Synthesis and Reactivity of Mononuclear Anionic Pentafluorophenyl Compounds of Rhodium(I) and Iridium(I). X-ray Structure of $[\{P(OPh)_3\}_2(C_6F_5)_2RhAg(PPh_3)]$

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Received August 4, 1994®

Arylation with $[Ag(C_6F_5)]$ or $(NBu_4)[Ag(C_6F_5)_2]$ of several rhodium or iridium substrates leads to new anionic complexes of type $[M(C_6F_5)Cl(L_2)]^-$ (M = Rh, $L_2 = (CO)_2$; M = Ir, L_2 = cod) or $[M(C_6F_5)_2(L_2)]^-$ (M = Rh, $L_2 = (CO)_2$, cod, $\{P(OPh)_3\}_2$; M = Ir, L_2 = cod) which have been isolated as benzyltriphenylphosphonium or tetrabutylammonium salts. The reactivity of some of these complexes have been explored. Addition of neutral ligands to $[Rh(C_6F_5)Cl(CO)_2]^-$ gives neutral rhodium(I) complexes $[Rh(C_6F_5)(PPh_3)(CO)_2]$ and $[Rh(C_6F_5)(CO)L]$ (L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)); with bis(diphenylphosphino)methane (dppm), the A-frame compound $[Rh_2(C_6F_5)_2(\mu\text{-}CO)(\mu\text{-dppm})_2]$ is prepared. Reactions of methyl iodide, $[Tl(C_6F_5)_2Cl]$, and $[Ag(PPh_3)]^+$ with the rhodium(I) complexes are described. The new compounds have been characterized by elemental analyses, MS, NMR, and conductivity and the heterobimetallic complex $[\{P(OPh)_3\}_2(C_6F_5)_2RhAg(PPh_3)]$ has also been characterized by a single-crystal X-ray diffraction study. The crystals are triclinic (space group $P\bar{1}$) having a unit cell of dimensions $a = 11.984(2)$ Å, $b = 12.752(2)$ Å, $c = 22.183(5)$ Å, $\alpha = 101.07(1)°$, $\beta = 104.14(1)°$, $\gamma = 103.06(1)°$, $V = 3090.7(10)$ Å^3, and $Z = 2$. The structure was solved by Patterson methods and refined by full-matrix least squares to $R = 0.064$, $R_w = 0.051$ for 5802 observed reflections ($F \geq 2\sigma(F)$). The rhodium atom is in a square-pyramidal environment, with two C_6F_5 (*cis*) and two $P(OPh)_3$ ligands in the square plane and a $Ag(PPh_3)$ moiety in the apical position. The complex contains a Rh–Ag bond [2.635(1) Å] unsupported by covalent bridges.

Introduction

One of our current research interests is the synthesis and reactivity of pentahalophenyl derivatives (C_6X_5; X = F, Cl) of rhodium and iridium. With the pentafluorophenyl group, we have reported a variety of neutral, anionic, mononuclear, and dinuclear complexes[1,2] of rhodium(III) prepared from the anionic complex[3] $[Rh(C_6F_5)_5]^{2-}$. However, only a few pentafluorophenyl complexes of rhodium(I) and iridium(I) are known. All of them are neutral compounds with stoichiometries *trans*-$[M(C_6F_5)L(PR_3)_2]$ (M = Rh, R = Ph, L = CO,[4,5] CS;[6] R = Cp, L = py, PPh_3, $H_2NCH_2CH_2NH_2$ (en);[7] M = Ir, R = Ph, L = CO,[4,8,9] CS[6]), $[Rh(C_6F_5)(cod)(PPh_3)]$,[4] $[Ir(C_6F_5)(PEt_2F)(PEt_3)_2]$,[10] and $[Ir(C_6F_5)(PMePh_2)_3]$.[8] To the best of our knowledge, no anionic complexes of rhodium(I) or iridium(I) with the pentafluorophenyl ligand have been described.

Due to the importance of anionic compounds for the synthesis of heterobinuclear complexes[11] as well as their use as starting materials for reactivity studies,[3] such as oxidative addition and substitution reactions, we have now focused our attention on the preparation of anionic pentafluorophenyl compounds of rhodium(I) and iridium(I). In this paper we wish to report (a) the synthesis of some anionic pentafluorophenyl rhodium(I) or iridium(I) complexes, (b) the reactivity of the rhodium derivatives toward a silver cation, (c) oxidation reactions to form monomeric rhodium(III) complexes, and (d) substitution reactions that allow the preparation of a variety of rhodium(I) complexes. In this context it is interesting to mention that, using the pentachlorophenyl group, we recently reported the synthesis of anionic and neutral iridium(I) and iridium(II)[12] as well as anionic rhodium(I) and neutral rhodium(II)[13] complexes.

Results and Discussion

Mono- and Bisarylated Mononuclear Anionic complexes: $[M(C_6F_5)Cl(L_2)]^-$ and $[M(C_6F_5)_2(L_2)]^-$. The preparation of pentafluorophenyl complexes of rhodium(I) and iridium(I) has been attempted by reaction of the dimers $[\{M(\mu\text{-}Cl)(L_2)\}_2]$ (M = Rh, Ir; L_2 = neutral ligands) with (pentafluorophenyl)lithium. In all cases, a reaction was observed but we could not isolate any product. Therefore, the arylation was

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® Abstract published in *Advance ACS Abstracts,* March 15, 1995.

(1) García, M. P.; Jiménez, M. V.; Lahoz, F. J.; Oro, L. A.; Tiripicchio, A.; López, J. A. *J. Chem. Soc., Dalton Trans.* **1990**, 1503.

(2) García, M. P.; Jiménez, M. V.; Oro, L. A. *J. Organomet. Chem.* **1992**, *438*, 229.

(3) García, M. P.; Oro, L. A.; Lahoz, F. J. *Angew. Chem.* **1988**, *100*, 1766; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1700.

(4) Bennett, R. L.; Bruce, M. I.; Gardner, R. C. F. *J. Chem. Soc., Dalton Trans.* **1973**, 2653.

(5) Deacon, G. B.; Faulks, S. J.; Miller, J. M. *Transition Met. Chem.* **1980**, *5*, 305. Nyholm, R. S.; Royo, P. *J. Chem. Soc., Chem. Commun.* **1969**, 421.

(6) Tresoldi, G.; Faraone, F.; Piraino, P. *J. Chem. Soc., Dalton Trans.* **1979**, 1053.

(7) Mukhedkar, A. J.; Mukhedkar, V. A.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 3158.

(8) Rausch, M. D.; Moser, G. A. *Inorg. Chem.* **1974**, *13*, 11.

(9) Clearfield, A.; Gopal, R.; Bernal, I.; Moser, G. A.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 2727.

(10) Blum, O.; Frolow, F.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1991**, 258.

(11) Usón, R.; Forniés, J. *Inorg. Chim. Acta* **1992**, *198–200*, 165.

(12) García, M. P.; Jimenez, M. V.; Oro, L. A.; Lahoz, F. J.; Alonso, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1527. García, M. P.; Jimenez, M. V.; Oro, L. A.; Lahoz, F. J.; Camellini Tiripicchio, M.; Tiripicchio, A. *Organometallics* **1993**, *12*, 4660.

(13) García, M. P.; Jimenez, M. V.; Oro, L. A.; Lahoz, F. J.; Casas, J. M.; Alonso, P. J. *Organometallics* **1993**, *12*, 3257.

0020-1669/95/1334-2153$09.00/0

carried out with mild arylating agents such as $[Ag(C_6F_5)]$[14] and $(NBu_4)[Ag(C_6F_5)_2]$.[15]

The results of the reaction of $[Ag(C_6F_5)]$ with several dinuclear compounds of rhodium and iridium $[\{M(\mu\text{-}Cl)(L_2)\}_2]$ ($M = Rh$, $L_2 = (CO)_2$, $\{P(OPh)_3\}_2$, 1,5-cyclooctadiene (cod); $M = Ir$, $L_2 =$ cod) depend on the nature of the dimer compound used. No reaction was observed for the complexes with rhodium as the metal and 1,5-cyclooctadiene or triphenyl phosphite as the neutral ligands. In spite of this, for $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ and $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ complexes, it is possible to transfer one pentafluorophenyl group, and after the addition of the cation benzyltriphenylphosphonium, anionic mononuclear monoarylated complexes can be isolated (eq 1).

$$[\{M(\mu\text{-}Cl)(L_2)\}_2] + 2[Ag(C_6F_5)] + 2PBzPh_3Cl \rightarrow \underset{\mathbf{1,2}}{2\textit{cis}\text{-}(PBzPh_3)[M(C_6F_5)Cl(L_2)]} + 2AgCl \quad (1)$$

$$M = Rh,\ L_2 = (CO)_2\ (\mathbf{1});\ M = Ir,\ L_2 = \text{cod}\ (\mathbf{2})$$

When carbon monoxide was bubbled through a dichloromethane solution of **2**, cod was displaced and the anionic biscarbonylated $[Ir(C_6F_5)Cl(CO)_2]^-$ (**3**) complex was formed.

By using $[Ag(C_6F_5)_2]^-$ as the arylating agent, both molecules of the perfluoroaryl ligand were transferred to the rhodium or iridium, yielding bisarylated complexes (eq 2).

$$[\{M(\mu\text{-}Cl)(L_2)\}_2] + 2(NBu_4)[Ag(C_6F_5)_2] = 2\textit{cis}\text{-}(NBu_4)[M(C_6F_5)_2(L_2)] + 2AgCl \quad (2)$$

$$M = Rh,\ L_2 = (CO)_2\ (\mathbf{4}),\ \text{cod}\ (\mathbf{5}),\ \{P(OPh)_3\}_2\ (\mathbf{6});\ M = Ir,\ L_2 = \text{cod}\ (\mathbf{7})$$

The analytical results (C, H, and N), mass spectra, and ^1H NMR spectra for complexes **1**–**7** are in agreement with the proposed formulations. The conductivities of the complexes, in acetone solutions, are those expected for 1:1 electrolytes.[16] The IR spectra show the characteristic bands near 1510, 1050, and 950 cm^{-1} of the pentafluorophenyl groups.[17] Complex **1** exhibits a $\nu(Rh-Cl)$ band at 302 cm^{-1}. The vibrations $\nu(CO)$ for compounds **1** and **4** (**1**: 2030, 1985 cm^{-1}, $\Delta\nu = 45$ cm^{-1}; **4**: 2050, 1985 cm^{-1}, $\Delta\nu = 65$ cm^{-1}) and the separation between them are consistent with a *cis* arrangement of the carbonyl ligands.[18] This disposition is also confirmed in compound **4** by the presence of two bands at 890 and 875 cm^{-1} for the pentafluorophenyl groups.[19] In compound **1** this region cannot be unambiguously assigned since the $PBzPh_3^+$ cation absorbs in this zone. The geometry of the diolefin also imposes a *cis* disposition in compounds **2**, **5**, and **7**. For complex **6** the IR absorption of the aryl ligand, in the 950 cm^{-1} region, overlaps that of the phosphite ligands. However, the same geometry is inferred from the $^{31}P\{^1H\}$ NMR spectrum. This consists of one doublet of multiplets at 135.0 ppm ($^1J(Rh-P) = 244$ Hz) which can be assigned to two equivalent phosphorus atoms coupling to a rhodium(I) center[20] and to the *ortho* F atoms of the pentafluorophenyl groups. These data are indicative of a phosphorus atom *trans* to a C_6F_5 group.[21]

The ^{19}F NMR spectra of all the complexes show only one signal for each type of *ortho* and *meta* fluorine atom. This can be understood in terms of fluxionality probably due to the rotation of the C_6F_5 ligand around the Rh–C bond or to the presence of a molecular symmetry plane coincident with the metal coordination plane.

Reactivity of the Anionic Complexes. The reactivity of these anions has also been examined. For this initial study the rhodium compounds were chosen. We have explored the reaction of the bisarylated complexes toward Ag^+; owing to their anionic nature, the metal center must have an excess of electron density and could act as a Lewis base toward Lewis acids, such as the Ag^+ cation in silver salts or complexes, to give heteronuclear derivatives with Rh–Ag bonds; this is the case for the reaction of complex **6** with $O_3ClOAgPPh_3$. The addition of solid $O_3ClOAgPPh_3$ to a toluene suspension of $[Rh(C_6F_5)_2\{P(OPh)_3\}_2]^-$ (**6**) (ratio 1:1), at 0 °C, gives a bright yellow solution together with a white solid (NBu_4ClO_4). From the solution the heterobinuclear $[\{P(OPh)_3\}_2(C_6F_5)_2RhAg(PPh_3)]$ (**8**) can be isolated. Complex **8** is not stable to the air in solution, but under nitrogen atmosphere, at -20 °C and in the absence of light, its solutions can be kept for several days. The ^{19}F NMR spectrum at room temperature gives two broad signals (at about -109 and -165.7 ppm) for the *ortho* and *meta* fluorine atoms of the pentafluorophenyl groups, respectively, and one signal, with the appearance of a triplet, at -164.17 ppm for the *para* fluorine atoms; from -40 to -85 °C, each of the signals for the *ortho* and *meta* fluorine atoms splits into two multiplets (at -106, -110.7 ppm and -163.8, -164.2 ppm) while the *para* fluorine signal remains unchanged. The $^{31}P\{^1H\}$ NMR spectrum of **8** consists of a doublet of multiplets due to the phosphite ligands and an AMX pattern, due to the PPh_3, arising from $^{107}Ag-^{31}P$ and $^{109}Ag-^{31}P$ and the rhodium atom spin couplings. The observed Ag–P coupling constants [$^1J(^{109}Ag-^{31}P) = 663$ Hz and $^1J(^{107}Ag-^{31}P) = 574$ Hz] are higher than the values reported in the literature[22] (ranging from 200 to 500 Hz), but the ratio of $J(^{109}Ag-^{31}P)/J(^{107}Ag-^{31}P)$ is consistently close to the $\mu(^{109}Ag)/\mu(^{107}Ag)$ ratio of 1.149.

According to the spectroscopic and analytical data complex **8** is formed by a donor–acceptor interaction between the rhodium center of the anionic $[Rh(C_6F_5)_2\{P(OPh)_3\}_2]^-$ complex and the $[Ag(PPh_3)]^+$ cationic fragment, resulting in a Rh–Ag bond. This fact was confirmed by the X-ray structure determination.

However, it has not been possible to form Rh–Ag bonds with the other anionic rhodium complexes. For example, the reactions of $[Rh(C_6F_5)_2(CO)_2]^-$ (**4**) or $[Rh(C_6F_5)_2(cod)]^-$ (**5**) with $O_3ClOAgPPh_3$ undergo decomposition even at -78 °C. The initial yellow solutions turned to red, and metallic silver was deposited on the Schlenk tube walls. From the solutions no Rh(III) complexes were isolated; instead, the known products $[Rh(C_6F_5)(CO)(PPh_3)_2]$[4,8] and $[Rh(C_6F_5)(cod)(PPh_3)]$,[4] respectively, were obtained and identified through their analytical and spectroscopic properties.

Substitution and Oxidation Reactions of Complex 1. The products derived from the reactions of complex **1** are summarized in Scheme 1. As can be seen, with neutral ligands,

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(14) Sun, K. K.; Miller, W. T. *J. Am. Chem. Soc.* **1970**, *92*, 3166.

(15) Usón, R.; Laguna, A.; Abad, J. A. *J. Organomet. Chem.* **1983**, *246*, 341.

(16) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(17) Long, D. A.; Steele, D. *Spectrochim. Acta* **1961**, *19*, 1955.

(18) Browning, J.; Goggin, P. L.; Goodfellow, R. J.; Norton, M. G.; Rattray, A. J. M.; Taylor, B. F.; Mink, J. *J. Chem. Soc., Dalton Trans.* **1977**, 2061.

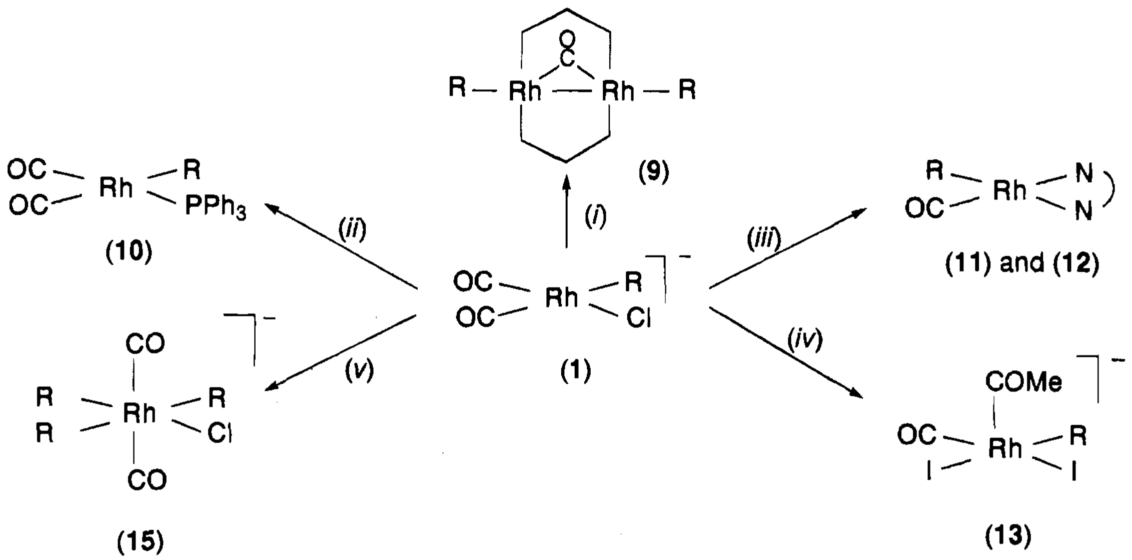
(19) Maslowsky, E., Jr. *Vibrational Spectra of Organometallic Compounds*; Wiley: New York, 1977, p 437 and references therein. Usón, R.; Forniés, J.; Gimeno, J.; Espinet, P.; Navarro, R. *J. Organomet. Chem.* **1974**, *81*, 115.

(20) Haines, L. M. *Inorg. Chem.* **1970**, *9*, 1517. Botrill, M.; Green, M. *J. Organomet. Chem.* **1976**, *111*, C6.

(21) Usón, R.; Forniés, J.; Gimeno, J.; Navarro, R.; Ortega, M. A. *J. Organomet. Chem.* **1987**, *334*, 389.

(22) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386.

Scheme 1[a]



[a] $R = C_6F_5$; $Q^+ = PBzPh_3$. Key: (*i*) dppm; (*ii*) PPh_3; (*iii*) 2,2′-bipyridine or 1,10-phenanthroline; (*iv*) CH_3I; (*v*) $[Tl(C_6F_5)_2]Br$.

such as dppm, PPh_3, 2,2′-bipy, or 1,10-phen, the chlorine is displaced as $PBzPh_3Cl$, yielding neutral rhodium(I) complexes. Reaction of **1** with dppm in dichloromethane affords orange crystals of the neutral A-frame compound $[\{Rh(C_6F_5)\}_2(\mu\text{-}dppm)_2(\mu\text{-}CO)]$ (**9**) which shows a strong ν(CO) band at 1795 cm^{-1} in the IR spectrum. Its ^{31}P NMR spectrum consists of a resonance pattern similar to that described for $[Rh_2Br_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$[23] with δ 26.6 ppm and $^1J(Rh-P) + {}^xJ(Rh-P) =$ 131 Hz. An acetone solution of **9** is nonconducting. On the basis of spectroscopic data, conductivity, and elemental analyses the proposed structure of this compound (Scheme 1), having a carbonyl ligand and a formal Rh–Rh bond, is analogous to the postulated for $[Rh_2X_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ (X = Cl, Br, I) and confirmed by X-ray structures of the chlorine[24] and bromine[23b] derivatives. The ^1H NMR spectrum of compound **9** exhibits two signals for the CH_2 protons of the dppm and the ^{19}F NMR shows two different resonances for the *ortho* F atoms as well as two for the *meta* F atoms of the C_6F_5 rings. These data indicate that the pentafluorophenyl groups are not coplanar with the A-frame skeleton of the molecule.

Triphenylphosphine also reacts with complex **1** in the stoichiometric ratio 1:1 to give the dicarbonyl neutral compound $[Rh(C_6F_5)(CO)_2(PPh_3)]$ (**10**). The IR spectrum of this compound, in CH_2Cl_2, shows two ν(CO) bands at 2060 and 1980 cm^{-1} ($\Delta\nu(CO) = 80\ cm^{-1}$), typical of *cis*-dicarbonyl derivatives of rhodium(I). The ^{31}P NMR spectrum of **10** consists of a doublet at δ 34.7 ppm with a $J(Rh-P)$ of 139 Hz. With 2 molar equiv of PPh_3, complex **1** gives the known $[Rh(C_6F_5)(CO)(PPh_3)_2]$[4,5] ($\nu(CO) = 1955\ cm^{-1}$) by additional displacement of one of the carbonyl groups.

The coordinated chlorine and one CO ligand can also be displaced, in complex **1**, by the bidentate neutral ligands 2,2′-bipyridine and 1,10-phenanthroline. Addition of the solid ligands to Cl_2CH_2 solutions of **1** resulted in the formation of $[Rh(C_6F_5)(CO)L]$ (L = bipy **11**, phen **12**). These compounds can also be prepared by reaction of $[Rh(C_6F_5)_2(CO)_2]^-$ (**4**) with the same ligands; in this case the displacement of a C_6F_5 group and a CO takes place. The IR spectra of complexes **11** and **12** show the ν(CO) band at 1970 and 1960 cm^{-1}, respectively. The ^1H NMR spectra of these complexes show one resonance for each proton of the nitrogen donor ligands, which corroborates the absence of symmetry elements in these molecules.

Oxidative addition reactions have also been carried out on complex **1** affording rhodium(III) compounds (Scheme 1). The solution of **1** in methyl iodide at room temperature led to a change in color of the reaction mixture from yellow to orange and to the formation of the acylrhodium(III) complex $(PBzPh_3)[Rh(C_6F_5)(I)_2(COMe)(CO)]$ (**13**). The elemental analyses, MS, and conductivity (1:1 electrolyte) are in agreement with the proposed formulation. Its IR spectrum shows a sharp terminal ν(CO) band at 2070 cm^{-1} and a broad band for the acetyl group at 1715 cm^{-1}, the ν(Rh–Cl) absorption of the starting complex **1** being absent. The room-temperature ^1H NMR spectrum shows a resonance at δ 3.2 ppm due to the methyl group of the acyl ligand.

It is known that square-pyramidal geometry appears to be the preferred arrangement for five-coordinated acylrhodium(III) complexes with the acetyl group occupying the apical coordination site.[25] Making this assumption, the reaction of **13** with $AgClO_4$ (1:1 ratio) with subsequent addition of neutral ligands, CO and Hpz (pyrazole), has been investigated, in an effort to elucidate the arrangement of the basal ligands as well as the migratory aptitude of the methyl group of the acyl ligand.

Complex **13** reacts with $AgClO_4$ in diethyl ether giving a solid, AgI and $[PBzPh_3]ClO_4$, and a yellow solution. The IR spectrum of the solution, either in diethyl ether or in CH_2Cl_2, gives only a ν(CO) terminal band and an acetyl band; no methyl migration has been observed. After the solution has been treated with CO, its IR spectrum shows the acetyl band at 1750 cm^{-1} and three terminal ν(CO) bands, at 2085, 2075, and 2010 cm^{-1}, which could be assigned to the tricarbonyl *mer*-$[Rh(C_6F_5)I(COMe)(CO)_3]$; unfortunately, this compound could not be isolated, so the three CO bands could also be due to the presence of more than one species, and consequently we cannot make a conclusive assignement of the basal ligands of compound **13**.

The reaction of compound **13** with $AgClO_4$ and Hpz led to the separation of AgI and $[PBzPh_3]ClO_4$ and to the formation of an orange, nonconducting acylrhodium(III) complex [Rh-

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[23] (a) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500. (b) *Ibid.* **1980**, *19*, 2508.

[24] Gelmini, L.; Stephan, D. W.; Loeb, S. J. *Inorg. Chim. Acta* **1985**, *98*, L3.

[25] Adams, H.; Bailey, N. A.; Mann, B. E.; Manuel, C. P. *Inorg. Chim. Acta* **1992**, *198–200*, 111. Bennett, M. A.; Jeffery, J. C.; Robertson, G. B. *Inorg. Chem.* **1981**, *20*, 330.

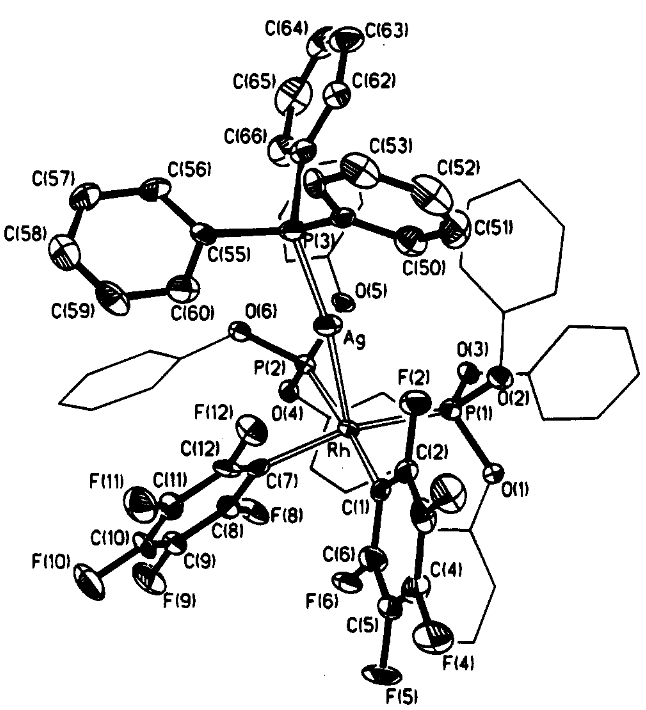

Figure 1. Molecular representation of $[\{P(OPh)_3\}_2(C_6F_5)_2RhAg(PPh_3)]$ (**8**) together with the atom-labeling scheme used. Phenyl rings of the $P(OPh)_3$ ligands are drawn in skeletal form for clarity (labeling for these rings comprises atoms between C(13) and C(48)).

$(C_6F_5)(I)(COMe)(CO)(Hpz)]$ (**14**). In the solid state IR spectrum of **14** there is a $\nu(NH)$ band at 3375 cm^{-1}, a sharp $\nu(CO)$ terminal absorption at 2088 cm^{-1}, and a strong $\nu(CO)$ acyl band at 1710 cm^{-1}. The ^1H NMR spectrum of **14**, in $CDCl_3$ at room temperature, shows the resonances due to the pyrazole ligand together with the methyl resonance of the acetyl group at δ 2.6 ppm. The elemental analyses, MS, and the ^{19}F NMR spectrum are in agreement with the proposed formulation.

By using $[Tl(C_6F_5)_2Cl]$ as oxidant, both pentafluorophenyl groups are transferred to the rhodium atom in complex **1**, yielding the white anionic complex $[Rh(C_6F_5)_3Cl(CO)_2]^-$ (**15**). IR spectrum: $\nu(CO)$, in CH_2Cl_2 solution, 2110 cm^{-1}; $\nu(Rh-Cl)$, in Nujol suspension, 310 cm^{-1}. The ^{19}F NMR spectrum shows two signals (2:1) for the *ortho* fluorine atoms and two signals (2:1) for the *para* fluorine atoms of the pentafluorophenyl ligands. The analytical and spectroscopic data indicate that the structure of compound **15** is similar to that of $(PBzPh_3)[Rh(C_6F_5)_4(CO)_2]$[3] with the anion exhibiting octahedral geometry and the CO groups in mutually *trans* positions.

Crystal and Molecular Structure of $[\{P(OPh)_3\}_2(C_6F_5)_2RhAg(PPh_3)]\cdot{}^1/_2CH_2Cl_2\cdot{}^1/_2C_6H_{14}$. In order to determine the molecular structure of **8**, a single-crystal X-ray diffraction study was undertaken. The molecular structure is shown in Figure 1, together with the labeling of the atoms; selected bond distances and angles are reported in Table 1. The molecule consists of a Rh atom displaying a slightly distorted square-pyramidal environment, the apical position being occupied by the Ag atom of the "$AgPPh_3$" moiety, while the basal plane is formed by the C_{ipso} atoms of the C_6F_5 groups (*cis*) and the P atoms of the phosphite ligands. The rhodium atom is situated 0.007(1) Å out of this basal plane. The angles between *cis* ligands range from 82.3(3) to 101.0(1)°; the angles between *trans* ligands are P(1)−Rh−C(7) 166.3(2)° and P(2)−Rh−C(1) 171.9(3)°. The dihedral angle between the planes defined by Rh, P(1) and P(2) and by Rh, C(1) and C(7) is 7.6(3)°. The Rh−C distances [Rh−C(1) 2.098(10) Å and Rh−C(7) 2.093(9) Å] are identical and very similar to that found for the basal C_6F_5 groups in closely related penta- or hexacoordinated Rh(III) complexes, either anionic,[3] $[Rh(C_6F_5)_5]^{2-}$ or $[Rh(C_6F_5)_4(CO)_2]^-$ (mean values 2.115(5) and 2.125(5) Å, respectively), or neutral[1] such as $[Rh(C_6F_5)_3(L)_2]$ (L = PEt_3, mean 2.087(10) Å; L = $AsPh_3$, mean 2.100(11) Å). This feature reveals that the basal Rh−C bond distances in rhodium pentafluorophenyl complexes seem to be only weakly influenced by the anionic character or the oxidation state of the rhodium center. The Rh−P bond distances, 2.232(3) and 2.222(3) Å, are in the range of values found[26] for other Rh(I)−triphenyl phosphite complexes.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $\mathbf{8}\cdot{}^1/_2CH_2Cl_2\cdot{}^1/_2C_6H_{14}$

Rh−Ag	2.635(1)	P(1)−O(1)	1.626(7)
Rh−P(1)	2.222(3)	P(1)−O(2)	1.614(5)
Rh−P(2)	2.232(3)	P(1)−O(3)	1.615(7)
Rh−C(1)	2.098(10)	P(2)−O(4)	1.621(6)
Rh−C(7)	2.093(9)	P(2)−O(5)	1.613(6)
Ag−P(3)	2.368(3)	P(2)−O(6)	1.606(7)
Ag···F(2)	2.816(5)	Ag···F(12)	2.862(5)
Ag−Rh−P(1)	95.92(8)	Rh−Ag−P(3)	172.41(8)
Ag−Rh−P(2)	79.67(7)	Rh−P(1)−O(1)	113.7(2)
Ag−Rh−C(1)	94.8(3)	Rh−P(1)−O(2)	123.4(3)
Ag−Rh−C(7)	91.2(3)	Rh−P(1)−O(3)	119.1(2)
P(1)−Rh−P(2)	101.0(1)	O(1)−P(1)−O(2)	91.7(3)
P(1)−Rh−C(1)	85.5(2)	O(1)−P(1)−O(3)	102.2(3)
P(1)−Rh−C(7)	166.4(2)	O(2)−P(1)−O(3)	101.8(3)
P(2)−Rh−C(1)	171.9(3)	Rh−P(2)−O(4)	119.4(2)
P(2)−Rh−C(7)	91.7(2)	Rh−P(2)−O(5)	115.8(2)
C(1)−Rh−C(7)	82.3(3)	Rh−P(2)−O(6)	120.1(3)
Ag−P(3)−C(49)	111.9(3)	O(4)−P(2)−O(5)	103.8(3)
Ag−P(3)−C(55)	113.6(3)	O(4)−P(2)−O(6)	97.2(3)
Ag−P(3)−C(61)	114.5(3)	O(5)−P(2)−O(6)	96.5(3)

The rhodium, $[Rh(C_6F_5)_2\{P(OPh)_3\}_2]$, and the silver, $[Ag(PPh_3)]$, fragments are bonded by a donor−acceptor Rh−Ag bond, unsupported by any other covalent bridging ligand, with an observed distance of 2.635(1) Å. This Rh−Ag distance is shorter than the distances found for other reported Rh−Ag complexes: 2.730(1) Å for $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgO_2CCH_3)]$,[27] 2.689(2) Å for $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgOPF_2O)]$,[28] 2.796(3) Å for $[(cod)_2Rh_2(\mu\text{-}C_7H_4NS_2)_2Ag(O_2ClO_2)]$,[29] and 2.822(1) Å (mean) for $[Rh_6C(CO)_{15}\{Ag(PPh_3)\}_2]$ or 2.823(1) Å (mean) for $[Rh_6C(CO)_{15}\{Ag(NCMe)\}_2]$.[30] This may be a direct consequence of the different coordination around the silver atom. In complex **8** there are only two ligands bonded to the silver metal center while in all the above referred compounds the coordination around the silver atom is higher. In accordance with this, the Rh−Ag bond distance in **8** is comparable to the values 2.636(1) and 2.651(1) Å found for the complex $[\{Rh(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(PPh_3)\}_2Ag]PF_6$, which has a nearly linear trimetal sequence Rh−Ag−Rh, with the silver center only linked to two rhodium atoms.[31] This shortening of the bond distance when the coordination number decreases has also been observed in related Pt−Ag compounds, ranging, for instance, from 2.787(1) Å for a hexacoordinated Ag atom,[32] in $[(NH_3)_8Pt_4(1MeUra)_4Ag]^{5+}$, to 2.637(1) Å in $[(C_6F_5)_3(SC_4H_8)PtAg(PPh_3)]$, where the silver atom is only bonded to a platinum

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(26) Trzeciak, A. M.; Ziolkowski, J. J.; Lis, T. *Polyhedron* **1989**, *8*, 2415.

(27) Lo Schiavo, S.; Bruno, G.; Piraino, P.; Faraone, F. *Organometallics* **1986**, *5*, 1400.

(28) Bruno, G.; Lo Schiavo, S.; Piraino, P.; Faraone, F. *Organometallics* **1985**, *4*, 1098.

(29) Ciriano, M. A.; Pérez-Torrente, J. J.; Oro, L. A.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1991**, 255.

(30) Fumagalli, A.; Martinengo, S. *J. Chem. Soc., Dalton Trans.* **1988**, 1237.

(31) Connelly, N. G.; Lucy, A. R.; Payne, J. D.; Galas, A. M. R.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1983**, 1879.

(32) Lippert, B.; Neugebauer, D. *Inorg. Chem.* **1982**, *21*, 451.

and a phosphorus atom.[33] In complex **8** the Rh−Ag bond deviates only 10.8(1)° from perpendicularity to the rhodium coordination plane. The silver atom is also bonded to a PPh_3 group, with the bond angle Rh−Ag−P(3) being 172.41(8)°.

Two *ortho* fluorine atoms of the C_6F_5 rings, F(2) and F(12), are oriented toward the silver atom; the Ag−F(2) and Ag−F(12) separations, 2.816(5) and 2.862(5) Å, respectively, suggest the presence of halogen−silver interactions as has been reported for related C_6F_5−Ag or C_6Cl_5−Ag complexes.[11,33] However, the values observed for compound **8** indicate that this interaction is relatively weak.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of nitrogen by using Schlenk tube techniques. Solvents were distilled under nitrogen from the appropriate drying agents. The starting materials $[\{M(\mu\text{-Cl})(L_2)\}_2]$ (M = Rh, L_2 = η^4-cod,[34] $(CO)_2$,[35] $(P(OPh)_3)_2$;[36] M = Ir, L_2 = η^4-cod[37]) were prepared by published methods.

Physical Measurements. IR spectra were recorded on a Perkin-Elmer 783 infrared spectrometer using Nujol mulls between polyethylene sheets or in solution in NaCl cells. NMR spectra were recorded on a Varian XL 200 spectrophotometer. Chemical shifts are expressed in parts per million upfield from Me_4Si (^1H), $CFCl_3$ (^{19}F), and 85% H_3PO_4 (^{31}P) as external references. C, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyzer. Molecular weights were determinated with a Knauer osmometer using chloroform solutions. Mass spectra were measured in a VG Autospec double-focusing mass spectrometer operated in the negative mode for anionic species and in the positive mode for neutral complexes; ions were produced with the standard Cs^+ gun at ca. 30 kV; 3-nitrobenzyl alcohol (NBA) or sulfolane were used as matrix; high-resolution FAB spectra are in accordance with the simulated isotopic pattern distribution.

$(PBzPh_3)[Rh(C_6F_5)Cl(CO)_2]$ (1) and $(PBzPh_3)[Ir(C_6F_5)Cl(cod)]$ (2). To a suspension of the dimer compounds $[\{MCl(L_2)\}_2]$ (M = Rh, L_2 = $(CO)_2$, 200 mg, 0.51 mmol; M = Ir, L_2 = cod , 100 mg, 0.15 mmol) in diethyl ether (10 mL) were added a solution of $[Ag(C_6F_5)]$ in the same solvent (20 mL) (Ag:M = 1:1) and benzyltriphenylphosphonium chloride; the reaction was carried out under nitrogen atmosphere and exclusion of light. The initial solids dissolved, and yellow solutions together with white solids (AgCl) were formed. After 30 min of stirring, the solvent was evaporated to dryness and CH_2Cl_2 was added. Filtration, evaporation of the solvent until ca. 1 mL, and addition of diethyl ether (20 mL) afforded compounds **1** and **2** which were filtered off, washed with diethyl ether, and vacuum dried. Data for **1**: pale yellow; yield 490 mg (67%). Anal. Calcd for $C_{33}H_{22}ClF_5O_2PRh$: C, 55.44; H, 3.10. Found: C, 55.30; H, 3.21. IR (CH_2Cl_2): ν(CO) 2030 s, 1985 s cm^{-1}. Λ_M (acetone, $C = 5.03 \times 10^{-4}$ mol L^{-1}): 127 Ω^{-1} cm^2 mol^{-1}. ^{19}F NMR (20 °C, $CDCl_3$), δ, ppm: *o*-F −113.0 (m), *m*-F −164.7 (ft), *p*-F −162.5 (ft). MS (FAB): *m*/*e*, 361 (M = $[Rh(C_6F_5)Cl(CO)_2]^-$, 100), 333 (M − (CO), 74), 305 (M − $(CO)_2$, 18). Data for **2**: yellow; yield 185 mg (72%). Anal. Calcd for $C_{39}H_{34}ClF_5IrP$: C, 54.70; H, 4.00. Found: C, 54.36; H, 4.45. Λ_M (acetone, $C = 5.99 \times 10^{-4}$ mol L^{-1}): 102 Ω^{-1} cm^2 mol^{-1}. ^{19}F NMR (20 °C, $CDCl_3$), δ, ppm: *o*-F −117.8 (m), *m*-F −166.7 (ft), *p*-F −166.2 (ft). ^1H NMR (20 °C, $CDCl_3$), δ, ppm: 7.7−6.8 (20H, phenyl), 4.4 (2H, $>CH_2$, $PBzPh_3^+$, ^2J(H−P) = 13.9), 3,4 (s, 4H, =CH, cod), 2.0, 1.4 (m, 8H, 4:4, $>CH_2$, cod).

$(PBzPh_3)[Ir(C_6F_5)Cl(CO)_2]$ (3). $(PBzPh_3)[Ir(C_6F_5)Cl(cod)]$ (**2**) (100 mg, 0.12 mmol) was dissolved in dichloromethane (15 mL), and the carbonyl derivative was prepared by bubbling CO into the solution for 15 min. After concentration to ca. 1 mL, an oily residue was obtained by addition of *n*-hexane (10 mL). The solution was removed, and the residue washed twice with *n*-hexane (5 mL). The pale yellow solid produced was stirred in *n*-hexane (15 mL), filtered off, washed with *n*-hexane, and vacuum dried. Yield: 57 mg (59%). Anal. Calcd for $C_{33}H_{22}ClF_5IrO_2P$: C, 49.29; H, 2.76. Found: C, 48.95; H, 3.12. IR (CH_2Cl_2): ν(CO) 2050 s, 1970 s cm^{-1}. Λ_M (acetone, $C = 4.87 \times 10^{-4}$ mol L^{-1}): 108 Ω^{-1} cm^2 mol^{-1}. ^{19}F NMR (20 °C, $CDCl_3$), δ, ppm: *o*-F −115.6 (m), *m*-F −165.0 (ft), *p*-F −162.4 (ft).

Table 2. Summary of Crystallographic Data for Complex $\mathbf{8}\cdot{}^1/_2CH_2Cl_2\cdot{}^1/_2C_6H_{14}$

formula	$C_{66}H_{45}AgF_{10}O_6P_3Rh\cdot{}^1/_2CH_2Cl_2\cdot{}^1/_2C_6H_{14}$
mol wt	1513.3
temp, K	150
symmetry	triclinic, $P\bar{1}$
a, Å	11.984(2)
b, Å	12.752(2)
c, Å	22.183(5)
α, deg	101.07(1)
β, deg	104.14(1)
γ, deg	103.06(1)
V, $Å^3$	3090(1)
Z	2
D, g cm^{-3}	1.626
F(000)	1524
λ(Mo Kα), Å	0.710 73
μ, cm^{-1}	7.78
R, R_w (obs data)[a]	0.0639, 0.0511 ($F \geq 2\sigma(F)$)
goodness-of-fit, S[b]	1.107

[a] $R = \Sigma(|F_o - F_c|)/\Sigma(F_o)$; $R_w = \Sigma(|F_o - F_c|w^{1/2})/\Sigma(F_o w^{1/2})$. [b] $S = [\Sigma(w|F_o - F_c|^2)/(\text{ref} - \text{par})]^{1/2}$.

$(NBu_4)[M(C_6F_5)_2L_2]$ (4−7) (M = Rh, L_2 = $(CO)_2$ (4), cod (5) $\{P(OPh)_3\}_2$ (6); M = Ir, L_2 = cod (7)). To a solution of $(NBu_4)[Ag(C_6F_5)_2]$ (0.2 mmol), in dichloromethane (10 mL), under exclusion of light, was added the stoichiometric amount (ratio 2:1) of the corresponding dinuclear compound $[\{MCl(L_2)\}_2]$. After 30 min the white solids formed were eliminated by filtration through Kieselguhr. Evaporation of the solutions under vacuum to 1 mL for **6**, addition of *n*-hexane, and stirring in the same solvent for **5** and **7** or addition of a 2-propanol/cyclohexane (1:1) mixture for **4** gave the complexes which were separated by filtration, washed with *n*-hexane or diethyl ether, and vacuum dried. Data for **4**: yellow; yield 58%. Anal. Calcd for $C_{30}H_{36}F_{10}NO_2Rh$: C, 48.99; H, 4.93; N, 1.90. Found: C, 49.26; H, 5.25; N, 1.95. IR (CH_2Cl_2): ν(CO) 2050 s, 1985 s cm^{-1}. Λ_M (acetone, $C = 6.12 \times 10^{-4}$ mol L^{-1}): 112 Ω^{-1} cm^2 mol^{-1}. ^{19}F NMR (20 °C, $CDCl_3$), δ, ppm: *o*-F −111.1 (m), *m*-F −165.2 (ft), *p*-F −163.1 (ft). MS (FAB): *m*/*e* 493 (M = $[Rh(C_6F_5)_2(CO)_2]^-$, 100), 465 (M− (CO), 58), 437 (M− $(CO)_2$, 78). Data for **5**: yellow; yield 52%. Anal. Calcd for $C_{36}H_{48}F_{10}NRh$: C, 54.89; H, 6.14; N, 1.78. Found: C, 55.30; H, 6.39; N, 1.90. Λ_M ($C = 5.07 \times 10^{-4}$ mol L^{-1}): 130 Ω^{-1} cm^2 mol^{-1}. ^{19}F NMR (20 °C, $CDCl_3$), δ ppm, *o*-F −111.2 (m), *m*-F and *p*-F −165.9/−163.1. ^1H NMR (20 °C, $CDCl_3$), δ, ppm: 4.1 (s, 4H, =CH, cod), 2.3, 1.9 (m, 8H, 4:4, $>CH_2$, cod), 3.1, 1.5, 1.3, 0.9 (36H, 8:8:8:12, NBu_4^+). Data for **6**: pale yellow; yield 64%. Anal. Calcd for $C_{64}H_{66}F_{10}NO_6P_2Rh$: C, 59.13; H, 5.12; N, 1.07. Found: C, 59.40; H, 5.30; N, 1.00. Λ_M (acetone, $C = 5.19 \times 10^{-4}$ mol L^{-1}): 92 Ω^{-1} cm^2 mol^{-1}. ^{19}F NMR (−60 °C, HDA), δ, ppm: *o*-F −111.2 (m), *m*-F −164.5(ft), *p*-F −163.8(ft).^1H NMR (20 °C, HDA), δ, ppm: 7.2−6.9 (m, 30H, $P(OPh)_3$), 3.4, 1.8, 1.4, 0.9 (36H, 8:8:8:12, NBu_4^+). ^{31}P NMR (20 °C, HDA), δ ppm, 135.0 (dm, ^1J(P−Rh) = 244). MS (FAB): *m*/*e* 1057 (M = $[Rh(C_6F_5)_2\{P(OPh)_3\}_2]^-$, 100), 437 (M − $2\{P(OPh)_3\}_2$, 40). Data for **7**: orange; yield 78%. Anal. Calcd for $C_{36}H_{48}F_{10}IrN$: C, 49.30; H, 5.52; N, 1.60. Found: C, 49.45; H, 5.84; N, 1.52. Λ_M (acetone, $C = 4.56 \times 10^{-4}$ mol L^{-1}): 98 Ω^{-1} cm^2 mol^{-1}. ^{19}F NMR (20 °C, $CDCl_3$), δ, ppm: *o*-F −116.1 (m), *m*-F −167.7 (ft), *p*-F −166.5 (m). ^1H NMR (20 °C, $CDCl_3$), δ, ppm: 2.1 (m, 4H, =CH, cod), 1.6 (m, 8H, $>CH_2$, cod), 3.1, 1.5, 1.3, 0.9 (36H, 8:8:8:12, NBu_4^+). MS (FAB): *m*/*e* 636 (M = $[Ir(C_6F_5)_2(cod)]^-$, 100).

$[\{P(OPh)_3\}_2(C_6F_5)_2RhAg(PPh_3)]$ (8). To a pale yellow suspension of **6** (100 mg, 0.08 mmol) in toluene (15 mL), at 0 °C under exclusion of light, was added solid $[O_3ClOAg(PPh_3)]$ (36.1 mg, 0.08 mmol). After 5 min most of the solid was dissolved, and the solution became bright yellow; a white solid was simultaneously formed which was filtered off after 30 min of stirring. The solvent was pumped off, and the residue was dissolved in dichloromethane (1 mL). The complex was

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(33) Cotton, F. A.; Falvello, L. R.; Usón, R.; Fornies, J.; Tomas, M.; Casas, J. M.; Ara, I. *Inorg. Chem.* **1987**, *26*, 1366.

(34) Giordano, G.; Crabtree R. H. *Inorg. Synth.* **1979**, *19*, 218.

(35) Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1968**, 211.

(36) Haines, L. M. *Inorg. Chem.* **1970**, *9*, 1517.

(37) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.

Table 3. Atomic Coordinates (×10^4; ×10^5 for Rh and Ag Atoms) and Equivalent Isotropic Displacement Coefficients (A^2 × 10^3; ×10^4 for Rh and Ag Atoms) for $[\{P(OPh)_3\}_2(C_6F_5)_2RhAg(PPh_3)]\cdot{}^1/_2CH_2Cl_2\cdot{}^1/_2C_6H_{14}$

atom	*x/a*	*y/b*	*z/c*	*U*(eq)[a]	atom	*x/a*	*y/b*	*z/c*	*U*(eq)[a]
Rh	15521(6)	22857(5)	26484(3)	190(3)	P(2)	2612(2)	1471(2)	3287(1)	20(1)
Ag	−1977(6)	7274(5)	27556(4)	281(3)	O(4)	4049(5)	2031(4)	3605(3)	23(2)
C(1)	406(8)	3053(7)	2137(4)	23(4)	O(5)	2485(5)	180(4)	2981(3)	23(2)
C(2)	−804(8)	2585(7)	1790(4)	25(4)	O(6)	2312(5)	1306(4)	3936(3)	25(2)
C(3)	−1550(8)	3134(8)	1514(4)	31(4)	C(31)	4873(7)	2260(7)	3265(4)	22(4)
C(4)	−1072(10)	4269(8)	1553(5)	41(5)	C(32)	4895(8)	1483(7)	2749(4)	24(4)
C(5)	99(10)	4777(7)	1885(5)	34(4)	C(33)	5774(8)	1733(8)	2454(5)	34(4)
C(6)	810(8)	4186(7)	2174(5)	32(4)	C(34)	6628(9)	2762(9)	2667(5)	40(5)
F(2)	−1351(4)	1484(4)	1730(2)	34(2)	C(35)	6616(9)	3534(8)	3204(5)	41(5)
F(3)	−2729(5)	2643(4)	1203(3)	46(3)	C(36)	5729(8)	3294(7)	3497(5)	29(4)
F(4)	−1780(6)	4842(5)	1281(3)	57(3)	C(37)	3008(8)	−550(7)	3271(4)	25(4)
F(5)	575(5)	5872(4)	1937(3)	51(3)	C(38)	3954(9)	−247(8)	3805(4)	36(4)
F(6)	1960(5)	4771(4)	2518(2)	37(2)	C(39)	4444(9)	−1060(8)	4020(5)	40(4)
C(7)	1472(7)	3428(6)	3441(4)	19(4)	C(40)	3949(9)	−2149(8)	3709(5)	40(5)
C(8)	2516(8)	4280(7)	3822(4)	24(4)	C(41)	3004(10)	−2442(8)	3169(6)	58(5)
C(9)	2498(9)	5159(7)	4283(4)	29(4)	C(42)	2491(8)	−1673(7)	2932(5)	43(4)
C(10)	1462(10)	5262(7)	4388(5)	35(4)	C(43)	2381(8)	2120(7)	4481(4)	24(4)
C(11)	413(8)	4440(7)	4038(5)	30(4)	C(44)	3490(9)	2799(7)	4891(4)	33(4)
C(12)	463(8)	3560(6)	3585(4)	24(4)	C(45)	3482(10)	3522(8)	5446(5)	43(5)
F(8)	3581(4)	4269(4)	3727(3)	38(2)	C(46)	2453(11)	3571(8)	5588(5)	47(5)
F(9)	3548(5)	5966(4)	4638(3)	50(2)	C(47)	1345(10)	2891(8)	5157(5)	42(5)
F(10)	1431(5)	6124(4)	4837(3)	54(3)	C(48)	1322(8)	2149(7)	4601(5)	30(4)
F(11)	−637(5)	4505(4)	4135(3)	49(3)	P(3)	−1716(2)	−524(2)	2992(1)	25(1)
F(12)	−622(4)	2795(4)	3253(2)	35(2)	C(49)	−3156(7)	−902(6)	2373(4)	20(3)
P(1)	1548(2)	1379(2)	1687(1)	23(1)	C(50)	−3150(9)	−910(7)	1751(5)	35(4)
O(1)	1835(5)	2187(4)	1225(3)	25(2)	C(51)	−4235(9)	−1247(8)	1263(5)	42(5)
O(2)	344(5)	588(4)	1134(3)	26(2)	C(52)	−5297(9)	−1528(8)	1391(6)	45(5)
O(3)	2475(5)	644(4)	1644(3)	22(2)	C(53)	−5317(9)	−1516(8)	2002(5)	40(4)
C(13)	2613(8)	3271(7)	1462(5)	31(4)	C(54)	−4242(8)	−1187(7)	2507(4)	29(4)
C(14)	2336(9)	4031(8)	1134(5)	43(5)	C(55)	−1995(8)	40(7)	3742(4)	27(4)
C(15)	3094(11)	5107(8)	1341(6)	66(6)	C(56)	−1838(10)	−391(8)	4260(5)	45(5)
C(16)	4115(10)	5425(9)	1868(7)	65(6)	C(57)	−2026(11)	121(8)	4825(5)	53(5)
C(17)	4347(10)	4649(8)	2189(6)	57(5)	C(58)	−2393(10)	1074(8)	4848(5)	48(5)
C(18)	3621(8)	3556(7)	1984(5)	33(4)	C(59)	−2571(8)	1518(8)	4336(5)	39(4)
C(19)	−285(7)	−479(7)	1114(4)	21(4)	C(60)	−2359(8)	1004(7)	3780(5)	35(4)
C(20)	35(8)	−996(7)	1609(4)	23(4)	C(61)	−1434(8)	−1859(7)	3042(4)	25(4)
C(21)	−652(8)	−2083(7)	1535(4)	29(4)	C(62)	−2272(8)	−2876(7)	2698(4)	32(4)
C(22)	−1604(9)	−2634(8)	987(5)	40(5)	C(63)	−1982(10)	−3869(8)	2722(5)	46(5)
C(23)	−1882(9)	−2088(8)	506(5)	43(4)	C(64)	−866(10)	−3848(9)	3084(5)	45(5)
C(24)	−1229(8)	−1025(7)	570(5)	34(4)	C(65)	−17(10)	−2856(10)	3411(5)	50(5)
C(25)	2734(8)	289(7)	1062(4)	27(4)	C(66)	−310(9)	−1855(8)	3387(5)	39(4)
C(26)	2068(8)	−764(7)	648(4)	27(4)	C(1S)	263(19)	4805(19)	9676(13)	108(22)
C(27)	2352(9)	−1097(8)	90(5)	35(4)	Cl(1S)	−805(6)	3919(4)	9872(3)	161(4)
C(28)	3283(9)	−432(9)	−45(5)	42(5)	C(2S)[b]	5280(24)	4229(24)	524(14)	189(11)
C(29)	3942(9)	602(8)	381(5)	39(5)	C(3S)[b]	5500(19)	3878(18)	101(12)	130(7)
C(30)	3667(8)	965(8)	933(4)	32(4)	C(4S)[b]	5098(28)	4509(25)	−216(15)	218(13)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Atoms involved in solvent disorder; refined isotropically.

crystallized by slow diffusion of *n*-hexane in a dichloromethane solution at −20 °C under nitrogen atmosphere and exclusion of light. Data for **8**: yellow; yield 63%. Anal. Calcd for $C_{66}H_{45}AgF_{10}O_6P_3Rh$: C, 55.52; H, 3.18. Found: C, 55.70; H, 3.25. ^{19}F NMR (−50 °C, $CDCl_3$), δ, ppm: *o*-F −106.7, −111.0 (m), *m*-F −164.2, −164.9 (m), *p*-F −162.7, −163.7 (ft). ^{31}P NMR (20 °C, $CDCl_3$), δ, ppm: 123.5 (dm, ^1J(P−Rh) = 194), 6.4 (complicated dm).

$[Rh(C_6F_5)(CO)_2(PPh_3)]$ (10). Addition of solid PPh_3 (0.14 mmol) to a solution of **1** (100 mg, 0.14 mmol) in tetrahydrofuran (5 mL) led to a suspension of a white solid. The solid was filtered off, and the oil residue obtained by evaporation of the solution till dryness was washed with two fractions of *n*-hexane (1 mL) and stirred in *n*-hexane (10 mL). The yellow solid obtained was separated by filtration, washed with *n*-hexane, and vacuum dried: yield 61%. Anal. Calcd for $C_{26}H_{15}F_5O_2PRh$: C, 53.08; H, 2.57. Found: C, 53.30; H, 2.82. IR (CH_2Cl_2): ν(CO) 2060, 1980 cm^{-1}. ^{19}F NMR (20 °C, $CDCl_3$), δ, ppm: *o*-F −113.0 (ft), *m*-F and *p*-F −162.3/−164.8. ^{31}P NMR (20 °C, $CDCl_3$), δ, ppm: 34.7 (dm, ^1J(P−Rh) = 139).

$[\{Rh(C_6F_5)\}_2(\mu\text{-dppm})_2(\mu\text{-CO})]$ (9) and $[Rh(C_6F_5)(CO)L]$ (L = 2,2′-bipy (11), phen (12)). Addition of the solid ligands (0.14 mmol) to yellow solutions of **1** (100 mg, 0.14 mmol) in dichloromethane (10 mL) led to changes of color. Evaporation of the solutions under reduced pressure to 1 mL and addition of methanol provided colored solids which were separated by filtration, washed with *n*-hexane, and vacuum dried. Data for **9**: orange; yield 72%. Anal. Calcd for $C_{63}H_{44}F_{10}OP_4Rh_2$: C, 56.61; H, 3.32. Found: C, 56.80; H, 3.54. IR (CH_2Cl_2): ν(CO) 1795 cm^{-1}. ^{19}F NMR (20 °C, $CDCl_3$), δ, ppm: *o*-F −110.5, −111.8 (1:1, fd), *m*-F −164.5, −165.1 (1:1, m), *p*-F −163.8 (ft). ^{1}H NMR (20 °C, $CDCl_3$), δ, ppm: 7.6−7 (40H, phenyl), 3.7 (m, 2H, >CH_2, dppm), 3.3 (m, 2H, >CH_2, dppm). ^{31}P NMR δ, ppm: 26.5 ([^1J(P−Rh) + ^xJ(P−Rh)] = 131). MS (FAB): *m/e* 1338 (M, 30). Data for **11**: brown; yield 85%. Anal. Calcd for $C_{17}H_8F_5N_2ORh$: C, 44.96; H, 1.77; N, 6.16. Found: C, 44.63; H, 1.58; N, 5.96. IR (Nujol mulls): 1970 s cm^{-1}. ^{19}F NMR (20 °C, HDA), δ, ppm: *o*-F −112.0 (m), *m*-F −166.3 (m), *p*-F −164.8 (ft). ^{1}H NMR (20 °C, HDA), δ, ppm: 8.9, 8.1 (H^3, $H^{3'}$), 7.6, 7.5 (H^4, $H^{4'}$), 8.3, 8.2 (H^5, $H^{5'}$), 8.5, 8.4 (H^6, $H^{6'}$). Data for **12**: brown; yield 89%. Anal. Calcd for $C_{19}H_8F_5N_2ORh$: C, 47.72; H, 1.69; N, 5.86. Found: C, 47.47; H, 1.72; N, 5.90. IR (Nujol mulls): ν(CO) 1960 s cm^{-1}. ^{19}F NMR (20 °C, HDA), δ, ppm: *o*-F −110.5 (fd), *m*-F −164.8 (ft), *p*-F −163.2 (ft). ^{1}H NMR (20 °C, HDA), δ, ppm: 9.3, 8.5, (d, 2H, H_2, H_9, ^3J = 4.6), 8.88, 8.82 (d, 2H, H_4, H_7, ^3J = 7.7), 8.2 (m, 2H, H_5, H_6), 8.0, 7.9 (ddm, 2H, H_3, H_8, ^3J = 7.7, 4.6).

$(PBzPh_3)[Rh(C_6F_5)I_2(COMe)(CO)]$ (13). A solution of **1** (100 mg, 0.14 mmol) in methyl iodide (3 mL) changed from yellow to orange after 6 h of stirring. The solvent was pumped off. The oily residue was washed with two fractions of *n*-hexane (1 mL) and stirred in *n*-pentane (10 mL). The orange solid formed was filtered off, washed with *n*-pentane, and vacuum dried. Data for **13**: orange; yield 78%. Anal. Calcd for $C_{34}H_{25}F_5I_2O_2PRh$: C, 43.07; H, 2.66. Found: C, 42.83; H, 2.52. IR (Nujol mulls): ν(CO) 2070 s, 1715 s cm^{-1}. Λ_M (acetone, $C = 5.23 \times 10^{-4}$ mol L^{-1}) 116 Ω^{-1} cm^2 mol^{-1}. ^{19}F NMR (20 °C, $CDCl_3$), δ, ppm: *o*-F −105.6 (dm), *m*-F −163.5 (m), *p*-F −161.8 (ft). ^{1}H NMR (20 °C, $CDCl_3$), δ, ppm: 7.7−6.8 (20H, phenyl), 4.4 (2H, >CH_2, $PBzPh_3^+$, ^2J(H−P) = 13.9), 3.2 (s, 3H, −CH_3). MS (FAB): *m*/*e* 595 (M = $[Rh(C_6F_5)I_2(COMe)(CO)]^-$, 45), 567 (M − (CO), 40), 539 (M − 2(CO), 100), 524 (M − (CO) − (COMe), 60).

[Rh(C_6F_5)I(COMe)(CO)(Hpz)] (14). To an orange suspension of **13** (75 mg, 0.077 mmol) in dry diethyl ether (10 mL), under exclusion of light, was added silver perchlorate (15.9 mg, 0.077 mmol). After 60 min the solid formed was eliminated by filtration through Kieselguhr, and solid pyrazole (5.2 mg, 0.077 mmol) was added. After 3 h of stirring, evaporation of the solution under vacuum to 1 mL and addition of *n*-pentane (15 mL) gave the orange complex, which was filtered off, washed with *n*-pentane and vacuum dried: yield 69%. Anal. Calcd for $C_{12}H_7F_5IN_2O_2Rh$: C, 26.89; H, 1.32; N 5.23. Found: C, 26.33; H, 1.27; N, 4.96. IR (Nujol mulls): ν(CO) 2088 s, 1710 s cm^{-1}; ν(NH) 3375 m cm^{-1}. ^{19}F NMR (20 °C, $CDCl_3$), δ, ppm: *o*-F −114.9 (m), *m*-F −161.8 (ft), *p*-F −158.3(m). ^{1}H NMR (20 °C, $CDCl_3$), δ, ppm: 12.2 (m, NH), 7.75, 7.25, 6.3 (m, H^3, H^4, H^5 Hpz), 2.6 (s, −CH_3). MS (FAB): *m*/*e* 535 (M, 42), 425 (M − (COMe) − (Hpz), 100), 397 (M − (CO) − (COMe) − (Hpz), 35)

($PBzPh_3$)[Rh(C_6F_5)$_3$Cl(CO)$_2$] (15). To a solution of **1** (100 mg, 0.14 mmol) in tetrahydrofuran (10 mL) was added solid $[Tl(C_6F_5)_2Cl]$ (79.7 mg, 0.14 mmol). After the reaction mixture was refluxed with stirring for 6 h, a white solid was formed, and the solution became almost colorless. The solid was filtered off, and the solvent was pumped off. The resulting oily residue was washed twice with *n*-hexane (1 mL) and stirred in *n*-hexane (15 mL). The white solid obtained was filtered off, washed with *n*-hexane, and vacuum dried: yield 61%. IR (CH_2Cl_2): ν(CO) 2110 s cm^{-1}. Anal. Calcd for $C_{45}H_{22}ClF_{15}O_2PRh$: C, 51.53; H, 2.11. Found: C, 51.36; H, 1.98. Λ_M (acetone, $C = 4.57 \times 10^{-4}$ mol L^{-1}): 94 Ω^{-1} cm^2 mol^{-1}. ^{19}F NMR (20 °C, HDA), δ, ppm: *o*-F −107.1, −109.2 (fd, 4:2), *m*-F −163.6 (ft), *p*-F −161.4, −161.7 (ft, 2:1). MS (FAB): *m*/*e* 695 (M = $[Rh(C_6F_5)_3Cl(CO)_2]^-$, 20), 639 (M − 2(CO), 100), 604 (M − 2(CO) − Cl, 35).

X-ray Crystal Structure Analysis of $8\cdot{}^1/_2CH_2Cl_2\cdot{}^1/_2C_6H_{14}$. Collection and Reduction of Data. Crystals suitable for X-ray study were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of **8** at −20 °C under nitrogen atmosphere and exclusion of light. A yellow transparent irregular block was mounted in an inert oil and put on a four-circle Siemens AED-2 difractometer at 150 K. Intensity data were collected with graphite-monochromated Mo Kα radiation, working in the $\omega/2\theta$ scan mode ($3 \le 2\theta \le 45°$). A summary of crystal and refinement data is reported in Table 2. Cell constants were obtained from the least-squares fit of the setting angles of 54 reflections in the range $20 \le 2\theta \le 37°$. The 8363 recorded reflections ($\pm h,\pm k,+l$) were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitored every 55 min of measuring time; no intensity decay was observed. An empirical method (ψ scan) was used to correct absorption effects.[38]

Structure Solution and Refinement. The structure was solved by Patterson and conventional Fourier techniques. Refinement was carried out by full-matrix least squares with initial isotropic thermal parameters. Two molecules of solvent, one of CH_2Cl_2 and one of C_6H_{14}, were found per unit cell. The *n*-hexane molecule was built up with three isotropic carbon atoms and the symmetry-related ones. The CH_2Cl_2 was modeled as two symmetry-related molecules with the chlorine atoms occupying equivalent positions. Further refinement was performed with anisotropic thermal parameters for all non-hydrogen atoms of the molecule. Hydrogen atoms of the complex were included in found positions and refined riding on carbon atoms with a common isotropic thermal parameter. The function minimized was $\Sigma(|F_o| - |F_c|)^2$ with the weight defined as $w^{-1} = \sigma^2(F_o) + 0.0006F_o^2$. Atomic scattering factors, corrected for anomalous dispersion for Rh, Ag, and P, were taken from ref 39. Final R and R_w values were 0.0639 and 0.0511, respectively. All calculations were performed by use of the SHELXTL-PLUS system of computer programs.[40] The final atomic coordinates for the non-hydrogen atoms are given in Table 3.

Acknowledgment. We thank the DGICYT (Dirección General de Investigación Científica y Técnica) for financial support (Proyect PB92 0032).

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen coordinates, experimental details of the X-ray study, bond distances and angles, selected least-squares planes, and interatomic distances (16 pages). Ordering information is given on any current masthead page.

IC940933U

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(38) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.
(39) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.
(40) *SHELXTL PLUS Program for Crystal Structure Determinations*; Siemens Analytical X-Ray Instruments: Madison, WI, 1990.