η^2-Bonded Methylenecyclopropane Complexes of Rhodium(I), Iridium(I), Platinum(0), and Platinum(II): Crystal and Molecular Structure of Acetylacetonatobis(η^2-methylenecyclopropane)rhodium(I)

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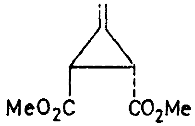
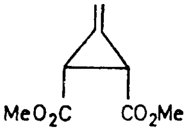
Reactions of methylenecyclopropane (1), *trans*-2,3-dimethoxycarbonylmethylenecyclopropane (2), or *cis*-2,3-dimethoxycarbonylmethylenecyclopropane (3) with the appropriate η^2-ethylene–metal complexes yield [Rh(un)$_2$(acac)] {un = (1)—(3)}, [{Rh(un)$_2$Cl}$_2$] {un = (2) or (3)}, [Rh(un)$_2$(η^5-C$_5$H$_5$)] [un = (2)], [Ir(un)$_2$(acac)] {un = (2) or (3)}, [Pt(un)(PPh$_3$)$_2$] {un = (1)—(3)}, and *trans*-[PtCl$_2$(un)(C$_5$H$_5$N)] {un = (2) or (3)}. The complexes [Rh(un)(CO)L] {un = (2); L = acac or η^5-C$_5$H$_5$} are described. ^{1}H, ^{13}C, and ^{31}P N.m.r. data are reported and discussed, and the complex [Fe(un)(CO)$_4$] {un = (3)} is shown to be stereochemically rigid at ambient temperature. An *X*-ray crystallographic determination of acetylacetonatobis(η^2-methylenecyclopropane)rhodium(I) (4a) establishes that the rhodium atom is in a square-planar configuration with two adjacent sites occupied by the acetylacetonate ligand. The methylenecyclopropane ligands are bonded with the exocyclic double-bond approximately perpendicular to the co-ordination plane of the rhodium atom and in converse orientation to one another. The plane of the cyclopropane ring lies normal to the valence direction of the rhodium–olefin bond.

THE transition-metal promoted opening-reactions of small, strained rings have aroused considerable recent interest, and the reactions of methylenecyclopropane and its derivatives with transition-metal systems have begun to be explored.[1-3]

Oligomerisation and co-dimerisation reactions of methylenecyclopropane, under the catalytic influence of zerovalent nickel complexes, have been reported to give products in which the integrity of the cyclopropane ring may be retained or destroyed.[1-3] The intermediates in these systems have been suggested to be η^2-bonded methylenecyclopropane complexes of Ni^0, and methylenenickelacyclobutane species arising from a formal oxidative insertion of Ni^0 into the 1,2-σ-bond of the cyclopropane ring.[1-3] Such oxidative insertion reactions, of other low-valent complexes of Pt^0,[4] Pt^{II},[5] Rh^I,[6] and Fe^0 (ref. 7) into the carbon–carbon σ-bonds of cyclopropane derivatives are well known.


(1)


(2)


(3)

[(un)$_2$RhX]
un X
(4) a; (1); acac
b; (2); acac
c; (3); acac
d; (2); Cl (dimer)
e; (3); Cl (dimer)
f; (2); η^5-C$_5$H$_5$

[(un)$_2$Ir(acac)]
(5) a; un = (2)
b; un = (3)

[(un)Pt(PPh$_3$)$_2$]
un
(6) a; (1)
b; (2)
c; (3)

trans-[(un)PtCl$_2$(C$_5$H$_5$N)]
un
(7) a; (2)
b; (3)

[(un)(OC)Rh(X)]
un X
(8) a; (2); acac
b; (2); η^5-C$_5$H$_5$

[(un)Fe(CO)$_4$]
un
(9) a; (2)
b; (3)

Phenyl-substituted methylenecyclopropanes have been shown to react with [Fe$_2$(CO)$_9$] to produce substituted tricarbonyl(trimethylenemethane)iron complexes; cleavage of the 2,3-bond of the cyclopropane ring is apparently preferred in this instance.[8]

In an attempt to clarify the factors governing these ring-opening reactions, the reactions of methylenecyclopropane (1) and the *trans*- and *cis*-dimethyl esters of Feist's acid, (2) and (3), with a variety of low-valent transition-metal systems have been explored.

RESULTS

Reaction of [Rh(C$_2$H$_4$)$_2$(acac)] with methylenecyclopropane (1), *trans*-2,3-dimethoxycarbonylmethylenecyclopropane (2), or *cis*-2,3-dimethoxycarbonylmethylenecyclopropane (3), at ambient temperatures in diethyl ether solution, resulted in displacement of ethylene, and the formation of complexes (4a), (4b), and (4c) respectively. Similarly, treatment of a pentane suspension of [{Rh(C$_2$H$_4$)$_2$Cl}$_2$] with (2) or (3) yielded the chloride-bridged dimeric complexes (4d) and (4e) respectively. Reaction of (4d) or (4e) with acetylacetonatothallium(I) yielded the monomeric complexes (4b) and (4c). Cyclopentadienylthallium(I) reacted with (4d) to yield the monomeric complex (4f).

Similarly, reaction of [Ir(C$_2$H$_4$)$_2$(acac)] with (2) or (3) yielded monomeric Ir^I complexes (5a) and (5b) respectively.

A benzene solution of [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] reacted readily with either (1), (2), or (3), displacing ethylene and forming the Pt^0 complexes (6a), (6b), and (6c). Similarly, reaction of *trans*-[Pt(C$_2$H$_4$)Cl$_2$(C$_5$H$_5$N)] with (2) or (3) yielded the Pt^{II} complexes (7a) and (7b).

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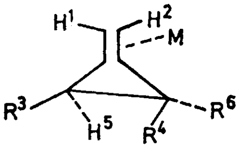
Setting aside, at −30 °C, a pentane solution containing equimolar amounts of (4b) and [Rh(CO)$_2$(acac)] resulted in the slow crystallisation of the mixed carbonyl–olefin complex (8a). Similarly, maintaining a pentane solution of (4f) and [Rh(CO)$_2$(η^5-C$_5$H$_5$)] at −30 °C resulted in crystallisation of complex (8b).

TABLE 1

^{1}H N.m.r. data (100 MHz; CDCl$_3$) for complexes (4)—(8)



Complex	R³	R⁴	R⁵	t/°C	H¹	H²	H³	H⁴	H⁵	H⁶	Other ligands
					τ (multiplicity); J [a]						
(4a)	H	H	H	−60	6.70(2)	8.06 (s)	8.62 (m)		9.08 (m)		Acac CH 4.67 (s) CH_3 8.02 (s)
(4b)	CO$_2$Me	H	CO$_2$Me	34	6.21 (s)	7.97 (s)	6.34 (s)	7.12 (d) J(4,5) 4	7.40 (d)	6.44 (s)	Acac CH 4.75 (s) CH_3 8.08 (s)
(4c)	CO$_2$Me	CO$_2$Me	H	−60	6.29 (s)	7.70 (s)	6.35 (s)		7.16 (s)		Acac CH 4.65 (s) CH_3 8.05 (s)
(4d)	CO$_2$Me	H	CO$_2$Me	34	6.70 (bs)	8.18 (bs)	6.05 (s)	7.53 (bs)		6.37 (s)	
(4e)	CO$_2$Me	CO$_2$Me	H	34	*ca*, 7.3 (b)		6.30 (s)		7.20 (s)		
(4f)	CO$_2$Me	H	CO$_2$Me	34	6.62 (s)	8.76 (s)	6.26 (s)	7.40 (d) J(4,5) 4	7.48 (d)	6.40 (s)	η^5-C$_5$H$_5$ 4.80 (s)
(5a)	CO$_2$Me	H	CO$_2$Me	34	6.29 (s)	8.06 (s)	6.33 (s)	7.47 (d) J(4,5) 4	7.61 (d)	6.47 (s)	Acac CH 4.52 (s) CH_3 7.98 (s)
(5b)	CO$_2$Me	CO$_2$Me	H	−60	*ca*. 6.3 [b]	7.84 (s)	6.30 (s)	6.35 (s)	7.64 (s)		Acac CH 4.42 (s) CH_3 7.92 (s)
(6a)	H	H	H	34			8.42 (m) [c]				PPh$_3$ 2.84 (m)
(6b)	CO$_2$Me	H	CO$_2$Me	34	7.09 (dd) ^3J(P–H) + ^3J(P′–H) 10, ^2J(Pt–H) 44	7.46 (dd) ^3J(P–H) + ^3J(P′–H) 10 ^2J(Pt–H) 44	6.35 (s)	8.40 (dd) [d]		7.46 (s)	PPh$_3$ 2.85 (m)
(6c)	CO$_2$Me	CO$_2$Me	H	34	7.83 (dd) ^3J(P–H) + ^3J(P′–H) 12 ^2J(Pt–H) 60		6.44 (s)		8.18 (dd) ^4J(P–H) 9 ^3J(Pt–H) 58		PPh$_3$ 2.85 (m)
(7a)	CO$_2$Me	H	CO$_2$Me	34	5.06 (s) ^2J(Pt–H) 62	5.11 (s) ^2J(Pt–H) 61	6.24 (s)	6.85 (d) J(4,5) 5 ^3J(Pt–H) 38	7.26 (d) ^3J(Pt–H) 27	6.28 (s)	Pyridine α-H 1.20 (m), J(Pt–H) 34 β-H 2.46 (m) γ-H 2.04 (m)
(7b)	CO$_2$Me	CO$_2$Me	H	34	5.20 (s) ^2J(Pt–H) 60		6.30 (s)		7.00 (s) ^3J(Pt–H) 30		Pyridine α-H 1.22 (m), J(Pt–H) 34 β-H 2.48 (m) γ-H 2.06 (m)
(8a)	CO$_2$Me	H	CO$_2$Me	34	*ca*. 6.2 [b]	8.03 (s)	6.13 (s)	7.10 (d) J(4,5) 4	7.20 (d)	6.28 (s)	Acac CH 4.60 (s) CH_3 7.90 (s) CH_3 8.11 (s)
(8b)	CO$_2$Me	H	CO$_2$Me	34	7.03 (s)	7.87 (s)	6.27 (s)	7.18 (d) J(4,5) 4	7.40 (d)	6.33 (s)	η^5-C$_5$H$_5$ 4.63 (s)

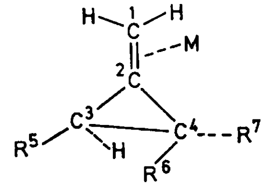
[a] Chemical shifts are quoted on τ scale. In Pt complexes, multiplicities given are for central peak system, excluding ^{195}Pt satellites. J values in Hz. [b] Obscured by resonances of H^3 and H^4. [c] Resonances of all protons in unsubstituted methylenecyclopropane ligand occur as complex unsymmetrical multiplet. [d] H^4 and H^5 are anisochronous. Separation between the outer lines of doublet of doublets is 14 Hz; ^{195}Pt satellites occur having the same multiplicity as the central peak, J(Pt–H) 58 Hz.

Complexes (4)—(8) were characterised by a combination of microanalytical data, ^{1}H n.m.r. (Table 1), ^{13}C n.m.r. (Table 2) and in the cases of complexes (6a—c), ^{31}P n.m.r. spectroscopy (Table 3). The spectroscopic data were fully compatible with the formulation of these complexes as η^2-bonded methylenecyclopropane complexes, in which no ring-opening reaction or oxidative insertion of the metal into the cyclopropane ring had occurred. The ^{1}H and ^{13}C n.m.r. spectra were particularly diagnostic in that, on co-ordination to the transition-metal centre, only the olefinic protons in the ^{1}H n.m.r. spectra, and the two olefinic carbon atoms in the ^{13}C n.m.r. spectra, experienced any pronounced upfield co-ordination shift.[9] Similarly, the observation that significant spin–spin coupling of either ^{103}Rh or ^{195}Pt only occurred to the olefinic protons, or carbon atoms, in complexes (4), (6), and (7), further substantiated this formulation as simple η^2-bonded olefin complexes.

The ^{1}H n.m.r. spectrum of complex (4a), in $CDCl_3$ at −60 °C, excluding those resonances attributable to the acac ligand, consisted of four resonances at τ 6.70, 8.06, 8.62, and 9.08 (ratio 2 : 2 : 4 : 4, see Table 1). On warming to ambient temperatures the resonances of the ' inner ' and ' outer ' olefinic protons coalesced to give a broad single resonance, indicating a rapid site-exchange between these two proton environments. These observations can be rationalised in terms of a rapid, propeller-type rotation[10] of

TABLE 2

^{13}C N.m.r. data (25.15 MHz; $CDCl_3$) for complexes (4a—c), (5a), (6b), (7a), and (9a,b)



					δ; J^a							
Complex	R^5	R^6	R^7	t/°C	C^1	C^2	C^3	C^4	R^5	R^6	R^7	Other ligands
(4a)	H	H	H	−50	47.96 J(Rh–C) 12 J(C–H) 160	72.88 J(Rh–C) 20	10.56 J(C–H) 163	9.46 J(C–H) 163				Acac CH_3; 27.24 J(C–H) 127 CH; 99.01 J(C–H) 157 C⋯O; 186.14
(4b)	CO_2Me	H	CO_2Me	34	45.36 J(Rh–C) 12	73.27 J(Rh–C) 21	31.71	30.56	OCH_3; 51.79 C=O; 170.16		OCH_3; 51.43 C=O; 169.80	Acac CH_3; 26.37; CH, 101.57; C⋯O; 186.48
(4c)	CO_2Me	CO_2Me	H	−50	47.81 J(Rh–C) 12	71.35 J(Rh–C) 30	31.20	30.00		OCH_3; 51.87 C=O; 168.49		Acac CH_3; 27.00; CH; 99.08; C⋯O, 186.94
(5a)	CO_2Me	H	CO_2Me	34	30.40	49.75	31.97	29.97	OCH_3; 51.75 C=O; 170.19		OCH_3; 51.39 C=O; 169.58	Acac CH_3, 26.80 CH, 100.90 C⋯O, 187.42
(6b)	CO_2Me	H	CO_2Me	34	28.21 [b] J(P–C) 40	54.90 [b] J(P–C) 65	32.40	30.21	OCH;3 51.39 C=O; 174.18		OCH_3; 50.48 C=O; 173.52	PPh_3; 134.39 133.90; 133.54 129.23; 127.84 127.47
(7a)	CO_2Me	H	CO_2Me	34	5.744 J(Pt–C) 136 [c]	80.92 J(Pt–C) 354 [c]	30.56 J(Pt–C) 18	29.71 J(Pt–C) 12	OCH_3; 52.64 C=O; 168.95		OCH_3; 52.64 C=O; 168.34	Pyridine α-C; 126.24 J(Pt–C) 35 β-C; 151.11 δ-C; 140.31
(9a)	CO_2Me	H	CO_2Me	−90 [d]	23.00	54.91	32.22	30.46	OCH_3; 52.24 C=O; 172.41		OCH_3; 52.24 C=O; 170.85	C≡O (ratio) 208.35 (2) 208.11 (1) 208.08 (1)
(9b)	CO_2Me	CO_2Me	H	−90 [d,e]	22.52	49.88	28.58		OCH_3; 51.88 C=O; 170.55			C≡O [e] (Ratio) 208.90 (1) 208.35 (2) 207.68 (1)

[a] δ Values p.p.m. downfield from internal tetramethylsilane; J values in Hz. [b] No ^{195}Pt satellites observed. [c] Corresponding values of J(Pt–C) for *trans*-[$PtCl_2$(δ-picoline)(η^2-$Me_2C{=}C^2{=}C^1H_2$)] are 114 and 277 Hz.[20] [d] In CD_2Cl_2 solution. [e] Identical spectrum obtained at 0 °C.

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the methylenecyclopropane ligands in (4a) at room temperature, and is further substantiated by the variable-temperature ^{13}C n.m.r. spectra of (4a) (Table 2). Similar variable-temperature behaviour was observed in the ^{1}H n.m.r. spectrum of (4c), but complex (4b) exhibited a temperature-independent ^{1}H n.m.r. spectrum. Apparently a barrier exists to rotation of the *trans*-2,3-dimethoxycarbonylmethylenecyclopropane ligands in (4b), which is not applicable to (4a) or (4c). Similar variable-temperature behaviour in the ^{1}H n.m.r. spectra of the analogous iridium complexes (5a) and (5b) was observed.

TABLE 3

^{31}P N.m.r. data (40.48 MHz; $CDCl_3$; 34 °C) for complexes (6)

Complex	δP^1 [a]	δP^2 [a]	$J(P^1–P^2)$ [b]	$J(Pt–P^1)$	$J(Pt–P^2)$
(6a)	32.49	30.02	35.4	3 410	3 231
(6b)	30.35	27.82	30.5	3 373	3 321
(6c)	30.17	27.85	32.9	3 380	3 358

[a] In p.p.m. downfield from external H_3PO_4. [b] J in Hz.

The ^{1}H and ^{13}C n.m.r. spectra of complexes (6) and (7) were fully consistent with their formulation as simple olefin complexes of Pt^0 and Pt^{II}.

The mixed olefin–carbonyl complexes (8a) and (8b) each exhibited a single terminal carbonyl stretching band in the i.r. spectrum (Nujol mull), and are analogous to the previously reported complex $[\{Rh(CO)(C_2H_4)Cl\}_2]$.[11]

During the course of this work the reaction of $[Fe_2(CO)_9]$ with (2) and (3) was reported to yield complexes (9a) and (9b) respectively, in which the substituted methylenecyclopropane ligands remained intact.[12] We have synthesised (9a) and (9b) and have recorded their variable-temperature ^{13}C n.m.r. spectra (Table 2).

At 34 °C the terminal carbonyl region in the ^{13}C n.m.r. spectrum of (9b) exhibited the expected three resonances (ratio 1 : 2 : 1) for a rigid trigonal bipyramidal structure, with the olefinic ligand constrained within the trigonal plane.[13] On cooling to 0 °C these resonances sharpened slightly. The terminal carbonyl region of the ^{13}C n.m.r. spectrum of (9a) at room temperature exhibited a single sharp resonance, which, on cooling to below −50 °C, split into three singlet resonances (ratio 2 : 1 : 1) [four carbonyl resonances are expected for the rigid trigonal bipyramidal structure for (9a); accidental overlap of two of these presumably accounts for the observed pattern]. Axial–equatorial carbonyl site-exchange therefore occurs rapidly above −50 °C in the case of (9a), but is still slow, on the n.m.r. time-scale, in complex (9b) at 34 °C.

Complexes (9a) and (9b) were reported [12] to possess remarkable thermal stability, rearranging only slowly when heated under reflux in toluene to yield (substituted-1,3-diene)tricarbonyliron complexes. Interestingly, the energy barrier for this rearrangement was significantly reduced by addition of excess of $[Fe_2(CO)_9]$, which caused the reaction to proceed smoothly at 40 °C.[12]

Similarly, the substituted methylenecyclopropane ligands in complexes of Rh^I, Pt^0, and Pt^{II} exhibited a high degree of thermal stability. Complexes (6a) and (6b) were recovered unchanged after heating under reflux for 12 h in benzene solution; similarly complex (7a) was stable in bromoform solution, in an n.m.r. tube, at temperatures up to 120 °C, decomposition to metallic platinum being preceded by dissociation of the pyridine ligand (evidenced by loss of ^{195}Pt coupling to the α-protons of the pyridine ligand). The Rh^I complexes (4b), (4c), (4f), (8a), and (8b) were also stable for several hours when heated under reflux in hexane, and were unaffected by prolonged u.v. irradiation in hexane solution.

In an effort to gain further insight into the stability and nature of bonding of methylenecyclopropanes towards transition metals, complex (4a) was subjected to a single-crystal *X*-ray crystallographic study.

The *X*-ray analysis (Tables 4—6) establishes that the molecule has the overall structure shown in Figure 1. The rhodium atom adopts an almost ideal square-planar configuration, with the two methylenecyclopropane ligands each η^2-bonded to the rhodium atom through the exocyclic double bond. The plane of the cyclopropane ring is symmetrically related to the metal–ligand bond, and the exocyclic double-bond in turn lies approximately perpendicular to the co-ordination plane of the rhodium atom, with the two methylenecyclopropane ligands in converse orientation to one another.

TABLE 4

Atomic positional (fractional co-ordinates) and thermal parameters for (4a), with estimated standard derivations in parentheses

Atom	x	y	z	$10^2U/Å^2$ *
Rh	0.455 73(6)	0.242 58(8)	0.214 09(6)	†
O(1)	0.3939(6)	0.0807(9)	0.0955(7)	3.9(2)
O(2)	0.5291(7)	0.0857(9)	0.3298(7)	4.1(2)
C(1)	0.4162(9)	−0.0572(12)	0.1072(9)	3.6(3)
C(2)	0.5317(10)	−0.0554(12)	0.3049(10)	4.0(3)
C(3)	0.4819(10)	−0.1205(13)	0.2040(10)	4.0(3)
H(3)	0.467	−0.224	0.183	6.3
C(11)	0.3636(11)	−0.1497(11)	0.0079(12)	5.5(3)
H(111)	0.279	−0.135	−0.012	6.3
H(112)	0.394	−0.107	−0.070	6.3
H(113)	0.384	−0.266	0.013	6.3
C(21)	0.5928(12)	−0.1451(16)	0.4045(12)	5.7(4)
H(211)	0.677	−0.098	0.422	6.3
H(212)	0.561	−0.130	0.477	6.3
H(213)	0.599	−0.259	0.382	6.3
C(4)	0.4106(10)	0.3954(13)	0.0748(10)	4.2(3)
H(401)	0.471	0.457	0.089	6.3
H(402)	0.432	0.334	−0.006	6.3
C(5)	0.3289(10)	0.3764(13)	0.1350(10)	4.1(3)
C(6)	0.2537(12)	0.4610(16)	0.1883(12)	5.7(4)
H(601)	0.255	0.454	0.281	6.3
H(602)	0.228	0.575	0.159	6.3
C(7)	0.2169(11)	0.3286(15)	0.1110(12)	5.2(3)
H(701)	0.195	0.228	0.144	6.3
H(702)	0.168	0.347	0.022	6.3
C(41)	0.4956(10)	0.3985(10)	0.3514(13)	4.2(3)
H(411)	0.442	0.480	0.335	6.3
H(412)	0.492	0.330	0.442	6.3
C(51)	0.5804(10)	0.3813(12)	0.2907(10)	3.7(3)
C(61)	0.6504(11)	0.4728(15)	0.2384(11)	5.1(3)
H(611)	0.647	0.457	0.145	6.3
H(612)	0.673	0.580	0.265	3.3
C(71)	0.6919(11)	0.3421(15)	0.3159(11)	5.1(3)
H(711)	0.719	0.239	0.282	6.3
H(712)	0.744	0.362	0.402	6.3

* $B = 8\pi^2U$. † Anisotropic thermal parameters in the form: $\exp\{-2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]\}$, with parameters (×$10^2$): U_{11} 3.57(5), U_{22} 2.84(5), U_{33} 3.49(5), U_{12} 0.05(4), U_{13} 0.39(3), and U_{23} 0.20(4).

Detailed examination of the bonding reveals features of peculiar interest. The two bonded atoms of the methylenecyclopropane ligand are not equidistant from the metal

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[11] J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 211.

[12] T. H. Whitesides and R. W. Slaven, *J. Organometallic Chem.*, 1974, **67**, 99.

[13] T. H. Whitesides, R. W. Slaven, and J. C. Calabrese, *Inorg. Chem.*, 1974, **13**, 1895.

TABLE 5

Bond lengths (Å) and angles (°) for (4a)

(*a*) Distances			
(i) Acetylacetonate ligand			
Rh–O(1)	2.061(8)	C(11)–H(111)	1.06
Rh–O(2)	2.049(8)	C(11)–H(112)	1.15
C(1)–O(1)	1.282(13)	C(11)–H(113)	1.08
C(2)–O(2)	1.314(14)	C(21)–H(211)	1.14
C(1)–C(3)	1.385(15)	C(21)–H(212)	1.04
C(2)–C(3)	1.356(15)	C(21)–H(213)	1.07
C(1)–C(11)	1.477(17)	C(3)–H(3)	0.98
C(2)–C(21)	1.499(17)		
(ii) Methylenecyclopropane (1)			
Rh–C(4)	2.131(12)	C(4)–H(401)	0.94
Rh–C(5)	2.073(11)	C(4)–H(402)	1.19
C(4)–C(5)	1.405(19)	C(6)–H(601)	1.09
C(5)–C(6)	1.479(21)	C(6)–H(602)	1.11
C(5)–C(7)	1.464(19)	C(7)–H(701)	1.05
C(6)–C(7)	1.518(19)	C(7)–H(702)	1.11
(iii) Methylenecyclopropane (2)			
Rh–C(41)	2.127(12)	C(41)–H(411)	1.00
Rh–C(51)	2.072(11)	C(41)–H(412)	1.25
C(41)–C(51)	1.440(19)	C(61)–H(611)	1.11
C(51)–C(61)	1.459(19)	C(61)–H(612)	1.04
C(51)–C(71)	1.437(18)	C(71)–H(711)	1.10
C(61)–C(71)	1.519(18)	C(71)–H(712)	1.10
(*b*) Angles			
(i) Acetylacetonate ligand			
O(2)–Rh–O(1)	90.6(3)	C(1)–C(3)–C(2)	128.9(11)
Rh–O(1)–C(1)	125.2(6)	C(3)–C(1)–C(11)	120.5(10)
Rh–O(2)–C(2)	123.7(7)	O(1)–C(1)–C(11)	114.6(9)
O(1)–C(1)–C(3)	124.9(10)	C(3)–C(2)–C(21)	121.1(11)
O(2)–C(2)–C(3)	126.2(10)	O(2)–C(2)–C(21)	112.6(10)
(ii) Methylenecyclopropane (1)			
O(1)–Rh–C(4)	86.5(4)	C(6)–C(5)–C(7)	62.1(9)
O(1)–Rh–C(5)	88.1(4)	C(5)–C(7)–C(6)	59.5(9)
C(4)–C(5)–C(6)	141.8(12)	C(5)–C(6)–C(7)	58.4(9)
C(4)–C(5)–C(7)	138.4(11)		
(iii) Methylenecyclopropane (2)			
O(2)–Rh–C(41)	87.3(4)	C(61)–C(51)–C(71)	63.3(9)
O(2)–Rh–C(51)	86.3(4)	C(51)–C(71)–C(61)	59.0(9)
C(41)–C(51)–C(61)	139.2(11)	C(51)–C(61)–C(71)	57.6(8)
C(41)–C(51)–C(71)	138.6(11)		

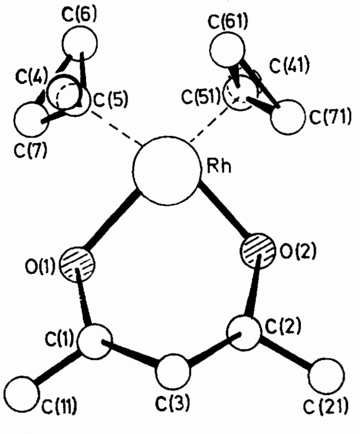

FIGURE 1 Molecular structure of (4a) showing the crystallographic numbering sequence

atom; the ring carbon atom (2.07 Å) is significantly nearer than the exocyclic carbon atom (2.13 Å). Furthermore, the co-ordination plane of the Rh atom [as defined by Rh, O(1), O(2)] does not intersect the olefinic bond at its mid-point, but much nearer to the exocyclic carbon (Table 6).

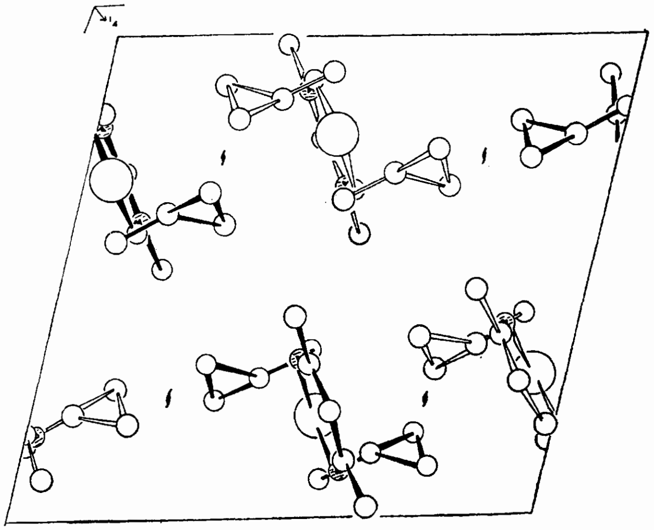

FIGURE 2 Projection of the contents of one unit cell of (4a) on the *ac* plane

TABLE 6

Equations of some least-squares planes and lines for (4a); distances (Å) of relevant atoms from these planes are given in square brackets.

(*a*) Plane (1): Rh, O(1), C(1), C(3), C(2), O(2)

$$11.758x + 1.067y - 6.840z = 4.104$$

[Rh 0.049, O(1) −0.040, C(1) −0.005, C(3) 0.039, C(2) 0.004, O(2) −0.047, C(11) −0.042, C(21) −0.055]

Plane (2): Rh, O(1), O(2)

$$11.840x + 0.489y - 6.844z = 4.049$$

[C(1) 0.117, C(3) 0.201, C(2) 0.133, C(11) 0.128, C(21) 0.130, C(4) 0.494, C(41) −0.392, C(5) −0.895, C(51) 1.109]

Plane (3): C(5), C(6), C(7)

$$0.358x - 5.441y + 9.148z = -0.695$$

[C(4) −0.625, Rh 1.497]

Plane (4): C(51), C(61), C(71)

$$-0.181x + 5.443y + 9.264z = 4.664$$

[C(41) 0.671, Rh −1.442]

Line (5): C(4), C(5)

$$x = 0.370 + 0.058t,\ y = 0.386 + 0.013t,\ z = 0.105 - 0.043t$$

[Rh 1.979, C(41) 2.947, C(51) 2.960]

Line (6): C(41), C(51)

$$x = 0.540 + 0.059t,\ y = 0.390 - 0.012t,\ z = 0.321 - 0.042t$$

[Rh 1.971, C(4) 2.956, C(5) 2.947]

(*b*) Angles (°) between normals to planes and lines

(1)–(2)	3.7	(2)–(3)	72.0	(2)–(4)	73.6
(5)–(3)	63.6	(5)–(2)	8.6	(5)–(1)	7.4
(6)–(4)	62.2	(6)–(2)	11.7	(6)–(1)	14.7

Also, the three-membered cyclopropane ring bends away from the metal atom and makes the ligand non-planar; the angle between the plane of the ring and the exocyclic double-bond is *ca.* 153°. Likewise, the exocyclic bond is not exactly perpendicular to the co-ordination plane of the rhodium atom, but bends away at some 80° to leave the internal carbon atom nearer the metal. This bending, and indeed the entire co-ordination geometry, is closely similar to that observed in 1,2-diene complexes.[14-16]

[14] P. Racanelli, G. Pantini, A. Immirzi, G. Allegra, and L. Porri, *Chem. Comm.*, 1969, 361.

[15] T. Kashigawa, N. Yasuoka, N. Kasai, and M. Kukudo, *Chem. Comm.*, 1969, 317.

[16] T. G. Hewitt, K. Anzenhofer, and J. J. de Boer, *Chem. Comm.*, 1969, 312.

A recent determination of the molecular structure of tetracarbonyl(η^2-*cis*-2,3-dimethoxycarbonylmethylenecyclopropane)iron[13] [complex (9b)] shows bond distances in the substituted cyclopropane moiety almost identical with those recorded here, but the angle of tilt between the plane of the ring and the exocyclic bond is 142°, as compared to 153° in complex (4a). Interestingly, both the methoxycarbonyl substituents are *endo* to the $Fe(CO)_4$ entity; it is therefore possible that steric interactions account for this diminution of the angle of tilt.

The acetylacetonate ligand is planar (Table 6), and shows C–C and C–O bond lengths intermediate between those of single and double bonds. This feature has been well established in many complexes.[17]

DISCUSSION

The molecular structure of (4a) shows considerable asymmetry in the bonding of methylenecyclopropane to Rh^I. Similar asymmetry in the metal–olefin bonding has been observed in the molecular structure of (9b),[13] and is a well documented feature of the bonding in η^2-bonded 1,2-diene complexes of Rh^I (refs. 14—16), Pt^0 (ref. 18), and Pt^{II} (ref. 19). This bonding asymmetry in (4a) manifests itself in solution, the coupling constants between ^{103}Rh and the endocyclic olefinic ^{13}C nucleus (20 Hz) and the exocyclic olefinic ^{13}C nucleus (14 Hz) being significantly different (Table 2); the greater J value to the endocyclic carbon presumably reflects both the shorter Rh–C distance and a higher % *s* character in the endocyclic carbon orbital involved in the rhodium–olefin bond.[9] A similar large difference in the coupling of ^{195}Pt to the corresponding carbon atoms in the ^{13}C n.m.r. spectrum of (7a) is also observed. Vastly different coupling of ^{195}Pt to the internal and external olefinic carbons in the ^{13}C n.m.r. spectrum of *trans*-[$PtCl_2$(η^2-1,1-dimethylallene)(γ-picoline)] has also been noted.[20] The very close similarity between the co-ordination geometry of methylenecyclopropanes and 1,2-dienes, as evidenced by *X*-ray crystallography, and presumably the hybridisation of the olefinic carbon atoms involved in bonding to transition metals, as evidenced both by *X*-ray crystallography and ^{13}C n.m.r. spectroscopy, is particularly interesting in view of the similarity of their chemical reactivity towards nucleophiles in the presence of Pd^{II} systems.[21]

The stability of the η^2-bonded methylenecyclopropane ligand towards heat and u.v. irradiation is remarkable, particularly since Rh^I (ref. 6), Pt^0 (ref. 4), and Pt^{II} (ref. 5) species have been shown to insert fairly readily into the C–C σ-bonds of cyclopropanes. No evidence for such oxidative insertion reactions has been found in the thermolysis of representative examples of complexes (4)—(8). The thermal stability of complexes (9) has received comment elsewhere,[12,13] and it is noteworthy that addition of an external reagent, [$Fe_2(CO)_9$], is required to effect a relatively low-energy opening reaction of the cyclopropane ring in complexes (9).[12]

The geometry of co-ordinated methylenecyclopropanes in (4a) and in (9b)[13] involves the cyclopropane ring bending away with respect to the η^2-olefin–metal bond; the result is that any interaction of the cyclopropane C–C σ-bonding orbitals with metal *d* orbitals which might give rise to a cleavage of the ring must be unfavourable. Thus, after co-ordination of the olefinic function of the methylenecyclopropane to a low-valent metal, the cyclopropane ring becomes inaccessible towards a direct, intramolecular, metal-induced ring-cleavage reaction. Addition of an external reagent, as in the case of complexes (9),[12] introduces the possibility of direct, extramolecular attack on the cyclopropane ring, and implies that the previously reported[1-3] transition-metal promoted ring-opening reactions of methylenecyclopropanes may either involve more than one metal centre, as has been suggested by Whitesides,[13] or may involve a transition-metal centre together with an intra- or extra-molecular nucleophilic reagent, as has been previously demonstrated.[21]

The variable-temperature ^1H and ^{13}C n.m.r. spectra of (4a) indicate that the methylenecyclopropane ligands undergo the well established propeller-type rotation[10] at ambient temperatures. Similar behaviour is also noted for the *cis*-dimethyl ester ligands of (4c) and (5b). The ^1H and ^{13}C n.m.r. spectra of (4b) and (5a), however, are temperature independent from −60 °C to +60 °C, indicating that the *trans*-dimethyl ester ligands in these complexes are locked in a rigid configuration. In complexes of *trans*-2,3-dimethoxycarbonylmethylenecyclopropane, one methoxycarbonyl substituent on each co-ordinated ligand must occupy a position *endo* with respect to the metal, whereas in the case of co-ordinated *cis*-2,3-dimethoxycarbonylmethylenecyclopropane both methoxycarbonyl groups must be either *endo* or *exo*. Examination of molecular models indicates that an *endo*-methoxycarbonyl substituent in such complexes interacts appreciably with the two ligands *cis* to itself. Such a steric interaction presumably accounts for the barrier to rotation of the olefinic ligands in (4b) and (5a), and since the olefinic ligands in (4c) and (5b) do rotate at ambient temperature it follows that the methoxycarbonyl substituents in these complexes must be *exo* with respect to the metal.

An interesting contrast can be found in the variable-temperature behaviour of the Fe^0 complexes (9a) and (9b), as evidenced by ^{13}C n.m.r. spectroscopy. It has been demonstrated that in order for exchange to occur between axial and equatorial carbonyl sites in [(olefin)-$Fe(CO)_4$] complexes *via* a pseudorotation mechanism, a concomitant 90° rotation of the equatorially situated olefinic ligand must also occur.[22,23] Any constraints

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placed upon such olefin rotation must therefore slow the rate of carbonyl site-exchange.[22,23] In complex (9b), carbonyl site-exchange is slow on the n.m.r. time-scale, even at ambient temperature, whereas complex (9a) must be cooled to below −50 °C before the rate slows sufficiently for the individual carbonyl environments to be resolved. The single *trans*-2,3-dimethoxycarbonylmethylenecyclopropane ligand in (9a) therefore rotates relatively easily at ambient temperatures, but the *cis*-2,3-dimethoxycarbonylmethylenecyclopropane ligand in (9b) which has both methoxycarbonyl substituents *endo* to the metal [13] is sterically impeded from doing so. It has been shown that the two *endo*-methoxycarbonyl substituents in (9b) interact appreciably with the axial carbonyl ligands in the solid state; [13] this interaction would also appear to be important in solution.

It is significant that complex (9b) contains a *cis*-2,3-dimethoxycarbonylmethylenecyclopropane ligand in which both methoxycarbonyl groups are *endo*,[13] whereas the complexes reported here apparently contain the same ligand with the substituents both *exo*. It has been suggested [13] that formation of (9b) occurs *via* an initial interaction of the iron atom with one of the ester carbonyl groups, with a subsequent stereochemical direction of the iron to yield what is presumably the thermodynamically less-favoured isomer. The observation that the thermodynamically more favoured *exo*-isomers are formed in square-planar d^8 and d^{10} systems, in which exchange between free and co-ordinated olefin ligands is expected to be relatively facile compared to that in a trigonal bipyramidal d^8 complex such as (9b), would seem to substantiate this suggestion.

EXPERIMENTAL

All reactions were carried out under dry, oxygen-free nitrogen.

^{1}H n.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 MHz, ^{13}C and ^{31}P n.m.r. spectra on a Jeol JNM PFT 100 spectrometer, operating in the Fourier-transform mode, at 25.15 and 40.48 MHz respectively. I.r. spectra were recorded on a Perkin-Elmer 257 instrument.

Methylenecyclopropane,[24] *trans*-2,3-dimethoxycarbonylmethylenecyclopropane,[25] *cis*-2,3-dimethoxycarbonylmethylenecyclopropane.[25] $[\{Rh(C_2H_4)_2Cl\}_2]$,[26] $[Rh(C_2H_4)_2(acac)]$,[27] $[Ir(C_2H_4)_2(acac)]$,[28] $[Pt(C_2H_4)(PPh_3)_2]$,[29] *trans*-$[PtCl_2(C_2H_4)(C_5H_5N)]$,[30] $[\{Rh(CO)_2Cl\}_2]$,[31] and $[Rh(CO)_2(acac)]$ [32] were prepared by literature methods. $[Fe(CO)_4(un)]$ {un = (2) or (3)} were prepared by the method of ref. 12.

Preparation and X-*Ray Crystal Structure of Acetylacetonatobis*(η^2-*methylenecyclopropane*)*rhodium*(I), (4a).—An excess of methylenecyclopropane (1.00 g, 18 mmol) was added to acetylacetonatobis(ethylene)rhodium(I) (0.66 g, 2.6 mmol) in diethyl ether (20 cm^3) at 0 °C. The resulting solution was stirred (0°, 1 h), warmed to room temperature, and solvent removed *in vacuo*. Recrystallisation of the residue from pentane (−30 °C) yielded *orange prisms* of (4a) (0.55 g, 70%), m.p. 88—89 °C (Found: C, 50.5; H, 6.2%. $C_{13}H_{19}O_2Rh$ requires: C, 50.3; H, 6.1%).

The crystal chosen for intensity measurements, 0.375 × 0.025 × 0.175 mm, was mounted on a Syntex $P2_1$ four-circle autodiffractometer, according to methods described earlier.[33] Of the total (2 466) reflections for $3.7° < 2\theta < 50°$, 1 684 having $I > 2.5\sigma(I)$ were considered observed and were used in the solution and refinement of the structure.

Crystal Data.—$C_{13}H_{19}O_2Rh$, $M = 310.2$, Monoclinic, $a = 12.810(5)$, $b = 9.054(3)$, $c = 11.855(4)$ Å, $\beta = 103.09(3)°$, $U = 1\,339$ Å^3, $D_m = 1.50$, $Z = 4$, $D_c = 1.54$ g cm^{-3}, $F(000) = 632$. Space group $P2_1/n$. Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 12.3 cm^{-1}.

The structure was solved by conventional heavy-atom methods and refined by full-matrix least-squares with anisotropic thermal parameters for the metal atom only. Weights were applied according to the scheme $1/w = (\sigma_F)^2$. Hydrogen atoms were incorporated at positions estimated from the electron-density maps, but neither their positional nor thermal parameters were refined. The refinement converged to R 0.066 (R' 0.075) and a final electron-density difference synthesis showed no peaks >0.6 or <−1.5 eÅ^{-3}, with a general background level very much less than this.

Positional and thermal parameters are in Table 4, interatomic distances in Table 5, and some least-squares planes in Table 6. No absorption correction was applied, and the atomic scattering factors were taken from ref. 34 for rhodium, carbon, and oxygen, and from ref. 35 for hydrogen. All computational work was carried out at the University of London Computing Centre with the '*X*-Ray' system of programmes.[36] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21385 (9 pp., 1 microfiche).*

Acetylacetonatobis(η^2-trans-2,3-*dimethoxycarbonylmethylenecyclopropane*)*rhodium*(I), (4b).—*trans*-2,3-Dimethoxycarbonylmethylenecyclopropane (0.32 g, 1.9 mmol) was added to a solution of acetylacetonatobis(ethylene)rhodium(I) (0.23 g, 0.9 mmol) in diethyl ether (10 cm^3), the solution stirred (10 min), and solvent removed *in vacuo*. Recrystallisation of the residue from diethyl ether–pentane (1 : 8 v/v) (−30 °C) yielded *orange prisms* of (4b) (0.43 g, 89%), m.p. 118—120 °C (Found: C, 46.6; H, 5.1. $C_{21}H_{27}O_{10}Rh$ requires C, 46.5; H, 5.0%).

A similar reaction with: (i) *cis*-2,3-dimethoxycarbonylmethylenecyclopropane (0.32 g, 1.9 mmol) and acetylacetonatobis(ethylene)rhodium(I) (0.23 g, 0.9 mmol) yielded *acetylacetonatobis*(η^2-cis-2,3-*dimethoxycarbonylmethylenecyclopropane*)*rhodium*(I), (4c), as *orange prisms* (0.40 g,

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* For details see Notice to Authors, No. 7, in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full size copies).

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[36] Technical Report TR 192, Computer Science Centre, University of Maryland, June 1972.

83%), m.p. 95—98 °C (Found: C, 46.3; H, 5.1. $C_{21}H_{27}O_{10}Rh$ requires C, 46.5; H, 5.0%); (ii) *trans*-2,3-dimethoxycarbonylmethylenecyclopropane (0.37 g, 2.2 mmol) and acetylacetonatobis(ethylene)iridium(I) (0.37 g, 1.1 mmol) yielded *acetylacetonatobis*(η^2-trans-2,3-*dimethoxycarbonylmethylenecyclopropane*)*iridium*(I), (5a), as *yellow prisms* (0.60 g, 89%), m.p. 105—107 °C (Found: C, 39.8; H, 4.5. $C_{21}H_{27}IrO_{10}$ requires C, 39.9; H, 4.3%); and (iii) *cis*-2,3-dimethoxycarbonylmethylenecyclopropane (0.20 g, 1.2 mmol) and acetylacetonatobis(ethylene)iridium(I) (0.20 g, 0.6 mmol) yielded *acetylacetonatobis*(η^2-cis-2,3-*dimethoxycarbonylmethylenecyclopropane*)*iridium*(I), (5b), as *yellow needles* (0.30 g, 83%), m.p. 87—89 °C (Found: C, 39.9; H, 4.3. $C_{21}H_{27}IrO_{10}$ requires C, 39.9; H, 4.3%).

Di-μ-chloro-tetrakis(η^2-trans-*dimethoxycarbonylmethylenecyclopropane*)*dirhodium*(I), (4d).—A suspension of di-μ-chloro-tetrakis(ethylene)dirhodium(I) (0.53 g, 1.8 mmol) in pentane (30 cm^3) was treated with *trans*-2,3-dimethoxycarbonylmethylenecyclopropane (1.00 g, 5.9 mmol) and stirred vigorously (15 h). The solid product was washed with pentane, and recrystallised from diethyl ether–pentane (−30 °C) to give (4d) as *orange prisms* (1.26 g, 72%), m.p. 145—150 °C (Found: C, 40.5; H, 4.3; Cl, 7.8. $C_{32}H_{40}Cl_2O_{16}Rh_2$ requires C, 40.2; H, 4.2; Cl, 7.4%).

A similar reaction with *cis*-2,3-dimethoxycarbonylmethylenecyclopropane (1.00 g, 5.9 mmol) and di-μ-chloro-tetrakis(ethylene)dirhodium(I) (0.53 g, 1.80 mmol) yielded *di-μ-chloro-tetrakis*(η^2-cis-2,3-*dimethoxycarbonylmethylenecyclopropane*)*dirhodium*(I), (4e), as *orange prisms* (1.16 g, 66%), m.p. 123—127 °C (Found: C, 40.4; H, 4.3. $C_{32}H_{40}Cl_2O_{16}Rh_2$ requires C, 40.2; H, 4.2%).

η^5-*Cyclopentadienylbis*(η^2-trans-2,3-*dimethoxycarbonylmethylenecyclopropane*)*rhodium*(I), (4f).—Cyclopentadienylthallium(I) (0.30 g, 1.1 mmol) was added to di-μ-chloro-tetrakis(η^2-*trans*-2,3-dimethoxycarbonylmethylenecyclopropane)dirhodium(I) (0.30 g, 0.31 mmol) in dichloromethane (30 cm^3), and the mixture stirred vigorously (30 min). The mixture was filtered (Kieselguhr) and the filtrate evaporated to dryness. Recrystallisation of the residue from pentane (−30 °C) yielded (4f) as pale *yellow prisms* (0.30 g, 94%), m.p. 147—150 °C (Found: C, 49.7; H, 5.1. $C_{21}H_{25}O_8Rh$ requires C, 49.6; H, 5.0%).

(η^2-*Methylenecyclopropane*)*bis*(*triphenylphosphine*)*platinum*(0), (6a).—Methylenecyclopropane (1.00 g, 18 mmol) was added to (ethylene)bis(triphenylphosphine)platinum(0) (0.60 g, 0.8 mmol) in benzene (10 cm^3), and the solution stirred (0 °C; 1 h). Removal of solvent *in vacuo* and recrystallisation of the residue from benzene–pentane yielded (6a) as *prisms* (0.48 g, 78%), m.p. 160—165 °C (decomp.) (Found: C, 62.3; H, 4.7. $C_{40}H_{36}P_2Pt$ requires: C, 62.1; H, 4.7).

A similar reaction with: (i) *trans*-2,3-dimethoxycarbonylmethylenecyclopropane (0.10 g, 0.6 mmol) and (ethylene)bis(triphenylphosphine)platinum(0) (0.45 g, 0.6 mmol) yielded (η^2-trans-2,3-*dimethoxycarbonylmethylenecyclopropane*)*bis*(*triphenylphosphine*)*platinum*(0), (6b), as white *prisms* (0.42 g, 79%), m.p. 166—168 °C (decomp.) (Found: C, 59.3; H, 4.5; P, 6.8. $C_{44}H_{40}O_4P_2Pt$ requires C, 59.4; H, 4.7; P, 7.0%); and (ii) *cis*-2,3-dimethoxycarbonylmethylenecyclopropane (0.11 g, 0.6 mmol) and (ethylene)bis(triphenylphosphine)platinum(0) (0.45 g, 0.6 mmol) yielded (η^2-cis-2,3-*dimethoxycarbonylmethylenecyclopropane*)*bis*(*triphenylphosphine*)*platinum*(0), (6c), as white *prisms* (0.44 g, 83%), m.p. 155—157 °C (decomp.) (Found: C, 59.2; H, 4.5; P, 7.6. $C_{44}H_{40}O_4P_2Pt$ requires C, 59.4; 4.5; P, 7.0%).

trans-*Dichloro*(η^2-trans-2,3-*dimethoxycarbonylmethylenecyclopropane*)(*pyridine*)*platinum*(II), (7a).—A solution of *trans*-dichloro(ethylene)(pyridine)platinum(II) (0.63 g, 1.7 mmol) in dichloromethane (20 cm^3) was treated with *trans*-2,3-dimethoxycarbonylmethylenecyclopropane (0.30 g, 1.8 mmol) and the solution stirred (30 min). Removal of solvent *in vacuo* and recrystallisation of the residue from dichloromethane–pentane yielded (7a) as *yellow prisms* (0.80 g, 92%), m.p. 120—125 °C (Found: C, 30.2; H, 2.9; Cl, 13.4; N, 2.7. $C_{13}H_{15}Cl_2NO_4Pt$ requires C, 30.3; H, 2.9; Cl, 13.7; N, 2.7%).

A similar reaction with *cis*-2,3-dimethoxycarbonylmethylenecyclopropane (0.25 g, 1.5 mmol) and *trans*-dichloro(ethylene)(pyridine)platinum(II) (0.52 g, 1.4 mmol) yielded trans-*dichloro*(η^2-cis-2,3-*dimethoxycarbonylmethylenecyclopropane*)(*pyridine*)*platinum*(II), (7b), as *yellow prisms* (0.60 g, 84%), m.p. 115—120 °C (decomp.) (Found: C, 30.3; H, 2.9; N, 2.8. $C_{13}H_{15}Cl_2NO_4Pt$ requires C, 30.3; H, 2.9; N, 2.7%).

Acetylacetonato(*carbonyl*)(η^2-trans-2,3-*dimethoxycarbonylmethylenecyclopropane*)*rhodium*(I), (8a).—Acetylacetonatodicarbonylrhodium(I) (0.26 g, 1.0 mmol) was added to a solution of acetylacetonatobis(η^2-*trans*-2,3-dimethoxycarbonylmethylenecyclopropane)rhodium(I) (0.54 g, 1.0 mmol) in hexane (50 cm^3) and the resulting mixture heated under reflux (15 h). Removal of solvent *in vacuo* and slow crystallisation of the residue from pentane (20 cm^3; −30 °C) yielded (8a) as *orange prisms* (0.40 g, 50%), m.p. 120—123 °C (Found: C, 42.3; H, 4.5. $C_{14}H_{17}O_7Rh$ requires C, 42.0; H, 3.3%); ν_{CO} (Nujol) 2 020 cm^{-1}.

Carbonyl-η^5-*cyclopentadienyl*-(η^2-trans-2,3-*dimethoxycarbonylmethylenecyclopropane*)*rhodium*(I), (8b).—A solution of di-μ-chloro-tetracarbonyldirhodium(I) (0.08 g, 0.3 mmol) and di-μ-chloro-tetrakis(η^2-*trans*-2,3-dimethoxycarbonylmethylenecyclopropane)dirhodium(I) (0.20 g, 0.2 mmol) in dichloromethane (50 cm^3) was treated with cyclopentadienylthallium(I) (0.28 g, 1.0 mmol) and the resulting mixture stirred vigorously (30 min). The mixture was filtered (Kieselguhr) and the filtrate evaporated to dryness. Slow crystallisation of the residue from pentane (20 cm^3; −30 °C) afforded (8b) as *yellow prisms* (0.15 g, 80%), m.p. 87—89 °C (Found: C, 46.2; H, 4.4. $C_{14}H_{15}O_5Rh$ requires C, 45.9; H, 4.1%); ν_{CO} (Nujol) 1 975 cm^{-1}.

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