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Ortho-Metalation of DPPE across a Dirhodium(II,II) Core. Synthesis and X-ray Crystal Structure of [Rh₂(form)(O₂CCF₃){(C₆H₅)₂P(CH₂)₂P(C₆H₅)(C₆H₄)}]-(DPPE)]CF₃COO (form = N,N'-Di-p-tolylformamidinate Anion, DPPE = 1,2-Bis(diphenylphosphino)ethane)

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The class of coordination compounds containing the Rh₂⁴⁺ core still represents an attractive field of research due to their many interesting structural, chemical,¹ catalytic,² and biochemical properties.³ While few additional data were reported on the Rh₂(carboxylate)₄ systems, there were a number of significant reports on Rh₂⁴⁺ complexes containing phosphorus donors⁴ and especially anionic bidentate nitrogen donors as bridging ligands.⁵ The presence of the latter ligands, on the one hand, enhances the metal-based redox processes facilitating the thermodynamic access to mixed-valent species. On the other hand, it makes the dirhodium(II,II) species even more inert toward equatorial substitution and in some cases it prevents axial reactivity too. For example, the complex Rh₂(form)₄ (form = N,N'-di-p-tolylformamidinate anion)⁵ is inert toward equatorial substitution and shows only poor axial reactivity for steric reasons. On the contrary, the complex Rh₂(form)₂(O₂CCF₃)₂(H₂O)₂⁶ has a rich chemistry and has proven to be an ideal starting material for the synthesis of other Rh₂⁴⁺ complexes. Its chemistry is characterized, in addition to an usual axial reactivity, also by a remarkable lability of the trifluoroacetate groups, which leads to mild conditions for the coordination of neutral ligands at the equatorial position. We recently reported conclusive evidence for such behavior synthesizing Rh₂⁴⁺ complexes containing monodentate (PPh₃, PCy₃)⁷ or bidentate neutral ligands (Ph₂PPy)⁸ in the equatorial position. In all the reactions performed the Rh–(form)₂–Rh fragment remains intact.

As a prelude to detailed investigation of the chemistry of Rh₂(form)₂(O₂CCF₃)₂(H₂O)₂ with bidentate phosphorus and nitrogen ligands, we have examined the reactivity of the above complex with dppe. This leads to an unexpected and novel result, namely an ortho-metalation under mild conditions of a diphosphine across a Rh–Rh bond. In this paper we report the synthesis and crystallographic characterization of the complex [Rh₂-(form)(O₂CCF₃){(C₆H₄)(C₆H₅)P(CH₂)₂P(C₆H₅)₂}(dppe)]-CF₃COO (dppe = 1,2-bis(diphenylphosphino)ethane), which represents the first example of a diphosphine ortho-metalated across a metal–metal bond as well as the first report on a dirhodium(II,II) complex supported by three different bridging ligands.

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Table I. Crystallographic Data

formula	C₇₁H₆₃F₆N₂O₄.₅P₄Rh₂	space group	*Pbca*
fw	1460	*T,* °C	23
a, Å	20.578 (4)	λ, Å	0.71073
b, Å	23.808 (4)	ρ_calcd, g cm⁻¹	1.52
c, Å	26.078 (4)	μ, cm⁻¹	6.4
V, Å³	12776.1	*Rᵃ*	0.049
Z	8	*R_wᵇ*	0.052

ᵃ R = [∑|F_o| − |F_c|]/∑|F_o|. ᵇ R_w = [∑w(|F_o| − |F_c|)²/∑w|F_o|²]^{1/2}; w = n/(σ²(F_o)).

Experimental Section

Rh₂(form)₂(O₂CCF₃)₂(H₂O)₂ was prepared according to the literature procedure.⁶ Other reagents and solvents were used as received. Infrared spectra were recorded on a Perkin-Elmer FT 43 instrument. Elemental analyses were performed by the Microanalytical Laboratory of the Organic Chemistry Institute of Milan and Analitische Laboratorien Malissa and Reuter, Elbach, West Germany.

Synthesis of [Rh₂(form)(O₂CCF₃){(C₆H₄)(C₆H₅)P(CH₂)₂P(C₆H₅)₂}-(dppe)]CF₃COO. Crude dppe (0.07 g, 0.17 mmol) was added to a stirred solution of Rh₂(form)₂(O₂CCF₃)₂(H₂O)₂ (0.081 g, 0.08 mmol) in diethyl ether (20 mL). The solution changed rapidly to a dark-green, red-orange, and again green color and then slowly to a red color. Stirring of the mixture was continued for 4 h whereupon a dark-red precipitate also formed. After the solvent was removed via a syringe, the residue was washed with diethyl ether and crystallized from CH₂Cl₂/heptane. Yield: 67%. Anal. Calcd for C₇₁H₆₂N₂P₄O₄F₆Rh₂: C, 58.73; H, 4.37; N, 1.92; P, 8.53; F, 7.84. Found: C, 57.89; H, 4.38; N, 2.06; P, 9.0; F, 8.0. Infrared spectrum (Nujol mull, cm⁻¹): ν(N=C=N) 1568; ν_asym(CO₂) 1683 (s), 1635 (s). Molar conductivity (Ω⁻¹ cm² M⁻¹): λ 62 (CH₂Cl₂, 5 × 10⁻⁴ M), 121 (CH₃CN, 5 × 10⁻⁴ M).

X-ray Data Collection and Structure Refinement. Suitable crystals of the title complex were obtained by slow evaporation of solvent from a CHCl₃–heptane solution. Diffraction measurements were made on Siemens R3m/v four-circle diffractometers using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Accurate unit-cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 25 strong reflections in the range 14° < 2θ < 28°. The compound crystallizes in the orthorhombic *Pbca* space group, with parameters as shown in Table I. Lorentz and polarization corrections were applied to the intensity data, but no absorption correction was made due to the low absorption coefficient and the fairly uniform dimensions of the crystal. The structure was solved by using Patterson methods, successive least-squares refinements, and difference Fourier maps. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were added at calculated positions and included in the structure factor calculations with fixed thermal parameters.

Scattering factors for non-hydrogen atoms were taken from ref 9 and for hydrogen atoms from ref 10. Anomalous dispersion corrections for Rh and P atoms were taken from ref 11. Of 12333 measured independent reflections, 5825 having I > 3σ(I) were used to refine 508 parameters to final residuals of R = 0.049 and R_w = 0.052, with w = 1.00/(σ²(F_o) + 0.001064F_o²), quality-of-fit indicator = 1.401, and the largest peak = 0.79 e Å⁻³.

All calculations were performed with the SHELX76¹² and PARST¹³ sets

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Table II. Selected Bond Distances (Å) and Angles (deg)

Distances

Rh(2)–Rh(1)	2.7331 (8)	Rh(2)–P(1)	2.265 (2)
Rh(2)–P(2)	2.195 (2)	Rh(2)–O(2)	2.147 (5)
Rh(2)–N(1)	2.072 (6)	Rh(1)–P(3)	2.327 (2)
Rh(1)–P(4)	2.367 (2)	Rh(1)–O(1)	2.235 (5)
Rh(1)–N(2)	2.149 (6)	Rh(1)–C(26)	2.020 (7)
P(1)–C(6)	1.825 (8)	P(1)–C(7)	1.837 (8)
P(1)–C(13)	1.839 (8)	C(5)–C(6)	1.52 (1)
C(5)–P(2)	1.860 (9)	P(2)–C(25)	1.829 (8)
P(2)–C(19)	1.814 (9)	P(3)–C(31)	1.812 (8)
P(3)–C(33)	1.838 (8)	P(3)–C(39)	1.831 (8)
C(31)–C(32)	1.54 (1)	C(32)–P(4)	1.826 (8)
P(4)–C(45)	1.842 (8)	P(4)–C(66)	1.834 (8)
C(1)–C(2)	1.54 (1)	C(1)–O(1)	1.24 (1)
C(1)–O(2)	1.24 (1)	C(2)–F(1)	1.25 (1)
C(2)–F(3)	1.22 (2)	C(2)–F(5)	1.30 (2)
C(3)–C(4)	1.54 (2)	C(3)–O(3)	1.19 (2)
C(3)–O(4)	1.20 (2)	C(4)–F(2)	1.26 (2)
C(4)–F(4)	1.25 (2)	C(4)–F(6)	1.35 (2)
N(1)–C(58)	1.31 (1)	N(1)–C(59)	1.41 (1)
C(58)–N(2)	1.31 (1)	N(2)–C(51)	1.44 (1)

Angles

O(2)–Rh(2)–N(1)	81.6 (2)	P(2)–Rh(2)–N(1)	94.9 (2)
P(2)–Rh(2)–O(2)	174.6 (2)	P(1)–Rh(2)–N(1)	157.2 (2)
P(1)–Rh(2)–O(2)	101.0 (2)	P(1)–Rh(2)–P(2)	83.75 (8)
Rh(1)–Rh(2)–N(1)	80.7 (2)	Rh(1)–Rh(2)–O(2)	90.8 (1)
Rh(1)–Rh(2)–P(2)	84.57 (6)	Rh(1)–Rh(2)–P(1)	121.68 (6)
Rh(2)–Rh(1)–C(26)	97.5 (2)	Rh(2)–Rh(1)–N(2)	84.3 (2)
Rh(2)–Rh(1)–O(1)	75.8 (1)	Rh(2)–Rh(1)–P(4)	163.06 (6)
Rh(2)–Rh(1)–P(3)	99.22 (6)	N(2)–Rh(1)–C(26)	85.3 (3)
O(1)–Rh(1)–C(26)	172.8 (2)	O(1)–Rh(1)–N(2)	91.2 (2)
P(4)–Rh(1)–C(26)	98.9 (2)	P(4)–Rh(1)–N(2)	93.0 (2)
P(4)–Rh(1)–O(1)	87.5 (1)	P(3)–Rh(1)–C(26)	89.5 (2)
P(3)–Rh(1)–N(2)	174.1 (2)	P(3)–Rh(1)–O(1)	94.4 (2)
P(3)–Rh(1)–P(4)	85.05 (7)	Rh(2)–P(1)–C(13)	96.9 (3)
Rh(1)–O(1)–C(1)	127.3 (5)	Rh(2)–O(2)–C(1)	112.9 (5)
O(3)–C(3)–O(4)	129 (1)	C(4)–C(3)–O(4)	116 (1)
N(1)–C(58)–N(2)	125.1 (7)	Rh(1)–N(2)–C(58)	115.8 (5)

Table III. Selected Fractional Atomic Coordinates

atom	x	y	z
Rh(2)	0.16523 (3)	0.30979 (2)	0.08856 (2)
Rh(1)	0.12899 (3)	0.20722 (2)	0.12594 (2)
P(1)	0.2391 (1)	0.36415 (9)	0.12960 (8)
C(5)	0.1371 (4)	0.3961 (3)	0.1889 (3)
C(6)	0.2099 (4)	0.3869 (3)	0.1924 (3)
P(2)	0.0981 (1)	0.34307 (9)	0.14645 (8)
P(3)	0.2186 (1)	0.18864 (9)	0.17764 (8)
C(31)	0.1974 (4)	0.1234 (3)	0.2092 (3)
C(32)	0.1784 (4)	0.0814 (3)	0.1665 (3)
P(4)	0.1072 (1)	0.10997 (8)	0.13384 (8)
C(1)	0.2124 (4)	0.2200 (4)	0.0256 (3)
C(2)	0.2440 (7)	0.1933 (4)	−0.0220 (4)
O(1)	0.1808 (3)	0.1873 (2)	0.0528 (2)
O(2)	0.2252 (3)	0.2704 (2)	0.0316 (2)
C(3)	0.2394 (6)	−0.0049 (4)	0.2804 (5)
C(4)	0.2519 (8)	−0.0283 (6)	0.3345 (6)
O(3)	0.1868 (5)	−0.0146 (4)	0.2635 (4)
O(4)	0.2841 (5)	0.0183 (5)	0.2603 (4)
F(1)	0.2725 (5)	0.1478 (3)	−0.0138 (3)
F(2)	0.2752 (7)	0.0068 (5)	0.3658 (3)
F(3)	0.2801 (7)	0.2232 (3)	−0.0470 (3)
F(4)	0.2066 (5)	−0.0547 (5)	0.3553 (4)
F(5)	0.1981 (5)	0.1776 (6)	−0.0533 (4)
F(6)	0.3018 (6)	−0.0652 (4)	0.3316 (4)
N(1)	0.0932 (3)	0.2901 (3)	0.0361 (2)
C(58)	0.0449 (4)	0.2557 (3)	0.0451 (3)
N(2)	0.0401 (3)	0.2229 (3)	0.0851 (2)

of programs on the IBM 4341 computer at the "Centro di Calcolo dell'Università di Messina".

Selected bond distances and angles and positional parameters are listed in Tables II and III, respectively. Complete tables of bond distances and
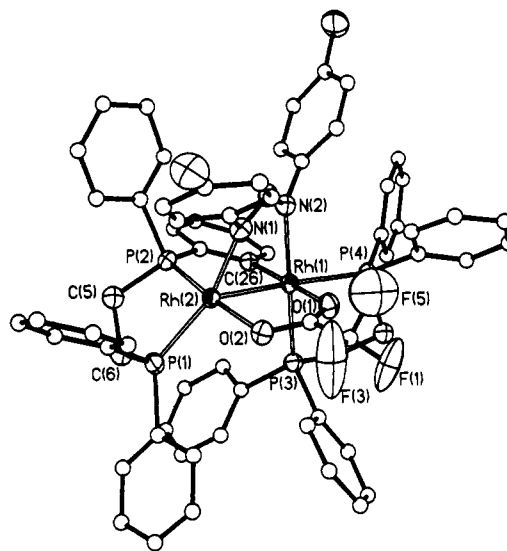
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Figure 1. ORTEP view of [Rh$_2$(form)(O$_2$CCF$_3$){(C$_6$H$_4$)(C$_6$H$_5$)P-(CH$_2$)$_2$P(C$_6$H$_5$)$_2$}(dppe)]CF$_3$COO, showing 40% probability thermal ellipsoids.

angles, positional parameters, hydrogen atom coordinates, anisotropic thermal parameters, and structure factors are available as supplementary material.

Results and Discussion

Addition of 2 equiv of dppe (1,2-bis(diphenylphosphino)ethane) to a diethyl ether solution of Rh$_2$(form)$_2$(O$_2$CCF$_3$)$_2$(H$_2$O)$_2$ results in several color changes which indicate that the reaction proceeds via several steps. Microanalysis of the red crystals, obtained after minimal manipulation in workup, shows that these crystals contain only one formamidinate group for the dimeric unit and have the formula Rh$_2$(form)(O$_2$CCF$_3$)$_2$(dppe)$_2$. The solid-state IR spectrum exhibits, in the 1600–1700-cm^{-1} region, two strong absorptions at 1635 and 1685 cm^{-1} give evidence of the presence of nonequivalent trifluoroacetate groups. The low-frequency value is consistent with those of chelating or bridging trifluoroacetate groups, while the band at 1685 cm^{-1} suggests the occurrence of monoligated or uncoordinated CF$_3$COO groups. On the other hand molar conductivity measurements, carried out in acetonitrile or dichloromethane, show unambiguously that the complex behaves as 1:1 electrolyte.

Cyclic voltammetric studies indicate irreversible electrochemical oxidations. The electrochemically generated species are diamagnetic, suggesting that the one-electron oxidation occurs with disruption of the dimeric unit.

The unequivocal identity of the title complex was ascertained by the X-ray analysis, which shows the presence of an ortho-metalated dppe. Ortho-metalation of aryl- or mixed aryl/alkylphosphines across a dirhodium(II,II) core is not unusual[14] whereas examples of phosphines ortho-metalated across other metal–metal systems are rarer.[14a,15]

Molecular Structure of [Rh$_2$(form)(O$_2$CCF$_3$){(C$_6$H$_5$)$_2$P-(CH$_2$)$_2$P(C$_6$H$_5$)(C$_6$H$_4$)}(dppe)]CF$_3$COO·0.5H$_2$O. The crystal structure of the title complex consists of discrete [Rh$_2$-(form)(O$_2$CCF$_3$){(C$_6$H$_5$)$_2$P(CH$_2$)$_2$P(C$_6$H$_5$)(C$_6$H$_4$)}(dppe)]$^+$ cations and CF$_3$COO anions. Figure 1 shows an ORTEP view of the cation, which consists of an unsymmetrical dirhodium unit bridged by three different ligands, a trifluoroacetate, a formamidinate,

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and an ortho-metalated dppe. A second chelated dppe completes the coordination sphere around Rh(1), which adopts a pseudooctahedral geometry, while the Rh(2) atom is in a distorted trigonal-bipyramidal geometry. The Rh–Rh bond distance [2.7331 (8) Å], which in dirhodium(II,II) complexes is the most salient feature, lies at the top range of distances observed in this class of compounds.[1] The reduced number of bridging ligands and the constraining effect of the bridging ortho-metalated dppe can explain the significant lengthening of the Rh–Rh bond distance in the title complex. A similar elongation of the metal–metal separation [2.770 (3) Å] has been recently found in the complex $[Rh_2(dppm)_2[(C_6H_5)_2(C_6H_4)P]_2Cl_2$,[16] where two ortho-metalated triphenylphosphines are present. Each diphosphine occupies an equatorial and an axial site. The Rh–P distances range from 2.195 (2) to 2.367 (2) Å, with the longest Rh–P trans to the Rh–Rh bond, and are comparable with the values found in other dirhodium(II,II) derivatives.[1]

The values of 163.06 (6) and 157.2 (2)° for the Rh(2)–Rh(1)–P(4) and N(1)–Rh(2)–P(1) bond angles are clearly imposed by the bidentate coordination of the dppe groups, which are then responsible for the distortion from the normal octahedral and square-pyramidal geometry around Rh(1) and Rh(2), respectively. All the bridging ligands are not planar with values of 10.0 (2), 10.2 (3), and 21.4 (3)° for the P(2)–Rh–Rh–C, O–Rh–Rh–O, and N–Rh–Rh–N torsion angles, respectively. The trifluoroacetate group is bonded to the dimetal unit by different Rh–O distances [Rh(1)–O(1) = 2.235 (5) Å; Rh(2)–O(2) = 2.147 (5) Å] with the longest value reflecting the trans influence of the C(26) ortho-metalated carbon atom. The formamidinate fragment is bonded to the dirhodium unit in the usual way, namely σ,σ-N,N′ with delocalized double bonds and by different Rh–N distances, the shortest being associated with the greatest deviation of the N(1)–Rh(2)–P(1) angle from linearity.

Although the mechanism of the reaction remains obscure, steric and electronic reasons might account for the ortho-metalation of one dppe. The formation of the title complex can be rationalized on the basis of initial bis-chelate dppe derivative generation. Given the steric demand of the phenyl and *p*-tolyl groups, one of the phenyl groups closely approaches the adjacent rhodium atom leading to formal transfer of an ortho proton to a formamidinate group followed by ortho-metalation and elimination of formamidine from the lantern structure.

It is worthwhile to mention that the analogous reaction of $Rh_2(O_2CCH_3)_4$ with dppe gives an insoluble material,[17] which, on the basis of analytical and IR data, was suggested to be a simple bis-axial adduct, while the complex $Mo_2(O_2CCH_3)_4$ gives with the diphosphine dmpe (dmpe = 1,1-bis(dimethylphosphino)ethane) infinite zigzag chains of $Mo_2(O_2CCH_3)_4$ units linked by the bidentate ligands.[18] The great tendency of dppe to form chelated complexes associated with the facile displacement of the trifluoroacetate groups from the lantern structure disfavor in the reaction reported here the formation of polymeric materials or simple axial adducts.

In conclusion the complex reported here shows some peculiar features. In fact, it represents the first example of ortho-metalation of a diphosphine across a metal–metal bond as well as the first report of a dirhodium(II,II) complex in which the Rh_2^{4+} core is supported by three different bridging ligands. A final comment concerns the formal oxidation state of the two rhodium atoms. The bridging trifluoroacetate and formamidinate as well as the ionic trifluoroacetate groups contribute three negative charges to the rhodium system, which charges are equally shared between the two rhodium atoms. Furthermore the ortho-metalated phenyl ring contributes one negative charge to Rh(2) so that the total charge on the two metal centers became unequally shared. On these bases, the title complex, owing to the asymmetric ar-

rangement of the ligands around the two rhodium atoms, may be best described as a formally mixed-valent complex with nonintegral oxidation states.

Supplementary Material Available: A fully numbered ORTEP diagram and Tables SI–SV, listing full crystal data, nonessential atomic distances and angles, hydrogen atom parameters, temperature factors, and complete positional parameters (10 pages); a table of calculated and observed structure factors (33 pages). Ordering information is given on any current masthead page.

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Photoredox Pathways to Spatially Restricted Metallopolymeric Films

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Introduction

There now exists an extensive body of synthesis[1–3] and applications-based[2–4] chemistry for redox-active metallopolymeric films. The applications include electrochemical catalysis, energy conversion, electrochromic displays, analysis, and molecular and ionic sensing.[2–4] Films for these purposes are most commonly assembled via electrochemically initiated radical polymerization pathways or, less often, by simple spin casting of preformed metallopolymers (or metal-free polymer backbones). Both approaches lead to films of more or less uniform composition, which effectively cover the entire available exposed surface support area.

In pursuit of additional applications (remote optical sensing and advanced electrochromics), we have devised an additional method for assembling films. The new approach, which is based on simple redox quenching processes following photochemical excitation, was designed to meet three specific requirements: (1) film assembly on transparent surfaces, (2) spatially selective assembly, and (3) assembly, if necessary, on insulating surfaces. Elements 1 and 2 were deemed desirable for electrochromic applications in which small multicomponent (multicolor) electrochromic images (alphanumerics, etc.) might be expanded and displayed via simple light projection through a transparent electrode surface. Element 3 (together with one or both of the others) could prove exceptionally important in analytical applications (for example, liquid chromatography detection) in which metallopolymer luminescence would be employed as a reporter for specific film-bound analytes. (Note that metallopolymer luminescence is often extensively or completely quenched (by energy transfer) when metallic or semiconducting support surfaces are used.) While some of these objectives can be achieved with existing synthetic or assembly methods, for any given system it is difficult to achieve all three simultaneously. As indicated below, however, we have been reasonably successful in reaching these goals by employing a straightforward photoredox approach.

Experimental Section

Materials. Reagent grade acetonitrile was used as received. Tetrabutylammonium perchlorate (TBAP) was purchased from GFS Chem-

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