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Mono- and bi-nuclear complexes of the rigid bidentate ligand 2-ethylthio-5-diphenylphosphinofuran

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Abstract

The reactions of 2-ethylthio-5-diphenylphosphino-furan (TPF) with $[Rh_2(CO)_4(\mu\text{-Cl})_2]$ (or with $[Ir_2(COD)_2Cl_2]$ under CO) have been shown to lead to $[Rh_2(TPF)_2(CO)_2(m\text{-Cl})_2]$, *trans*-$[Rh(TPF)_2(CO)Cl]$ or the cationic $[M(TPF)_2(CO)_3]^+$ species ($M = Rh$, Ir), all with monodentate phosphorus-bound ligands. The latter gives rhodium-silver and rhodium-iridium heterobinuclear head-to-head $[(CO)_3Rh(\mu\text{-TPF})_2Ag]^{2+}$ and $[(CO)_3Ir(\mu\text{-TPF})_2Rh(CO)_3]^{2+}$ derivatives. A monomeric $[Au(TPF)_2Cl]$ derivative with monodentate P-bound ligands has also been prepared, and shown to react with $[Rh_2(CO)_4(\mu\text{-Cl})_2]$ to yield rhodium-gold heterobinuclear adducts as mixtures of head-to-head and head-to-tail isomers.

Introduction

A number of binuclear rhodium and iridium complexes containing the rigid ligand 2,5-bis(diphenylphosphino)furan have been previously described and shown to possess especially favoured orientation for a defined intermetallic separation [1]. Heterobinuclear derivatives present a greater challenge and one route to them which might work involves the use of mixed-donor ligands. Here we present information on one such ligands, namely 2-ethylthio-5-diphenylphosphinofuran (**1**), which is closely related to the diphosphine mentioned above. The ligand is expected to bind preferentially through phosphorus, with the result that uncoordinated sulfur atoms will be present in such molecules, thus offering the possibility of ready coordination to a second different metal ion to form binuclear species.

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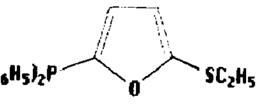
Experimental

NMR spectra (in dichloromethane-d_2) were recorded on a JEOL FX 90 Q FT and on a 400 MHz Bruker spectrometers. The ^{31}P NMR spectra were proton decoupled, and referenced to external 85% phosphoric acid; the high-frequency-positive convention was used for chemical shifts. IR spectra were recorded in Nujol mulls or dichloromethane solutions on a Perkin-Elmer 781 spectrometer. Elemental analyses were made by Mr. L. Turiaco, University of Padova. The complexes [Rh(NBD)(acac)] [2], $[Ir_2(COD)_2(\mu\text{-}Cl)_2]$ [3], $[Rh_2(CO)_4(\mu\text{-}Cl)_2]$ [4] and [Au(CO)Cl] [5] were prepared by standard routes. 2-Ethylthiofuran was prepared by a published method from 2-lithiofuran, sulfur, and iodoethane [6].

2-Ethylthio-5-diphenylphosphinoethane (TPF) (1). A solution of 1.4 ml of 2-ethylthiofuran (11.5 mmol) in 10 ml of diethyl ether was treated with 4.5 ml of of n-butyllithium (2.7 *M*) in petroleum ether (12 mmol). The red solution was stirred for 1 h at room temperature then a solution of 6 ml of chlorodiphenylphosphine (33 mmol) in 10 ml of toluene was added. The colorless mixture was refluxed for 2 h, then cooled and shaken successively with aqueous NH_4Cl, aqueous, NaOH, and water. The organic layer was dried over sodium sulfate, and evaporated to dryness.



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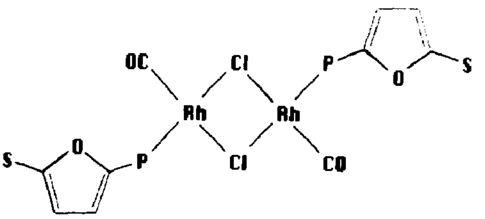

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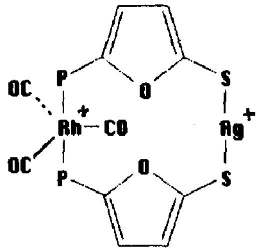
The yellow oily product was purified by column chromatography on flash silica gel (ether/benzene 1/1, RT 0.5). A spectroscopically pure product was obtained in a 50% yield. Anal. Found: C, 77.2; H, 5.1. $C_{18}H_{17}OPS$ calcd.: C, 77.06; H, 5.09%. ^{31}P NMR, δ: -29.4 ppm. ^{1}H NMR, δ: 1.25 (t, SCH_2CH_3), 2.75 (q, SCH_2CH_3), 6.50 and 6.65 (m, furan 3- and 4-protons), 7.4 ppm (m, C_6H_5).

$[Rh_2(TPF)_2(CO)_2(\mu\text{-}Cl)_2]$ (2). The ligand TPF (220 mg, 0.69 mmol) and $[Rh_2(CO)_4(m\text{-}Cl)_2]$ (135 mg, 0.35 mmol) were mixed in dichloromethane. After addition of 2-propanol to the resulting orange solution a yellow-orange solid slowly separated (yield 65%). Anal. Found: C, 46.2; H, 3.7. $C_{38}H_{34}Cl_2O_4P_2S_2Rh_2$ calcd.: C, 46.42; H, 3.58%. ^{31}P NMR, δ: 28.1 ppm (d, J(PRh) 177 Hz. ν(CO) 1985 cm^{-1}.

$[Rh(TPF)_2(CO)Cl]$. The ligand TPF (350 mg, 1.12 mmol) and $[Rh_2(CO)_4(\mu\text{-}Cl)_2]$ (115 mg, 0.29 mmol) were mixed in dichloromethane. After addition of 2-propanol, a yellow powder slowly separated (yield 55%). Anal. Found: C, 56.2; H,



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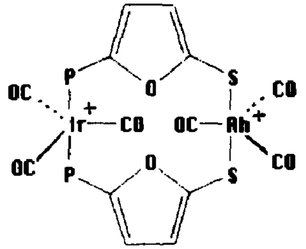

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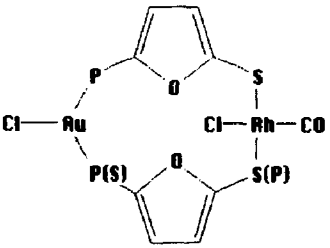

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4.2. $C_{37}H_{34}ClO_2PSRh$ calcd.: C, 56.16; H, 4.33%. ^{31}P NMR, δ: 10.8 ppm (d, J(PRh) 129 Hz). ν(CO) 1982 cm^{-1}.

[Ir(TPF)₂(CO)₃]BF₄. The ligand TPF (300 mg, 0.96 mmol) was added to an ethanol solution of $[Ir_2(COD)_2(\mu\text{-}Cl)_2]$ (160 mg, 0.28 mmol) under a carbon monoxide atmosphere to give a yellow solution, to which a three-fold excess of $AgBF_4$ was added. The solution was filtered and the filtrate was diluted with diethyl ether to precipitate the colourless product (yield 65%). Anal. Found: C, 47.1; H, 3.4. $C_{39}H_{34}BF_4O_5P_2S_2Ir$ calcd.: C, 47.41; H, 3.44%. ^{31}P NMR, δ: −21.1 ppm (s). ν(CO) 2070, 2005 and 1975 cm^{-1}.

$[(CO)_3Ir(\mu\text{-}TPF)_2Rh(CO)_3](BF_4)_2$ (4). To a dichloromethane solution of $[Ir(TPF)_2(CO)_3]BF_4$ (250 mg, 0.25 mmol) was added a solution of [Rh(NBD)(acac)] (75 mg, 0.25 mmol). The mixture was stirred for 1 h under carbon monoxide and then trityl tetrafluoroborate was added. After addition of 2-propanol, a yellow solid separated (yield 40%). Anal. Found: C, 40.2; H, 3.1. $C_{42}H_{34}B_2F_8O_8P_2S_2IrRh$ calcd.: C, 39.93; H, 2.78%. ^{31}P NMR, δ: 20.9 ppm (s). ν(CO) 2000 cm^{-1} (broad).

$[Au(TPF)_2Cl]$. A solution of chloroauric acid (480 mg, 1.22 mmol of Au) in ethanol was slowly added to an ethanolic solution of TPF (900 mg, 2.88 mmol).

Some white product separated, and precipitation was completed by addition of diethyl ether (yield 55%). Anal. Found: C, 50.5; H, 4.1. $C_{36}H_{34}ClOPSAu$ calcd.: C, 50.48; H, 4.11%. ^{31}P NMR, δ: 12.8 ppm (s).

Results and discussion

The ligand 2-ethylthio-5-diphenylphosphino-furan (TPF,**1**) was prepared in fair yield by selective lithiation of 2-ethylthio-furan [6] at the 5-position followed by condensation with chlorodiphenylphosphine.

The reaction of $[Rh_2(CO)_4(m\text{-}Cl)_2]$ with TPF yields either the dimeric $[Rh(TPF)(CO)Cl]_2$ (**2**) or the monomeric $[Rh(TPF)_2(CO)Cl]$, the stoichiometry of the reaction determining the identity of the product. In the ^1H NMR spectra of monomeric $[Rh(TPF)_2(CO)Cl]$ the quartet pertaining to the SCH_2CH_3 protons is found at 2.70 ppm, in practically the same position as that for the free ligand, indicating that the sulfur remains uncoordinated; this resonance is quite sensitive to the coordination of sulfur, being significantly shifted downfield by 0.2–0.3 ppm upon coordination [7]. ^{31}P NMR evidence confirms coordination of the phosphorus atoms in a *trans* P-Rh-P configuration (J (PRh) 129 Hz).

On contrast, the substantially larger P–Rh coupling constant found for the dimeric species (177 Hz) apparently rules out a mutual *trans* position of the phosphorus donors. This, and the fact that the SCH_2CH_3 resonance is again unchanged, strongly suggests a dimeric structure with two bridging Cl ligands *trans* to monodentate phosphorus-bound ligands. The NMR data are hardly consistent with possible alternative structures, containing bridging TPF (both *cis* and *trans*), such as have been reported for a number of binuclear derivatives containing rigid diphosphines [8] and hybrid ligands [9]. It is noteworthy that the related non-rigid phosphino-thioether $Ph_2P(CH_2)_nSPh$ (*PS*) ligands yield, upon reaction with $[Rh_2(CO)_4(m\text{-}Cl)_2]$ (*PS*/Rh 1/1) only mononuclear [Rh(*PS*)(CO)Cl] complexes, containing a chelating *PS* ligand [10], rather than dimeric derivatives.

The monomeric complex $[Rh(TPF)_2(CO)Cl]$ can be readily dechlorinated in dichloromethane solution by addition of $AgBF_4$, and when this is done under a carbon monoxide atmosphere the expected *trans*-$[Rh(TPF)_2(CO)_3]^+$ cation, with $\nu(CO)$ at 2030 cm^{-1} and $\delta(^{31}P)$ at 13.0 ppm (d, J(PRh) 80 Hz), is formed. Addition of another equivalent of $AgBF_4$ results in the immediate formation of a clear, yellow solution and a marked change in the NMR spectrum. In particular, the significant downfield shift of the methylene protons of the thioethyl groups (from 2.70 to 3.00 ppm) strongly suggests coordination of the silver ion to sulfur. The phosphorus moiety remains bound to rhodium, as demonstrated by the presence in the ^{31}P NMR spectra of the doublet at 15.5 ppm (J(PRh) 87 Hz). A binuclear, head-to-head, rhodium-silver derivative (**3**) is probably formed, in which the silver ion appears to be selectively coordinated to the sulfur: no ^{31}P NMR signals attributable to silver-bound phosphorus atoms were observed [1c]. Removal of the carbon monoxide atmosphere leads to breakdown of the tricarbonyl adduct and immediate precipitation of the $AgBF_4$.

Attempts to obtain similar binuclear derivatives with Cu^I, Au and Hg^{II} were unsuccessful. Neither $[Cu(CH_3CN)_4]BF_4$ (or CuCl) nor [Au(CO)Cl] react with the $[Rh(TPF)_2(CO)_3]^+$ cation. It should be noted however, that stable adducts between

TPF and both copper(I) and gold(I) (vide infra) were obtained in which the metals are invariably coordinated to the phosphorus donors.

Addition of $HgCl_2$ to $[Rh(TPF)_2(CO)_3]^+$ or $[Rh(TPF)_2(CO)Cl]$ yields red solutions (dichloromethane), which slowly deposit yellow products of variable composition. In no case could participation of either sulfur or phosphorus in the coordination of mercury be demonstrated, but the thioethyl methylene proton resonance is found at the same position as in the free TPF, whereas the ^{31}P NMR spectra exhibit only doublets, with no evidence of satellites, corresponding to $^{31}P-^{199}Hg$ coupling [9]. In the light of the usual behavior of Hg^{II} halides, it is likely that chloro-bridged adducts are formed with rhodium, and eventually become insoluble, as the molecular complexity increases.

In contrast to the rhodium complexes discussed above, the iridium tricarbonyl cation is, as usual [11], very stable even in the absence of a carbon monoxide atmosphere. Thus we succeeded in isolating in the solid state the compound $[Ir(TPF)_2(CO)_3]BF_4$, which probably contains two phosphorus-bound monodentate ligands in *trans* disposition. Dichloromethane solutions of the compound dissolve one equivalent of $AgBF_4$, but NMR evidence does not provide unequivocal confirmation of coordination of silver, since both the ^{31}P and ^1H spectra are practically unchanged.

If, instead, the $[Ir(TPF)_2(CO)_3]^+$ cation is treated with simple rhodium(I) complexes under CO, a binuclear rhodium-iridium $[(CO)_3Ir(\mu\text{-}TPF)_2Rh(CO)_3]^{2+}$ (**4**) derivative can be isolated as a solid. The ^{31}P spectra exhibited only a single resonance, suggesting selective formation of the head-to-head isomer, with phosphorus-bound to iridium. Coordination of rhodium to the sulfur is confirmed by the appearance of the methylene protons resonance of the thioethyl group at 2.95 ppm, downfield with respect to the free ligand.

The reaction of excess TPF with chloroauric acid results in the formation of the tri-coordinate neutral derivative $[Au(TPF)_2Cl]$, containing two dangling ligands bound through the phosphorus donors to the metal. The SCH_2CH_3 quartet is found at 2.70 ppm (^1H NMR), indicating uncoordinated sulfur.

Addition of $[Rh_2(CO)_4(\mu\text{-}Cl)_2]$ to the above gold derivative (Rh/Au = 1/1), in chloroform does not lead to reaction at room temperature, but quantitative formation of products takes place upon prolonged heating (24 h) at 50 ° C, as shown by the disappearance of the $\nu(CO)$ bonds of $[Rh_2(CO)_4(\mu\text{-}Cl)_2]$, which are completely replaced by a single broad band centered at 1990 cm^{-1}. ^{31}P NMR spectra of the reaction mixture exhibits two singlet signals, at 12.6 (2P) and at 15.8 ppm (1P), and a doublet, centred at 28.7 ppm (1P) and diagnostic for phosphorus-coordination to rhodium. The spectral patterns could be accounted for by assuming the formation of a binuclear rhodium-gold derivative (**5**), present as head-to-head (phosphorus-bound to gold) and head-to-tail isomers. In this latter, the rhodium-bound phosphorus moiety appears to be *trans* to a sulfur atom (and not to phosphorus), as indicated by the high value of the $^{31}P-^{103}Rh$ coupling constant (180 Hz). The ^1H NMR spectral data are consistent with this scheme, since the diagnostic SCH_2CH_3 quartet is shifted downfield (2.85 ppm), indicating sulfur coordination. Yellow products were isolated from the solutions, but variable analyses prevented more accurate characterization.

Acknowledgment

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