Synthesis of Heterobimetallic Complexes containing Cobalt–Platinum or Rhodium–Platinum Dative Bonds. Molecular Structure of $[(\eta^5\text{-}C_5H_5)(CO)_2Rh\rightarrow Pt(C_6F_5)_2(CO)]$†

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The complexes $[(\eta^5\text{-}C_5R_5)(CO)LM\rightarrow Pt(C_6F_5)_2(CO)]$ (R = H or Me; M = Co or Rh; L = CO or PPh_3) have been obtained by reacting the bases $[M(\eta^5\text{-}C_5R_5)(CO)L]$ with *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ (thf = tetrahydrofuran). Their structures are discussed on the basis of ^1H, ^{19}F, and ^{31}P n.m.r. and i.r. data. The molecular structure of the complex $[(\eta^5\text{-}C_5H_5)(CO)_2Rh\rightarrow Pt(C_6F_5)_2(CO)]$ has been determined by an *X*-ray diffraction study: orthorhombic, space group $P2_12_12_1$ with a = 7.632 1(10), b = 16.415 1(17), c = 16.520 0(43) Å, Z = 4; R = 0.027, R' = 0.028 for 3 676 reflections with $I \geqslant 3\sigma(I)$ having $2 < 2\theta < 60°$. The structure shows that the basic $(\eta^5\text{-}C_5H_5)(CO)_2Rh$ group is co-ordinated to the $Pt(C_6F_5)_2(CO)$ moiety forming a binuclear complex with an unbridged Rh–Pt bond of length 2.750(1) Å. Platinum is in an almost square-planar environment with the C_6F_5 groups mutually *cis*. The ^{19}F n.m.r. spectra of the complexes reveal fluxional behaviour leading to equivalence of the two C_6F_5 groups. The reaction of $[(\eta^5\text{-}C_5R_5)(CO)_2Rh\rightarrow Pt(C_6F_5)_2(CO)]$ (R = H or Me) with PPh_3 yields $[Rh(\eta^5\text{-}C_5R_5)(CO)_2]$ and *cis*-$[Pt(C_6F_5)_2(CO)(PPh_3)]$; reacting $[(\eta^5\text{-}C_5H_5)(CO)_2\text{-}Rh\rightarrow Pt(C_6F_5)_2(CO)]$ with bis(diphenylphosphino)methane (dppm) gives $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ and $[Pt(C_6F_5)_2(dppm)]$.

Heterobimetallic complexes containing an asymmetric metal–metal bond have received considerable recent attention.[1] A very useful method of synthesising such compounds is the use of transition-metal complexes displaying basic properties which can act as a ligand towards other metal centres, thereby forming compounds with donor–aceptor metal–metal bonds. We have recently described the synthesis of polynuclear Pt–Ag complexes of this type,[2–5] formed by reaction of anionic platinum pentafluorophenyl derivatives with $AgClO_4$ or $Ag(OClO_3)L$, L = PPh_3, PPh_2Me, or PEt_3, and most of these compounds contain unsupported Pt–Ag bonds. We now report a different route to unsupported M–M′ bonds.

Half-sandwich 18-electron complexes $[M(\eta^5\text{-}C_5R_5)L_2]$ (R = H or Me; M = Co or Rh; L = CO or PR'_3; R′ = Ph, Et, or Me) have previously been used as ligands towards other metal compounds to produce species with asymmetric metal–metal bonds.[6–16] This paper describes the reactions of $[M(\eta^5\text{-}C_5R_5)L_2]$ (M = Co or Rh) with *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$[17] (thf = tetrahydrofuran) where the basic nature of the metal centre M produces displacement of the weakly co-ordinated thf ligand and yields the heterobimetallic complexes of the type $[(\eta^5\text{-}C_5R_5)L_2M\rightarrow Pt(C_6F_5)_2(CO)]$, containing metal–metal bonds unsupported by any bridging ligands. The structure of $[(\eta^5\text{-}C_5H_5)(CO)_2Rh\rightarrow Pt(C_6F_5)_2(CO)]$ has been established by single-crystal *X*-ray diffraction.

Results and Discussion

Syntheses.—The reaction between *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ and $[M(\eta^5\text{-}C_5R_5)LL']$ (molar ratio 1:1) in CH_2Cl_2 at room temperature yields the binuclear heterometallic complexes (**1**)—(**5**), equation (1) [M = Co, R = H, L = L′ = CO (**1**); L = CO, L′ = PPh_3 (**2**); M = Rh, R = H, L = L′ = CO (**3**); L = CO, L′ = PPh_3 (**4**); R = Me, L = L′ = CO (**5**)].

$$[M(\eta^5\text{-}C_5R_5)LL'] + cis\text{-}[Pt(C_6F_5)_2(CO)(thf)] \longrightarrow [(\eta^5\text{-}C_5R_5)LL'M\rightarrow Pt(C_6F_5)_2(CO)] + thf \quad (1)$$

Thus, the formally five-co-ordinated 18-electron complexes $[M(\eta^5\text{-}C_5R_5)LL']$ (M = Co or Rh), acting as a ligand, cause displacement of the weakly co-ordinated thf of *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ giving rise to complexes with a donor–acceptor M–Pt bond in which the M centre is formally six-co-ordinated and the Pt centre is four-co-ordinated.

The reactions must be carried out in a non-donor solvent (CH_2Cl_2) since otherwise the basic nature of the solvent precludes formation of the binuclear complexes. In fact the i.r. spectrum [ν(CO) region] of a thf solution containing $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ and *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ shows only absorptions due to ν(CO) in the starting materials and none due to the binuclear derivative (**3**). However if this solution is evaporated to dryness, complex (**3**) is obtained.

Complexes (**1**)—(**5**) can be isolated by partial evaporation of the CH_2Cl_2 solutions and addition of n-hexane. Complexes (**1**) and (**2**) are stable in the solid state but decompose in CH_2Cl_2 solution at room temperature. Complexes (**3**)—(**5**) are more stable and do not decompose in CH_2Cl_2 solutions at room temperature over a few days. Analytical and other data are collected in Table 1. Molecular weight determinations in $CHCl_3$ confirm the binuclear nature of these complexes. The i.r. spectra of complexes (**1**)—(**5**) in the ν(CO) region (see Table 2) show only absorptions due to terminal carbonyl groups thus indicating that the M–Pt bonds are unsupported by CO bridges.

Infrared Spectra.— (*i*) ν(CO) *Region.* Complexes (**1**)—(**5**) show two or three absorptions (see Table 2) due to ν(CO) in the

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† 1,2,2-Tricarbonyl-2-(η^5-cyclopentadienyl)-1,1-bis(pentafluorophenyl)platinumrhodium (*Pt–Rh*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

Table 1. Analytical results (calculated values in parentheses) and other characteristic data

Complex	C	H	M^a	Colour	Yield (%)
(1) $[(\eta^5\text{-}C_5H_5)(CO)_2Co{\rightarrow}Pt(C_6F_5)_2(CO)]$	33.30 (32.60)	1.00 (0.70)	*b*	Orange-brown	35
(2) $[(\eta^5\text{-}C_5H_5)(CO)(PPh_3)Co{\rightarrow}Pt(C_6F_5)_2(CO)]$	45.00 (45.75)	2.10 (2.05)	1 055 (971)	Garnet	54
(3) $[(\eta^5\text{-}C_5H_5)(CO)_2Rh{\rightarrow}Pt(C_6F_5)_2(CO)]$	30.25 (30.75)	0.70 (0.65)	782 (781)	Yellow	65
(4) $[(\eta^5\text{-}C_5H_5)(CO)(PPh_3)Rh{\rightarrow}Pt(C_6F_5)_2(CO)]$	43.60 (43.75)	2.10 (2.00)	1 079 (1 015)	Orange	78
(5) $[(\eta^5\text{-}C_5Me_5)(CO)_2Rh{\rightarrow}Pt(C_6F_5)_2(CO)]$	35.00 (35.25)	1.75 (1.75)	890 (851)	Green	79

[a] In $CHCl_3$ solution. [b] Decomposition of complex (**1**) in $CHCl_3$ precludes molecular weight determination.

Table 2. Relevant i.r. absorptions

Complex	$\nu(CO)_{solid}$	ν(CO) in $[M(\eta^5\text{-}C_5R_5)(CO)L]^a$	*X*-sensitive C_6F_5
(1)	2 092, 2 057, 1 991	2 019, 1 958	800, 791
(2)	2 087, 2 075, 1 978 (2 066, 1 985)^b	1 937	792, 783
(3)	2 091, 2 073, 2 032	2 051, 1 987	801, 790
(4)	2 066, 2 006	1 957	795, 785
(5)	2 088, 2 077, 2 053, 2 019, 2 009 (2 080, 2 059, 2 015)^b	2 000, 1 950	796, 787

[a] ν(CO) in *cis*-$[Pt(C_6F_5)_2(CO)(thf)]$ 2 124 cm^{-1}. [b] In CH_2Cl_2 solution.

solid state. In some cases [complexes (**2**) and (**5**)] the number of observed ν(CO) absorptions is higher than expected but the i.r. spectra of CH_2Cl_2 solutions show the expected number of absorptions.

Although an unequivocal assignment of ν(CO) absorptions cannot be made, a decrease of ν(CO) for the carbonyl group bonded to platinum and an increase of ν(CO) for those bonded to M is observed, thus indicating that the formation of the binuclear complexes produces an increase and a decrease of the electronic density around the platinum and the M centres respectively.[18]

(*ii*) *Absorptions due to the* C_6F_5 *groups.* All the i.r. spectra show bands characteristic of the C_6F_5 group near 1 500, 1 050, 950, and 800 cm^{-1}, the last one assigned to an *X*-sensitive mode, and are of structural interest.[19,20] The absorptions due to the i.r.-active vibrations for the *X*-sensitive modes for complexes (**1**)—(**5**) are collected in Table 2. Two absorptions of the same intensity are observed in all cases which indicates[21] that, as for the starting platinum complex, the C_6F_5 groups are mutually *cis*. The molecular structure of complex (**3**) (which is discussed below) confirms this point.

N.M.R. Spectra.—Proton, ^{19}F, and ^{31}P n.m.r. spectra for complexes (**1**)—(**5**) were recorded in $CDCl_3$, and the chemical shifts and coupling constants are collected in Table 3.

Complexes (**3**) and (**4**) show signals due to C_5H_5 as a doublet because of the coupling Rh–H. The ^2J(Rh–H) values are similar to those found for the starting Rh complexes.[22] For complex (**4**) no coupling with the P nucleus is observed. Complex (**5**) shows a singlet due to the methyl groups of C_5Me_5, *i.e.* no coupling with rhodium is observed; however in this case platinum satellites [^4J(Pt–H) 4.92 Hz] are observed. Phosphorus-31 n.m.r. spectra of complexes (**2**) and (**4**) in $CDCl_3$ show a broad singlet [(**2**)] and a doublet [(**4**)] as expected (see Table 3).

The ^{19}F n.m.r. spectra of complexes (**2**)—(**5**) show three multiplet signals (2:1:2 ratio) which can be assigned to the two *ortho*-fluorines (isochronous), to the *para*-fluorine, and to the two *meta*-fluorines (isochronous); $^3J(Pt\text{–}F_o)$ and $^5J(Pt\text{–}F_p)$ are observed in all cases. This indicates that in $CDCl_3$ both C_6F_5 groups are equivalent. Since i.r. and crystallographic data indicate that both C_6F_5 groups are mutually *cis* and so inequivalent, a fluxional process must be operating in solution in order to make both C_6F_5 groups equivalent. It must be noted that, since Pt–F couplings are observed in all cases and that for complex (**5**) H–Pt coupling is observed, the Pt–C_6F_5 and M–Pt bonds must be preserved throughout this fluxional process. All these facts can adequately be explained if the process takes place according to the Scheme. The activation energy of this process must be very low since for complex (**3**) no changes in the n.m.r. spectra are observed at −40 °C.

The ^{13}C n.m.r. spectrum of complex (**3**) (the more soluble and stable in $CDCl_3$ solution) was recorded at room temperature with two different instruments (Varian XL-200 and Bruker AC-300). Neither the signals due to C_6F_5 nor to CO merge from the baseline and only the cyclopentadienyl signals [92.13 p.p.m., d, $J(^{103}Rh\text{–}^{13}C)$ = 3.6 Hz] can be observed. The i.r. spectra of the solids show intense ν(CO) bands in the CO(terminal) region, but dichloromethane solutions of complexes (**2**), (**3**), and (**5**) additionally show weak absorptions in the CO(bridge) region [at 1 857 (**2**), 1 843 (**3**), or 1 865 (**5**) cm^{-1} respectively], which support the proposed mechanism.

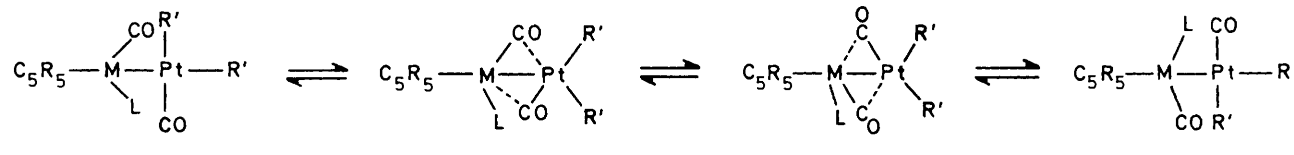
Reaction with L.—The reactions of heterobimetallic complexes containing donor–acceptor metal–metal bonds with neutral ligands L usually produce fission of the M–M′ bond.[15,16,23,24] Complexes (**3**) and (**5**) react in CH_2Cl_2 with PPh_3 (molar ratio 1:1) at room temperature yielding $[Rh(\eta^5\text{-}C_5R_5)(CO)_2]$ [R = H (**3**) or Me (**5**)] and *cis*-$[Pt(C_6F_5)_2(CO)(PPh_3)]$.[21] The reaction of complex (**3**) with bis(diphenylphosphino)methane (dppm) yields $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ and *cis*-$[Pt(C_6F_5)_2(dppm)]$.[25] This indicates a higher nucleophilic character of these phosphines compared to the metallic bases $[Rh(\eta^5\text{-}C_5R_5)(CO)_2]$.

Molecular Structure of $[(\eta^5\text{-}C_5H_5)(CO)_2Rh{\rightarrow}Pt(C_6F_5)_2(CO)]$ (**3**).—The structure of complex (**3**) has been established by *X*-ray diffraction studies (see Experimental section). Single crystals were grown by slow diffusion (*ca.* 2 weeks) of n-hexane into a CH_2Cl_2 solution of the complex at −25 °C. The molecular structure is shown in the Figure. Selected bond distances and angles are collected in Table 4. As can be seen, the 18-electron complex $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$ acts as a donor ligand toward the platinum atom of the $Pt(C_6F_5)_2(CO)$ moiety, forming an unsupported Rh–Pt bond of length 2.750(1) Å. The Pt–Rh distances in the cluster compounds $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta^5\text{-}C_5H_5)_2]$,[11] $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(PPh_3)(\eta^5\text{-}C_5Me_5)_2]BF_4$,[26] and $[PtRh_4(\mu\text{-}CO)_4(\eta^5\text{-}C_5Me_5)_4]$[27] are in the range 2.616(2)—2.805(2) Å.

Table 3. Hydrogen-1, ^{19}F, and ^{31}P n.m.r. data for complexes (**2**)—(**5**)*

Complex	δ(H)	^{2}J(Rh–H)	^{4}J(Pt–H)	δ(P)	^{1}J(Rh–P)	δ(F_o)	δ(F_p)	δ(F_m)	^{3}J(Pt–F_o)	^{5}J(Pt–F_p)
(**2**)	5.24 (s)			53.62 (s)		−119.3	−161.8	−164.6	340.9	39.9
(**3**)	5.92 (d)	0.60				−119.2	−160.1	−163.8	388.6	39.9
(**4**)	5.62 (d)	0.85		40.99 (d)	156.5	−118.9	−162.0	−164.8	358.8	40.1
(**5**)	2.09 (s)		4.92			−117.8	−160.0	−164.3	366.2	40.1

* The rapid decomposition of complex (**1**) in solution precludes an n.m.r. study.



Scheme. R = H or Me, R′ = C_6F_5

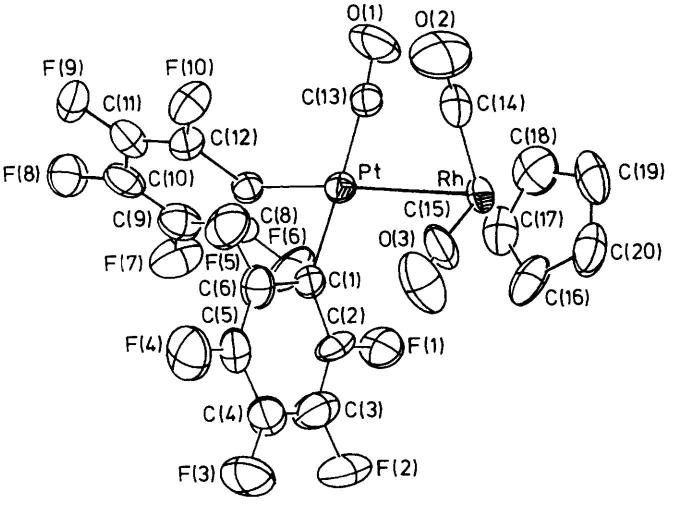


Figure. Molecular structure of [$(\eta^5\text{-}C_5H_5)(CO)_2Rh{\rightarrow}Pt(C_6F_5)_2(CO)$] (**3**) showing the atom labelling scheme

Platinum is in an approximately square-planar environment, the C_6F_5 groups are mutually *cis*. Angles between Pt and *cis*-ligand bonds are in the range 87.4—93.6°. The Pt–C pentafluorophenyl [Pt–C(1) 2.062(7), Pt–C(7) 2.025(7)] and carbonyl [Pt–C(13) 1.860(9)] distances are similar to those found for *cis*-[$Pt(C_6F_5)_2\{SC(S)P(C_6H_{11})_3\}(CO)$].[28] The Pt–C(1) distance (C_6F_5 group *trans* to CO) is slightly longer than Pt–C(7) (C_6F_5 *trans* to Rh). If the cyclopentadienyl group is considered to occupy three co-ordination sites, the rhodium(I) centre has a roughly octahedral environment, and the C(14)–Rh–Pt, C(15)–Rh–Pt, C(14)–Rh–C(15) angles are in the range 82.0—91.9°. The average of the Rh–C(cyclopentadienyl) distances is 2.25(7) Å, similar to that found in other cyclopentadienyl rhodium complexes;[28] the separation of the rhodium atom from the C_5H_5 plane is 1.9002(9) Å.[29] The distances between the C atoms of the carbonyl groups bonded to the rhodium atom and the platinum atom are 3.112(10) and 3.237(10) Å, which indicates no interaction between these carbonyl groups and the platinum centre.[15]

Experimental

Carbon and H analyses, i.r. spectra, ^{1}H, ^{19}F, and ^{31}P n.m.r. spectra, and molecular weight determinations were performed as described elsewhere.[25] Standard methods were used to prepare the following complexes: [$Co(\eta^5\text{-}C_5H_5)(CO)_2$],[30] [$Co(\eta^5\text{-}C_5H_5)(CO)(PPh_3)$],[22,31] [$Rh(\eta^5\text{-}C_5H_5)(CO)(PPh_3)$],[22,31] [$Rh(\eta^5\text{-}C_5Me_5)(CO)_2$],[32] and [$Rh(\eta^5\text{-}C_5H_5)(CO)_2$].[33-35] *cis*-[$Pt(C_6F_5)_2(CO)(thf)$][17] was prepared by reacting equimolecular amounts of *cis*-[$Pt(C_6F_5)_2(thf)_2$][21] and *cis*-[$Pt(C_6F_5)_2(CO)_2$][21] in CH_2Cl_2 at room temperature for 30 min. The solution was evaporated to dryness and the residue was dissolved in Et_2O and crystallized by addition of n-hexane. All the reactions were carried out under N_2. Hexane and dichloromethane were distilled, under N_2, from sodium or P_2O_5 respectively.

[$(\eta^5\text{-}C_5H_5)(CO)_2Co{\rightarrow}Pt(C_6F_5)_2(CO)$] (**1**).—To a red solution of [$Co(\eta^5\text{-}C_5H_5)(CO)_2$] (20.4 μl, 0.158 mmol) in CH_2Cl_2 (15 cm^3), [$Pt(C_6F_5)_2(CO)(thf)$] (0.100 g, 0.158 mmol) was added and the mixture stirred at room temperature for 30 min. The solution was evaporated almost to dryness and the oily residue was stirred with n-hexane (10 cm^3). The resulting solid was recrystallized from CH_2Cl_2–hexane.

Complexes (**2**), (**4**), and (**5**) were prepared in a similar way. Complex (**2**): [$Co(\eta^5\text{-}C_5H_5)(CO)(PPh_3)$], 0.0684 g (0.165 mmol); *cis*-[$Pt(C_6F_5)_2(CO)(thf)$], 0.104 g (0.165 mmol). Complex (**4**): [$Rh(\eta^5\text{-}C_5H_5)(CO)(PPh_3)$], 0.052 g (0.113 mmol); *cis*-[$Pt(C_6F_5)_2(CO)(thf)$], 0.0714 g (0.113 mmol). Complex (**5**): [$Rh(\eta^5\text{-}C_5Me_5)(CO)_2$], 0.077 g (0.262 mmol); *cis*-[$Pt(C_6F_5)_2(CO)(thf)$], 0.1647 g (0.262 mmol). Complexes (**2**), (**4**), and (**5**) were not recrystallized. Complex (**5**) was heated at 58 °C under vacuum for 16 h to remove CH_2Cl_2.

[$(\eta^5\text{-}C_5H_5)(CO)_2Rh{\rightarrow}Pt(C_6F_5)_2(CO)$] (**3**).—To a CH_2Cl_2 solution (25 cm^3) of [$\{Rh(\mu\text{-}Cl)(CO)_2\}_2$][36] (0.050 g, 0.119 mmol), was added $Tl(C_5H_5)$ (0.0693 g, 0.257 mmol) and the mixture stirred at room temperature for 90 min. The TlCl was filtered off, *cis*-[$Pt(C_6F_5)_2(CO)(thf)$] was added to the resulting solution and the mixture stirred at room temperature for 30 min. The solution was evaporated almost to dryness and the residue was stirred with n-hexane (10 cm^3) to render a solid.

X-*Ray Structure Determination of Complex* (**3**).—*Crystal data*. $C_{20}H_5F_{10}O_3PtRh$, M = 782, orthorhombic, space group $P2_12_12_1$, a = 7.632 1(10), b = 16.415 1(17), c = 16.520 0(43) Å, U = 2 069 $Å^3$ (refined from 25 reflections, $14 < \theta < 15°$), Mo-K_α radiation (λ = 0.710 69 Å), Z = 4, D_c = 2.51 g cm^{-3}. Crystal dimensions 0.3 × 0.35 × 0.45 mm, μ = 73.4 cm^{-1}, $F(000)$ = 1 448.

Data collection and processing. Enraf-Nonius CAD4 dif-

Table 4. Bond distances (Å) and angles (°) in compound (**3**)

Rh–Pt	2.750(1)	C(1)–Pt	2.062(7)	C(10)–F(8)	1.325(8)	C(11)–F(9)	1.342(10)
C(7)–Pt	2.025(7)	C(13)–Pt	1.860(9)	C(12)–F(10)	1.349(9)	C(13)–O(1)	1.162(10)
C(14)–Rh	1.889(10)	C(15)–Rh	1.867(10)	C(14)–O(2)	1.096(11)	C(15)–O(3)	1.147(11)
C(16)–Rh	2.254(6)	C(17)–Rh	2.236(7)	C(2)–C(1)	1.390(10)	C(6)–C(1)	1.364(10)
C18)–Rh	2.240(7)	C(19)–Rh	2.261(7)	C(3)–C(2)	1.354(12)	C(4)–C(3)	1.346(15)
C(20)–Rh	2.269(7)	C(2)–F(1)	1.358(9)	C(5)–C(4)	1.406(15)	C(6)–C(5)	1.369(12)
C(3)–F(2)	1.324(11)	C(4)–F(3)	1.351(10)	C(8)–C(7)	1.359(9)	C(12)–C(7)	1.401(10)
C(5)–F(4)	1.362(10)	C(6)–F(5)	1.358(9)	C(9)–C(8)	1.407(11)	C(10)–C(9)	1.355(13)
C(8)–F(6)	1.345(9)	C(9)–F(7)	1.353(10)	C(11)–C(10)	1.380(12)	C(12)–C(11)	1.368(11)
C(1)–Pt–Rh	93.6(2)	C(7)–Pt–Rh	171.8(2)	C(5)–C(4)–F(3)	118.5(1)	C(5)–C(4)–C(3)	119.3(8)
C(7)–Pt–Cl	87.4(3)	C(13)–Pt–Rh	87.7(2)	C(4)–C(5)–F(4)	118.5(8)	C(6)–C(5)–F(4)	122.7(9)
C(13)–Pt–Cl	177.0(3)	C(13)–Pt–C(7)	91.7(3)	C(6)–C(5)–C(4)	118.6(8)	C(1)–C(6)–F(5)	121.0(7)
C(14)–Rh–Pt	82.0(3)	C(15)–Rh–Pt	86.8(3)	C(5)–C(6)–F(5)	115.3(7)	C(5)–C(6)–C(1)	123.5(8)
C(15)–Rh–C(14)	91.9(4)	C(16)–Rh–Pt	103.6(2)	C(8)–C(7)–Pt	120.8(5)	C(12)–C(7)–Pt	123.5(5)
C(16)–Rh–C(14)	165.5(3)	C(16)–Rh–C(15)	101.7(4)	C(12)–C(7)–C(8)	115.6(6)	C(7)–C(8)–F(6)	119.9(7)
C(17)–Rh–Pt	80.9(2)	C(17)–Rh–C(14)	134.0(3)	C(9)–C(8)–F(6)	117.6(7)	C(9)–C(8)–C(7)	122.5(8)
C(17)–Rh–C(15)	129.3(4)	C(17)–Rh–C(16)	36.9(1)	C(8)–C(9)–F(7)	120.2(9)	C(10)–C(9)–F(7)	119.8(7)
C(18)–Rh–Pt	97.7(2)	C(18)–Rh–C(14)	104.8(3)	C(10)–C(9)–C(8)	119.9(7)	C(9)–C(10)–F(8)	121.2(8)
C(18)–Rh–C(15)	163.2(4)	C(18)–Rh–C(16)	61.5(2)	C(11)–C(10)–F(8)	119.5(8)	C(11)–C(10)–C(9)	119.3(7)
C(18)–Rh–C(17)	37.0(1)	C(19)–Rh–Pt	134.5(2)	C(10)–C(11)–F(9)	119.2(7)	C(12)–C(11)–F(9)	121.1(8)
C(19)–Rh–C(14)	105.3(3)	C(19)–Rh–C(15)	136.4(3)	C(12)–C(11)–C(10)	119.7(7)	C(7)–C(12)–F(10)	119.6(6)
C(19)–Rh–C(16)	61.2(2)	C(19)–Rh–C(17)	61.5(2)	C(11)–C(12)–F(10)	117.5(7)	C(11)–C(12)–C(7)	122.9(7)
C(19)–Rh–C(18)	36.8(1)	C(20)–Rh–Pt	139.5(2)	O(1)–C(13)–Pt	175.4(8)	O(2)–C(14)–Rh	177.6(10)
C(20)–Rh–C(14)	134.6(3)	C(20)–Rh–C(15)	105.2(4)	O(3)–C(15)–Rh	176.0(10)	C(17)–C(16)–Rh	70.9(2)
C(20)–Rh–C(16)	36.6(1)	C(20)–Rh–C(17)	61.3(2)	C(20)–C(16)–Rh	72.3(2)	C(16)–C(17)–Rh	72.3(2)
C(20)–Rh–C(18)	61.3(2)	C(20)–Rh–C(19)	36.5(1)	H(16)–C(16)–Rh	122.5(2)	C(17)–C(18)–Rh	71.3(1)
C(2)–C(1)–Pt	124.3(5)	C(6)–C(1)–Pt	121.0(5)	C(18)–C(17)–Rh	71.7(2)	C(18)–C(19)–Rh	70.8(2)
C(6)–C(1)–C(2)	114.7(7)	C(1)–C(2)–F(1)	119.2(7)	H(17)–C(17)–Rh	121.8(2)	C(16)–C(20)–Rh	71.1(2)
C(3)–C(2)–F(1)	116.7(7)	C(3)–C(2)–C(1)	124.0(8)	C(19)–C(18)–Rh	72.4(2)	H(18)–C(18)–Rh	122.0(2)
C(2)–C(3)–F(2)	121.4(9)	C(4)–C(3)–F(2)	118.7(9)	H(19)–C(19)–Rh	122.8(2)	C(20)–C(19)–Rh	72.1(1)
C(4)–C(3)–C(2)	119.6(9)	C(3)–C(4)–F(3)	122.1(1)	C(19)–C(20)–Rh	71.4(1)	H(20)–C(20)–Rh	123.1(2)

Table 5. Fractional atomic co-ordinates ($\times 10^4$) with standard deviations for (**3**)

Atom	x	y	z
Pt	4 149(1)	8 629(1)	2 928(1)
Rh	2 729(1)	9 914(1)	2 085(1)
F(1)	797(6)	7 756(3)	2 070(3)
F(2)	578(8)	6 796(4)	779(4)
F(3)	3 481(10)	6 298(4)	−15(4)
F(4)	6 674(9)	6 792(4)	494(4)
F(5)	6 968(6)	7 785(4)	1 781(3)
F(6)	1 926(6)	7 236(3)	3 700(3)
F(7)	2 742(9)	6 023(4)	4 748(4)
F(8)	6 131(9)	5 795(3)	5 192(3)
F(9)	8 673(7)	6 760(3)	4 604(3)
F(10)	7 879(6)	7 992(3)	3 600(3)
O(1)	4 844(12)	9 768(4)	4 327(5)
O(2)	6 158(10)	10 689(5)	2 486(5)
O(3)	4 174(17)	9 165(5)	560(5)
C(1)	3 892(9)	7 830(4)	1 972(4)
C(2)	2 299(10)	7 535(5)	1 688(5)
C(3)	2 135(13)	7 020(6)	1 053(6)
C(4)	3 574(16)	6 782(5)	645(6)
C(5)	5 234(13)	7 031(6)	919(5)
C(6)	5 328(10)	7 541(5)	1 573(5)
C(7)	4 847(9)	7 660(4)	3 615(4)
C(8)	3 617(10)	7 137(4)	3 906(5)
C(9)	4 025(14)	6 509(4)	4 453(5)
C(10)	5 708(13)	6 387(5)	4 684(4)
C(11)	7 004(11)	6 889(5)	4 383(5)
C(12)	6 570(10)	7 509(4)	3 867(5)
C(13)	4 509(10)	9 344(5)	3 785(5)
C(14)	4 893(12)	10 402(6)	2 356(6)
C(15)	3 676(14)	9 441(5)	1 155(6)
C(16)	−123(8)	9 577(4)	1 971(4)
C(17)	370(8)	9 545(4)	2 799(4)
C(18)	865(8)	10 342(4)	3 042(4)
C(19)	678(8)	10 867(4)	2 364(4)
C(20)	67(8)	10 394(4)	1 702(4)

fractometer, monochromated Mo-K_α radiation, 5 595 data measured ($2\theta_{max.} = 60°$); 3 676 with $F > 6\sigma(F)$ used for all calculations; empirical absorption correction applied.[37]

Structure analysis and refinement. Metal atoms located by analysis of Patterson synthesis. All other non-H atoms by iterative full-matrix least-squares refinement and ΔF syntheses. Refinement on F to $R = 0.027$, $R' = 0.028$ [non-H atoms anisotropic, cyclopentadienyl ring as rigid group, and H atoms incorporated using riding model with C–H 0.96 Å]. Group U values for H atoms (0.10 Å^2); weighting scheme, $w^{-1} = \sigma^2(F) + 0.0005 F^2$; 308 parameters. The enantiomorph was chosen on the basis of a lower weighted R factor. All calculations were performed by using the SHELX 76 package.[38] Final atomic co-ordinates are given in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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