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Notes

Synthesis and NMR Investigation of Dirhodium(II) Formamidinate Complexes Containing Bidentate Phosphorus Donors. X-ray Crystal Structure of the Ortho-Metalated Complex $Rh_2(form)(\mu\text{-}O_2CCF_3)[(C_6H_4)(C_6H_5)P(CH_2)_2P(C_6H_5)_2](\sigma\text{-}O_2CCF_3)(p\text{-toluidine})$

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Introduction

In a previous work we reported that the Rh_2^{4+} complex $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ (form = *N*,*N′*-di-*p*-tolylformamidinate anion) easily reacts with 1,2-bis(diphenylphosphino)ethane (dppe), molar ratio 1:2, giving the species $[Rh_2(form)(O_2CCF_3)\{(C_6H_4)(C_6H_5)P(CH_2)_2P(C_6H_5)_2\}dppe]CF_3COO$ (**1**) containing one diphosphine ortho-metalated across the dirhodium core.[1] This species represents the first example of a diphosphine ortho-metalated across a metal−metal bond as well as the first report on a dirhodium(II) complex supported by three different bridging ligands. It also represents a further example of the propensity of P-donor ligands to undergo ortho-metalation across the Rh−Rh bond. This observation is supported by work carried out by Cotton and Lahuerta who showed that P-donors such as $P(C_6H_5)_3$,[2] $P(m\text{-}CH_3C_6H_4)_3$,[3] $P(C_6H_5)_2(C_6F_4Br)$,[4] and $P(o\text{-}ClC_6H_4)(C_6H_5)_2$[5] undergo, under more or less vigorous conditions, ortho-metalation across the Rh−Rh bond of the complexes $Rh_2(O_2CCH_3)_4$ and $Rh_2(O_2CCF_3)_4$. A search of the literature for reactions of this type reveals that the aforementioned reactions are rare for other metal−metal-bonded complexes.[6] The mechanism invoked for these reactions[2c] contains three main features: (i) axial coordination of the phosphorus ligand, (ii) axial−equatorial isomerization (very likely this is the crucial step of these reactions since it allows the close approach of one phenyl ring at the adjacent rhodium atom), and (iii) formal transfer of a proton from a phenyl group to an acetate or formamidinate fragment.

In order to assess the generality of such reactions and to evaluate the influence of the chain length on the reaction products, we now report the results of the 1:1 reactions between $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ and the diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ ($n = 1−4$). We report also the X-ray analysis of the ortho-metalated complex $Rh_2(form)(\mu\text{-}O_2CCF_3)[(C_6H_4)(C_6H_5)P(CH_2)_2P(C_6H_5)_2](\sigma\text{-}O_2CCF_3)(p\text{-toluidine})$.

Experimental Section

$Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ was prepared according to literature procedure.[7] 1,2-bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(diphenylphosphino)propane (dppp), and 1,2-bis(diphenylphosphino)butane (dppb) were all obtained from Strem and were used without further purification. Other reagents and solvents were used as received. Infrared spectra were recorded on a Perkin-Elmer FT 43 instrument. ^{31}P NMR spectra were obtained on a Perkin-Elmer AMX 300 instrument.

Synthesis of $Rh_2(form)_2(\mu\text{-}O_2CCF_3)(dppm)(\sigma\text{-}O_2CCF_3)$ (2). To a diethyl ether solution (20 mL) of $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ (0.2 g, 0.21 mmol) was added 0.017 g (0.21 mmol) of solid 1,2-bis(diphenylphosphino)methane (dppm). The resulting green solution was stirred at room temperature for 3 h. The filtrate was evaporated to dryness and the green powder obtained was crystallized from $CHC1_3$/n-heptane giving green needles of **2**. Yield: 113 mg. Anal. Calcd for $C_{59}H_{52}N_4P_2O_4F_6Rh_2$: C, 56.11; H, 4.15; N, 4.43; P, 4.90; F, 9.02. Found: C, 55.89; H, 4.31; N, 4.39; P, 5.11; F, 8.94. Infrared spectrum (Nujol mull, cm^{-1}): $\nu_{asym}(CO_2)$ 1645 (s), 1687 (s); (CH_3CN) $\nu_{asym}(CO_2)$ 1645 (s), 1695 (s). Molar conductivity (Ω^{-1} cm^2 M^{-1}): 180 (CH_3CN, 5×10^{-4} M). ^{31}P NMR ($CDCl_3$, *J* (Hz)): δ 7.37 ddd ($^1J_{Rh-P} = 123$; $^2J_{Rh-P} = 3.5$; $J_{P-P} = 52.6$), 18.81 ddd ($^1J_{Rh-P} = 137$; $^2J_{Rh-P} = 4$); (CD_3CN, AA′XX′ spin system): δ 15.5

Synthesis of $Rh_2(form)(\mu\text{-}O_2CCF_3)[(C_6H_4)(C_6H_5)P(CH_2)_2P(C_6H_5)_2](\sigma\text{-}O_2CCF_3)(p\text{-toluidine})$ (3). This complex was prepared by reacting a diethyl ether solution of $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ (0.091 g, 0.1 mmol) with solid dppe (0.04 g, 0.1 mmol) at room temperature for 4 h. After this time stirring was stopped and the resulting dichroic green−red solution was left standing for an additional 16 h, leading to the formation of **3** as red crystals. Yield: 59%. Anal. Calcd for $C_{60}H_{54}N_4P_2O_4F_6Rh_2$: C, 56.44; H, 4.26; N, 4.38; P, 4.85. Found: C, 56.04; H, 4.16; N, 4.28; P, 5.00. Infrared spectrum (Nujol mull, cm^{-1}): $\nu_{asym}(CO_2)$ 1716 (s), 1647 (s). Molar conductivity (Ω^{-1} cm^2 M^{-1}): 140 (CH_3CN, 5×10^{-4} M). ^{31}P NMR ($CDCl_3$, *J* (Hz)): δ 37.56 ddd ($^1J_{Rh-P} = 145.8$; $^2J_{Rh-P} = 3.6$; $J_{P-P} = 25.2$); 52.4 ddd ($^1J_{Rh-P} = 131.9$; $^2J_{Rh-P} = 3.8$).

Synthesis of $Rh_2(form)_2(O_2CCF3)_2(dppb)$ (4). Crude dppb (0.047 g, 0.1 mmol) was added to a stirred solution of $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ (0.1 g, 0.1 mmol) in CH_2C1_2 (30 mL). The solution changed rapidly to a dark green and then slowly to a yellow-red color. Stirring of the mixture was continued for 3 h. After the solvent was removed, the residue was crystallized from benzene/heptane. Yield: 63%. Anal. Calcd for $C_{62}H_{58}N_4P_2O_4F_6Rh_2$: C, 57.68; H, 4.52; N, 3.25; P, 4.79. Found: C, 57.40; H, 4.52; N, 3.21; P, 4.79. Infrared spectrum (Nujol mull, cm^{-1}): $\nu_{asym}(CO_2)$ 1632 (vs), 1657 (s). ^{31}P NMR ($CDCl_3$, *J* (Hz)): δ 30.67 dd ($^1J_{Rh-P} = 135$; $^2J_{Rh-P} = 5.8$).

X-ray Data Collection and Structure Refinement. Suitable crystals of complex **3** were obtained by slow evaporation of solvent from a $CHCl_3$−heptane solution. A summary of the crystallographic data and the structure refinement is listed in Table 1. The reflection

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Table 1. Crystallographic Data for $Rh_2(form)(\mu\text{-}O_2CCF_3)[(C_6H_5)_2P(CH_2)_2P(C_6H_5)(C_6H_4)](\sigma\text{-}CF_3COO)(p\text{-toluidine})$

formula	$C_{52}H_{47}F_6N_3O_4P_2Rh_2$
fw	1159.7
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	11.118(2)
b, Å	12.324(2)
c, Å	19.753(2)
α, deg	76.87(2)
β, deg	80.33(2)
γ, deg	72.11(2)
V, Å^3	2494.2(7)
Z	2
F(000)	1172
ρ_{calcd}, g/cm^3	1.54
μ, mm^{-1}	0.796
rel transm	0.813−0.841
λ(graphite monochromated), Å	0.710 73 (Mo Kα)
T, °C	23
2θ range, deg	3−54
no. of data colld ($2\theta-\omega$)	11734
no. of data refined	7632 [$F \geq 6\,\sigma(F)$]
no. of variables	628
R^a	0.035
$R_w{}^b$	0.045
GOF^c	1.33

^{a} $R = [\sum|F_o| - |F_c|]/\sum|F_o|$. ^{b} $R_w[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. ^{c} GOF $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{var})]^{1/2}$.

intensities were evaluated by the learnt-profile procedure[8] and then corrected for Lorentz−polarization and absorption effects.[9]

The structure was solved by standard methods with the SHELXTL-PLUS system.[10] Neutral-atom scattering factors and anomalous dispersion corrections come from ref 11. The final geometrical calculations and drawings were carried out with the PARST program[12] and the XP utility of the Siemens package,[10] respectively. Selected bond distances and bond angles are listed in Table 2. An Ortep view of the molecular structure of **3** with the corresponding atom-labeling scheme is shown in Figure 2.

Results and Discussion

The reactions of the dirhodium(II) complex $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ with the diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1-4$) show an evolution which is critically dependent on the aliphatic chain length of the ligand.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $Rh_2(form)(\mu\text{-}O_2CCF_3)[(C_6H_5)_2P(CH_2)_2P(C_6H_5)(C_6H_4)](\sigma\text{-}CF_3COO)(p\text{-toluidine})$

Rh(1)−Rh(2)	2.606(1)	Rh(1)−P(1)	2.189(1)
Rh(1)−P(2)	2.249(1)	Rh(1)−O(2)	2.169(3)
Rh(1)−N(2)	2.064(4)	Rh(2)−O(1)	2.204(3)
Rh(2)−O(3)	2.125(3)	Rh(2)−N(1)	2.148(3)
Rh(2)−N(3)	2.039(4)	Rh(2)−C(40)	1.992(4)
P(1)−C(33)	1.841(5)	P(1)−C(34)	1.818(4)
P(1)−C(41)	1.807(4)	P(2)−C(20)	1.831(4)
P(2)−C(26)	1.818(4)	P(2)−C(32)	1.821(4)
O(1)−C(1)	1.234(5)	O(2)−C(1)	1.250(5)
O(3)−C(3)	1.229(5)	O(4)−C(3)	1.244(6)
N(1)−C(46)	1.440(5)	N(2)−C(5)	1.426(4)
N(2)−C(12)	1.310(6)	N(3)−C(12)	1.321(4)
N(3)−C(13)	1.441(6)		

Rh(2)−Rh(1)−P(1)	86.9(1)	Rh(2)−Rh(1)−P(2)	105.3(1)
P(1)−Rh(1)−P(2)	84.8(1)	Rh(2)−Rh(1)−O(2)	89.3(1)
P(1)−Rh(1)−O(2)	176.1(1)	P(2)−Rh(1)−O(2)	97.0(1)
Rh(2)−Rh(1)−N(2)	85.1(1)	P(1)−Rh(1)−N(2)	92.4(1)
P(2)−Rh(1)−N(2)	169.0(1)	O(2)−Rh(1)−N(2)	86.5(1)
Rh(1)−Rh(2)−O(1)	81.1(1)	Rh(1)−Rh(2)−O(3)	91.4(1)
O(1)−Rh(2)−O(3)	90.8(1)	Rh(1)−Rh(2)−N(1)	169.1(1)
O(1)−Rh(2)−N(1)	88.0(1)	O(3)−Rh(2)−N(1)	87.7(1)
Rh(1)−Rh(2)−N(3)	86.6(1)	O(1)−Rh(2)−N(3)	87.0(1)
O(3)−Rh(2)−N(3)	177.2(1)	N(1)−Rh(2)−N(3)	93.9(1)
Rh(1)−Rh(2)−C(40)	98.1(1)	O(1)−Rh(2)−C(40)	178.3(1)
O(3)−Rh(2)−C(40)	90.8(1)	N(1)−Rh(2)−C(40)	92.8(1)
N(3)−Rh(2)−C(40)	91.5(1)	Rh(1)−P(1)−C(33)	111.5(1)
Rh(1)−P(1)−C(34)	115.2(1)	Rh(1)−P(1)−C(41)	114.7(1)
Rh(1)−P(2)−C(20)	102.4(2)	Rh(1)−P(2)−C(26)	128.0(2)
Rh(1)−P(2)−C(32)	109.7(2)	Rh(2)−O(1)−C(1)	123.5(2)
Rh(1)−O(2)−C(1)	115.7(2)	Rh(2)−O(3)−C(3)	126.7(3)
Rh(2)−N(1)−C(46)	122.3(2)	Rh(1)−N(2)−C(5)	117.9(3)
Rh(1)−N(2)−C(12)	122.5(2)		

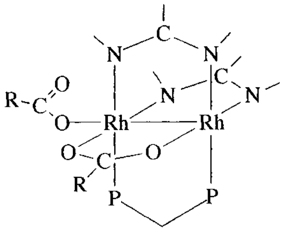

Figure 1. Proposed solid-state structure for $Rh_2(form)_2(\mu\text{-}O_2CCF_3)(dppm)(\sigma\text{-}O_2CCF_3)$.

Addition of 1 equiv of dppm to a solution of $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ results in the immediate formation of a green solution from which the complex $Rh_2(form)_2(\mu\text{-}O_2CCF_3)(dppm)(\sigma\text{-}O_2CCF_3)$ (**2**) was easily isolated. The solid IR spectrum of **2** shows two strong absorptions at 1645 and 1687 cm^{-1} evidencing the presence of nonequivalent trifluoroacetate groups. The high energy band is shifted to 1695 cm^{-1} in CH_3CN, where **2** behaves as 1:1 electrolyte, while it is little affected in CH_2Cl_2, where **2** behaves as a nonelectrolyte. Comparison of the properties of **2** with those of the complex $Rh_2(form)_2(O_2CCF_3)_2(PPh_2Py)$[13] shows a number of similar features and suggests that **2** adopts in the solid state a similar geometry (Figure 1) The complex, which in CH_2Cl_2 or benzene retains the same geometry, in CH_3CN, according to conductivity and solution IR data, exhibits a different structure. This can be interpreted in terms of dissociation of the monoligated trifluoroacetate group so that the species existing in acetonitrile solution is $[Rh_2(form)_2(\mu\text{-}O_2CCF_3)(\mu\text{-}dppm)(L)_2](CF_3COO)$ (L = CH_3CN).

In agreement with this suggestion the ^{31}P NMR spectra in $CDCl_3$ and CH_3CN are different. The ^{31}P NMR spectrum in $CDCl_3$ is temperature invariant from −25 to +25 °C and is consistent with the structure shown in Figure 1. In particular, the resonance of the phosphorus atoms appears as two well formed doublets of doublets of doublets centered at 7.37 and 18.81 ppm with one large (123−137 Hz) and one small (3.5−4 Hz) $^1J_{Rh-P}$ and $^2J_{Rh-P}$ coupling constant. As already reported[14] these values provide conclusive evidence for the equatorial coordination of both the phosphorus atoms. When the ^{31}P NMR spectrum is measured in CD_3CN a different spin system appears. At room temperature the spectrum reveals the expected ten lines of an AA′XX′ spin system (A,A′ = ^{103}Rh; X,X′ = ^{31}P). Analysis of the XX′ portion of the AA′XX′ pattern yielded the following parameters: δ 15.5 ($^1J_{Rh-P} = 123.1$; $^2J_{Rh-P} = 3.85$; $J_{P-P} = 53.8$; $J_{Rh-Rh} = -11.8$ Hz).

In contrast to $Rh_2(form)_2(O_2CCF_3)_2(PPh_2Py)$, complex **2** does not react further with a second equivalent of dppm. The synthesis of the complexes $Rh_2(O_2CCH_3)_2(dppm)_2Cl_2$ and Rh_2-

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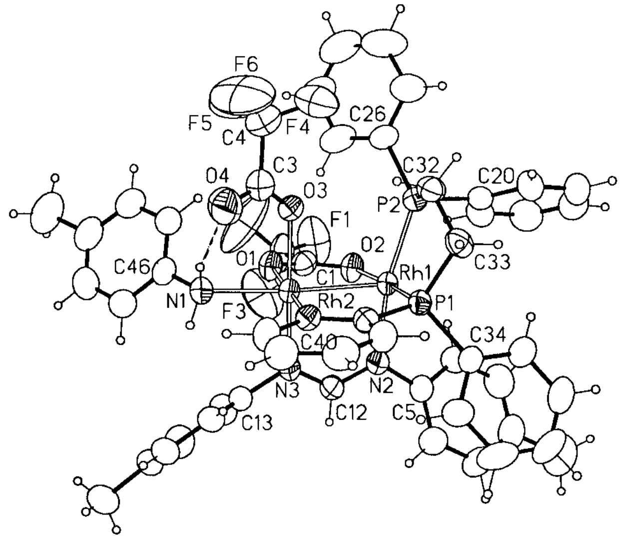

Figure 2. View of the asymmetric unit represented by one discrete molecule $Rh_2(form)(\mu\text{-}O_2CCF_3)[(C_6H_5)_2P(CH_2)_2P(C_6H_5)(C_6H_4)](\sigma\text{-}O_2CCF_3)(p\text{-toluidine})$ with numbering scheme. Thermal ellipsoids are drawn at the 50% probability level while the hydrogen atom size is arbitrary.

$[(C_6H_4)(C_6H_5)_2P]_2(dppm)_2Cl_2$, recently reported by Cotton et al.,[15] shows that *cis*-coordination of two dppm ligands across the Rh_2^{4+} core is possible. The reactions reported by Cotton are promoted by $(CH_3)_3SiCl$ whose function is to remove two acetate groups from the equatorial position of the complexes $Rh_2(O_2CCH_3)_4$ and $Rh_2(O_2CCH_3)_2[(C_6H_5)_2P(C_6H_4)]_2$, respectively. This synthetic route leaves unoccupied four equatorial sites where two dppm molecules are easily accommodated. Although we do not have spectroscopic evidences on the mechanism operating during the formation of complex **2**, on the basis of the literature data,[13,14] we suggest that the reaction leading to **2** proceeds through the following steps: (i) preliminary coordination of the phosphorus donor at one axial position of the parent complex; (ii) axial−equatorial isomerization followed by ring closure of the uncoordinated phosphorus atom at the second rhodium atom. The reaction of **2** with a second equivalent of dppm ought to proceed in a similar way. But space-filling models show that the first step is hindered. The presence of two phenyl and two *p*-tolyl groups does not leave the metal centers open to axial attack by the phosphorus atom of a second dppm molecule.

The reaction of $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ with dppe in a 1:1 mole ratio proceeds in a different way, namely via ortho-metalation of the diphosphine across the Rh_2^{4+} core. Microanalysis of the red crystals, obtained by minimal manipulation in workup, shows that these crystals contain only one formamidinate group per dimeric unit and analyze as $Rh_2(form)(O_2CCF_3)_2[(C_6H_4)(C_6H_5)P(CH_2)_2P(C_6H_5)_2](C_7H_9N)$ (**3**). Once formed, complex **3** reacts with a further equivalent of dppe giving an ionic species which analyzes as $[Rh_2(form)(O_2CCF_3)\{(C_6H_4)(C_6H_5)P(CH_2)_2P(C_6H_5)_2\}dppe]CF_3COO$ (**3D**).

The solid state IR spectrum of **3** shows, in addition to the bands associated with the formamidinate fragment, two strong ν(O−C−O) absorptions at 1716 and 1647 cm^{-1}. These absorptions are also present in dichloromethane where **3** is not conducting. In acetonitrile, where **3** behaves as 1:1 electrolyte, a very strong band appears at 1695 cm^{-1}. The ^{31}P NMR spectrum of **3**, taken in CD_3CN at room temperature, exhibits two doublets of doublets of doublets centered at 37.56 and 52.4 ppm with coupling constants to ^{103}Rh of 145.8 and 3.6 Hz and 131.9 and 3.8 Hz, respectively. Spectroscopic and conductivity data were not helpful in assigning the structure of **3**, which was elucidated only by an X-ray investigation.

Molecular Structure of $Rh_2(form)(\mu\text{-}O_2CCF_3)[(C_6H_5)_2P(CH_2)_2P(C_6H_5)(C_6H_4)](\sigma\text{-}O_2CCF_3)(p\text{-toluidine})$. In the crystal structure of the title complex, illustrated in Figure 2, the asymmetric unit comprises one discrete $Rh_2(form)(\mu\text{-}O_2CCF_3)[(C_6H_5)_2P(CH_2)_2P(C_6H_5)(C_6H_4)](\sigma\text{-}O_2CCF_3)(p\text{-toluidine})$ molecule. The dinuclear complex is mainly characterized by a central unsymmetrical dirhodium unit bridged by three different ligands: a trifluoroacetate, a formamidinate, and an ortho-metalated 1,2-bis(diphenylphosphino)ethane which is also chelated to Rh(1) through the two phosphorus atoms. A second trifluoroacetate group, monocoordinated at one equatorial position, and a *p*-toluidine, located at one axial position, complete the coordination around the Rh(2) atom which adopts a pseudooctahedral arrangement for its six bonds. The geometry of the 5-coordinated Rh(1) atom might be described as a distorted square-pyramid with the equatorial plane orthogonal to the dirhodium axis. The Rh−Rh separation of 2.606(1) Å, which is considerably longer than the distances found in most of the dirhodium(II) complexes,[16] is significantly shorter than the value [2.7331(8) Å] found in the complex $[Rh_2(form)(\mu\text{-}O_2CCF_3)\{(C_6H_5)_2P(CH_2)_2P(C_6H_5)(C_6H_4)\}(dppe)]CF_3COO$ (**1**), which exhibits essentially the same set of bridging ligands.

The Rh(1)−P(2) and Rh(1)−P(1) bond lengths are 2.189(1) and 2.249(1) Å, respectively, with the longer Rh−P distance reflecting the influence of the trans nitrogen. The Rh(2)−Rh(1)−P(2) bond angle is significantly larger than Rh(2)−Rh(1)−P(1) [105.3(1) vs 86.9(1)°]. This difference may be explained in terms of rigidity of the bridging fragment C(40)−C(41)−P(1) and steric interactions between one phenyl rings ligated to P(2) atom and the fluorine atoms of the adjacent trifluoroacetate ligand. However the Rh(2)−Rh(1)−P(2) bond angle is significantly smaller than the corresponding value found in **1** [121.68(6)°] where the steric requirement of the ligands force the 5-coordinated rhodium to assume a different geometry, namely distorted trigonal-bipyramidal instead of square-pyramidal.

The formamidinate fragment is bonded to the dirhodium unit in the usual way, namely σ,σ-N,N′ with delocalized double bonds. As expected the Rh(2)−N(*p*-toluidine) bond length [2.148(3) Å] is significantly longer than both Rh−N(form) bond lengths. In addition the hydrogen atoms of the *p*-toluidine fragment are involved in intramolecular interactions: the most significant hydrogen bond acts on the uncoordinated oxygen of the adjacent mono-coordinated trifluoroacetate [H(1A)···O(4) = 1.93(4) Å; N(1)···O(4) = 2.834(6) Å; N(1)−H(1A)···O(4) = 156(3)°].

The formation of the *p*-toluidine fragment is the likely result of the fragmentation of the neutral *p*-tolylformamidine produced during the ortho-metalation. Although fragmentation of neutral formamidines is a known process in organic chemistry, no corresponding reactions are found in the chemistry of metal coordination complexes. The only similar example, reported by Cotton, concerns the fragmentation of a *p*-tolylformamidine with formation of a *p*-toluido fragment.[17]

NMR Studies. Once the solid-state structure of **3** had been established, we monitored its formation by ^{31}P NMR spectros-

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(16) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, J Claredon Press: Oxford, England, 1993. (b) Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *29*, 73. (c) Boyar, E. B.; Robinson, S. D. *Coord. Chem. Rev.* **1983**, *50*, 109.

(17) Cotton, F. A.; Poli, P. *Inorg. Chim. Acta* **1986**, *122*, 243.

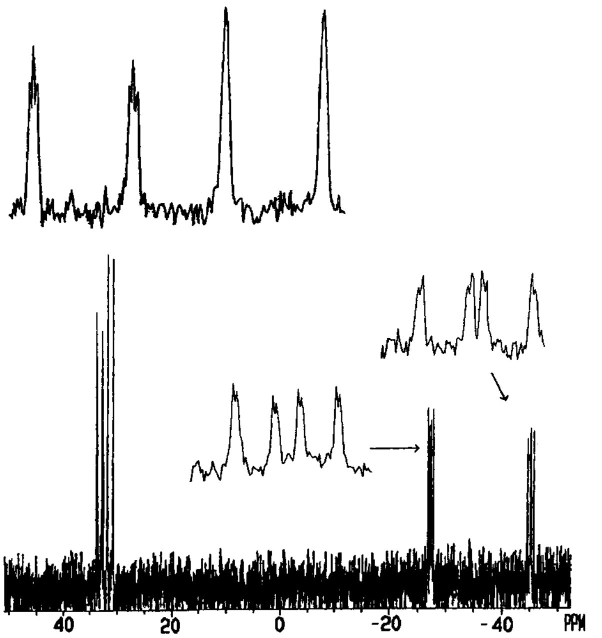
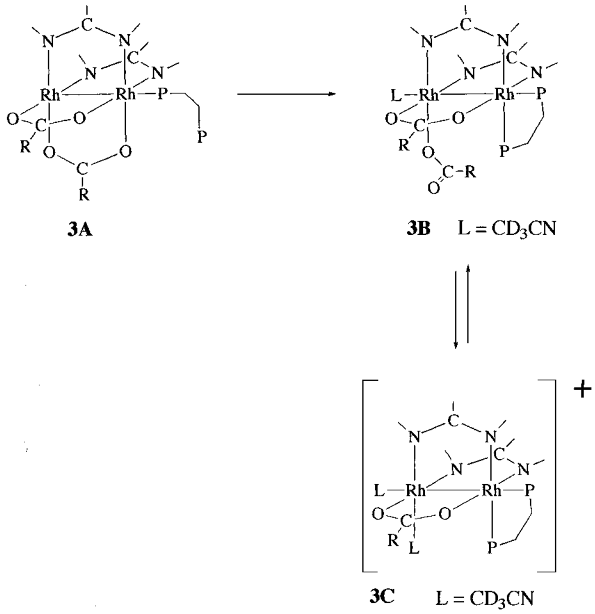


Figure 3. ^{31}P NMR spectrum at 240 K of the reaction mixture used to form **3** in CD_3CN. Insets show the expansions of the region around +30, −30, and −50 ppm.

Scheme 1



3A

3B L = CD_3CN

3C L = CD_3CN

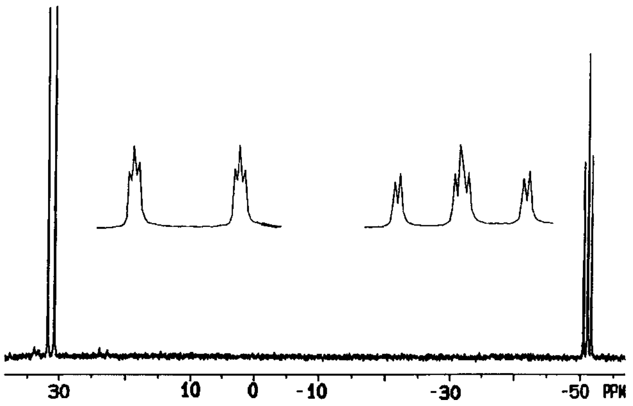


Figure 4. ^{31}P NMR spectrum at 245 K of the reaction mixture used to form **3** in $CDCl_3$. Insets show expansions of the region around +30 and −50 ppm.

copy in order to provide information about the reaction sequence leading to complex **3**. These experiments were performed in a ^{31}P NMR tube by adding at room temperature, *via* syringe, an acetonitrile solution of dppe to a solution of $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ dissolved in the same solvent, molar ratio 1:1, immediately after the reaction mixture was cooled to 240 K. The spectrum recorded at this temperature clearly shows the presence of two axial−equatorial adducts. No signals due to uncoordinated phosphorus atoms were detected. The negative region of the spectrum, shown in Figure 3, shows two sets of resonances of similar intensity falling at −45.74 ($^1J_{Rh-P} = 80$, $^2J_{Rh-P} = 63.2$, $J_{P-P} = 6.3$ Hz) and −27.4 ppm ($^1J_{Rh-P} = 77.8$, $^2J_{Rh-P} = 50.5$, $J_{P-P} = 4.2$ Hz). Both the chemical shifts and coupling constants are consistent with the presence of axially coordinated phosphorus atoms (class I adduct according to Andersen description)[18] with a linear Rh−Rh−P fragment. The positive region of the ^{31}P NMR spectrum at 240 K consists of two closely spaced groups of resonances: a doublet of triplets falling at 33.2 ppm ($^1J_{Rh-P} = 124.1$, $^2J = 4.4$ Hz) and a broad doublet at 31.72 ppm ($J = 122.1$ Hz). These two sets of resonances display similar intensity. All of these parameters are consistent with the formation of equatorial adducts with a bent arrangement of the Rh−Rh−P fragment (class II).

According to Scheme 1, we suggest that the reaction pattern could involve sequential axial coordination of dppe through one phosphorus atom with formation of the axial monoadduct **3A** followed by chelation of the dangling phosphorus at the same rhodium atom with partial displacement of one trifluoroacetate group from the equatorial position. In CD_3CN at 240 K the labile monocoordinated CF_3COO group is partially dissociated leading to the formation of two species: one neutral (**3B**) which resonates at −45.74 and 33.2 ppm, and another one, monocationic (**3C**), with resonances at −27.4 and 31.72 ppm. To confirm this suggestion the same experiment was performed in a noncoordinating solvent such as chloroform. The spectrum in this solvent (Figure 4) is invariant from 230 to 270 K and shows only two signals of similar intensity arising from **3B**: the low-field one, centered at 30.3 ppm, appears as a doublet of triplets ($^1J_{Rh-P} = 124.8$; $^2J_{Rh-P} = 5.1$ Hz) while the high-field shows a doublet of doublets of doublets centered at −50.37 ppm ($^1J_{Rh-P} = 74$; $^2J_{Rh-P} = 68$, $J_{P-P} = 6$ Hz). When the sample was warmed to 273 K, the spectra became more complicated, showing the presence of several interconverting species. No attempts were made to assign these signals which were not helpful in clarifying the reaction sequence. However the chemical shift of these signals, which fall in the range 30−55 ppm, clearly indicates that all the phosphorus atoms are equatorially coordinated. At 295 K the spectrum in CD_3CN reveals only the presence of the signals centered at 37.56 and 52.4 ppm due to the formation of **3**. Very likely **3B** and **3C** undergo the well established axial−equatorial isomerization with formation of a bis-equatorial adduct which was not detected in the spectra. These species undergo ortho-metalation followed by formal transfer of an ortho-proton of one phenyl group, closely approaching the adjacent rhodium atom, to a formamidinate group with consequent elimination of formamidine from the "lantern" structure. After one day, these signals also disappear and are replaced by a pair of doublets centered at 48.16 ppm indicating that in CD_3CN complex **3** evolves toward unidentified species still containing equatorially bonded phos-

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(18) Girolami, G. S.; Mainz, V. V.; Andersen, R. A. *Inorg. Chem.* **1980**, *18*, 805.

phorus atoms. The latter species is not formed in $CDCl_3$ even after 6 days.

Once formed, complex **3** easily reacts with a further equivalent of dppe giving the ionic complex $[Rh_2(form)(O_2CCF_3)\{(C_6H_4)(C_6H_5)P(CH_2)_2P(C_6H_5)_2\}dppe]CF_3COO$ (**3D**) whose analytical, spectroscopic and conductivity data resemble those of **1**. The reaction very likely involves initial displacement of the labile, equatorially coordinated CF_3COO^- group by one phosphorus atom of a second dppe molecule followed by ring closure by the second phosphorus at the axial site. Ortho-metalation of a second dppe molecule is prevented. At first sight it would appear that the synthesis of **3** allows us to elucidate the overall reaction leading to complex **1**. Careful comparison of the structure of **1** with that of **3D** shows that **1** and **3D** do not display the same arrangement of ligands around the Rh_2^{4+} core.

When the parent complex is allowed to react with 1,2-bis(diphenylphosphino)propane (dppp), molar ratio 1:1, a reaction similar to that of dppe was observed. But, although analytical data and the intensity of the IR and ^1H NMR absorptions of the formamidinate fragment indicate that this reaction also proceeds by elimination of a formamidine ligand, we were not able to obtain the compound in an acceptable pure form. By following the reaction by ^{31}P NMR spectroscopy from 250 to 308 K, we found a possible explanation. The sequence of the ^{31}P resonances is essentially the same as that observed for the dppe derivative and a species with resonances similar to those exhibited by **3** was detected. By this time, this species evolves toward a compound of unknown composition with a resonance centered at 8.93 ppm as a doublet of doublets.

The reaction between $Rh_2(form)_2(O_2CCF_3)_2(H_2O)_2$ and 1,2-bis(diphenylphosphino)butane (dppb), molar ratio 1:1, proceeds in a different way. With this long and fexible ligand the reaction occurs without ortho-metalation and leads to the formation of the complex $Rh_2(form)_2(O_2CCF_3)_2(dppb)$ (**4**). The ^{31}P NMR spectrum of **4** exhibits only one resonance, as a double doublet, centered at 30.67 ppm with coupling constants to ^{103}Rh of 135 and 5.8 Hz. The values of the chemical shift and coupling constants strongly suggest that in complex **4** both phosphorus atoms are equivalent and that dppb is chelated in equatorial positions to one rhodium atom. Complex **4**, which is moderately stable in solution and insoluble in polar solvents, does not undergo ortho-metalation. This failure may be due to the flexible organic backbone of dppb which orientates the phenyl groups away from the rhodium atoms thereby disfavoring the ortho-metalation. The formation of equatorial adducts prevents the formation of polymeric, zigzag, or linear chain compounds.

Acknowledgment. Financial support from MURST and Italian CNR is gratefully acknowledged.

Supporting Information Available: Tables S1−S6, giving crystal data, anisotropic thermal parameters, hydrogen atom coordinates, atomic coordinates, and full listing of bond lengths and bond angles for **3** (11 pages). Ordering information is given on any current masthead page.

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