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"To Bend or not To Bend?" Both! The Planar and Bent Structures of $[(Ph_3P)_4Rh_2(\mu\text{-}F)_2]$

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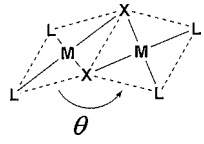
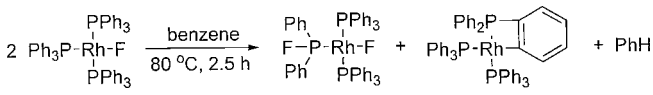
The first experimental evidence is presented for planar–bent isomerism of complexes of the type $[L_4M_2(\mu\text{-}X)_2]$. Both the planar and bent forms have been detected for *the same composition*, $[(Ph_3P)_4Rh_2(\mu\text{-}F)_2]$, with full exclusion of any variation in such factors as the nature of the metal, ligand, counterion, and solvent of co-crystallization. Computational studies point to weak C–H···F intramolecular bonding as an additional factor affecting the choice between the planar and bent geometries.

In 1998, two of us published a paper entitled "To Bend or Not To Bend: Dilemma of the Edge-Sharing Binuclear Square Planar Complexes of d^8 Transition Metal Ions".[1] This publication provided a structural and theoretical analysis of complexes of the type $[L_4M_2(\mu\text{-}X)_2]$ which are ubiquitous in the chemistry of catalytically important metals such as Ni, Pd, Pt, Rh, and Ir.[1–3] A remarkable feature of such dinuclear complexes is their ability to exist in either planar or bent forms, with the bending angle θ (Scheme 1) showing a bimodal distribution with maxima at 130 and 180°. Analysis of well over 100 X-ray structures of $[L_4M_2(\mu\text{-}X)_2]$ (X = halogen or chalcogen) indicated that for M = Rh, Pd, and Pt, both bent and planar geometries are commonly observed.[1] The energy cost of bending for such complexes is normally low, often only a few kcal mol^{-1},[1,4] suggesting that both forms could be found experimentally for a single species. Both almost planar and more bent molecules have been found in the crystal structure of *non-square-planar* $[Co_2(\mu\text{-}PPh_2)_2(CO)_6]$.[5] The $Pt_2(\mu\text{-}S)_2$ moiety in complexes of the type $[L_4Pt_2(\mu\text{-}S)_2]$ is commonly bent,[1] though for L = 2-(diphenylphosphanyl)pyridine, a planar structure was reported.[6] Depending on the nature of the counterion X in $[Pt_2(NH_3)_4(\mu\text{-}OH)_2]X_2$, both the planar (X = NO_3[7] or 1/2CO_3, dihydrate[8]) and bent (X = ClO_4[9]) forms of the cation can exist in the crystalline state. The angle θ for these structures is apparently governed by H-bonding interactions involving the anion, as well as by different packing requirements for different X. There have been no literature reports describing a compound of the type $[L_4M_2(\mu\text{-}X)_2]$, for which *both* planar and bent forms have been detected for *the same composition*, with full exclusion of any variation in the ligand, counterion, solvent of crystallization, and so forth. In this communication, we report the first example of such a complex, $[(Ph_3P)_4Rh_2(\mu\text{-}F)_2]$.



Scheme 1.

Some of us recently reported[10,11] that the fluoro congener of Wilkinson's catalyst, $[(Ph_3P)_3RhF]$, exhibits intriguing reactivity patterns. For instance, heating of $[(Ph_3P)_3RhF]$ in benzene (at 80 °C for 2.5 h) leads to F transfer to one of the P atoms, as shown in Equation (1).[10]



(1)

The reaction occurs by reversible Ph/F exchange as the first key step.[11] In order to determine if the resulting fluoride complex, *trans*-$[(Ph_3P)_2(Ph_2PF)RhF]$, was also capable of undergoing such Ph/F exchange, the thermolysis was conducted for longer periods of time. After 5–6 h at 80 °C, complex reaction mixtures were produced, as judged by ^{19}F

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and ^{31}P NMR analysis. Because the NMR spectroscopic data did not allow for unambiguous characterization of new compounds, a series of attempts were made to isolate some of the products by fractional crystallization. After the reaction solutions were concentrated and treated with ether and/or hexane, single crystals were obtained. X-ray analysis of one of the gold-yellow square plates revealed the structure of ideally planar (θ = 180°) $[(Ph_3P)_4Rh_2(\mu\text{-}F)_2]$ (**1**).[12] Poor quality, disordered structures of $\mathbf{1}\cdot 2C_6H_6$ and $\mathbf{1}\cdot 2C_6H_5CH_3$ have been mentioned before.[10] The formation of $[(PPh_3)_4Rh_2(\mu\text{-}F)_2]$ is easily accounted for by dissociation and decomposition of the (in its free form[13,14]) unstable Ph_2PF from $[(Ph_3P)_2(Ph_2PF)RhF]$ to give "$[(PPh_3)_2RhF]$" which would undergo dimerization to **1**.

In another experiment under similar reaction and crystallization conditions, growth of very thin, "two-dimensional" looking yellow plates was noticed. Although the bulkiest crystal in the batch appeared to be only ca. 0.005 mm thick, its X-ray analysis was achieved with a Bruker Smart Apex-II CCD instrument. To our surprise, the crystal was comprised of the same dimer $[(Ph_3P)_4Rh_2(\mu\text{-}F)_2]$ but in a *bent* form (θ = 133.7°). The planar (**1-p**) and bent (**1-b**) structures are shown in Figures 1 and 2, respectively.[12] The quality of the structure of **1-b** was limited by the crystal size/shape, and structure subtleties such as bond lengths and angles should be looked at with care. Most importantly, the bent geometry was established beyond any doubt.

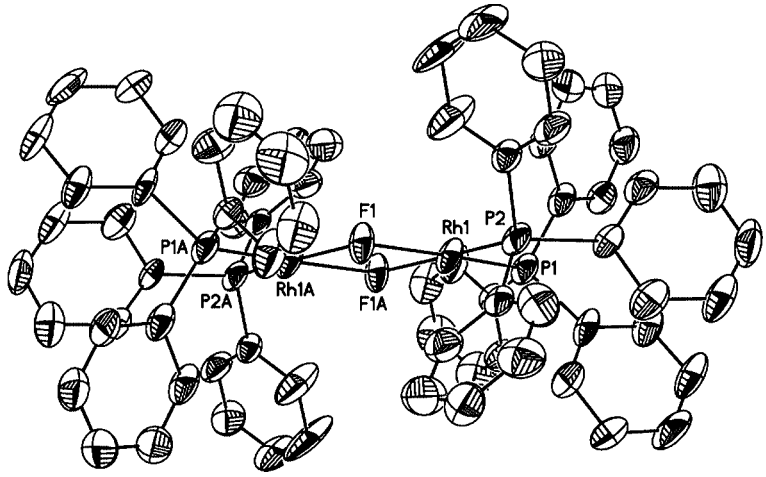


Figure 1. ORTEP view of the planar form of **1** (**1-p**) with thermal ellipsoids drawn to the 50% probability level. Selected bond lengths [Å] and angles [°]: Rh(1)–F(1) 2.131(5), Rh(1)–F(1A) 2.141(5), Rh(1)–P(1) 2.161(3), Rh(1)–P(2) 2.185(3); F(1)–Rh(1)–F(1A) 77.3(2), F(1)–Rh(1)–P(1) 171.4(2), F(1A)–Rh(1)–P(1) 94.2(1), F(1)–Rh(1)–P(2) 93.2(2), F(1A)–Rh(1)–P(2) 170.1(1), P(1)–Rh(1)–P(2) 95.4(1).

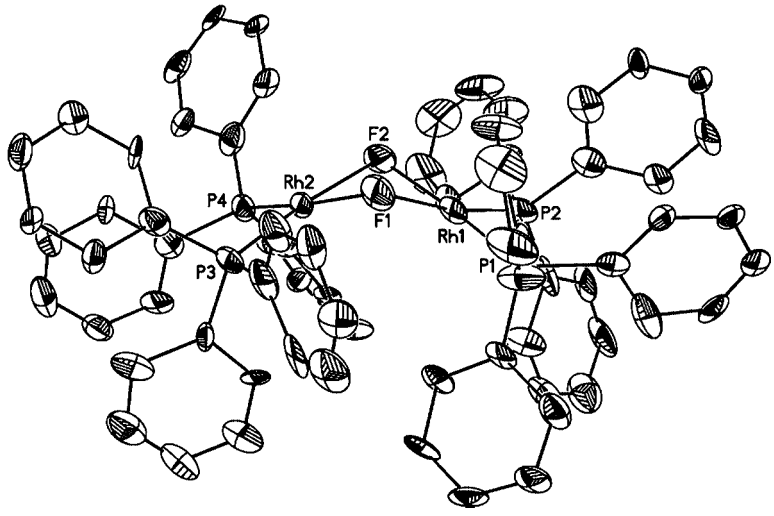


Figure 2. ORTEP view of the bent form of **1** (**1-b**) with thermal ellipsoids drawn to the 50% probability level. Selected bond lengths [Å] and angles [°]: Rh(1)–F(1) 2.02(1), Rh(1)–F(2) 2.07(1), Rh(1)–P(2) 2.116(6), Rh(1)–P(1) 2.146(7), Rh(1)–Rh(2) 2.972(6), Rh(2)–F(1) 2.04(1), Rh(2)–F(2) 2.08(1), Rh(2)–P(4) 2.109(6), Rh(2)–P(3) 2.115(6); F(1)–Rh(1)–F(2) 76.1(5), F(1)–Rh(1)–P(2) 169.8(4), F(2)–Rh(1)–P(2) 95.7(3), F(1)–Rh(1)–P(1) 93.9(4), F(2)–Rh(1)–P(1), 170.0(3), P(2)–Rh(1)–P(1) 94.3(2), F(1)–Rh(1)–Rh(2) 43.1(4), F(2)–Rh(1)–Rh(2) 44.5(3), P(2)–Rh(1)–Rh(2) 133.0(2), P(1)–Rh(1)–Rh(2) 126.82(14), F(1)–Rh(2)–F(2) 75.6(5), F(1)–Rh(2)–P(4) 167.7(3), F(2)–Rh(2)–P(4) 92.1(4), F(1)–Rh(2)–P(3) 95.6(4), F(2)–Rh(2)–P(3) 170.6(4), P(4)–Rh(2)–P(3) 96.6(2), F(1)–Rh(2)–Rh(1) 42.8(3), F(2)–Rh(2)–Rh(1) 44.3(4), P(4)–Rh(2)–Rh(1) 126.6(2), P(3)–Rh(2)–Rh(1) 126.6(2).

The structures of **1-p** and **1-b** were carefully examined to see if the Rh centers could be bridged by OH, rather than F. There was no evidence from the X-ray data that either structure contained OH based upon occupancy refinement or the location of hydrogen atoms from difference maps. However, the X-ray data from structures of this quality cannot rule out completely the presence of OH either partially or fully occupied in the bridging position. While direct X-ray evidence cannot be obtained for the lack of OH in the crystals, a number of experimental facts support the formulation $[(Ph_3P)_4Rh_2(\mu\text{-}F)_2]$. Complex **1** has been found[15a] uncommonly stable toward hydrolysis. Rigorously anhydrous conditions[11] were used all through the experiments, from the thermolysis to the fractional crystallization steps. The starting material, $[(Ph_3P)_3RhF]$, was free of $[(Ph_3P)_4Rh_2(\mu\text{-}OH)_2]$ (NMR), the "would-be" product of its hydrolysis. Because there is no fast exchange between $[(Ph_3P)_3RhF]$ and $[(Ph_3P)_4Rh_2(\mu\text{-}OH)_2]$,[15a] the presence of the latter would have been easily detected. The reaction mixtures were studied by ^{19}F and ^{31}P NMR prior to fractional crystallization in a dry-box. The NMR spectra indicated the presence of **1**[10] and no detectable amounts of $[(Ph_3P)_4Rh_2(\mu\text{-}OH)_2]$ with the characteristic chemical shift and J(Rh–P) coupling constant.[15b] It is also noteworthy that unlike **1**, $[(Ph_3P)_4Rh_2(\mu\text{-}OH)_2]$ crystallizes with 2 molecules of benzene under similar conditions.[15c] Measuring NMR spectra of the crystals in bulk supported the formulation $[(Ph_3P)_4Rh_2(\mu\text{-}F)_2]$.[10] The ultimate solution to the problem, however (as also suggested by a referee), would be obtaining NMR spectroscopic data for the very crystals used in the X-ray determination. This, however, is not experimentally feasible. The masses of the crystals of **1-p** ($0.420 \times 0.420 \times 0.030$ mm; $d = 1.454$ g cm^{-3}) and **1-b** ($0.320 \times 0.300 \times$ ca. 0.005 mm; $d = 1.618$ g cm^{-3}) were ca. 0.0077 mg and 0.00078 mg, respectively. Such quantities are not amenable to a solution NMR study.

The difference in energy between the planar and bent forms (ΔE) of **1** is expected to be small. For instance, the ΔE value from the ab initio (MP2) study of the planar ($\theta = 180°$) and bent ($\theta = 139.1°$) forms of $[(PH_3)_4Rh_2(\mu\text{-}F)_2]$ has been computed at about 3 kJ mol^{-1},[1] the smallest difference among the series of analogous halide-bridged rhodium complexes. This small value suggests that the observed deviation from the planar geometry of **1** may be easily forced by weak ligand–ligand interactions or different crystal-packing requirements, e.g., due to co-crystallization with different solvents. Remarkably, however, both X-ray-analyzed crystals contained only molecules of **1** and no other co-crystallized species. Examination of the X-ray structures of **1-p** and **1-b** did not reveal any conclusive evidence that the crystal packing might influence the bending along the F···F hinge.

Both structures exhibit intramolecular CH···F close contacts, as defined by being shorter than the sum of the van der Waals radii (2.67 Å). Such CH···F interactions are common for late transition metal fluoride complexes.[16] In the planar form (**1-p**) each F atom interacts with *two ortho*-hydrogen atoms of two different phenyl groups of the same phosphane ligand with the H···F distances of 2.45 and 2.49 Å and corresponding C···F distances of 3.11 and 3.21 Å. In contrast, each fluorine atom of the bent form (**1-b**) exhibits only *one* short CH···F contact. Within the bent molecule, the two non-symmetry related H···F distances are observed at 2.26 and 2.64 Å with C···F distances of 3.02 and 2.92 Å, respectively. At difference with the planar form, the bent form (**1-b**, Figure 2) presents three intermolecular contacts shorter than 3.0 Å to the bridging fluorine atoms. It should be emphasized that because of the limited quality of the structures the presented H···F distances should be interpreted with care.

The unusual existence of both the planar and the bent forms of $[(Ph_3P)_4Rh_2(\mu\text{-}F)_2]$ prompted us to perform exploratory electronic structure calculations in search for an explanation, using DFT at the B3LYP level.[17] First, we verified that the DFT calculations do reproduce the qualitative expectations of the higher level MP2 calculations, using the simplified model complexes $[(R_3P)_4Rh_2(\mu\text{-}F)_2]$ (R = H, Me) in which the phenyl rings in the phosphane ligands were substituted by the computationally affordable H atoms or Me groups. Energy optimization of their bent and planar forms tells us that the two geometries correspond to two nearly isoenergetic minima (characterized through a vibrational analysis; geometries provided in the Supporting Information). We note also that B3LYP calculations have been shown to provide excellent results for the analysis of bending of dinuclear complexes similar to the ones studied here.[18]

These results, combined with the structural information of the short contacts between the bridging fluoride ions and the phenyl groups of the phosphanes, suggest that the F···Ph interactions may govern the choice between the planar and bent forms. Therefore, we studied the interaction between $[(H_3P)_4Rh_2(\mu\text{-}F)_2]$ and an independent benzene molecule. Two energy minima were found for the $[(H_3P)_4Rh_2(\mu\text{-}F)_2]\cdots C_6H_6$ adduct. In one of them, one C–H···F contact is formed while the Rh_2F_2 core remains practically planar ($\theta = 165°$). The slight degree of bending is most likely an artefact of the choice of only one benzene ring to study this interaction, because in the experimental planar structure each fluorine atom interacts with one phenyl proton at each side of the molecular plane. In the other minimum found for the adduct, two C–H···F contacts appear between two *ortho*-hydrogen atoms of the *exo*-phenyl group and the two bridging fluorine atoms, quite similar to the intermolecular interaction found in the experimental bent structure **1b**. Moreover, the optimized adduct presents a minimum only at a bent geometry ($\theta = 148°$), thus giving support to the idea that the intermolecular C–H···F contacts favor the bent structure.[19] Further support to the effect of the weak hydrogen bonds governing the molecular geometry comes from calculations on $[(H_2PhP)_4Rh_2(\mu\text{-}F)_2]$, in which the phenyl substituents pointing to the central part of the molecule have been retained. This complex has only one energy minimum with a planar geometry and two short intramolecular F···H contacts (2.14 Å) per fluorine atom.

Let us concisely review the factors influencing the bending in $[L_4M_2(\mu\text{-}X)_2]$,[1] as applied to **1**.

The Nature of the Metal. Of the metals that may present both planar and bent structures (Rh, Ir, Pd, and Pt), rhodium is the one that favors the most diverse distribution. For the other metals, planar structures prevail for palladium and platinum, while only bent structures are found for iridium.

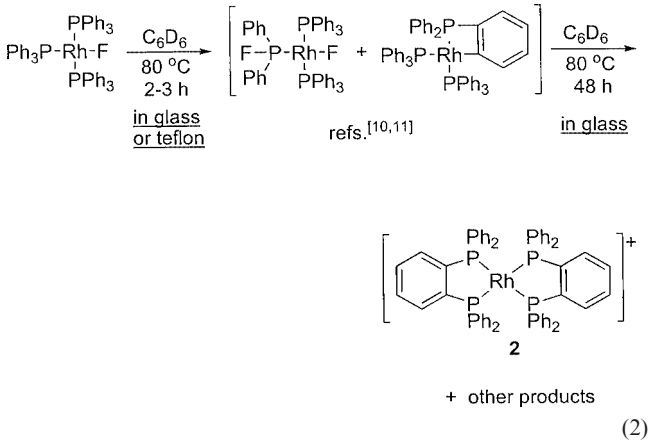
The Nature of the Bridging Atom. Of all the halogens, fluorine is apparently the one, for which the smallest ΔE value is expected. The ab initio (MP2) calculated values for ΔE in $[(PH_3)_4Rh_2(\mu\text{-}X)_2]$ are 3, 17, 26, and 31 kJ mol^{-1}, for X = F, Cl, Br, and I, respectively.[1]

The Nature of the Terminal Ligand. It has been concluded[1] that bent structures for $[L_4M_2(\mu\text{-}X)_2]$ are favored by monodentate ligands L that are good σ-donors/π-acceptors. Strongly σ-donating organic tertiary phosphanes R_3P are also recognized[20] as π-acids, the combination of electronic properties that might be important for stabilization of the M–F bond in late transition metal fluorides.[15a] With regards to steric properties, the bending in **1** is surprising due to the presence of four bulky PPh_3 ligands which normally favor only planar structures.[1]

The Substituents of the Phosphane Ligand. Given the small energy difference between the planar and bent forms to be expected for the $[(PR_3)_4Rh_2(\mu\text{-}F)_2]$ compounds, the ability of the R groups to form weak hydrogen bonds with the bridging fluorine atoms, combined with the different orientation of the PR_3 groups in the planar and bent forms, may stabilize the form with the larger number of short H···F contacts for R = Ph, but not for R = Me.[19]

Very poor solubility of **1** precludes its low-temperature NMR studies in solution. More easily soluble Werner's Rh–F dimer $[(i\text{Pr}_3P)_4Rh_2(\mu\text{-}F)_2]$[21] has been found[11,15a] planar in the solid state. A detailed solution NMR study[21] did not reveal the presence of two or more isomers of $[(i\text{Pr}_3P)_4Rh_2(\mu\text{-}F)_2]$ at room temperature. Because the ^{19}F and ^{31}P spectral parameters of **1** are similar,[10] the barrier to planar–bent isomerization of both $[(i\text{Pr}_3P)_4Rh_2(\mu\text{-}F)_2]$ and **1** may be low enough to regard **1-p** and **1-b** as conformational isomers.

It is worth mentioning in this communication one more unexpected result obtained during our studies of decomposition of $[(Ph_3P)_3RhF]$ at prolonged heating. After a benzene solution of $[(Ph_3P)_3RhF]$ in glass had been kept at 80 °C for 48 h, the formation of well-shaped yellow crystals was noticed. Although the amount of these crystals was insufficient for full characterization in bulk, single-crystal X-ray analysis was carried out to reveal the astounding structure of a cationic Rh^I complex $[(dppbz)_2Rh]^+X^-$ (**2**)[12] where dppbz = 1,2-bis(diphenylphosphanyl)benzene [Equation (2); Figure 3].[22] The nature of the counterion X^- could not be established unambiguously. In the X-ray analysis, the anion refined well as tetrahedral $[F_3SiO]^-$. Indeed, when the experiment was repeated in a teflon reactor, no precipitation was observed, indicating that the bis(chelate) was not produced. Although the formation of $[(dppbz)_2Rh]^+$ from $[(Ph_3P)_3RhF]$ in glass is certainly remarkable, we did not carry out a detailed study of this reaction [Equation (2)], as it was beyond the scope of this project. It is noteworthy, however, that monitoring the long-term decomposition of $[(Ph_3P)_3RhF]$ by ^{31}P and ^{19}F NMR spectroscopy indicated intermediate formation of several Rh species bearing $PhPF_2$ as a ligand, i.e. triplets of multiplets with large triplet coupling constants of ca. 900–1100 Hz in the ^{31}P NMR spectra. Hence, the originally formed Ph_2PF ligand [Equation (1)] is apparently capable of undergoing further Ph/F exchange with fluoride on Rh, albeit at considerably slower rates.



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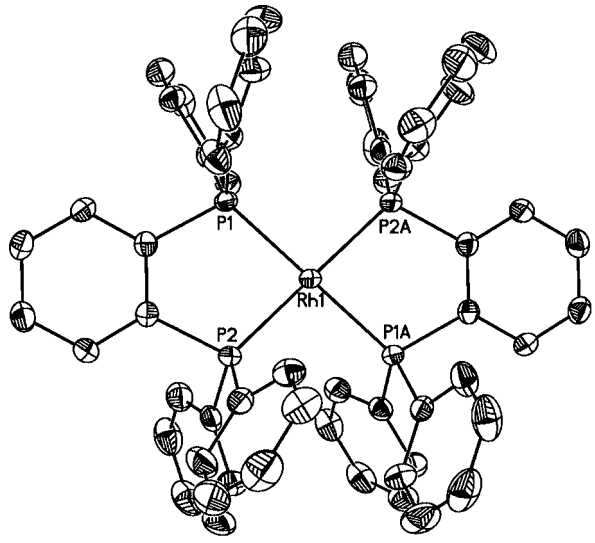

Figure 3. ORTEP view of the cation of **2** with thermal ellipsoids drawn to the 50% probability level. Selected bond lengths [Å] and angles [°]: Rh(1)–P(2A) 2.2807(7), Rh(1)–P(2) 2.2807(7), Rh(1)–P(1) 2.2975(7), Rh(1)–P(1A) 2.2976(7); P(2A)–Rh(1)–P(2) 174.93(3), P(2A)–Rh(1)–P(1) 95.03(2), P(2)–Rh(1)–P(1) 85.00(2), P(2A)–Rh(1)–P(1A) 85.00(2), P(2)–Rh(1)–P(1A) 95.03(2), P(1)–Rh(1)–P(1A) 179.29(3).

In conclusion, we have obtained the first experimental evidence for the existence of a single compound of the type $[L_4M_2(\mu\text{-}X)_2]$ in *both* planar and bent forms. Most importantly, the two forms have been detected for *the same composition*, $[(Ph_3P)_4Rh_2(\mu\text{-}F)_2]$, with full exclusion of any varia-

tion in such factors as the nature of the metal, ligand, counterion, and solvent of co-crystallization. For the first time, experimental support has been provided to the previous theoretical results predicting a very small difference in energy between the planar and bent forms for dimers of the type $[L_4M_2(\mu\text{-}X)_2]$. The preliminary DFT study suggests that the hydrogen bonding pattern will govern whether the planar or bent form is isolated.

Supporting Information (see footnote on the first page of this article): Tables containing atomic coordinates of the B3LYP optimized geometries of $[(H_3P)_4Rh_2(\mu\text{-}F)_2]$ and $[(Me_3P)_4Rh_2(\mu\text{-}F)_2]$ in their planar and bent conformations, of the adducts formed by benzene and $[(H_3P)_4Rh_2(\mu\text{-}F)_2]$ in the *exo* and *endo* orientations, and of $[(H_2PhP)_4Rh_2(\mu\text{-}F)_2]$. Figures showing the energy of interaction between a benzene molecule and $[Rh_2(\mu\text{-}F)_2(PH_3)_4]$ as a function of the intermolecular F···H distance, calculated at the B3LYP and MP2 levels, and the relative B3LYP energy of $[(Me_3P)_4Rh_2(\mu\text{-}F)_2]$ as a function of the bending angle θ.

Acknowledgments

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[12] Data for all structures were collected at –100 °C using a Bruker APEX-II CCD system equipped with Mo-K_α radiation. Indexing and integration were performed using the Bruker APEX-II software suite and the structures were solved and refined on $|F^2|$ using the SHELXTL software suite. All of the hydrogen atoms were idealized using a riding model. Extra redundant reflections were collected and a SADABS correction was applied to help minimize absorption effects. Specific parameters are as follows. **1-p:** Square plate, $0.42\times0.42\times0.03$ mm, triclinic, $P\bar{1}$, a = 9.130(7), b = 13.311(10), c = 14.106(11) Å, α = 67.872(14), β = 71.577(16), γ = 72.832(18)°, V = 1476(2) Å^3, $\rho_{calcd.}$ = 1.454 g/cm^3, μ(Mo) = 0.72 mm^{-1}, total data = 18279, unique data = 5507, 2θ range = 3.20–51.40°, parameters = 362, R indices [$I>4\sigma(I)$]: R_1 = 0.089, wR_2 = 0.203, R indices (all data): R_1 = 0.166, wR_2 = 0.223, max. difference peak/hole = 2.55/–2.11 e/Å^3. **1-b:** Thin plate, $0.320\times0.300\times$ca. 0.005 mm, monoclinic, $P21/c$, a = 13.32(3), b = 34.39(8), c = 13.04(3) Å, β = 117.31(4)°, V = 5307(21) Å^3, $\rho_{calcd.}$ = 1.618 g/cm^3, μ(Mo) = 0.80 mm^{-1}, total data = 32033, unique data = 10735, 2θ range = 3.64–52.74°, parameters = 716, restraints = 1365, R indices [$I>4\sigma(I)$]: R_1 = 0.168, wR_2 = 0.347, R indices (all data): R_1 = 0.274, wR_2 = 0.381, max. difference peak/hole = 2.97/–2.62 e/Å^3. The overall quality of this structure was poor due to the small crystal size. A number of restraints were used to help stabilize the refinement including SAME, FLAT, SIMU and ISOR commands. **2:** Irregular block, $0.17\times0.17\times0.12$ mm, monoclinic, $C2/c$, a = 16.062(3), b = 15.054(3), c = 23.422(4) Å, β = 104.797(3)°, V = 5475.6(18) Å^3, $\rho_{calcd.}$ = 1.425 g/cm^3, μ(Mo) = 0.50 mm^{-1}, total data = 21929, unique data = 6807, 2θ range = 3.60–56.66°, parameters = 383, restraints = 13, R indices [$I>4\sigma(I)$]: R_1 = 0.039, wR_2 = 0.094, R indices (all data): R_1 = 0.064, wR_2 = 0.101, max difference peak/hole = 0.62/–0.60 e/Å^3. CCDC-295809 (**1-p**), -295810 (**1-b**), and -295811 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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