# Synthesis and Electrochemical Studies of New Ferrocene-labelled Dinuclear Rhodium(II) Complexes. Crystal Structures of $[Rh_2(O_2CMe)_2\{[(C_6H_4)PhP(C_5H_4)]Fe(C_5H_5)\}_2(HO_2CMe)_2]$ and $[Rh_2(O_2CMe)_2\{[(C_6H_4)PhP(C_5H_4)]_2Fe\}(HO_2CMe)]\cdot CH_2Cl_2$ †

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The reaction of diphenylphosphinoferrocene and 1,1'-bis(diphenylphosphino)ferrocene with $[Rh_2(O_2CMe)_4(MeOH)_2]$ (1:1 and 1:2 molar ratio respectively) yields the monoadducts $[Rh_2(O_2CMe)_4\{(Ph_2PC_5H_4)Fe(C_5H_5)\}]$ **1** and $[\{Rh_2(O_2CMe)_4(MeOH)\}_2\{(Ph_2PC_5H_4)_2Fe\}]$ **2**. By thermal treatment of **1** in refluxing toluene–acetic acid (10:3) the monometallated product $[Rh_2(O_2CMe)_3\{[(C_6H_4)PhP(C_5H_4)]Fe(C_5H_5)\}(HO_2CMe)_2]$ **3** was obtained in practically quantitative yield. Compound **3** reacts with $[Fe(C_5H_5)(C_5H_4PPh_2)]$ (1:1 molar ratio) giving the adduct $[Rh_2(O_2CMe)_3\{[(C_6H_4)PhP(C_5H_4)]Fe(C_5H_5)\}\{(Ph_2PC_5H_4)Fe(C_5H_5)\}]$ **4**, which reacts thermally in toluene–acetic acid (10:3) yielding the doubly metallated product $[Rh_2(O_2CMe)_2\{[(C_6H_4)PhP(C_5H_4)]Fe(C_5H_5)\}_2(HO_2CMe)_2]$ **5** as a mixture of conformational isomers. An X-ray determination of **5** has been carried out: space group *Pbca* (orthorhombic), $a = 18.065(3)$, $b = 20.606(4)$, $c = 26.242(5)$ Å, $Z = 8$, and $R = 0.038$. The crystal structure shows that the two metallated phosphines are in a head-to-tail configuration. Thermal treatment of a mixture of $[Rh_2(O_2CMe)_4(MeOH)_2]$ and $[Fe(C_5H_4PPh_2)_2]$ (1:1 molar ratio) in acetic acid yields the compound $[Rh_2(O_2CMe)_2\{[(C_6H_4)PhP(C_5H_4)]_2Fe\}(HO_2CMe)]\cdot CH_2Cl_2$ **6** after purification and crystallization from a $CH_2Cl_2$–hexane–acetic acid mixture. An X-ray diffraction investigation showed that this compound crystallizes in space group $P2_1/c$ (monoclinic) with $a = 12.735(4)$, $b = 16.811(5)$, $c = 20.161(8)$ Å, $\beta = 95.17(4)°$, $Z = 4$ and $R = 0.089$. The two $PPh_2$ fragments of the ferrocene ligand act as bridging orthometallated ligands in a head-to-head configuration. Two well defined oxidation processes were detected by cyclic voltammetry for all the complexes in $CH_2Cl_2$ solution: the first one, in the range 0.6–0.7 V, is due to the couple $Fe^{2+}$–$Fe^{3+}$ while the second one, in the range 0.9–1.32 V, is due to the couple $Rh_2^{4+}$–$Rh_2^{5+}$.

The synthesis of new complexes which can display multiple electron-transfer processes has been a focus of considerable attention,[1a-c] mainly due to their potential to act as electron-transfer catalysts.[1d] The electrochemical investigation of several rhodium(II) carboxylates $[Rh_2(O_2CR)_4]$ indicated[2] that all exhibit a reversible one-electron oxidation, $Rh_2^{5+}$ being the only oxidized species detected. The value of the redox potential is strongly affected by the nature of the bridging and axial ligands.[2] Some of these $Rh_2^{5+}$ species, generated by electrochemical methods, have been characterized '*in situ*' by EPR[3] and Raman spectroscopy.[4] To our knowledge, only one $Rh_2^{5+}$ compound has been structurally characterized by X-ray methods.[5]

One particular example of $Rh_2^{4+}$ complexes are the orthometallated rhodium(II) species. Several compounds with bridging orthometallated triaryl- or alkylaryl-phosphines have been described[6,7] where the metallation always occurs at aromatic carbons.

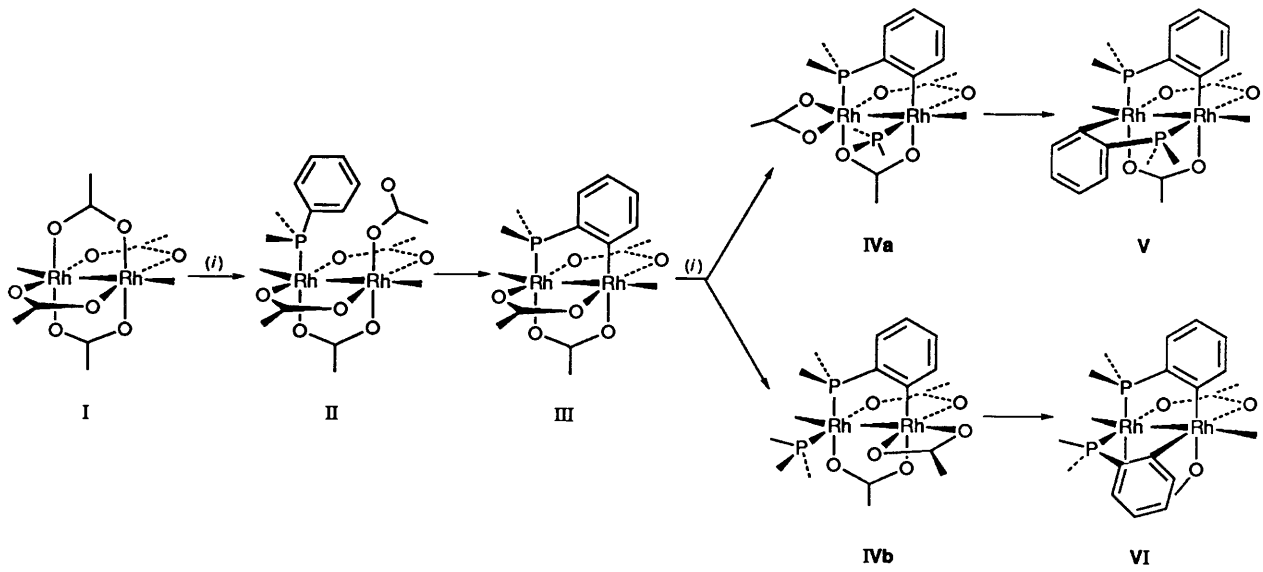
Scheme 1 shows the general reaction pathway found for the metallation of $[Rh_2(O_2CMe)_4]$ and arylphosphines[6] yielding doubly metallated compounds with head-to-tail (**V**) or head-to-head (**VI**) configurations. Different compounds of types **III**, **V** and **VI** have been isolated and characterized by X-ray methods.[7] Species of the structural type **IVa** have been isolated and the crystal structure has been solved for one compound of this type.[7c] Species of structure **IVb**[7d] have been only spectroscopically detected in a few systems but no observation of any intermediate of type **II** has been made until now.

We describe in this paper the reactivity of $[Rh_2(O_2CMe)_4]$ with the ferrocenyl-substituted phosphines $[Fe(C_5H_5)(C_5H_4PPh_2)]$ and $[Fe(C_5H_4PPh_2)_2]$. The isolation of a new monometallated compound, the crystal structure of two compounds of structural types **V** and **VI** and the electrochemical behaviour of these multielectron-transfer species is also discussed.

## Experimental

*General Comments.*—The complexes $[Rh_2(O_2CMe)_4(MeOH)_2]$,[8] $[Rh_2(O_2CMe)_3(C_6H_4PPh_2)(HO_2CMe)_2]$,[7e] and $[Rh_2(O_2CMe)_2(C_6H_4PPh_2)_2(HO_2CMe)_2]$ in the head-to-tail[6c] (H-T) and head-to-head[7k] (H-H) configurations were prepared according to literature methods. Commercially available ferrocene, $LiBu^n$ and 1,1'-bis(diphenylphosphino)ferrocene were used as purchased (Aldrich). All solvents were of analytical grade and were degassed prior to use. Diethyl ether was freshly distilled from sodium–benzophenone prior to use. All the

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.




**Scheme 1** (*i*) Phosphine

reactions were performed under an argon atmosphere. The NMR measurements were made on AC-200 Bruker ($^{31}P$) and UNITY400 Varian spectrometers ($^{13}C$ and $^{1}H$).

*Electrochemical Measurements*.—The electrochemical experiments were carried out in a three-electrode cell; the working and auxiliary electrodes were platinum, the reference electrode was a saturated calomel electrode electrically connected to the solution by a 'salt bridge' containing a saturated solution of the supporting electrolyte and the solvent. Cyclic voltammograms were obtained with a 305 HQ programming function generator connected to a Amel potentiostat, and were recorded on a Riken-Denshi F-35 *x-y* recorder. The solvent was $CH_2Cl_2$ which had been freshly distilled from $P_2O_5$. The supporting electrolyte, $NBu_4PF_6$, was recrystallized from ethanol and dried at 80 °C under vacuum for 48 h. Controlled-potential electrolysis was carried out in a three-compartment cell separated by glass frits. The working and auxiliary electrodes were platinum mesh. The charge transferred was calculated by recording intensity *versus* time and carrying out an integration. The system was calibrated against ferrocene.

*Crystallography*.—Crystallographic constants and experimental details for both structures **5** and **6** are collected in Table 1. Data collection was carried out on an Enraf-Nonius CAD4 single-crystal diffractometer equipped with a graphite-crystal monochromator and Mo-K$\alpha$ radiation ($\lambda$ = 0.710 73 Å). Unit-cell dimensions were determined from the angular settings of 25 reflections. Space groups determined from systematic absences. The $\omega$–2$\theta$ scan technique and a variable scan rate with a maximum scan time of 60 s per reflection were employed. Three standard reflections were monitored every 60 min. Profile analysis was performed on all reflections;[9,10] a semiempirical absorption correction, $\psi$-scan based,[11] was applied to **6**. Some doubly measured reflections were averaged. Lorentz and polarization corrections were applied.

Structures were solved by Patterson interpretation, using the program SHELX 86[12] and expanded with DIRDIF.[13] Isotropic least-squares refinement, using a locally modified version of the program SHELX 76[14] was used. An empirical absorption correction was applied.[15] Further anisotropic refinements followed by a Fourier difference synthesis allowed the location of some hydrogen atoms. During the final stages of the refinement the positional parameters and the anisotropic thermal parameters of the non-hydrogen atoms were refined. The positions of most hydrogen atoms were calculated geometrically and included in the refinement. All hydrogens were refined as rigid groups riding on their parent atoms, with a common isotropic thermal parameter. Atoms of the dichloromethane molecule in **6** have high thermal parameters; the high anisotropy for this molecule indicates the presence of thermal disorder.

Atomic scattering factors were taken from ref. 16.

**Table 1** Crystallographic data for compounds **5** and **6**

| Compound | **5** | **6** |
|---|---|---|
| $M$ | 1180.4 | 1021.25 |
| Crystal colour | Red | Dark red |
| Crystal size (mm) | 0.33 × 0.23 × 0.17 | 0.20 × 0.20 × 0.10 |
| Formula | $C_{52}H_{50}Fe_2O_8P_2Ph_2$ | $C_{40}H_{36}FeO_6P_2Rh_2\cdot CH_2Cl_2$ |
| Crystal symmetry | Orthorhombic | Monoclinic |
| Space group | *Pbca* | $P2_1/c$ |
| $a$/Å | 18.065(3) | 12.735(4) |
| $b$/Å | 20.606(4) | 16.811(5) |
| $c$/Å | 26.242(5) | 20.161(8) |
| $\beta$/° | — | 95.17(4) |
| $U$/Å$^3$ | 9769(3) | 4299(3) |
| $Z$ | 8 | 4 |
| $D_c$/g cm$^{-3}$ | 1.61 | 1.58 |
| $\mu$(Mo-K$\alpha$)/cm$^{-1}$ | 13.52 | 13.21 |
| $\theta$ limits/° | 0–25 | 0–25 |
| *hkl* range | (0,0,0)–(21,24,31) | (−15,0,0)–(15,19,23) |
| $R_{int}$[a] | 0.021 | 0.064 |
| Drift correction | 1.00–1.04 | 0.98–1.02 |
| Measured reflections | 9464 | 8017 |
| Unique reflections | 8530 | 7493 |
| Observed reflections [$I > 3\sigma(I)$] | 3825 | 2761 |
| $F$(000) | 4767 | 2044 |
| Absorption correction | | |
| $\psi$ scans | — | 0.93–1.00 |
| DIFABS | 0.90–1.23 | 1.19–0.78 |
| $R$ | 0.038 | 0.089 |
| $R'$[b] | 0.036 | 0.089 |
| $g$ | 0.0002 | Unit weights |
| Maximum shift/error | 0.21 | 0.01 |
| Maxinum, minimum/e Å$^{-3}$ | 0.79, −0.48 | 0.66, −0.75 |
| Number of variables | 597 | 488 |

[a] $R_{int} = \Sigma(I - \langle I\rangle)/\Sigma I$. [b] $\Sigma w(F_o - F_c)^2$, $w = 1/[\sigma^2(F_o) + gF_o^2]$.

Geometrical calculations were made with PARST.[17] Drawings were made using the EUCLID package.[18] All calculations made on a MicroVax 3400 computer at the Scientific Computer Center of the University of Oviedo.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

*Synthesis of Compounds.*—$[Fe(C_5H_5)(C_5H_4PPh_2)]$. Butyllithium (17 $cm^3$, 27 mmol), in hexane (1.6 mol $dm^{-3}$), was added to ferrocene (5 g, 26 mmol) dissolved in diethyl ether (200 $cm^3$). The mixture was stirred for 15 h yielding a brown-red solution. Chlorodiphenylphosphine (5 $cm^3$, 27 mmol) was slowly added and the new solution was stirred for 12 h. After removal of the white precipitate of LiCl by filtration, an orange solution was obtained. It was evaporated to dryness under vacuum, and the resulting orange solid dissolved in hexane. The solution was transferred to a chromatography column (30 × 2 cm) packed with silica gel in hexane. Elution with hexane separated a yellow band of ferrocene. Further elution with $CH_2Cl_2$–hexane (1 : 1) separated one yellow-orange band which was collected. A minor band containing $[Fe(C_5H_4PPh_2)_2]$ was discarded. The solvent of the collected fraction was reduced under vacuum to 50% and crystals of analytically pure $[Fe(C_5H_5)(C_5H_4PPh_2)]$ were obtained (2.88 g, 30%). $\delta_H(CDCl_3)$ 4.07 (5 H, s, $C_5H_5$), 4.12 (2 H, s, $C_5H_4$), 4.37 (2 H, s, $C_5H_5$) and 7.2–7.5 (10 H, m, aromatics); $\delta_P(CDCl_3)$ −16.2; $\delta_C(CDCl_3)$ 69.09 (5 C, s, $C_5H_5$), 70.72 [2 C, d, $J$(PC) 4.25], 72.81 [2 C, d, $J$(PC) 14.65], 75.46 (1 C, s), 128.0–128.5 (aromatics, m), 133.0–133.7 (aromatics, m) and 138.81 [aromatic, d, $J$(PC) 8.24 Hz].

*Compound* **1**. The complex $[Rh_2(O_2CMe)_4(MeOH)_2]$ (110 mg, 0.21 mmol) and $[Fe(C_5H_5)(C_5H_4PPh_2)]$ (75 mg, 0.21 mmol) were dissolved in $CHCl_3$ (25 $cm^3$). The resulting red solution was concentrated to half of the initial volume under vacuum. Addition of hexane (10 $cm^3$) yielded a red-brown precipitate of $[Rh_2(O_2CMe)_4\{(PhPC_5H_4)Fe(C_5H_5)\}]$ **1** which was recrystallised from $CH_2Cl_2$–hexane (190 mg, 95%). $\delta_H(CDCl_3)$ 1.81 (12 H, s, Me), 4.12 (5 H, s, $C_5H_5$), 4.51 (2 H, m, $C_5H_4$), 4.65 (2 H, m, $C_5H_4$) and 7.2–7.8 (10 H, m, aromatics); $\delta_P(CDCl_3)$ −44.5 [$^1J$(RhP) 97, $^2J$(RhP) 31 Hz]; $\delta_C(CDCl_3)$ 23.76 (s, Me), 69.34–73.4 (m, $C_5H_5$), 127.25–133.89 (m, aromatics) and 190.63 (s, OCO) (Found: C, 44.7; H, 3.65. Calc. for $C_{30}H_{31}FeO_8PRh_2$: C, 44.4; H, 3.80%).

*Compound* **2**. This adduct was obtained in solution by adding the phosphine ligand $[Fe(C_5H_4PPh_2)_2]$ to $[Rh_2(O_2CMe)_4(MeOH)_2]$ (1 : 2) in $CH_2Cl_2$ (10 $cm^3$). The $^{31}P$ NMR spectrum was recorded from the resulting solution.

*Compound* **3**. The complex $[Rh_2(O_2CMe)_4(MeOH)_2]$ (165 mg, 0.315 mmol) and $[Fe(C_5H_5)(C_5H_4PPh_2)]$ (112.5 mg, 0.315 mmol) were dissolved in toluene–acetic acid (10 : 3, 40 $cm^3$). The solution was refluxed for 6 h and the colour changed to red-brown. The solvent was reduced to dryness under vacuum, and the resulting red-brown solid was dissolved in $CH_2Cl_2$. This solution was transferred to a chromatography column (30 × 2 cm) packed with silica gel in hexane. Elution with hexane–$CH_2Cl_2$–acetic acid (20 : 10 : 2) separated a red band and a minor green band which were collected. The green band contained the starting compound $[Rh_2(O_2CMe)_4(MeOH)_2]$. The red solution was evaporated to dryness and the solid containing $[Rh_2(O_2CMe)_3\{[(C_6H_4)PhP(C_5H_4)]Fe(C_5H_5)\}(HO_2CMe)_2]$ **3** was precipitated in $CH_2Cl_2$–hexane. The same results were obtained when compound **1** was refluxed under similar conditions. Yield 233 mg (85%). $\delta_H(CDCl_3)$ 1.05 (3 H, s, Me), 1.51 (3 H, s, Me), 2.13 (6 H, s, Me), 2.23 (3 H, s, Me), 3.69 (5 H, s, $C_5H_5$), 4.16 (1 H, s, $C_5H_5$), 4.23 (1 H, s, $C_5H_5$), 4.35 (1 H, s, $C_5H_5$), 4.43 (1 H, s, $C_5H_5$), 7.01–7.46 (8 H, m, aromatics) and 8.65 (1 H, m, aromatics); $\delta_P(CDCl_3)$ 15.43 [$^1J$(RhP) 148, $^2J$(RhP) 5.9 Hz]; $\delta_C(CDCl_3)$ 21.95 (s, Me), 22.62 (s, Me), 23.42 (s, Me), 24.01 (s, Me), 69.23–75.22 (m, $C_5H_5$), 121.6–137.04 (m, aromatics), 163.8 (dd, $J$ 33, 22 Hz), 179.70 (s, OCO), 182.25 (s, OCO) and 189.46 (s, OCO) (Found: C, 45.00; H, 4.40. Calc. for $C_{32}H_{35}FeO_{10}PRh_2$: C, 44.05; H, 4.05%).

*Compound* **4**. This adduct was obtained in $CH_2Cl_2$ solution by adding $[Fe(C_5H_5)(C_5H_4PPh_2)]$ to **3** (1 : 1 molar ratio). The $^{31}P$ NMR spectrum was recorded from the resulting solution.

*Compound* **5**. The complex $[Rh_2(O_2CMe)_4(MeOH)_2]$ (110 mg, 0.21 mmol) and $[Fe(C_5H_5)(C_5H_4PPh_2)]$ (150 mg, 0.42 mmol) were refluxed in toluene–acetic acid (10 : 3, 40 $cm^3$) for 4 h. The resulting red-brown solution was reduced to dryness under vacuum, and the crude solid was dissolved in $CH_2Cl_2$. The solution was transferred to a chromatography column (30 × 2 cm) packed with silica gel in hexane. By elution with hexane–$CH_2Cl_2$–acetic acid (20 : 10 : 2) a red band separated. Further elution with hexane–$CH_2Cl_2$–acetic acid (20 : 10 : 4) separated a green band which contained the starting compound $[Rh_2(O_2CMe)_4(MeOH)_2]$. The red solution was evaporated to dryness and the crude solid recrystallized from $CH_2Cl_2$–hexane. Elemental analysis data confirmed the formula $[Rh_2(O_2CMe)_2\{[(C_6H_4)PhP(C_5H_4)]Fe(C_5H_5)\}_2(HO_2CMe)_2]$ **5** (136 mg, 55%). $\delta_P(CDCl_3)$ (three isomers) 15.43 [$^1J$(RhP) 148, $^2J$(RhP) 6.3 Hz] (Found: C, 52.85; H, 4.40. Calc. for $C_{52}H_{50}Fe_2O_8P_2Rh_2$: C, 52.80; H, 4.25%).

*Compound* **6**. The complex $[Rh_2(O_2CMe)_4(MeOH)_2]$ (140 mg, 0.277 mmol) and $[Fe(C_5H_4PPh_2)_2]$ (154 mg, 0.277 mmol) were gently refluxed in acetic acid (40 $cm^3$) for 4 h. The resulting dark red solution was concentrated to dryness under vacuum. The crude solid was purified by column chromatography in a similar way to that described for compound **2**. Elution with hexane–$CH_2Cl_2$–acetic acid (40 : 20 : 2) allowed the separation of a main red band which contained $[Rh_2(O_2CMe)_2\{[(C_6H_4)PhP(C_5H_4)]_2Fe\}(HO_2CMe)]\cdot CH_2Cl_2$ **6**. Slow evaporation of the solvent mixture gave after 3 d single crystals suitable for X-ray diffraction analysis. Yield 178 mg (63%). $\delta_H(CDCl_3)$ 1.44 (6 H, s, Me), 2.12 (3 H, s, Me), 4.06 (2 H, s, $C_5H_5$), 4.15 (2 H, s, $C_5H_5$), 4.47 (2 H, s, $C_5H_5$), 5.23 (2 H, s, $C_5H_5$), 5.33 (2 H, s, $CH_2Cl_2$) and 6.8–8.0 (18 H, m, aromatics); $\delta_P(CDCl_3)$ 19.12 [$^1J$(RhP) 154.4, $^2J$(RhP) 9.1 Hz]; $\delta_C(CD_2Cl_2)$ 22.14 (s, Me), 23.50 (s, Me), 69.34–73.4 (m, $C_5H_5$), 127.25–133.89 (m, aromatics) and 190.63 (s, OCO) (Found: C, 48.70; H, 3.90. Calc. for $C_{41}H_{38}ClFeO_6P_2Rh_2$: C, 48.20; H, 3.75%).

## Results and Discussion

The complexes $[Rh_2(O_2CMe)_4(MeOH)_2]$ and $[Fe(C_5H_5)(C_5H_4PPh_2)]$ in 1 : 1 molar ratio react in chloroform solution at room temperature yielding the monoadduct **1**. The $^{31}P$ NMR spectrum in $CDCl_3$ solution shows a doublet of doublets centred at δ −44.5 [$^1J$(Rh–P) = 97, $^2J$(Rh–P) = 31 Hz]. The value of $^2J$(Rh–P) changes with the solvent, probably due to the replacement of the second axial ligand.

The complex $[Rh_2(O_2CMe)_4(MeOH)_2]$ reacts with $[Fe(C_5H_4PPh_2)_2]$ (2 : 1 molar ratio) in chloroform solution. The $^{31}P$ NMR spectrum of the resulting solution only shows a doublet of doublets centred at δ −44.3 [$^1J$(Rh–P) = 98, $^2J$(Rh–P) = 33 Hz]. This suggests a structure with the axial phosphine ligand bridging two $Rh_2$ units (compound **2**). Very insoluble products are obtained if higher amounts of phosphine are used. The low solubility of these products prevented us from making a detailed spectroscopic study in solution.

If compound **1** is refluxed for 6 h in toluene–acetic acid (10 : 3), $[Rh_2(O_2CMe)_3\{[(C_6H_4)PhP(C_5H_4)]Fe(C_5H_5)\}(HO_2CMe)_2]$ **3** can be isolated in practically quantitative yield. This compound shows $^1H$, $^{13}C$ and $^{31}P$ NMR data quite similar to those observed for other monometallated compounds.[7d–g] Owing to its low symmetry, the $^1H$ NMR spectrum shows one methyl resonance for each bridging acetate group as well as for each proton of the substituted cyclopentadienyl ring. The observation of only one signal for the two axial acetic acid ligands is probably due to a rapid dissociation equilibrium occurring at room temperature which has already been

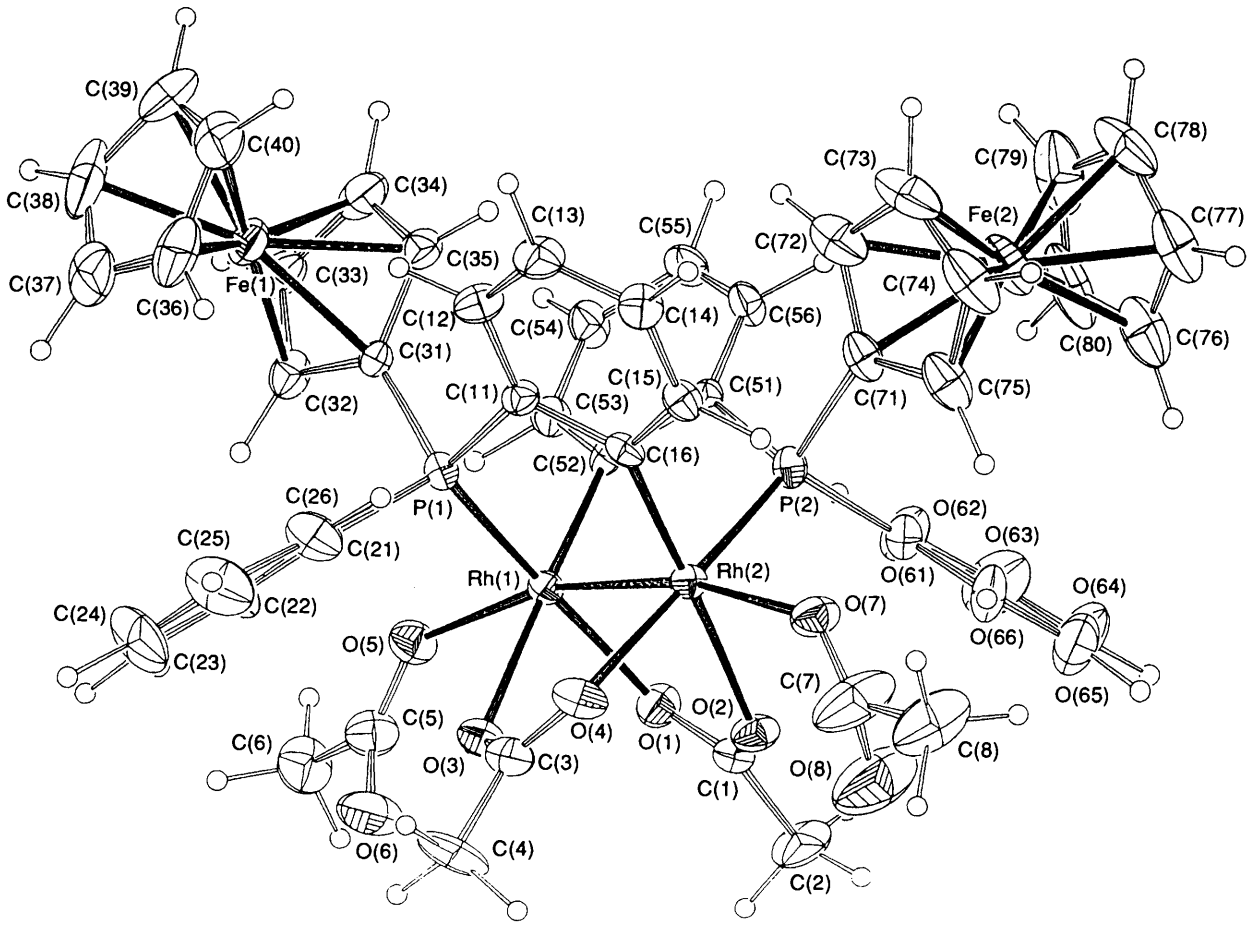


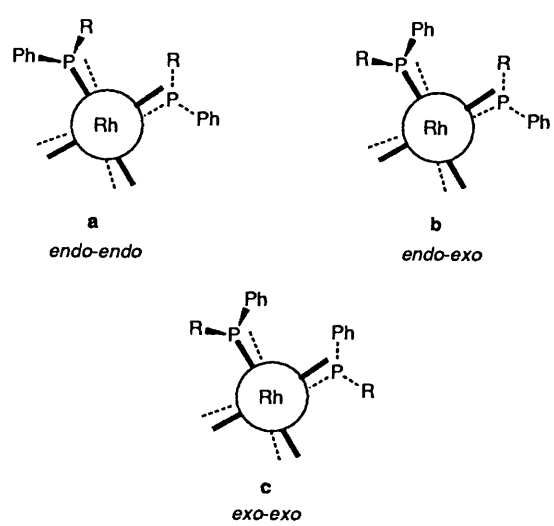

**Fig. 1** A PLATON diagram for compound **5**

observed for other related species.[7] The $^{31}P$ NMR spectrum shows the characteristic doublet of doublets centred at δ 15.4 [$^1J$(Rh–P) = 148, $^2J$(Rh–P) = 5.9 Hz]. The unique metallated carbon atom shows a doublet of doublets at δ 163.8 with coupling constants of 33 and 22 Hz.

If the reaction **1** ⟶ **3** is monitored by $^{31}P$ NMR spectroscopy, three sets of signals at $\delta_P$ 29.56 [d, $^1J$(Rh–P) = 157.1], 22.72 [d, $^1J$(Rh–P) = 122.7] and 22.04 [d, $^1J$(Rh–P) 126.2 Hz] can be detected in solution. These signals can be attributed to the existence of different rotational isomers with the phosphine occupying an equatorial non-metallated co-ordination, stabilized in solution due to the rotational barrier introduced by the bulky ferrocenyl group attached to the phosphine. These three NMR signals disappear at different rates, consistent with the fact that, for sterical reasons, not all the possible equatorial isomers can undergo easy metallation. These intermediate species are of relative short life and cannot be isolated.

We have recently observed in other related dirhodium(II) compounds that the axial-to-equatorial rearrangement of one phosphine can be quantitatively promoted by photochemical irradiation of the starting phosphine adducts. Compound **1** in $CDCl_3$ was exposed to mercury lamp irradiation and the chemical evolution followed by $^{31}P$ NMR spectroscopy. The formation of compound **3** in solution was clearly detected after 5 min of irradiation. The reaction is complete in about 6 h but under these conditions the equatorial intermediates are only detected in very minor amounts.

When compound **3** reacts with $[Fe(C_5H_5)(C_5H_4PPh_2)]$ in 1:1 molar ratio the adduct $[Rh_2(O_2CMe)_3\{[(C_6H_4)PhP(C_5H_4)]Fe(C_5H_5)\}\{(Ph_2PC_5H_4)Fe(C_5H_5)\}(HO_2CMe)]$ **4** is formed. Thermal reaction of **4** in toluene–acetic acid (10:3) generates the doubly metallated species $[Rh_2(O_2CMe)_2\{[(C_6H_4)PhP(C_5H_4)]Fe(C_5H_5)\}_2(HO_2CMe)_2]$ **5**. The $^{31}P$ NMR spectrum indicates the existence of three main species which we were unable to separate by conventional methods (recrystallization and column chromatography). The analysis of complex **5** is consistent with the above formula. The three different species detected by $^{31}P$ NMR spectroscopy must be the three possible diastereoisomers shown in Scheme 2.




**Scheme 2** R = $(C_5H_4)Fe(C_5H_5)$

These three isomers can also be obtained by direct thermal reaction of $[Rh_2(O_2CMe)_4(MeOH)_2]$ and $[Fe(C_5H_5)(C_5H_4PPh_2)]$ (1:2 molar ratio) in refluxing toluene–acetic acid (7:3). Each of these two metallation reactions yields slightly different

**Table 2** Selected bond lengths (Å) and angles (°) for complex **5** with estimated standard deviations (e.s.d.s) in parentheses

| | | | | | | |
|---|---|---|---|---|---|---|
| Rh(1)–Rh(2) | 2.504(1) | Rh(1)–P(1) | 2.196(2) | Rh(1)–O(1) | 2.158(6) | |
| Rh(1)–O(3) | 2.182(6) | Rh(1)–O(5) | 2.295(6) | Rh(1)–C(52) | 1.996(8) | |
| Rh(2)–P(2) | 2.205(2) | Rh(2)–O(2) | 2.202(6) | Rh(2)–O(4) | 2.169(6) | |
| Rh(2)–O(7) | 2.392(6) | Rh(2)–C(16) | 2.011(8) | Fe(1)–C(31) | 2.043(8) | |
| Fe(1)–C(32) | 2.042(9) | Fe(1)–C(33) | 2.02(1) | Fe(1)–C(34) | 2.03(1) | |
| Fe(1)–C(35) | 2.05(1) | Fe(1)–C(36) | 2.06(1) | Fe(1)–C(37) | 2.01(1) | |
| Fe(1)–C(38) | 2.00(1) | Fe(1)–C(39) | 2.02(1) | Fe(1)–C(40) | 2.03(1) | |
| Fe(2)–C(71) | 2.054(8) | Fe(2)–C(72) | 2.04(1) | Fe(2)–C(73) | 2.041(9) | |
| Fe(2)–C(74) | 2.06(1) | Fe(2)–C(75) | 2.064(9) | Fe(2)–C(76) | 2.06(1) | |
| Fe(2)–C(77) | 2.09(1) | Fe(2)–C(78) | 2.04(1) | Fe(2)–C(79) | 2.04(1) | |
| Fe(2)–C(80) | 2.05(1) | P(1)–C(11) | 1.805(8) | P(1)–C(21) | 1.848(8) | |
| P(1)–C(31) | 1.827(9) | P(2)–C(51) | 1.805(8) | P(2)–C(61) | 1.844(8) | |
| P(2)–C(71) | 1.829(8) | O(1)–C(1) | 1.25(1) | O(2)–C(1) | 1.27(1) | |
| O(3)–C(3) | 1.27(1) | O(4)–C(3) | 1.27(1) | O(5)–C(5) | 1.16(1) | |
| O(6)–C(5) | 1.40(1) | O(7)–C(7) | 1.18(1) | O(8)–C(7) | 1.34(1) | |
| P(1)–Rh(1)–Rh(2) | 88.3(1) | O(1)–Rh(1)–Rh(2) | 87.2(2) | C(1)–O(2)–Rh(2) | 120.2(6) | C(3)–O(4)–Rh(2) 118.8(6) |
| O(1)–Rh(1)–P(1) | 175.4(2) | O(3)–Rh(1)–Rh(2) | 84.2(2) | C(51)–P(2)–Rh(2) | 112.8(3) | C(61)–P(2)–Rh(2) 113.0(3) |
| O(3)–Rh(1)–P(1) | 95.0(2) | O(3)–Rh(1)–O(1) | 83.7(2) | C(7)–O(7)–Rh(2) | 128.5(7) | C(71)–P(2)–Rh(2) 114.6(3) |
| O(5)–Rh(1)–Rh(2) | 167.5(2) | O(5)–Rh(1)–P(1) | 99.9(2) | C(15)–C(16)–Rh(2) | 120.1(6) | C(11)–C(16)–Rh(2) 123.2(6) |
| O(5)–Rh(1)–O(1) | 84.3(2) | O(5)–Rh(1)–O(3) | 85.7(2) | C(12)–C(11)–P(1) | 123.1(6) | C(16)–C(11)–P(1) 114.6(6) |
| C(52)–Rh(1)–Rh(2) | 97.1(2) | C(52)–Rh(1)–P(1) | 87.8(2) | C(22)–C(21)–P(1) | 120.0(6) | C(26)–C(21)–P(1) 120.6(7) |
| C(52)–Rh(1)–O(1) | 93.6(3) | C(52)–Rh(1)–O(3) | 177.0(3) | C(32)–C(31)–P(1) | 122.9(8) | C(35)–C(31)–P(1) 128.4(7) |
| C(52)–Rh(1)–O(5) | 92.6(3) | P(2)–Rh(2)–Rh(1) | 88.2(1) | C(31)–P(1)–C(11) | 107.9(4) | C(31)–P(1)–C(21) 104.5(4) |
| O(2)–Rh(2)–Rh(1) | 84.1(2) | O(2)–Rh(2)–P(2) | 94.9(2) | C(21)–P(1)–C(11) | 103.5(4) | C(52)–C(51)–P(2) 115.4(6) |
| O(4)–Rh(2)–Rh(1) | 87.0(2) | O(4)–Rh(2)–P(2) | 175.2(2) | C(56)–C(51)–P(2) | 122.8(6) | C(62)–C(61)–P(2) 120.7(7) |
| O(4)–Rh(2)–O(2) | 84.3(2) | O(7)–Rh(2)–Rh(1) | 165.6(2) | C(66)–C(61)–P(2) | 120.1(7) | C(73)–C(71)–P(2) 126.5(7) |
| O(7)–Rh(2)–P(2) | 100.4(2) | O(7)–Rh(2)–O(2) | 83.7(2) | C(75)–C(71)–P(2) | 124.9(6) | C(61)–P(2)–C(51) 105.0(4) |
| O(7)–Rh(2)–O(4) | 84.3(2) | C(16)–Rh(2)–Rh(1) | 96.4(2) | C(71)–P(2)–C(51) | 106.3(4) | C(71)–P(2)–C(61) 104.3(4) |
| C(16)–Rh(2)–P(2) | 86.9(2) | C(16)–Rh(2)–O(2) | 178.2(3) | O(2)–C(1)–O(1) | 125.3(9) | C(2)–C(1)–O(1) 117.8(9) |
| C(16)–Rh(2)–O(4) | 94.0(3) | C(16)–Rh(2)–O(7) | 95.6(3) | C(2)–C(1)–O(2) | 116.9(9) | O(4)–C(3)–O(3) 124.2(9) |
| C(11)–P(1)–Rh(1) | 112.6(3) | C(21)–P(1)–Rh(1) | 113.2(3) | C(4)–C(3)–O(3) | 118.2(9) | C(4)–C(3)–O(4) 117.6(9) |
| C(1)–O(1)–Rh(1) | 118.5(6) | C(3)–O(3)–Rh(1) | 120.9(6) | O(6)–C(5)–O(5) | 115(1) | C(6)–C(5)–O(5) 130(1) |
| C(5)–O(5)–Rh(1) | 130.9(8) | C(31)–P(1)–Rh(1) | 114.4(3) | C(6)–C(5)–O(6) | 109(1) | O(8)–C(7)–O(7) 123(1) |
| C(51)–C(52)–Rh(1) | 123.2(6) | C(53)–C(52)–Rh(1) | 121.0(6) | C(8)–C(7)–O(7) | 125(1) | C(8)–C(7)–O(8) 112(1) |

**Table 3** Selected bond lengths (Å) and angles (°) for complex **6** with e.s.d.s in parentheses

| | | | | | | |
|---|---|---|---|---|---|---|
| Rh(2)–Rh(1) | 2.508(4) | Rh(2)–O(2) | 2.24(2) | Rh(2)–O(3) | 2.20(2) | |
| Rh(2)–O(6) | 2.26(2) | Rh(2)–C(1) | 1.94(3) | Rh(2)–C(7) | 2.01(3) | |
| Rh(1)–P(1) | 2.218(9) | Rh(1)–P(2) | 2.230(9) | Rh(1)–O(1) | 2.14(2) | |
| Rh(1)–O(4) | 2.12(2) | Fe–C(25) | 2.00(3) | Fe–C(26) | 2.07(3) | |
| Fe–C(27) | 2.13(3) | Fe–C(28) | 2.09(4) | Fe–C(29) | 2.02(3) | |
| Fe–C(30) | 2.01(3) | Fe–C(31) | 2.03(3) | Fe–C(32) | 2.05(4) | |
| Fe–C(33) | 2.05(3) | Fe–C(34) | 2.08(4) | P(1)–C(8) | 1.80(3) | |
| P(1)–C(13) | 1.85(3) | P(1)–C(30) | 1.80(3) | P(2)–C(6) | 1.78(3) | |
| P(2)–C(19) | 1.80(3) | P(2)–C(25) | 1.81(4) | O(1)–C(36) | 1.31(4) | |
| O(2)–C(36) | 1.19(4) | O(3)–C(38) | 1.31(4) | O(4)–C(38) | 1.25(4) | |
| O(5)–C(39) | 1.30(4) | O(6)–C(39) | 1.22(4) | | | |
| O(2)–Rh(2)–Rh(1) | 83.8(6) | O(3)–Rh(2)–Rh(1) | 84.3(6) | C(6)–P(2)–Rh(1) | 112(1) | C(19)–P(2)–Rh(1) 112(1) |
| O(3)–Rh(2)–O(2) | 83.1(8) | O(6)–Rh(2)–Rh(1) | 167.2(6) | C(25)–P(2)–Rh(1) | 115(1) | C(36)–O(2)–Rh(2) 120(2) |
| O(6)–Rh(2)–O(2) | 85.8(8) | O(6)–Rh(2)–O(3) | 87.1(8) | C(38)–O(4)–Rh(1) | 122(2) | C(39)–O(6)–Rh(2) 127(3) |
| C(1)–Rh(2)–Rh(1) | 96.0(9) | C(1)–Rh(2)–O(2) | 93(1) | C(2)–C(1)–Rh(2) | 121(2) | C(6)–C(1)–Rh(2) 125(2) |
| C(1)–Rh(2)–O(3) | 176(1) | C(1)–Rh(2)–O(6) | 92(1) | C(8)–C(7)–Rh(2) | 122(2) | C(12)–C(7)–Rh(2) 121(2) |
| C(7)–Rh(2)–Rh(1) | 96.3(9) | C(7)–Rh(2)–O(2) | 176(1) | C(38)–O(3)–Rh(2) | 121(2) | C(1)–C(6)–P(2) 116(2) |
| C(7)–Rh(2)–O(3) | 93(1) | C(7)–Rh(2)–O(6) | 94(1) | C(29)–C(25)–P(2) | 130(3) | C(5)–C(6)–P(2) 122(3) |
| C(7)–Rh(2)–C(1) | 91(1) | P(1)–Rh(1)–Rh(2) | 90.1(2) | C(7)–C(8)–P(1) | 120(2) | C(9)–C(8)–P(1) 119(3) |
| P(2)–Rh(1)–Rh(2) | 88.5(2) | P(2)–Rh(1)–P(1) | 96.5(3) | C(14)–C(13)–P(1) | 118(3) | C(18)–C(13)–P(1) 123(3) |
| O(1)–Rh(1)–Rh(2) | 86.8(6) | O(1)–Rh(1)–P(1) | 169.9(6) | C(20)–C(19)–P(2) | 121(3) | C(24)–C(19)–P(2) 121(3) |
| O(1)–Rh(1)–P(2) | 93.1(6) | O(4)–Rh(1)–Rh(2) | 86.8(6) | C(25)–P(2)–C(19) | 101(1) | C(30)–P(1)–C(13) 104(1) |
| O(4)–Rh(1)–P(1) | 88.1(6) | O(4)–Rh(1)–P(2) | 173.4(6) | C(13)–P(1)–C(8) | 108(1) | C(30)–P(1)–C(8) 102(1) |
| C(8)–P(1)–Rh(1) | 109(1) | C(36)–O(1)–Rh(1) | 119(2) | C(19)–P(2)–C(6) | 105(2) | C(25)–P(2)–C(6) 111(2) |
| C(13)–P(1)–Rh(1) | 107(1) | C(30)–P(1)–Rh(1) | 125(1) | C(26)–C(25)–P(2) | 122(2) | O(4)–Rh(1)–O(1) 82.1(8) |

mixtures of doubly metallated diastereoisomers. By slow diffusion of hexane in a dichloromethane solution of **5** single crystals suitable for X-ray analysis were obtained.

Thermal treatment of adduct **2**, in refluxing toluene–acetic acid, gave $[Rh_2(O_2CMe)_4]$ and the doubly metallated species $[Rh_2(O_2CMe)_2\{[(C_6H_4)PhP(C_5H_4)]_2Fe\}(HO_2CMe)]$. The same species can be obtained in higher yield by reaction of $[Rh_2(O_2CMe)_4(MeOH)_2]$ and $[Fe(C_5H_4PPh_2)_2]$ (1:1) in refluxing acetic acid during 4 h. Purification of the resulting solution (as described in the Experimental section) yields compound **6**. The $^{31}P$ NMR spectrum consists of a signal at $\delta_P$ 19.12 [double doublet, $^1J(Rh–P)$ = 154.4, $^2J(Rh–P)$ = 9.1 Hz] which indicates that the two phosphorus atoms are magnetically equivalent. The data suggest that the two phosphorus atoms are in a head-to-head conformation which has been confirmed by X-ray diffraction methods.

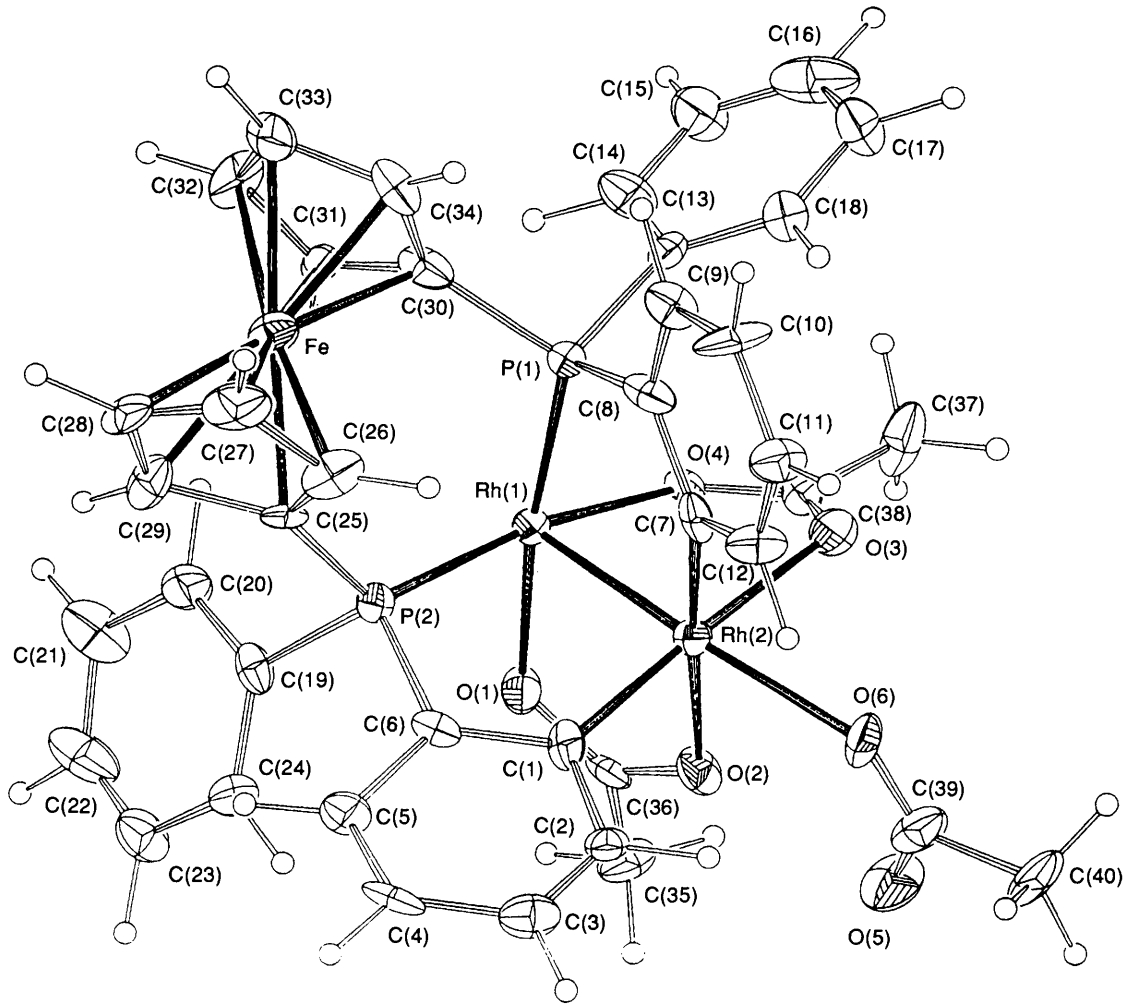



**Fig. 2** A PLATON diagram for compound **6**

*Molecular Structures of* $[Rh_2(O_2CMe)_2\{[(C_6H_4)PhP(C_5H_4)]Fe(C_5H_5)\}_2(HO_2CMe)_2]$ **5** *and* $[Rh_2(O_2CMe)_2\{[(C_6H_4)PhP(C_5H_4)]_2Fe\}(HO_2CMe)]\cdot CH_2Cl_2$ **6**. Views of the molecular structures of complexes **5** and **6** are shown in Figs. 1 and 2, respectively. Important bond distances and angles are listed in Tables 2 and 3 and positional parameters are given in Tables 4 and 5. In the structure of **5** the two rhodium atoms are bridged by two acetate groups and two diphenylphosphinoferrocenes metallated in one phenyl ring; two oxygens of two acetic acid molecules occupying the axial positions complete the slightly distorted octahedral co-ordination [angles in the range 83.8(2)–96.3(3)°] around the metals. The metallated phosphines are in a head-to-tail configuration. The value of the Rh–Rh bond distance, 2.504(1) Å, falls within the range reported for dirhodium compounds of comparable structure.[7]

The rather long Rh–O bond distances involving the axial acetic acid molecules, 2.392(6) and 2.295(6) Å, are indicative of the high *trans* effect of the metal–metal bond. The equatorial Rh–O distances are in the range 2.158(6)–2.202(7) Å, those *trans* to carbon being longer than the rest, in agreement with the expected order of *trans* effect of M–C and M–P bonds. No significant differences are found for the Rh–P, Rh–C and Rh–O distances around each rhodium atom.

According to the torsion angles observed about the rhodium–rhodium bond [falling in the range 12.8(2)–15.3(2)°], the two rhodium atoms are far from a totally eclipsed configuration. The torsion angle for the four atoms O(5)–Rh(1)–Rh(2)–O(7) is 1.0(9)° (see Fig. 1). The Rh–Rh–O axial angles, 165.5(2) and 167.4(2)°, deviate from linearity, as in other doubly metallated complexes.[6d,7c,h] It was suggested that steric interactions between the non-metallated phenyl rings and the axial ligands are responsible for these deviations.[6d] Fig. 1 shows the crystal structure of one of the three possible diastereoisomers for **5** which has been represented schematically as *a* in Scheme 2.

The crystal structure of complex **6** confirms the presence of one $Fe(C_5H_4PPh_2)_2$ ligand metallated in one of the two phenyl rings attached to each $PPh_2$ group. The two metallated carbon atoms are bonded to the same Rh atom. Two cisoid bridging acetate groups complete the co-ordination. The co-ordination sphere around each rhodium atom is different. Excluding the metal–metal bond the Rh atoms have $O_3C_2$ and $P_2O_2$ environments. The absence of axial ligands for one of the atoms must be due to the strong steric hindrance produced by the bidentate phosphine ligand. The rhodium–rhodium bond length is 2.508(4). The equatorial Rh–O distances are in the range 2.12(2)–2.24(2) Å, and again those *trans* to carbon are longer than those *trans* to P. The axial Rh–O bond distance involving the acetic acid molecule is 2.26(2), only slightly longer than the Rh–O equatorial bond, unlike what is observed for **3** and related complexes.

The torsion angles about the rhodium–rhodium bond are in the range 10.7(9)–20(3)° indicating a conformation closer to eclipsed than to alternated. The Rh–Rh–O axial angle, 167.2(6)°, deviates from linearity, as in other doubly metallated complexes.[6d,7c,h]

*Electrochemical Results.*—The results of electrochemical measurements for the described compounds are summarized in Table 6. The cyclic voltammograms always exhibit two consecutive oxidation peaks at about 0.7 V due to the $Fe^{2+}$–$Fe^{3+}$ couple and at about 1.20 V associated with the $Rh_2^{4+}$–$Rh_2^{5+}$

**Table 4** Fractional positional parameters for complex **5**

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Rh(1) | 0.216 84(3) | 0.242 24(3) | 0.709 62(2) | C(26) | 0.003 7(4) | 0.259 9(5) | 0.790 2(4) |
| Rh(2) | 0.125 71(3) | 0.227 03(3) | 0.638 75(2) | C(31) | 0.177 3(5) | 0.374 7(5) | 0.781 0(3) |
| Fe(1) | 0.144 62(8) | 0.429 40(8) | 0.841 88(6) | C(32) | 0.227 9(5) | 0.366 8(6) | 0.823 0(4) |
| Fe(2) | 0.146 62(8) | 0.420 82(7) | 0.499 32(5) | C(33) | 0.256 0(6) | 0.427 9(7) | 0.833 8(4) |
| P(1) | 0.136 2(1) | 0.306 2(1) | 0.747 00(8) | C(34) | 0.226 3(6) | 0.473 8(6) | 0.801 5(5) |
| P(2) | 0.189 2(1) | 0.298 6(1) | 0.594 16(8) | C(35) | 0.176 0(6) | 0.441 2(5) | 0.767 6(4) |
| O(1) | 0.289 2(3) | 0.177 2(3) | 0.668 8(2) | C(36) | 0.083 7(7) | 0.389 4(7) | 0.900 1(5) |
| O(2) | 0.196 7(3) | 0.144 2(3) | 0.618 2(2) | C(37) | 0.124 5(7) | 0.443 5(8) | 0.916 4(5) |
| O(3) | 0.169 2(3) | 0.152 5(3) | 0.739 3(2) | C(38) | 0.104 3(9) | 0.496 9(8) | 0.889 2(6) |
| O(4) | 0.070 2(3) | 0.157 4(3) | 0.687 6(2) | C(39) | 0.048 0(8) | 0.476(1) | 0.855 3(5) |
| O(5) | 0.302 2(3) | 0.232 0(3) | 0.773 9(2) | C(40) | 0.038 2(7) | 0.410 2(9) | 0.862 0(6) |
| O(6) | 0.272 6(6) | 0.136 9(5) | 0.802 0(4) | C(51) | 0.250 3(4) | 0.347 1(4) | 0.633 1(3) |
| O(7) | 0.046 3(3) | 0.184 5(3) | 0.573 9(2) | C(52) | 0.265 5(4) | 0.321 8(4) | 0.682 0(3) |
| O(8) | 0.099 9(5) | 0.088 5(4) | 0.562 3(3) | C(53) | 0.319 8(4) | 0.356 0(4) | 0.711 0(3) |
| C(1) | 0.261 3(6) | 0.139 3(4) | 0.636 7(4) | C(54) | 0.352 7(5) | 0.411 3(4) | 0.692 7(3) |
| C(2) | 0.309 6(6) | 0.083 8(5) | 0.616 7(4) | C(55) | 0.336 5(5) | 0.435 5(4) | 0.645 1(4) |
| C(3) | 0.105 4(6) | 0.133 8(4) | 0.725 3(3) | C(56) | 0.285 8(5) | 0.402 9(4) | 0.614 8(3) |
| C(4) | 0.068 9(6) | 0.080 2(5) | 0.754 9(4) | C(61) | 0.249 8(5) | 0.260 8(4) | 0.546 0(3) |
| C(5) | 0.324 7(8) | 0.186 3(7) | 0.794 8(6) | C(62) | 0.325 9(5) | 0.267 9(5) | 0.548 6(4) |
| C(6) | 0.381 0(6) | 0.181 1(6) | 0.834 3(5) | C(63) | 0.370 2(6) | 0.239 1(6) | 0.510 5(5) |
| C(7) | 0.044 0(6) | 0.131 0(6) | 0.557 3(4) | C(64) | 0.339 7(8) | 0.202 9(6) | 0.472 9(5) |
| C(8) | −0.015 0(6) | 0.105 7(5) | 0.523 5(4) | C(65) | 0.264 1(8) | 0.192 6(6) | 0.471 3(4) |
| C(11) | 0.068 3(4) | 0.338 0(4) | 0.703 2(3) | C(66) | 0.219 3(5) | 0.221 8(4) | 0.507 5(3) |
| C(12) | 0.020 5(4) | 0.388 8(4) | 0.715 4(3) | C(71) | 0.132 5(5) | 0.355 7(4) | 0.557 8(3) |
| C(13) | −0.037 7(5) | 0.404 6(4) | 0.683 0(3) | C(72) | 0.038 2(5) | 0.393 8(5) | 0.506 3(4) |
| C(14) | −0.048 9(5) | 0.366 7(4) | 0.639 5(3) | C(73) | 0.085 3(5) | 0.340 5(5) | 0.516 1(3) |
| C(15) | −0.001 2(5) | 0.316 6(4) | 0.627 9(3) | C(74) | 0.055 3(6) | 0.442 7(5) | 0.543 0(4) |
| C(16) | 0.058 5(4) | 0.300 7(4) | 0.658 4(3) | C(75) | 0.112 7(5) | 0.418 8(4) | 0.574 4(3) |
| C(21) | 0.079 6(4) | 0.264 2(4) | 0.795 5(3) | C(76) | 0.255 2(7) | 0.421 6(8) | 0.475 4(5) |
| C(22) | 0.113 5(5) | 0.235 4(5) | 0.837 2(3) | C(77) | 0.210 2(8) | 0.403 0(7) | 0.434 5(5) |
| C(23) | 0.070 6(7) | 0.204 5(6) | 0.874 3(4) | C(78) | 0.159 6(9) | 0.452 9(9) | 0.426 2(4) |
| C(24) | −0.003 9(7) | 0.202 5(6) | 0.870 6(5) | C(79) | 0.172 6(9) | 0.504 8(7) | 0.462 2(6) |
| C(25) | −0.037 0(6) | 0.229 3(6) | 0.829 1(5) | C(80) | 0.232 9(8) | 0.484 7(7) | 0.490 8(4) |

**Table 5** Fractional positional parameters for complex **6**

| Atom | *x* | *y* | *z* | Atom | *x* | y | z |
|---|---|---|---|---|---|---|---|
| Rh(1) | 0.7802(2) | 0.3105(1) | 0.1242(1) | C(15) | 1.127(3) | 0.329(3) | 0.027(2) |
| Rh(2) | 0.7208(2) | 0.3365(1) | 0.2375(1) | C(16) | 1.188(3) | 0.381(2) | 0.061(2) |
| Fe | 0.8908(4) | 0.0716(3) | 0.1140(2) | C(17) | 1.182(3) | 0.395(2) | 0.125(2) |
| P(1) | 0.9300(6) | 0.2596(5) | 0.1705(4) | C(18) | 1.106(3) | 0.360(2) | 0.161(2) |
| P(2) | 0.6882(6) | 0.1975(5) | 0.1210(4) | C(19) | 0.566(2) | 0.207(2) | 0.069(2) |
| Cl(1) | 0.329(1) | 0.3663(9) | 0.2998(8) | C(20) | 0.565(3) | 0.223(2) | 0.002(2) |
| Cl(2) | 0.328(1) | 0.2058(9) | 0.256(1) | C(21) | 0.476(3) | 0.234(3) | −0.040(2) |
| O(1) | 0.647(1) | 0.379(1) | 0.086(1) | C(22) | 0.382(4) | 0.225(2) | −0.015(2) |
| O(2) | 0.569(2) | 0.371(1) | 0.180(1) | C(23) | 0.376(3) | 0.207(3) | 0.052(3) |
| O(3) | 0.764(2) | 0.460(1) | 0.218(1) | C(24) | 0.470(3) | 0.199(2) | 0.096(2) |
| O(4) | 0.853(2) | 0.424(1) | 0.132(1) | C(25) | 0.749(3) | 0.115(2) | 0.081(2) |
| O(5) | 0.679(2) | 0.513(1) | 0.316(1) | C(26) | 0.819(2) | 0.126(2) | 0.030(2) |
| O(6) | 0.647(2) | 0.383(1) | 0.328(1) | C(27) | 0.847(3) | 0.051(2) | 0.011(2) |
| C(1) | 0.673(2) | 0.229(2) | 0.252(1) | C(28) | 0.809(3) | −0.008(2) | 0.048(2) |
| C(2) | 0.648(3) | 0.203(2) | 0.318(2) | C(29) | 0.743(3) | 0.030(2) | 0.093(2) |
| C(3) | 0.601(3) | 0.130(2) | 0.332(2) | C(30) | 0.963(2) | 0.155(2) | 0.173(1) |
| C(4) | 0.579(4) | 0.078(2) | 0.277(2) | C(31) | 0.915(3) | 0.098(2) | 0.212(2) |
| C(5) | 0.602(2) | 0.097(2) | 0.212(2) | C(32) | 0.958(3) | 0.021(3) | 0.200(2) |
| C(6) | 0.652(2) | 0.170(2) | 0.201(2) | C(33) | 1.035(3) | 0.033(2) | 0.156(2) |
| C(7) | 0.860(2) | 0.314(2) | 0.289(2) | C(34) | 1.043(3) | 0.114(2) | 0.138(2) |
| C(8) | 0.945(2) | 0.285(2) | 0.258(1) | C(35) | 0.471(3) | 0.428(3) | 0.084(2) |
| C(9) | 1.047(3) | 0.273(2) | 0.295(2) | C(36) | 0.569(2) | 0.390(2) | 0.123(2) |
| C(10) | 1.054(3) | 0.286(2) | 0.361(2) | C(37) | 0.843(3) | 0.563(2) | 0.159(2) |
| C(11) | 0.966(3) | 0.319(2) | 0.392(2) | C(38) | 0.825(2) | 0.477(2) | 0.171(2) |
| C(12) | 0.876(2) | 0.330(2) | 0.357(1) | C(39) | 0.642(3) | 0.452(2) | 0.346(2) |
| C(13) | 1.039(2) | 0.307(2) | 0.130(2) | C(40) | 0.585(3) | 0.466(2) | 0.408(2) |
| C(14) | 1.047(3) | 0.289(2) | 0.064(2) | C(41) | 0.385(4) | 0.293(4) | 0.257(3) |

couple. All the processes are electrochemically reversible at the sweep rate of 0.1 V $s^{-1}$.

For compound **3** both oxidation peaks are of equal intensity and, after exhaustive electrolysis at +0.70 V, 1F $mol^{-1}$ of dimer is consumed. The resulting solution shows one oxidation and one reduction peak indicating a relative stability for the intermediate cationic species $\mathbf{3}^{+}$. A similar electrochemical behaviour is observed for complex **5**; however, in this case the first peak, corresponding to the simultaneous oxidation of the two ferrocenyl groups present, is approximately twice the intensity of the second one.

We have also studied the electrochemistry of singly and

**Table 6** Electrochemical data

| Compound | $E_p$*/V *vs.* SCE | |
|---|---|---|
| | $Fe^{2+}$–$Fe^{3+}$ | $Rh_2^{4+}$–$Rh_2^{5+}$ |
| **7** | | 1.02 |
| **8** (H-T) | | 0.90 |
| **9** (H-H) | | 0.84 |
| **3** | 0.68 | 1.18 |
| **5** | 0.60 | 1.20 |
| **6** | 0.82 | 1.12 |

* Sweep rate = 0.1 $V s^{-1}$.

doubly metallated compounds with triphenylphosphine $[Rh_2(O_2CMe)_3(C_6H_4PPh_2)(HO_2CMe)_2]$ **7**, $[Rh_2(O_2CMe)_2(C_6H_4PPh_2)_2(HO_2CMe)_2]$ (head-to-tail structure) **8** and $[Rh_2(O_2CMe)_2(C_6H_4PPh_2)_2(HO_2CMe)_2]$ (head-to-head structure) **9**, which have been crystallographically identified.[6d,7f] Complexes **7**–**9** in $CH_2Cl_2$ solution show, by cyclic voltammetry one-electron reversible oxidation processes corresponding to the couple $Rh_2^{4+}$–$Rh_2^{5+}$ (see Table 6). From the electrochemical data summarized in Table 6 we conclude that for compounds **7**–**9** the oxidation $Rh_2^{4+} \longrightarrow Rh_2^{5+}$ occurs at lower potentials than for the structurally analogous **3**, **5** and **6** with ferrocenyl groups in the metallated phosphine. Also, the doubly metallated compound **8** oxidizes at a lower potential than that for **7**; the reverse trend is observed for the isostructural compounds with $Fe(C_5H_5)(C_5H_4PPh_2)$, **3** and **5**. So, it is quite evident that the presence of one ferrocenyl group in one metallated phosphine increases the oxidation potential of the $Rh_2^{4+}$–$Rh_2^{5+}$ couple indicating that the two redox centres are mutually influenced.

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