Synthesis of Three-co-ordinate Mono-, Bis-, and Tris-olefin Complexes of Platinum with Dimethyl or Diethyl Fumarate, Dimethyl Maleate, or Maleic Anhydride Ligands

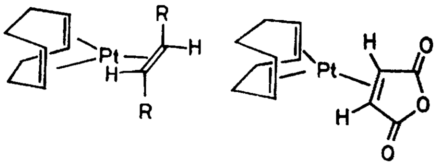
By **M. Teresa Chicote, Michael Green, John L. Spencer, F. Gordon A. Stone,* and Jose Vicente,** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Bis(cyclo-octa-1,5-diene)platinum, $[Pt(cod)_2]$, reacts with dimethyl or diethyl fumarate (dmf or def) or maleic anhydride (ma) to give the complexes [Pt(cod)(olefin)] (olefin = dmf, def, or ma). Dimethyl or diethyl maleate (dmm or dem) yield the fumarate complexes [Pt(cod)(olefin)] (dmf or def). In the presence of 1 mol equivalent of Bu^tNC or PPh_3, complexes of the type $[PtL(olefin)_2]$ (L = $CNBu^t$ or PPh_3; olefin = dmf, def, dmm, or ma) are produced. With an excess of Bu^tNC the complexes $[Pt(CNBu^t)_2(olefin)]$ are formed. The latter species can also be obtained from the triplatinum complex $[Pt_3(CNBu^t)_6]$ and the respective olefin. Addition of tricyclohexylphosphine to $[Pt(CNBu^t)(dmf)_2]$ gives $[Pt(CNBu^t)(dmf)\{P(C_6H_{11})_3\}]$. The tris(olefin) complexes $[Pt(C_2H_4)(olefin)_2]$ (olefin = dmf or dmm) and $[Pt(olefin)_3]$ (olefin = dmf or def) are formed by treating $[Pt(C_2H_4)_3]$ with the respective olefin. Tetra-alkylammonium halides react with a mixture of [Pt(cod)(dmf)] and dmf to give ionic complexes $[NR_4][PtX(dmf)_2]$ (X = Cl, Br, or I). Protonation of [Pt(cod)(dmf)] with trifluoroacetic acid gives selectively the platinum(II) σ-bonded complex $[Pt\{CH(CO_2Me)CH_2(CO_2Me)\}(O_2CCF_3)(cod)]$.

THERE are many known mononuclear nickel,[1] palladium,[2] and platinum [3] olefin complexes but there are as yet relatively few [1,4-7] which do not contain supporting ligands such as tertiary phosphines or phosphites. The observation [8] that an excess of ethylene will displace both cyclo-octa-1,5-diene ligands from $[M(cod)_2]$ (M = Pd or Pt; cod = 1,5-C_8H_{12}) to give the complexes $[M(C_2H_4)_3]$ suggested that related reactions might occur with other olefins, particularly those carrying electronegative substituents.[9] Accordingly, reactions between $[Pt(cod)_2]$ or $[Pt(C_2H_4)_3]$ and dimethyl or diethyl fumarate (dmf or def), dimethyl or diethyl maleate (dmm or dem), and maleic anhydride (ma) were investigated.[10] It has recently been reported [11] that $[Ni(cod)_2]$ reacts with dimethyl fumarate or maleate in acetonitrile to afford the complexes $[Ni(NCMe)(olefin)_2]$ (olefin = dmf or dmm).

RESULTS AND DISCUSSION

Addition of $[Pt(cod)_2]$ to a diethyl ether solution of 1 mol equivalent of dmf, def, or ma led to rapid displacement at room temperature of one of the cod ligands with formation of the thermally stable white crystalline complexes (1)—(3), respectively, characterised by elemental analysis and i.r. and ^1H n.m.r. spectroscopy (Tables 1 and 2). In the i.r. spectra the position of the C=O bands



(1) R = CO_2Me
(2) R = CO_2Et

(3)

TABLE 1

Platinum olefin complexes

	Complex [a]	M.p. (θ_c/°C)	Yield (%)	Analyses (%) [b] C	H	N	I.r. (cm^{-1}) [c] ν(C=O)	ν(NC)
(1)	[Pt(cod)(dmf)]	122—124	81	37.9 (37.6)	4.7 (4.5)		1 700vs, 1 690vs	
(2)	[Pt(cod)(def)]	82—84	96	40.1 (40.4)	5.0 (5.1)		1 685vs	
(3)	[Pt(cod)(ma)]	142—145	92	35.7 (35.9)	3.6 (3.5)		1 860vs, 1 730vs	
(4)	$[Pt(CNBu^t)(dmf)_2]$	88	37	36.2 (36.1)	4.5 (4.5)	2.3 (2.5)	1 710vs	2 215s
(5)	$[Pt(CNBu^t)(dmm)_2]$	104—108	66	36.1 (36.1)	4.5 (4.5)	2.4 (2.5)	1 700vs	2 210vs
(6)	$[Pt(CNBu^t)(def)_2]$	80—82	70	40.3 (40.5)	5.4 (5.3)	2.3 (2.3)	1 700vs	2 205vs
(7)	$[Pt(CNBu^t)(ma)_2]$	143 (decomp.)	70	32.5 (32.9)	3.0 (3.0)	2.7 (3.0)	1 820s, 1 770vs	2 125vs
(8)	$[Pt(PPh_3)(def)_2]$	110	60	51.0 (50.9)	5.1 (4.9)		1 705vs	
(9)	$[Pt(CNBu^t)_2(dmf)]$	108	64	38.0 (38.0)	5.1 (5.2)	5.4 (5.5)	1 700vs	2 195vs, 2 155vs
(10)	$[Pt(CNBu^t)_2(dmm)]$	80	80	37.7 (38.0)	5.2 (5.2)	5.3 (5.5)	1 718vs	2 180vs, 2 150vs
(11)	$[Pt(CNBu^t)_2(def)]$	84—86	70	40.2 (40.2)	5.8 (5.6)	5.1 (5.2)	1 700vs	2 080vs, 2 075vs
(12)	$[Pt(CNBu^t)_2(ma)]$	140—142	80	36.3 (36.6)	4.4 (4.4)	6.0 (6.1)	1 813vs, 1 745vs	2 200vs, 2 170vs
(13)	$[Pt(PPh_3)_2(def)]$	192	75	58.9 (59.3)	5.1 (4.8)		1 690s, 1 680vs	
(14)	$[Pt(CNBu^t)(dmf)\{P(C_6H_{11})_3\}]$	210	70	49.1 (49.6)	7.2 (7.2)	2.0 (2.0)	1 705vs, 1 695vs	2 150vs
(15)	$[Pt(C_2H_4)(dmf)_2]$	60 (decomp.)	50	33.1 (32.9)	4.1 (4.0)		1 725vs, 1 705vs	
(16)	$[Pt(C_2H_4)(dmm)_2]$	79 (decomp.)	60	32.8 (32.9)	4.0 (4.0)		1 700br,vs	
(17)	$[Pt(dmf)_3]$	99 (decomp.)	62	34.2 (34.5)	3.9 (3.9)		1 730vs, 1 718vs	
(18)	$[Pt(def)_3]$	42 (decomp.)	50	40.5 (40.5)	5.3 (5.1)		1 723vs	
(19)	$[NEt_3(CH_2Ph)][PtCl(dmf)_2]$	104—106	78	42.2 (42.2)	5.5 (5.4)	2.0 (2.0)	1 790br,vs	
(20)	$[NMe_4][PtBr(dmf)_2]$	144—146	72	30.4 (30.2)	4.5 (4.4)	2.2 (2.2)	1 690br,s	
(21)	$[NEt_4][PtI(dmf)_2]$	100—102	65	32.6 (32.4)	5.2 (4.9)	1.9 (1.9)	1 700vs	

[a] dmf = *trans*-$CH(CO_2Me)=CH(CO_2Me)$, def = *trans*-$CH(CO_2Et)=CH(CO_2Et)$, dmm = *cis*-$CH(CO_2Me)=CH(CO_2Me)$, and ma = $\overline{CH=CHC(O)OC}(O)$. [b] Calculated values are given in parentheses. [c] In Nujol.

were not significantly different from those in the free ligand, indicating that the ester groups in (1) and (2) are not co-ordinated. When these reactions were carried out with an excess of the olefins there was no evidence for displacement of the second cod ligand to give [Pt(olefin)$_3$] complexes. Reaction of excess of dimethyl or diethyl maleate with [Pt(cod)$_2$] gave the fumarate complexes (1) and (2), demonstrating that *cis* to *trans* isomerisation of these olefins readily occurs.

TABLE 2

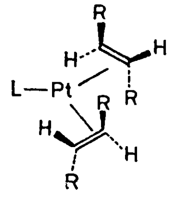
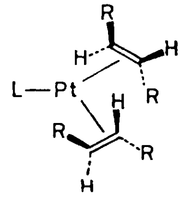
Hydrogen-1 and carbon-13 n.m.r. data [a]

Complex [b]	Solvent and temperature [c]	^{1}H	^{13}C
(1) [Pt(cod)(dmf)]	A	4.85 [m, 4 H, CH, cod, *J*(PtH) 63], 5.96 [s, 2 H, CH=CH, *J*(PtH) 82], 6.68 (s, 6 H, Me), 8.73 (m, 8 H, CH$_2$)	172 (C=O), 95 [CH, cod, *J*(PtC) 101], 94 [CH, cod, *J*(PtC) 102], 51 (Me), 44 (CH, dmf), 30 (CH$_2$), 29 (CH$_2$)
(2) [Pt(cod)(def)]	A	4.92 [m, 4 H, CH, cod, *J*(PtH) 63], 5.88 [s, 2 H, CH=CH, *J*(PtH) 80], 6.06 [q, 4 H, C*H*$_2$CH$_3$, *J*(HH) 7], 8.74 (m, 8 H, CH$_2$), 9.00 [t, 6 H, CH$_2$C*H*$_3$, *J*(HH) 7]	172 (C=O), 95 [CH, cod, *J*(PtC) 102], 94 [CH, cod, *J*(PtC) 104], 59 (CH$_2$, def), 44.5 (CH, def), 31 (CH$_2$, cod), 29 (CH$_2$, cod), 15 (Me, def)
(3) [Pt(cod)(ma)]	C	4.40 [m, 4 H, CH, cod, *J*(PtH) 38], 6.28 [s, 2 H, CH=CH, ma, *J*(PtH) 76], 7.68 (m, 8 H, CH$_2$)	171 (C=O), 100 [CH, cod, *J*(PtC) 104], 97 [CH, cod, *J*(PtC) 102], 42 [CH, ma, *J*(PtC) 337], 30 (CH$_2$)
(4) [Pt(CNBu^t)(dmf)$_2$]	A	5.36—5.56 [AB system CH=CH, *J*(AB) 10, *J*(PtA) 52, *J*(PtB) 64], 6.82 (s, 12 H, Me, dmf), 9.29 (s, 9 H, Me, CNBu^t)	170 [C=O, *J*(PtC) 41], 52—55 (br, CH, dmf), 52 (Me), 30 (Me, CNBu^t)
(5) [Pt(CNBu^t)(dmm)$_2$]	B	6.00 [s, 4 H, CH=CH, *J*(PtH), 60], 6.56 (s, 12 H, Me, dmm), 8.96 (s, 9 H, Me, CNBu^t)	169 [C=O, *J*(PtC) 37], 53 [CH, dmm, *J*(PtC) 188], 51 (Me, dmm), 30 (Me, CNBu^t)
(6) [Pt(CNBu^t)(def)$_2$]	A	4.56—4.77 [AB system, CH=CH, *J*(AB) 10, *J*(PtA) 56, *J*(PtB) 68], 6.00 [q, 4 H, CH$_2$, *J*(HH) 7], 6.10 [q, 4 H, CH$_2$, *J*(HH) 7], 8.92 [t, 6 H, Me, *J*(HH) 7], 9.05 [t, 6 H, Me, *J*(HH) 7], 9.14 (s, 9 H, Me, CNBu^t)	170 (C=O), 169 (C=O), 60.5 (CH$_2$), 60.3 (CH$_2$), 58 (NC), 55 [CH, def, *J*(PtC) 142], 51 [CH, def, *J*(PtC) 190], 29 (Me, CNBu^t), 14.6 ,14.2 (Me, def)
(7) [Pt(CNBu^t)(ma)$_2$]	D	5.16 [s, CH=CH, 4 H, *J*(PtH) 62], 8.28 (s, 9 H, Me, CNBu^t)	54 [CH, ma, *J*(PtC) 168], 30 (Me)
(9) [Pt(CNBu^t)$_2$(dmf)]	B	5.78 [s, 2 H, CH=CH, *J*(PtH) 60], 6.52 (s, 6 H, Me, dmf), 9.12 (s, 18 H, CNBu^t)	174 [C=O, *J*(PtC) 43], 57 (CMe$_3$), 50 (Me, dmf), 39 [CH, dmf, *J*(PtC) 247], 30 (Me, CNBu^t)
(10) [Pt(CNBu^t)$_2$(dmm)]	B	6.44 (s, 6 H, Me, dmm), 6.48 [s, 2 H, CH=CH, *J*(PtH) 60], 9.08 (s, 18 H, CNBu^t)	173 [C=O, *J*(PtC) 43], 57 (CMe$_3$), 51 (Me, dmm), 38 [CH, dmm, *J*(PtC) 288], 30 (Me, CNBu^t)
(11) [Pt(CNBu^t)$_2$(def)]	B	5.76 [s, 2 H, C*H*=CH, *J*(PtH) 64], 5.88 [q, 4 H, CH$_2$, *J*(HH) 7], 8.92 [t, 6 H, C*H*$_3$CH$_2$, *J*(HH) 7], 9.1 (s, 18 H, CNBu^t)	174 [C=O, *J*(PtC) 43], 59 (CH$_2$), 57 (CMe$_3$), 40 [CH, def, *J*(PtC 245), 30 (Me, CNBu^t)], 15 (Me, def)
(12) [Pt(CNBu^t)$_2$(ma)]	D	6.52 [s, 2 H, CH=CH, *J*(PtH) 62], 8.40 (s, 18 H, CNBu^t)	173 [C=O, *J*(PtC) 43], 59 (CMe$_3$), 36 [CH, ma, *J*(PtC) 265], 30 (Me, CNBu^t)
(14) [Pt(CNBu^t)(dmf){P(C$_6$H$_{11}$)$_3$}]	C	6.40 (s, 3 H, Me, dmf), 6.50 (s, 3 H, Me, dmf), 6.66 and 6.86 [H$_A$, H$_B$, ABX system with ^{195}Pt satellites, CH=CH, *J*(AB) 9, *J*(AP) 10, *J*(BP) 2, *J*(PtA) 55, *J*(PtB) 62], 8.20—8.73 [m, 33 H, P(C$_6$H$_{11}$)$_3$], 8.52 (s, 9 H, CNBu^t)	
(15) [Pt(C$_2$H$_4$)(dmf)$_2$]	B	5.12 [s, 4 H, CH=CH, dmf, *J*(PtH) 60], 6.12 [(AB)$_2$ system, 4 H, C$_2$H$_4$], 6.72 (s, 12 H, Me, dmf)	168 [C=O, *J*(PtC) 43], 75 [C$_2$H$_4$, *J*(PtC) 80], 58 [CH, dmf, *J*(PtC) 163], 51 (Me, dmf)
(16) [Pt(C$_2$H$_4$)(dmm)$_2$]	B	5.64 [s, 4 H, C$_2$H$_4$, *J*(PtH) 52], 5.80 [s, 4 H, CH=CH, dmm, *J*(PtH) 66], 6.56 (s, 12 H, Me, dmm)	168 (C=O), 80 [C$_2$H$_4$, *J*(PtC) 76], 57 [CH, dmm, *J*(PtC) 200], 52 (Me, dmm)
(17) [Pt(dmf)$_3$]	B	4.36 [s, 6 H, CH=CH, *J*(PtH) 58], 6.68 (s, 18 H, Me, dmf)	166 [C=O, *J*(PtC) 41], 68 [CH, dmf, *J*(PtC) 130], 52 (Me, dmm)
(18) [Pt(def)$_3$]	B	4.28 [s, 6 H, CH=CH, *J*(PtH) 58], 6.10 [q, 12 H, CH$_2$, *J*(HH) 7], 9.00 [t, 18 H, CH$_3$, *J*(HH) 7]	165 (C=O), 68 [s, CH, def, *J*(PtC) 131], 61 (s, CH$_2$), 14 (s, Me)
(19) [NEt$_3$(CH$_2$Ph)][PtCl(dmf)$_2$]	C	2.48 (s, 5 H, C$_6$H$_5$), 5.50 (s, 2 H, C$_6$H$_5$C*H*$_2$), 5.00 (m, CH=CH), 6.42 (s, 12 H, Me, dmf), 6.74 (m, 6 H, CH$_3$C*H*$_2$), 8.56 (m, 9 H, C*H*$_3$CH$_2$)	

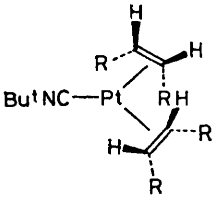
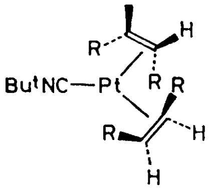
[a] ^{1}H and ^{13}C chemical shifts are relative to SiMe$_4$ (τ, 10.0 and 0.0 p.p.m. respectively), *J* values in Hz. [b] See footnote *a*, Table 1. [c] A = [^{2}H$_8$]toluene at −80 °C, B = [^{2}H$_6$]benzene at room temperature, C = [^{2}H]chloroform at room temperature, and D = [^{2}H$_6$]acetone at room temperature

In the solid, complexes (1)—(3) most likely adopt the configuration shown, with the carbon atoms of the olefin, the platinum atom, and the midpoints of the C=C bonds of the cod group being essentially coplanar. *X*-Ray crystallographic studies on several complexes of the type [PtL_2(olefin)] have shown this kind of arrangement to be favoured.[12]

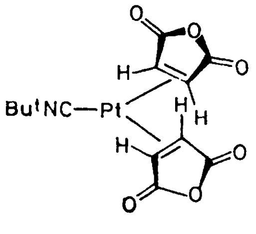
The ^1H n.m.r. spectra of (1) and (2) at room temperature showed broad olefinic resonances for the dmf and def groups; however, on cooling (—80 °C) sharp singlet resonances with ^{195}Pt satellites were observed. In contrast, both the ^1H and ^{13}C spectra of the maleic anhydride complex (3) show at room temperature the expected ^{195}Pt–^1H and ^{195}Pt–^{13}C coupling with the CH=CH group of the mono-olefin. Evidently (3) does not undergo dynamic behaviour, unlike (1) and (2). The nature of the process causing line broadening in the spectra of (1) and (2) at room temperature is unclear. It cannot be due to simple olefin rotation because the ^1H sites remain equivalent. A dissociative mechanism is eliminated because of the observation in the room-temperature ^{13}C spectra of two sharp olefinic resonances for the cod ligand.

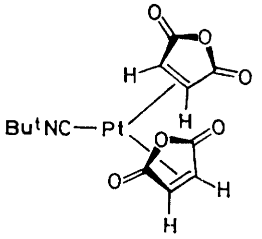



	R	L	
(4a)	CO_2Me	$CNBu^t$	(4b)
(6a)	CO_2Et	$CNBu^t$	(6b)
(8a)	CO_2Et	PPh_3	(8b)

(5a) R = CO_2Me (5b)


(7a)

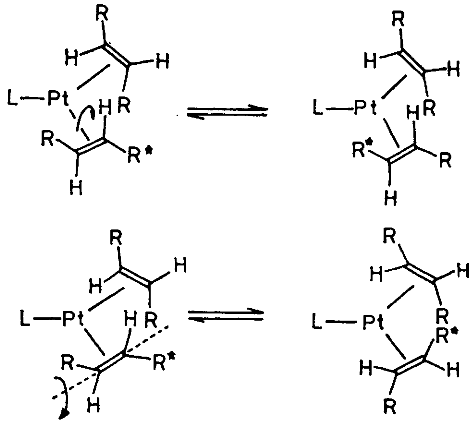

(7b)

A palladium analogue of complex (3) has recently been prepared by adding cyclo-octa-1,5-diene and maleic anhydride to the dibenzylideneacetone complex [Pd_2(dba)$_3$]·$CHCl_3$.[7]

Formation of the complexes (1)—(3) from the 18-electron species [$Pt(cod)_2$] presumably involves capture of a 16-electron species, containing η^4- and η^2-bonded cod ligands formed by a dissociative process. As mentioned above, the remaining cod ligand in the 16-electron complexes (1)—(3) is not displaced by an excess of the mono-olefin. However, addition of 1 mol equivalent of Bu^tNC or PPh_3 in the presence of excess of the olefin affords the crystalline complexes (4)—(8). Under these conditions a dmm complex (5) can be isolated, although longer reaction times (4 d) give a mixture of (4) and (5).

For each bis(olefin) complex (4)—(8) four isomeric forms are possible [13] but only two are illustrated for each complex. These are the pairs in which the olefinic carbon atoms, the platinum, and the ligated C or P atoms of the $CNBu^t$ or PPh_3 groups are all in the same plane. The alternative set of two isomers for each complex can be generated by rotating the olefins through 90° about the metal–η^2-C_2 axis. However, the latter situation is likely to be unstable with respect to the former,[14] *X*-ray crystallographic studies on the complexes [$Ni(C_2H_4)_2$-$\{P(C_6H_{11})_3\}$] [15] and [$Pt(C_2H_4)(C_2F_4)\{P(C_6H_{11})_3\}$] [16] revealing coplanar arrangements for the metal, the phosphorus, and the olefinic carbon atoms.

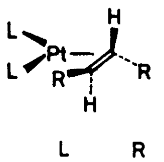
Examination of the ^1H n.m.r. spectrum of the reaction mixture which produced complex (4) showed the presence of two isomers. After crystallisation and redissolving the solid only one isomer was detected. In contrast, complexes (5)—(8) form as single isomers. On the basis of the observations it is impossible to distinguish between structures (a) and (b). However, the complex [$Pt(dmf)_2$-(PBu^t_2Ph)] has been shown [13] to have no plane of symmetry and a structure analogous to (a) has been proposed. At room temperature the ^1H spectra of (5) and (7) showed sharp singlet signals for the olefinic CH resonances, implying dynamic behaviour, but since crystallisation occurred on cooling variable-temperature studies were precluded. Further evidence for fluxional behaviour came from the spectra of (4) and (6) where broad olefinic resonances observed at ambient temperatures sharpened at —80 °C to an AB system. If it is assumed that olefin rotation does not occur *via* rotation about an axis through the C–C bond of the olefin (Scheme 1),[17] then these observations indicate that either the complexes are very stable to dissociation or that the mixture



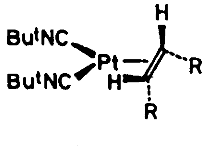
Scheme 1 R = CO_2Me

obtained reflects a thermodynamically controlled reaction.

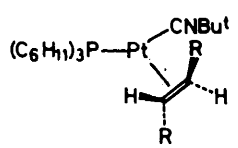
In the reaction of [Pt(cod)$_2$] with the olefins in the presence of Bu^{t}NC or PPh$_3$, if an excess of these ligands is used then (9)—(13) are obtained as stable crystalline complexes, characterised by the data given in Table 1 and 2. Their spectroscopic properties are similar to those reported for the corresponding nickel and palladium complexes.[18,19] The t-butyl isocyanide complexes were also formed by treating [Pt$_3$(CNBu^t)$_6$] [20] with the appropriate olefin. Reaction with dmf was faster than that with dmm, and there was no evidence for *cis* to *trans* olefin isomerisation in these reactions.



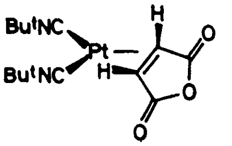
	L	R
(9)	CNBu^t	CO$_2$Me
(11)	CNBu^t	CO$_2$Et
(13)	PPh$_3$	CO$_2$Et



(10) R = CO$_2$Me

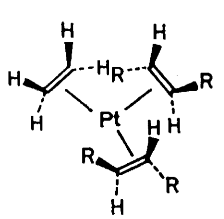


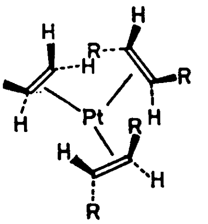
(14)



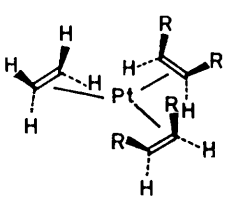
(12)

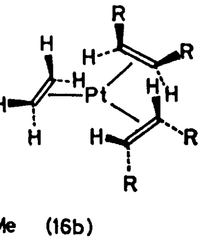
Addition of 1 mol equivalent of tricyclohexylphosphine to complex (4) led to the preferential displacement of dmf, and the formation of the crystalline three-co-ordinate complex (14), containing three different ligands. The presence of sharp olefinic ^{1}H resonances as an ABX system with ^{195}Pt satellites in the room-temperature n.m.r. spectrum suggests that olefin rotation does not occur.





(15a) R = CO$_2$Me (15b)



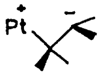


(16a) R = CO$_2$Me (16b)

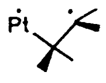
Tris(olefin) complexes (15)—(18) were prepared by treating the corresponding olefin with the labile complex [Pt(C$_2$H$_4$)$_3$].[8] Depending on the solvent, two or all three ethylene molecules were displaced. The tris(fumarate) complexes (17) and (18) were also obtained using an excess of dimethyl or diethyl maleate, respectively. However, it is interesting that it was possible to isolate bis(dimethyl maleate)ethyleneplatinum (16).

Structure (15a) may be assigned to the bis(dimethyl fumarate) complex on the basis of the room-temperature ^{1}H and ^{13}C n.m.r. results. Only one signal is seen for the olefinic protons and only one for the olefinic carbon atoms of the fumarate, implying rapid rotation of these ligands. Under these conditions the ethylene must also be expected to rotate and, therefore, the observation of a complex AA'BB' multiplet ^{1}H signal for this ligand is consistent only with the chiral diastereoisomer (15a) and its enantiomer.

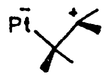
Isomerisation of maleate to fumarate species observed in our work requires a reaction path to an intermediate, in which the bond order of the co-ordinated C=C bond is reduced sufficiently to allow rotation. There are three conceivable ways this could be achieved (A)—(C). An intermediate (C) seems unlikely in view of the fact that the platinum is already in a zerovalent state before charge transfer occurs. It is difficult to distinguish between the first two alternatives; however, it is interesting to note that the intermediacy of species of this type have been invoked [9,21] to explain a variety of reactions of electronegatively substituted olefins and acetylenes with low-valent metal species.



(A)



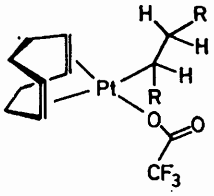
(B)



(C)

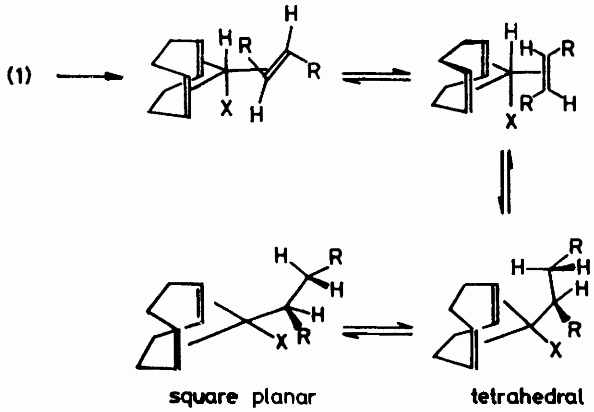
Addition (room temperature) of a tetra-alkylammonium chloride, bromide, or iodide to (cyclo-octa-1,5-diene)(dimethyl fumarate)platinum (1) in acetone in the presence of an excess of dimethyl fumarate afforded the white crystalline salts (19)—(21). Elemental analysis and i.r. and ^{1}H n.m.r. spectra indicated the formation of the anions [PtX(dmf)$_2$]$^-$. Addition of an excess of Bu^{t}NC to the salts regenerated the ammonium halides and formed complex (9). The i.r. spectrum of (19) in the 200—400 cm^{-1} region showed a single Pt–Cl stretch at 289 cm^{-1}, which was replaced by a band at 203 cm^{-1} in the spectrum of (20). In the case of the iodide there was no band at $>$200 cm^{-1}. The Pt–Cl band was asymmetric to low frequency, compatible with the ^{37}Cl,^{35}Cl isotope effect observed with a single Pt–Cl bond in the set. A binuclear structure with bridging chloride ligands would not be expected to give this pattern. The related complexes [NEt$_4$][NiBr(dmf)$_2$] and [PPh$_4$][NiBr(dmf)$_2$] have also been reported [11] and assigned mononuclear structures.

Protonation of [Pt(cod)$_2$] affords the cation [Pt(1-σ,4—5-η-C$_8$H$_{13}$)(cod)]$^+$ probably *via* direct attack on a cod ligand.[22] It was of interest, therefore, to examine the corresponding reaction of complex (1). Addition of trifluoroacetic acid at room temperature afforded air-stable crystals of the platinum(II) complex (22). Examination of the ^{1}H n.m.r. spectrum, and that of the corresponding [^{2}H]derivative (from addition of CF_3CO_2D), showed that protonation had occurred exclusively on the fumarate to give the illustrated σ-bonded derivative.



(22) R = CO_2Me

A plausible reaction path is illustrated in Scheme 2, the initial step being a *trans*-oxidative addition of CF_3CO_2H. The nature of the stereochemistry of the intermediates is hard to define because of the availability of low-energy polytopal rearrangement paths involving various square-pyramidal and trigonal-bipyramidal isomers. Following the discussion of Thorn and Hoffmann,[23] and assuming a trigonal-bipyramidal geometry, the strong σ-donating hydride ligand would be expected to show a preference for an axial site, the co-ordinated dimethyl fumarate preferring a planar orientation over an upright one thus maximising backbonding. In order for migration of the hydrogen to occur the mono-olefin must rotate to form a less-stable isomer so as to be able to achieve an essentially coplanar configuration. As shown, the hydrogen is equally well placed to migrate on to co-ordinated cod or on to dmf, and there is no obvious stereochemical reason why the latter is preferred.



SCHEME 2 R = CO_2Me, X = CF_3CO_2

EXPERIMENTAL

N.m.r. measurements (Table 2) were made on JEOL PFT and PS 100 spectrometers. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer. Experiments were conducted in Schlenk tubes in a dry oxygen-free nitrogen atmosphere, using solvents which were dried and distilled under nitrogen prior to use. Light petroleum refers to that fraction of b.p. 40—60 °C. Analytical data and other data for the complexes are given in Table 1.

Preparations.—[Pt(cod)(olefin)] *complexes*. Bis(cycloocta-1,5-diene)platinum (0.35 g, 0.85 mmol) was added portionwise with stirring (room temperature) to a solution of dimethyl fumarate (0.12 g, 0.85 mmol) in diethyl ether (15 cm^3). After 15 min the solution was filtered, the volume of solvent reduced (10 cm^3) *in vacuo*, and the solution cooled (−20 °C) to give white *crystals* of (cyclo-octa-1,5-diene)(dimethyl fumarate)platinum (1). Addition of light petroleum to the filtrate gave a further crop of crystals. A similar method afforded (cyclo-octa-1,5-diene)(diethyl fumarate)platinum (2) and (cyclo-octa-1,5-diene)(maleic anhydride)platinum (3).

[Pt(CNBu^t)(olefin)$_2$] *complexes*. To a solution of dimethyl fumarate (0.21 g, 1.56 mmol) in diethyl ether (15 cm^3) was added portionwise [Pt(cod)$_2$] (0.30 g, 0.73 mmol). After stirring for 15 min at room temperature the mixture was cooled (−20 °C), and t-butyl isocyanide (0.061 g, 0.73 mmol) in diethyl ether (5 cm^3) added dropwise. The reaction mixture was allowed to warm to room temperature, and then the solvent was removed *in vacuo* to give, after washing with light petroleum, a 1 : 1 mixture of two isomers of (4) (0.30 g, 74%). Recrystallisation (−78 °C) from diethyl ether (0.30 g, from 15 cm^3) gave *crystals* of one isomer of bis(dimethyl fumarate)(t-butyl isocyanide)platinum (4).

Similarly, reaction of dimethyl maleate (0.29 g, 2 mmol) in diethyl ether (20 cm^3) with [Pt(cod)$_2$] (0.41 g, 1.0 mmol) and Bu^{t}NC (0.083 g, 1.0 mmol) gave, from diethyl ether (10 cm^3, −20 °C), white *crystals* of bis(dimethyl maleate)(t-butyl isocyanide)platinum (5). Diethyl fumarate (0.34 g, 2 mmol) in diethyl ether (20 cm^3) with [Pt(cod)$_2$] (0.41 g, 1 mmol) and Bu^{t}NC (0.083 g, 1 mmol) gave *crystals* of bis(diethyl fumarate)(t-butyl isocyanide)platinum (6). Maleic anhydride (0.17 g, 1.7 mmol) in diethyl ether (15 cm^3) with [Pt(cod)$_2$] (0.35 g, 0.85 mmol) and Bu^{t}NC (0.071 g, 0.85 mmol) afforded (−20 °C) white *crystals* of bis(maleic anhydride)(t-butyl isocyanide)platinum (7).

Bis(diethyl fumarate)(triphenylphosphine)platinum (8). In a similar way, treatment of diethyl fumarate (0.038 g, 2.18 mmol) in diethyl ether (20 cm^3) with [Pt(cod)$_2$] (0.30 g, 0.73 mmol) and triphenylphosphine (0.19 g, 0.73 mmol) at room temperature gave white *crystals* of (8) on cooling (−20 °C).

[PtL(L′)(olefin)] *complexes*. Addition of [Pt$_3$(CNBu^t)$_6$] (0.18 g, 0.17 mmol) at room temperature to a solution of dimethyl fumarate (0.072 g, 0.5 mmol) in diethyl ether (15 cm^3) led to an immediate change in colour from red to colourless. After 0.5 h the solution was filtered, light petroleum (5 cm^3) added, and the solution cooled (−20 °C) to give white *crystals* of (dimethyl fumarate)bis(t-butyl isocyanide)platinum (9). Similar reactions between [Pt$_3$(CNBu^t)$_6$] and dimethyl maleate, diethyl fumarate, or maleic anhydride gave, respectively, (dimethyl maleate)bis(t-butyl isocyanide)platinum (10), (diethyl fumarate)bis(t-butyl isocyanide)platinum (11), and (maleic anhydride)bis(t-butyl isocyanide)platinum (12). Reaction (room temperature) of [Pt(cod)$_2$] (0.2 g, 0.48 mmol) with diethyl fumarate (0.084 g, 0.48 mmol) and PPh$_3$ (0.25 g, 0.96 mmol) in diethyl ether (10 cm^3) gave, after 1 h and cooling (−20 °C), white *crystals* of (diethyl fumarate)bis(triphenylphosphine)platinum (13).

To a solution of complex (4) (0.23 g, 0.4 mol) in diethyl ether solution (15 cm^3) was added tricyclohexylphosphine

(0.4 mmol) in diethyl ether (5 cm^3). After stirring at room temperature for 0.5 h the resulting white precipitate was collected and washed with diethyl ether to give *crystals* of (dimethyl fumarate)(t-butyl isocyanide)(tricyclohexylphosphine)platinum (14).

Tris(olefin)platinum complexes. (*a*) *Bis(dimethyl fumarate)(ethylene)platinum* (15). Dimethyl fumarate (0.25 g, 1.75 mmol) was added (0 °C) with stirring to a solution of tris(ethylene)platinum (0.24 g, 0.87 mmol) in diethyl ether (20 cm^3) under an atmosphere of ethylene. When the addition was complete the ethylene atmosphere was replaced with one of nitrogen, and the reaction mixture allowed to warm to room temperature. After 18 h the mixture was filtered, concentrated (5 cm^3) *in vacuo*, and cooled (−78 °C) to give white *crystals* of (15).

(*b*) *Bis(dimethyl maleate)(ethylene)platinum* (16). Similarly, reaction of [$Pt(C_2H_4)_3$] (0.28 g, 1.0 mmol) and dimethyl maleate (0.29 g, 2 mmol) in diethyl ether–light petroleum (1 : 1, 20 cm^3) gave after 4 h at room temperature a brown solid which on recrystallisation (−78 °C) from diethyl ether–light petroleum gave white *crystals* of (16).

(*c*) *Tris(dimethyl fumarate)platinum* (17). Addition of dimethyl fumarate (0.38 g, 2.61 mmol) to [$Pt(C_2H_4)_3$] (0.24 g, 0.87 mmol) in diethyl ether (15 cm^3) at room temperature gave (3 h), on concentrating (10 cm^3) *in vacuo* and cooling (−90 °C), white *crystals* of (17).

(*d*) *Tris(diethyl fumarate)platinum* (18). A similar reaction between [$Pt(C_2H_4)_3$] (0.31 g, 1.12 mmol) and diethyl fumarate (1.42 g, 2 mmol) in diethyl ether (20 cm^3) gave from light petroleum (−20 °C) colourless *crystals* of (18).

Anionic complexes of the type [NR_3R'][$PtX(olefin)_2$]. Benzyltriethylammonium chloride (0.10 g, 0.45 mmol) was added at room temperature to a stirred solution of complex (1) (0.20 g, 0.45 mmol) and dimethyl fumarate (0.065 g, 0.45 mmol) in acetone (20 cm^3). After 2 h, solvent was removed *in vacuo*. The resulting oil was triturated with diethyl ether (5 cm^3) and acetone (0.5 cm^3) to give white *crystals* of benzyltriethylammonium chlorobis(dimethyl fumarate)platinate (19). Similar reactions afforded tetramethylammonium bromobis(dimethyl fumarate)platinate (20) and tetraethylammonium bis(dimethyl fumarate)-iodoplatinate (21) as white crystalline *materials*.

Reaction of Trifluoroacetic Acid with (Cyclo-octa-1,5-diene)(dimethyl fumarate)platinum.—Trifluoroacetic acid (1.0 cm^3) was added to complex (1) (0.20 g, 0.45 mmol) and the resulting yellow solution stirred at room temperature. After 1 h excess of CF_3CO_2H was removed *in vacuo*. The resulting oil was dissolved in diethyl ether (3 cm^3) and light petroleum (10 cm^3) added to give white *crystals* of (22) (0.77 g, 68%), m.p. 54 °C (decomp.) (Found: C, 34.3; H, 3.9. $C_{16}H_{21}F_3O_6Pt$ requires C, 34.2; H, 3.8%); $\nu_{max.}$ (Nujol) at 1 735s, 1 700vs, 1 410s, 1 320m, 1 240(sh), 1 185vs, 1 140vs, 1 080m, 1 028w, 1 010m, 990w, 970w, 912w, 895m, 870w, 850m, 822w, 808vw, 795w, 788m, 770m, 730s, 620vw, 578vw, 540(sh), 520w, and 420w cm^{-1}. N.m.r. spectra: ^{1}H in [^{2}H]toluene, τ 5.22 (m, 4 H, CH=CH), 6.46 (s, 3 H, CO_2Me), 6.66 (s, 3 H, CO_2Me), 7.12 [d, 2 H, CH_2CO_2Me (*H*$_2$), *J*(HH) 4.0], 7.22 [t, 1 H, C*H*CO_2Me, *J*(HH) 4.0 Hz], and 8.38 (m, 8 H, CH_2); ^{19}F in $CDCl_3$, relative to CCl_3F, 76.0 p.p.m. (s, 3 F, CF_3CO_2); ^{13}C in C_6D_6 of the complex from CF_3CO_2D, 175, 173 (C=O), 160—161 (*C*F_3CO_2 and CF_3*C*O_2), 112.7, 112.4 [*C*H=CH, *trans* to $C_6H_8DO_4$, *J*(PtC) 47.3], 87,85 [*C*H=CH, *trans* to CF_3CO_2, *J*(PtC) 226], 51.4, 51.2 (Me), 34.3 [PtCH*C*H_2, *J*(PtC) 39.7], 34.0 [PtCH*C*HD, *J*(DH) 38.1], 31.8 and 30.8 [CH_2(cod), *trans* to $CH(CO_2Me)$-$CHD(CO_2Me)$, *J*(PtC) 21], 31.5 [Pt*C*HCH_2, *J*(PtC) 639], 27.8 and 27.2 p.p.m. [CH_2(cod), *trans* to CF_3CO_2, *J*(PtC) 21 Hz].

We thank the S.R.C. for support, the CSIC (Spain) and Royal Society for the award of a European Exchange Fellowship (to J. V.), and Dr. P. L. Goggin for discussion of the low-wavelength i.r. spectra of the halogeno-complexes.

[8/1167 *Received, 23rd June*, 1978]

REFERENCES

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

[2] P. M. Maitlis, 'The Organic Chemistry of Palladium,' Academic Press, New York, 1971, vol. 1 and refs. therein.

[3] U. Belluco, 'Organometallic and Co-ordination Chemistry of Platinum,' Academic Press, New York, 1974, and refs. therein.

[4] T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, and J. A. Ibers, *J. Organometallic Chem.*, 1974, **65**, 253; Y. Ishii, S. Hasegawa, S. Kimura, and K. Itoh, *ibid.*, vol. **73**, p. 411.

[5] M. C. Mazza and C. G. Pierpont, *Inorg. Chem.*, 1973, **12**, 2955; 1974, **13**, 1891.

[6] K. Moseley and P. M. Maitlis, *J.C.S. Dalton*, 1974, 169.

[7] K. Itoh, F. Ueda, K. Harai, and Y. Ishii, *Chem. Letters*, 1977, 877.

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

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

[10] M. T. Chicote, M. Green, J. L. Spencer, F. G. A. Stone, and J. Vicente, *J. Organometallic Chem.*, 1977, **137**, C8.

[11] F. Guerrieri and G. Salerno, *J. Organometallic Chem.*, 1976, **114**, 339.

[12] S. D. Ittel and J. A. Ibers, *Adv. Organometallic Chem.*, 1976, **14**, 33.

[13] T. Yoshida and S. Otsuka, *J. Amer. Chem. Soc.*, 1977, **99**, 2134.

[14] N. Rösch and R. Hoffmann, *Inorg. Chem.*, 1974, **13**, 2656.

[15] C. Krüger and Y.-H. Tsay, *J. Organometallic Chem.*, 1972, **34**, 387.

[16] J. A. K. Howard, P. Mitrprachachon, and P. Woodward, unpublished work.

[17] B. F. G. Johnson and J. A. Segal, *J.C.S. Chem. Comm.*, 1972, 1312.

[18] S. Otsuka, T. Yoshida, and Y. Tatsuno, *J. Amer. Chem. Soc.*, 1971, **93**, 6462.

[19] S. D. Ittel, *Inorg. Chem.*, 1977, **16**, 2589.

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

[21] F. G. A. Stone, *Pure Appl. Chem.*, 1972, **30**, 551.

[22] M. Green, D. M. Grove, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 2228.

[23] D. L. Thorn and R. Hoffmann, *J. Amer. Chem. Soc.*, 1978, **100**, 2079.