Two signals (relative intensity 4 : 3) were observed at 73.6 [J(PtF) 15.6 Hz] and 74.7 p.p.m. [J(PtF) <5 Hz], with chemical shifts and coupling constants very similar to those found in the spectrum of (2).

The susceptibility of [Pt(cod)$_2$] to electrophilic attack by acetyl-, trifluoroacetyl-, and hexafluoroacetyl-acetone suggested that strong protonic acids might protonate this complex. Successful protonation of [Ni(cod)$_2$] without loss of one C_8 ligand does not seem to have been reported. At 0 °C, tetrafluoroboric acid in trifluoroacetic anhydride reacted readily with [Pt(cod)$_2$] to give a pale yellow air-stable complex (6a), characterised by analysis and its ^{13}C n.m.r. spectrum. The latter (Table 1) showed 16 well defined resonances, six of which at low field [J(PtC) 17—157 Hz] were characteristic of η^2-bonded olefinic groups, and ten at high field were indicative of the sp^3-carbon atoms of the cation. Moreover, whereas nine of the higher-field signals possessed platinum–carbon couplings in the range 10—60 Hz, the tenth signal (46.1 p.p.m.) had J(PtC) 543 Hz, as expected for a carbon–platinum σ bond. Comparison of

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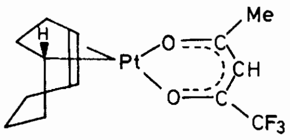
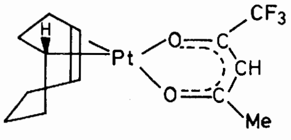
[9] G. K. Barker, M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1976, **98**, 3373.

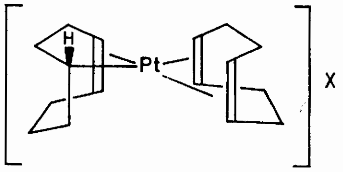
the spectrum with that of (2) and other complexes containing an identical C_8H_{13} ligand allowed the assignments for (6a) made in Table 1. Using HPF_6 the salt (6b) was also prepared, and had an identical ^{13}C spectrum.



(5a)



(5b)



(6a) X = BF_4
(6b) X = PF_6

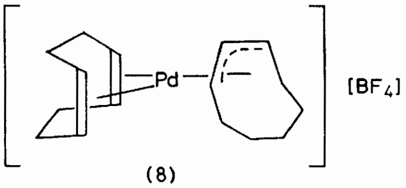
Bis(cyclo-octa-1,5-diene)platinum dissolved in trifluoroacetic acid to form bright yellow solutions from which (7) was isolated as air-sensitive crystals. The ^{19}F n.m.r. spectrum showed a single broad peak (75.8 p.p.m.) that did not sharpen on cooling to −50 °C. The chemical shift of this signal is close to that of CF_3CO_2H (76.5 p.p.m.) and to those observed in the spectra of the complexes[10] $[Pt(O_2CCF_3)_2\{(CF_3)_2CNH\}(Ph_3P)_2]$ (76.1 p.p.m.) and $[Pt(O_2CCF_3)H\{(CF_3)_2CNMe\}(Ph_3P)_2]$ (75.0 p.p.m.). The ^{13}C n.m.r. spectrum of (7) at 40 °C showed a large number of broad ill defined peaks, but on cooling (−50 °C) sharp resonances appeared corresponding to the cation $[Pt(1\text{-}\sigma,4\text{—}5\text{-}\eta\text{-}C_8H_{13})(cod)]^+$, as found in (6a) and (6b). Repeated elemental analyses were consistent with a formulation $[Pt(C_8H_{13})(cod)][CF_3CO_2{\cdot}CF_3CO_2H]$ (7). At ambient temperatures, both in solution and the solid state, some association of a molecule of trifluoroacetic acid with the cation appears to take place, as reflected in the ^{13}C n.m.r. spectrum and in the i.r. (Nujol) spectrum ($\nu_{max.}$ at 1 645s and 1 660s,br cm^{-1}).

In the reactions of $[Pt(cod)_2]$ with HBF_4, HPF_6, or CF_3CO_2H, where neither of the cod ligands is displaced, the structure of $[Pt(cod)_2]$ makes initial attack of the proton at the metal unlikely. Therefore, protonation probably involves direct attack on a cod ligand as observed with $[Rh(cod)(\eta\text{-}C_5H_5)]$.[11] Moreover, in the case of the rhodium complex, the initially formed $1\text{-}\sigma,4\text{—}5\text{-}\eta\text{-}C_8H_{13}$ species rearranges to a $1\text{—}3\text{-}\eta\text{-}C_8H_{13}$ bonding mode. No such isomerisation occurs with (6) or (7), presumably because the β-elimination reaction required to generate an η^3-allyl complex is less ready. With the β-diketones rapid displacement of one cod ligand is likely to occur first, as with hexafluoroacetone,[6] leading subsequently to transfer of the hydrogen *via* the metal from the β-diketone to the cod.

It was of interest that complex (6a) was also formed when $[PtCl_2(cod)]$ in dichloromethane was treated with $Ag[BF_4]$ in the presence of excess of cyclo-octa-1,5-diene. The mechanism for formation of (6a) in this manner is unknown, but the existence of the thermally unstable dicationic acetonitrile complex $[Pt(cod)(CH_3CN)_2][BF_4]_2$[12] suggests that $[Pt(cod)_2]^{2+}$ may be an intermediate. This square-planar intermediate is apparently electrophilic, abstracting hydride from the free cyclo-octa-1,5-diene present. Reaction of $[PtCl_2(cod)]$ with $Ag[BF_4]$ in the presence of cyclo-octa-1,3-diene, bicyclo[2.2.1]heptene, or cyclopentadiene failed to give any isolable organoplatinum species, apart from cyclo-octa-1,3-diene which gave (6a) in low yield.

Halide abstraction from $[PtCl_2L_2]$ (L_2 = cyclo-octatetraene or cyclo-octa-1,3,5-triene) with $Ag[BF_4]$ in the presence of cod also generated (6a), in these instances by ligand displacement.

Treatment of $[PdCl_2(cod)]$ in dichloromethane with $Ag[BF_4]$ and cod gave an air-stable solid, characterised by analysis and ^{13}C n.m.r. spectroscopy as $[Pd(1\text{—}3\text{-}\eta\text{-}C_8H_{13})(cod)][BF_4]$ (8). The formation of a 1—3-η-allyl rather than a 1-σ,4—5-η-enyl system, as found with platinum, is typical of the known chemistry of palladium and its propensity to bond in this manner. Treatment of $[Pd(cod)_2]$[2] with HBF_4 also gave (8), but it was difficult to purify the product obtained by this route.



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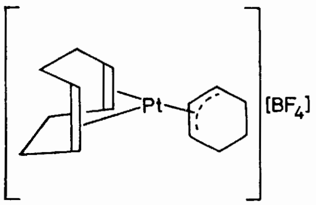

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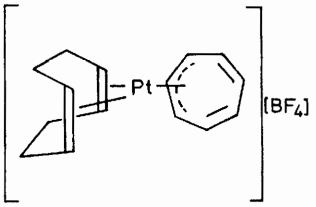

(10)

The acetonitrile complex $[Pt(cod)(CH_3CN)_2][BF_4]_2$[12] was treated with cyclohexa-1,3-diene to ascertain whether a mono- or di-cationic platinum complex would form. The product was identified as $[Pt(1\text{—}3\text{-}\eta\text{-}C_6H_9)(cod)][BF_4]$ (9) by analysis, and from the ^{13}C n.m.r. spectrum (Table 1). The observed inequivalence of the *C*H⁚*C*H groups of the cod ligand established that (9) was rigid with respect to rotation of the C_6H_9 ligand about the platinum–η^3-allyl axis. The C_6H_9 group

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[10] J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc. (A)*, 1970, 3161.

[11] J. Evans, B. F. G. Johnson, and J. Lewis, *Chem. Comm.*, 1971, 1252.

[12] R. Roulet and R. Vouillamaz, *Helv. Chim. Acta*, 1974, **57**, 2139.

showed features typical of a 1—3-η-allyl system with a resonance at 111.9 p.p.m. [J(PtC) 46.4 Hz] attributable to the central carbon of the η^3-C_3 system, and a signal due to the terminal carbon atoms of the allyl group at 82.3 p.p.m. [J(PtC) 161 Hz].

Since [Pt(cod)$_2$] is known to undergo displacement reactions with donor ligands,[3,4] and, as shown above, is also susceptible to electrophilic attack, reaction between the platinum complex and tropylium tetrafluoroborate was studied. Treatment of [Pt(cod)$_2$] with [C_7H_7][BF_4] in acetone afforded a mauve-red air-stable solid, insoluble in non-polar solvents. Microanalysis and ^{1}H and ^{13}C n.m.r. studies identified this product as [Pt(cod)(C_7H_7)][BF_4] (10). The ^{1}H spectrum showed a single sharp resonance at τ 4.25 [J(PtH) 17 Hz] due to the C_7H_7 ligand and broad signals attributable to the cod ligand. The ^{13}C spectrum (Table 1) at 30 °C had only one signal [108.5 p.p.m., J(PtC) 44 Hz] for the C_7 ring. Moreover, the sp^2- and sp^3-carbon atoms of the cod ligand appeared as only two signals. Thus complex (10) shows dynamic behaviour in solution. Even at −90 °C the resonance due to the C_7 ring remained a sharp singlet. Presumably the C_7H_7 ligand in the static structure is bonded in the 1—3-η mode as shown (10), although 1-σ,2—3-η or 1-σ,4—5-η attachments of the cycloheptatrienyl ring are also possible. The barrier to the fluxional process is evidently very low, as the instantaneous structure could not be established. It was hoped that substitution of one of the hydrogen atoms in the C_7H_7 ring with a phenyl group would slow down the dynamic behaviour. Accordingly, [Pt(cod)$_2$] was treated with [C_7H_6Ph][BF_4] affording the complex [Pt(cod)(C_7H_6Ph)][BF_4] (11). Unfortunately, examination of the ^{13}C spectrum of (11) over the range 30 to −90 °C showed no change in the pattern. Complexes (10) and (11) were insufficiently soluble in a mixture of $(CD_3)_2CO$ and $CHClF_2$ to study their spectra at −120 °C.

Although the mode of bonding of the C_8H_{13} ligands is different, the cations (6) are isoelectronic with the previously reported[13] η^3-allylcobalt complex [Co(cod)(1—3-η-C_8H_{13})], first synthesised by reduction of cobalt(II) chloride with sodium in the presence of pyridine and cyclo-octa-1,5-diene. With the cobalt complex several reactions have been carried out[13] which demonstrate the mobility of a hydrogen atom, as in the reaction with CO followed by tertiary phosphines and phosphites which yields hydrido-complexes [CoH(CO)L_3]. In view of these results a study was made of the reactions of (6a) with donor molecules.

With triphenylphosphine, t-butyl isocyanide, and 1,2-bis(diphenylphosphino)ethane reactions occurred, but pure products could not be isolated. However, triphenyl phosphite afforded the salt [PtH{(PhO)$_3$P}$_3$][BF_4] (12) [ν(PtH) at 2 075w cm^{-1}] in good yield. Several other four-co-ordinate cationic platinum hydrides are known.[14] The ^{31}P-{H} n.m.r. spectrum of (12) consists of an AB_2 pattern superimposed on the AB_2X pattern due to the presence of ^{195}Pt nuclei, and is consistent with the expected square-planar structure for the cation. The spectrum was temperature invariant in the range 30 to −90 °C in the absence of added ligand, as expected.[15] The ^{1}H spectrum showed a doublet signal at τ 15.84 [$J(P_{trans}H)$ 257 Hz] characteristic of a platinum-bonded hydride. Some coupling to the two *cis*-phosphorus nuclei produced further splitting which was not resolved.

In view of the isolation of (12), reactions of (6a) with trimethyl and triethyl phosphite were studied. Unexpectedly, five-co-ordinate cationic hydrido-complexes [PtH{(RO)$_3$P}$_4$][BF_4] [R = Me (13) or Et (14)] were produced in good yield. Both salts form stable solutions in polar solvents at room temperature. They are stable in the solid state in an inert atmosphere for several days in the absence of light at room temperature. Infrared bands due to Pt–H stretches are observed at 2 107 (13) and 2 119 cm^{-1} (14). These simple five-co-ordinate cationic species are unique amongst isolated hydride complexes of the nickel triad. Recent evidence has shown that [MHL_4]$^+$ (M = Ni, Pd, or Pt; L = Et_3P) species may be formed in solution at low temperatures from [MHL_3]$^+$ and excess of ligand.[15] The [$NiHL_4$]$^+$ species has also been reported to exist in acidic media.[16] There are a limited number of platinum(II) complexes with hydrido-ligands which are five-co-ordinate, including the anionic species[17] [PtH($SnCl_3$)$_2$(Et_3P)$_2$]$^-$ and [PtH($SnCl_3$)$_4$]$^{3-}$.

Complexes (13) and (14) undergo dynamic behaviour in solution, as revealed by variable-temperature studies on their ^{1}H and ^{31}P n.m.r. spectra. The n.m.r. data (Table 2) are in accord with earlier observations[18] on complexes [MHL_4] (M = Co, Rh, or Ir; L = F_3P). At room temperature the ^{31}P spectra show broad singlets with poorly defined ^{195}Pt satellite peaks, an observation indicating rapid fluxionality which equilibrates the ^{31}P environments. The room-temperature ^{1}H n.m.r. spectra examined over the range τ 10—40 failed to reveal a signal for Pt*H*, presumably due to the corresponding broadness of the ^{31}P signals in (13) and (14). At *ca.* −50 °C the ^{31}P and ^{1}H spectra of (13), and the ^{31}P spectrum of (14), showed sharp resonances with platinum satellites indicating that ligand dissociation was minimal. Both spectra showed equivalence of the ^{31}P nuclei on the n.m.r. time scale. Further cooling caused broadening of the signals. At *ca.* −120 °C the resonances in the spectra of (13) became sharp once more; the ^{31}P spectrum revealed two phosphorus environments in the relative intensity of 3 : 1, with J(PP) and J(PPt) couplings consistent with C_{3v} symmetry. The ^{1}H spectrum of (13) at −120 °C with a high-field (τ 24.05) signal gave confirmatory evidence

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[13] S. Otsuka and M. Rossi, *J. Chem. Soc.* (*A*), 1968, 2630; 1969, 497.

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[17] R. D. Cramer, R. V. Lindsey, C. T. Prewitt, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 1965, **87**, 658.

[18] P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1972, **94**, 5271.

for a trigonal-bipyramidal or pseudo-tetrahedral structure. Evidently these hydrides undergo ligand-site exchange *via* a Berry process or a tetrahedral-jump mechanism.

TABLE 2

Hydrogen-1 and ^{31}P n.m.r. data for the cationic species (13) and (14) [a]

$[PtH\{(MeO)_3P\}_4]^+$	(*a*) ^{1}H n.m.r. (τ):	O–CH_3; 40 to −90 °C, invariant, 6.3 (s)
		Pt–H; 40 °C, not observed
		−50 °C, 23.85 [q, *J*(PH) 57, *J*(PtH) 532]
		−90 °C, collapsed spectrum with outer lines of quintet remaining
		−120 °C,[b] 24.05 [d, *J*(PH) 230, *J*(PtH) 470]
	(*b*) ^{31}P n.m.r. (δ):	40 °C, 100.3 [br, s, *J*(PPt) 4 116]
		−50 °C, 100.1 [s, *J*(PPt) 3 972]
		−90 °C, 100.3 [br, s, *J*(PPt) 3 970, low-field satellite collapsed]
		−120 °C,[b,c] 90.8 [q, *J*(PP) 52, *J*(PtP) 2 995] and 103.6 [d, *J*(PP) 52, *J*(PtP) 4 274]
$[PtH\{(EtO)_3P\}_4]^+$	(*a*) ^{1}H n.m.r. (τ):	O–*CH*$_2$CH$_3$; 40 °C, 5.9 [q, 2 H, *J*(HH) 7] and 8.7 [t, 3 H, *J*(HH) 7]
		Pt–H; 40 °C, not observed
	(*b*) ^{31}P n.m.r. (δ):[d]	−60 °C, 94.15 [d, *J*(PH) 37, *J*(PtP) 3 950]
		−94 °C, 94.8 [br, s, *J*(PtP) 3 950, low-field satellite collapsed]

[a] Measured in $(CD_3)_2CO$ unless otherwise stated; ^{31}P chemical shifts (δ) in p.p.m. relative to external H_3PO_4 [with all protons decoupled (13); Et protons only decoupled (14)], *J* values in Hz. [b] In $CHClF_2$–$(CD_3)_2CO$ solution. [c] Spectrum not first order. [d] Low-temperature limiting spectrum not obtained.

Complexes (13) and (14) did not react with carbon tetrachloride, or undergo an insertion reaction with tetrafluoroethylene under mild conditions; this lack of reactivity is presumably due to the absence of a vacant co-ordination site. We attempted unsuccessfully to prepare (13) by direct protonation of $[Pt\{(MeO)_3P\}_4]$ with HBF_4, but hydrogen was evolved from the reaction mixture.

EXPERIMENTAL

Infrared spectra were recorded on Perkin-Elmer 457 and 257 spectrophotometers using Nujol mulls. Hydrogen-1 n.m.r. spectra ($CDCl_3$ solutions unless otherwise stated) were obtained on Varian HA100 and T60 spectrometers, ^{1}H-decoupled ^{19}F, ^{31}P, and ^{13}C spectra on a JEOL PFT-100 Fourier-transform spectrometer using a ^{2}H lock. All the reactions were carried out under an atmosphere of dry oxygen-free nitrogen using freshly distilled deoxygenated solvents. Bis(cyclo-octa-1,5-diene)platinum was prepared as described previously.[2] The tropylium salts were obtained from cycloheptatriene and phenylcycloheptatriene.[19] Light petroleum refers to that fraction of b.p. 30—40 °C.

*Reactions of Bis(cyclo-octa-*1,5*-diene)platinum with* β*-Diketones*.—(*a*) *Acetylacetone*. A mixture of $[Pt(cod)_2]$ (0.205 g, 0.5 mmol) and Hacac (1 cm^3, *ca*. 10 mmol) in diethyl ether (4 cm^3) was stirred at 25 °C for 24 h. The brown suspension, after concentration (*ca*. 1.5 cm^3) *in vacuo*, was chromatographed on alumina. Elution with light petroleum and concentration afforded pale yellow needle-like *crystals* of (1b) (15 mg, 7.5%) (Found: C, 39.2; H, 5.4. $C_{13}H_{20}O_2Pt$ requires C, 38.7; H, 5.0%), $\nu_{max.}$ at 1 582s, 1 510s [ν(CO)], 1 245s, 1 000s, 910w, 880w, 850w, 805m, 780m, 745m, 670w, 600m, 485m, and 440m cm^{-1}.

(*b*) *Hexafluoroacetylacetone*. To a stirred suspension of $[Pt(cod)_2]$ (0.205 g, 0.5 mmol) in diethyl ether (15 cm^3) at 0 °C was added Hhfacac (0.1 cm^3, *ca*. 0.75 mmol). The mixture was allowed to warm to room temperature (1 h), and the solvent was removed *in vacuo*. The yellow residue was extracted with light petroleum leaving a white insoluble material, and the solution was evaporated to dryness. The yellow solid thereby obtained was crystallised from light petroleum at −78 °C to give yellow cubic *crystals* of (2) (0.13 g, 63%), m.p. 129—131 °C (Found: C, 30.9; H, 3.0. $C_{13}H_{14}F_6O_2Pt$ requires C, 30.5; H, 2.7%), $\nu_{max.}$ at 1 625s, 1 605m, 1 550m, 1 525m [ν(CO)], 1 340w, 1 320s, 1 210s, 1 160s, 1 100s, 1 030m, 905w, 875m, 812m, 755m, 690m, 600m, 585w, 530w, 480w, and 430m cm^{-1}. N.m.r. spectra: ^{19}F, 73.9 [s, CF_3, *J*(PtF) 14.6] and 75.1 p.p.m. [s, CF_3, *J*(PtF) <5 Hz]; ^{1}H, τ 3.8 (s, 1 H), 4.9 [s, 2 H, *J*(PtH) 95 Hz], and 7.0—9.0 (br m, 11 H).

The much less soluble white material was recrystallised from chloroform–diethyl ether at −40 °C to give white *crystals* of (4) (35 mg, 15%), m.p. 115—120 °C (decomp.) (Found: C, 29.5; H, 3.2; F, 22.4. $C_{13}H_{14}F_6O_2Pt$ requires C, 30.5; H, 2.7; F, 22.3%), $\nu_{max.}$ at 3 400br [ν(OH)], 1 340w, 1 295w, 1 260s, 1 250s, 1 205m, 1 195m, 1 180m, 1 170s, 1 115s,br, 1 070m, 1 000w, 935w, 870w, 795m, 775w, 715m, 660m, and 620w cm^{-1}. Fluorine-19 n.m.r.: 75.8 [s, CF_3, *J*(PtF) 58.8] and 82.4 p.p.m. [s, CF_3, *J*(PtF) 14.9 Hz].

(*c*) *Trifluoroacetylacetone*. To a solution of Htfacac (0.5 cm^3) in diethyl ether (5 cm^3) was added $[Pt(cod)_2]$ (0.12 g, 0.29 mmol) at 25 °C with stirring. After 20 min, solvent was removed *in vacuo*, and the residue extracted with light petroleum. The solution was filtered and evaporated to give yellow *microcrystals* (from diethyl ether at −78 °C) of (5) (98 mg, 61%), m.p. 125—128 °C (Found: C, 34.2; H, 3.9. $C_{13}H_{17}F_3O_2Pt$ requires C, 34.1; H, 3.7%), $\nu_{max.}$ at 1 625s,br, 1 602m, 1 510m,br [ν(CO)], 1 275s, 1 205w, 1 155m, 1 125s,br, 1 010m, 915w, 855w, 810w, 775m, 720w, 610w, and 580w cm^{-1}. N.m.r. spectra: ^{19}F, 73.6 [s, CF_3, *J*(PtF) 15.6 Hz] and 74.7 p.p.m. (s, CF_3) (relative intensity 4 : 3); ^{1}H, τ 4.2 (s, 1 H), 5.05 [s, 2 H, *J*(PtH) 90 Hz], 7.0—9.0 (br m, 14 H), 7.75 (s, CH_3), and 7.90 (s, CH_3).

*Protonation of Bis(cyclo-octa-*1,5*-diene)platinum*.—(*a*) *With tetrafluoroboric acid*. Trifluoroacetic anhydride (2 cm^3) was cooled to −60 °C and HBF_4 (0.5 cm^3, 40% in water) added. After warming to room temperature, the clear solution was cooled (0 °C) and $[Pt(cod)_2]$ (0.205 mg, 0.5 mmol) added portionwise. After stirring for 5 min, solvent was removed *in vacuo* from the yellow solution. The resulting oil was washed with light petroleum and diethyl ether to give a yellow solid. This solid was purified by repeated precipitation from a solution in chloroform by adding diethyl ether and afforded a yellow salt (6a) (0.22 g, 88%),

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[19] H. J. Dauben, L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, 1960, **25**, 1442.

decomp. >150 °C (Found: C, 38.1; H, 5.2. $C_{16}H_{25}BF_4Pt$ requires C, 38.4; H, 5.0%), $\nu_{max.}$ at 1 285s,br, 1 180w, 1 090s,br, 1 050s,br, 910vw, and 900vw cm^{-1}. Hydrogen-1 n.m.r.: τ 3.1 [br, 2 H, *J*(PtH) 75], 4.3 [br s, 4 H, *J*(PtH) 75 Hz], and 6.9—8.4 (br m, 19 H; main peaks at 7.25, 7.4, and 8.05).

(*b*) *With hexafluorophosphoric acid.* Similarly, (6b) (90% yield) was prepared as a 1 : 1 adduct with diethyl ether from [Pt(cod)$_2$] and HPF$_6$, decomp. >120 °C (Found: C, 38.0; H, 5.1. $C_{16}H_{25}F_6PPt{\cdot}C_4H_{10}O$ requires C, 38.0; H, 5.5%), $\nu_{max.}$ (PF) at 1 080m and 1 045s cm^{-1}.

(*c*) *With trifluoroacetic acid.* To a solution of CF_3CO_2H (2 cm^3) in diethyl ether (3 cm^3) at *ca.* 10 °C was added [Pt(cod)$_2$] (0.41 g, 1 mmol). After 5 min, solvent was removed *in vacuo*, giving a yellow oil. The latter was dissolved in diethyl ether (5 cm^3) to which light petroleum (0.5 cm^3, b.p. 80—100 °C) had been added. The solution was evaporated until a pale yellow precipitate started to form. Cooling (−78 °C) then afforded, after washing with light petroleum, yellow *crystals* (7) (0.44 g, 71%), m.p. 70—77 °C, stable under nitrogen (Found: C, 37.3; H, 4.1; F, 17.1. $C_{20}H_{26}F_6O_4Pt$ requires C, 37.6; H, 4.1; F, 17.8%), $\nu_{max.}$ at 1 660s,br, 1 645s [ν(CO)], 1 280w, 1 200s, 1 180w, 1 155s, 1 090w, 1 020w, 990vw, 855m, 805w, 790w, and 730m cm^{-1}. Hydrogen-1 n.m.r.: τ 3.2 (2 H), 4.4 (m, 4 H), and 6.8—8.3 (m, 19 H, maxima at 7.5 and 8.1).

Other Reactions of Bis(*cyclo-octa*-1,5-*diene*)*platinum.*—(*a*) *With tropylium tetrafluoroborate.* To a stirred solution of [Pt(cod)$_2$] (60 mg, 0.15 mmol) in diethyl ether (15 cm^3) at 0 °C was slowly added [C_7H_7][BF$_4$] (28 mg, 0.16 mmol). The dark red precipitate so formed was allowed to settle after 15 min. The supernatant liquid was removed and the solid washed with diethyl ether (2 × 5 cm^3). Precipitation of the product at 0 °C from an acetone solution (3 cm^3) by dropwise addition of light petroleum (b.p. 40—60 °C) removed trace amounts of [C_7H_7][BF$_4$]. After washing the precipitate with diethyl ether, the product was dried *in vacuo* to give a mauve-red *solid* (10) (60 mg, 83%), m.p. >119 °C (decomp.) (Found: C, 37.4; H, 4.0. $C_{15}H_{19}BF_4Pt$ requires C, 37.4; H, 4.0%), $\nu_{max.}$ (BF) at 1 050s,br cm^{-1}. Hydrogen-1 n.m.r. in $(CD_3)_2CO$: τ 4.25 [s, 7 H, *J*(PtH) 17 Hz], 6.1 (br s, 4 H), and 7.55 (br m, 8 H).

(*b*) *With phenyltropylium tetrafluoroborate.* To a stirred suspension of [Pt(cod)$_2$] (0.205 g, 0.5 mmol) in acetone (5 cm^3) at 0 °C was added solid [C_7H_6Ph][BF$_4$] (0.127 g, 0.5 mmol). After 10 min the deep red solution was concentrated *in vacuo* to *ca.* 0.5 cm^3, and added to diethyl ether (*ca.* 30 cm^3) with vigorous stirring. The dark red precipitate so produced was filtered off, washed with diethyl ether, and dried *in vacuo*. Dissolution in a minimum of acetone and repetition of the precipitation procedure afforded a brick-red *powder* (11) (0.22 g, 79%), m.p. >110 °C (decomp.) (Found: C, 43.7; H, 4.5. $C_{21}H_{23}BF_4Pt$ requires C, 45.3; H, 4.2%), $\nu_{max.}$ at 3 050w, 1 560w, 1 320w, 1 285w, 1 245w, 1 185w, 1 170w, 1 090s,br, 1 050s [ν(BF)], 895w, 855w, 790w, 775m, 710m, 670m, and 520w cm^{-1}. Hydrogen-1 n.m.r.: τ 2.5 (br s, 5 H, C_6H_5), 3.5—5.0 (br m, 10 H), and 7.0—8.2 (m, 8 H).

Reaction of Bis(*cyclo-octa*-1,5-*diene*)*palladium with Silver Tetrafluoroborate and Cyclo-octa*-1,5-*diene.*—To a suspension of [PdCl$_2$(cod)] (0.285 g, 1 mmol) in dichloromethane (5 cm^3) at 0 °C was added cod (0.5 cm^3) and Ag[BF$_4$] (0.39 g, 2 mmol), and the mixture was stirred in the dark for 1 h. The mixture was then briefly refluxed, cooled to 0 °C, filtered, and the residue washed with dichloromethane (3 cm^3). The filtrate and the washings were combined and all the solvent removed *in vacuo*. The sticky solid so formed was washed with light petroleum and diethyl ether. The solid was dissolved in chloroform (4 cm^3), filtered, and the filtrate added to diethyl ether (25 cm^3) giving a yellow precipitate. This was collected and dried *in vacuo* affording a pale yellow *powder* (8) (0.25 g, 60%), m.p. >70 °C (decomp.) (Found: C, 46.7; H, 6.2. $C_{16}H_{25}BF_4Pd$ requires C, 46.8; H, 6.1%), $\nu_{max.}$ at 1 540w, 1 320w, 1 280w, 1 220w, 1 180w, 1 080m,br, 1 040s,br [ν(BF)], 860w, 850w, 830w, 760m, 735m, 512m, and 420w cm^{-1}. N.m.r. spectra: ^1H, τ 4.3 (br m, 7 H) and 7.4 (br m, 18 H); ^{13}C in $CDCl_3$, 113.4 (:CH, cod), 117.6 (η^3-CH*C*HCH), 92.6 (η^3-*C*HCH*C*H), 31.8 (CH$_2$, C_8H_{13}), 29.7 (CH$_2$, cod), 26.3, and 22.5 p.p.m. (CH$_2$, C_8H_{13}).

Complex (6a) was similarly prepared (80—90%) from [PtCl$_2$(cod)], Ag[BF$_4$], and cod in CH_2Cl_2 at 25 °C.

Reaction of [Pt(cod)(MeCN)$_2$][BF$_4$]$_2$ *with Cyclohexa*-1,3-*diene.*—To acetonitrile (6 cm^3) was added [PtCl$_2$(cod)] (0.375 g, 1.0 mmol) and the suspension cooled to −20 °C. Solid [Ag(BF$_4$)(MeCN)$_2$] (0.562 g, 2 mmol) was added and the mixture stirred at *ca.* −15 °C for 2 h. Solvent was removed *in vacuo* at 0 °C and the white solid extracted with acetone (50 cm^3). To the acetone solution at 0 °C was added cyclohexa-1,3-diene (0.75 cm^3) and the mixture stirred at room temperature (15 min). After concentration (*ca.* 5 cm^3) and filtration, addition of diethyl ether (20 cm^3) at 0 °C gave a pale yellow precipitate which was collected, washed with diethyl ether, and recrystallised from chloroform–diethyl ether at −40 °C to give a pale yellow *powder* (9) (0.14 g, 30%), m.p. 155—160 °C (decomp.) (Found: C, 35.9; H, 4.4. $C_{14}H_{21}BF_4Pt$ requires C, 35.7; H, 4.5%), $\nu_{max.}$ at 1 320w, 1 290w, 1 080m,br, 1 050s [ν(BF)], 865w, 830w, 795w, 770w, 520w, and 450w cm^{-1}. Hydrogen-1 n.m.r.: τ 4.0 (br m, 7 H) and 7.5 (br m, 14 H).

Reactions of Complex (6a).—(*a*) *With triphenyl phosphite.* To a stirred solution of triphenyl phosphite (0.5 g, 1.6 mmol) in tetrahydrofuran (thf) (2 cm^3) at 0 °C was added slowly complex (6a) (100 mg, 0.205 mmol) to form a colourless solution. This was then warmed to room temperature (18 h) affording a white precipitate. Concentration *in vacuo* to *ca.* 1 cm^3 and addition of diethyl ether (5 cm^3) produced a heavy precipitate which was filtered off and washed with diethyl ether (3 × 5 cm^3). Crystallisation from chloroform–diethyl ether at −40 °C gave white *crystals* of (12) (0.185 g, 72%), m.p. 135—140 °C (decomp.) (Found: C, 53.9; H, 4.2. $C_{54}H_{46}BF_4O_9P_3Pt$ requires C, 53.4; H, 3.7%), $\nu_{max.}$ at 2 075w [ν(PtH)], 1 595w, 1 585m, 1 375m, 1 290w, 1 190s, 1 160s, 1 100m, 1 060s, 1 025w, 955s,br, 775m, 690m, 585w, and 500m cm^{-1}. N.m.r. spectra: ^1H, τ 2.6 (m, 9 H), 3.1 (m, 2 H), and 3.4 (m, 4 H) (Ph ring resonances), 15.9 [m, 1 H, *J*(PH) 257 Hz]; ^{31}P, −106.05 [d, 2 P, *J*(PP) 44, *J*(PPt) 4 614] and −116.92 p.p.m. [t, 1 P, *J*(PP) 44, *J*(PPt) 3 427 Hz].

(*b*) *With trimethyl phosphite.* A solution of trimethyl phosphite (1 cm^3, 8 mmol) in thf (5 cm^3) at 0 °C was slowly added to (6a) (0.215 g, 0.43 mmol), and the mixture stirred for 18 h. After filtering, the solution was concentrated (*ca.* 0.5 cm^3), and diethyl ether (*ca.* 3 cm^3) added. The mixture was cooled to −78 °C and the supernatant liquid removed. The solid was washed with diethyl ether and light petroleum, dried, and crystallisation from nitromethane–diethyl ether at −40 °C gave white *microcrystals* of (13) (0.25 g, 74%), m.p. 105—110 °C (decomp.) (Found: C, 18.6; H, 4.8. $C_{12}H_{37}BF_4O_{12}P_4Pt$ requires C, 18.5; H, 4.8%), $\nu_{max.}$ at 2 107m [ν(PtH)], 1 175m,br, 1 040s,br, 970m, 790m,br, 735m,br, 520m,br, 440w, and 395w cm^{-1}. N.m.r. data are in Table 2.

(*c*) *With triethyl phosphite*. The hydride complex (14) (77%), decomp. >110 °C (Found: C, 30.9; H, 6.7. $C_{24}H_{61}BF_4O_{12}P_4Pt$ requires C, 30.5; H, 6.5%), was similarly prepared, $\nu_{max.}$ (PtH) at 2 119m cm^{-1}. N.m.r. data are in Table 2.

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