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# Synthesis and Evaluation of the Bonding Properties of 2,5-Bis(2-(diphenylphosphino)ethyl)thiophene: A New Potentially Tridentate Ligand

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The new ligand 2,5-bis(2-(diphenylphosphino)ethyl)thiophene (**1**) has been synthesized in four steps from thiophene, and its bonding capabilities have been evaluated. Compound **1** displaces the cycloheptatriene ligand in $Mo(CO)_3$-(cycloheptatriene) to give [*fac*-$Mo(CO)_3$(**1**)] (**2**), but the complex slowly converts in solution to [*mer*-$Mo(CO)_3$(**1**)] (**3**). The structure of **2** has been established by an X-ray structure determination. Crystallographic data for **2**: monoclinic $C_{2h}^5$-$P2_1/n$, $a = 10.294(1)$ Å, $b = 16.470(1)$ Å, $c = 18.878(2)$ Å, $\beta = 93.62(1)°$, $V = 3194$ Å$^3$, $Z = 4$; $R = 0.032$, $R_w = 0.043$ for 4124 observations and 379 variable parameters. Ligand **1** is tripodal, bonded through the two phosphorus atoms and sulfur atom. With cobalt, the complex [$Co(CO)_3$(**1**)[$BPh_4$] (**4**) has been isolated. In this complex, ligand **1** is bidentate, with the two phosphorus atoms *trans*. In refluxing butanone, the bonding of the sulfur atom is achieved by CO displacement, giving the complex [$Co(CO)_2$(**1**)][$BPh_4$] (**5**), which has been isolated and characterized. With (COD)Rh(acac) in the presence of perchloric acid, the complex [(COD)Rh-(**1**)][$ClO_4$] (**6**) is obtained, in which ligand **1** is bidentate. 1,5-Cyclooctadiene in this complex can be displaced by CO, leading to the two complexes [$(CO)_2Rh$(**1**)][$ClO_4$] (**7**) and [(CO)Rh(**1**)][$ClO_4$] (**8**), which are in equilibrium, depending on the partial pressure of CO. In the two complexes, ligand **1** is tridentate, and the structure of **8** has been established by an X-ray structure determination. Crystallographic data for **8**: triclinic $C_i^1$-$P\bar{1}$, $a = 10.940(3)$ Å, $b = 16.215(3)$ Å, $c = 9.548(2)$ Å, $\alpha = 97.93(2)°$, $\beta = 107.76(2)°$, $\gamma = 89.29(2)°$, $V = 1613$ Å$^3$, $Z = 2$; $R = 0.040$, $R_w = 0.042$ for 4021 observations and 220 variable parameters.

## Introduction

The synthesis of polydentate phosphines and the study of their binding properties are of interest, as these ligands are expected to exert more control of the coordination sphere of the metal with the possible consequence of new catalytic properties for the resulting complexes.[1,2]

With this goal, a special class of polydentate ligands was recently developed which associates phosphorus and oxygen donor atoms. In their complexes, tertiary phosphorus atoms are tightly bound to the metal and the oxygen atoms (provided by an ether, a keto, or an ester function, for instance) form weak metal–oxygen bonds which may be cleaved reversibly to open a coordination site on the metal to induce catalytic activity.[3] An additional property of the transient direct metal–oxygen bond is its ability to increase the electron density at the metal, faciliting oxidative addition of a substrate.[4] The use of such ligands has met with some success in catalysis, leading, for instance, to active systems for the oligomerization and polymerization of ethylene,[5] the carbonylation of methanol,[6] and the hydrogenation of olefins.[7]

The study of bonding properties of ligands associating trivalent phosphorus with sulfur donor atoms is less developed.[8] In this connection, one may mention the increased reactivity toward the insertion of alkynes into the metal–metal bond in a bimetallic palladium complex bridged by two ((benzylthio)methyl)diphenylphosphine ligands compared with a similar complex bridged by the bis(diphenylphosphino)methane ligand.[8b]

To broaden our knowledge of polydentate P–S ligands, we have thought to use as a source of the sulfur donor atom the thiophene ring, as it can offer several advantages:[9,10] (1) the sulfur atom is a weak nucleophile, which implies weak metal–sulfur bonds; (2) the thiophene ring is also able to coordinate a metal with a labile bond in an $\eta^4$ or $\eta^5$ mode, and with the 2,5-positions of the ring being easily functionalized, the ring can serve as a template for building new polydentate ligands.

In a first approach, we have built $Ph_2P(CH_2)_n(C_4H_3S)$ ligands, but these ligands have shown only a weak tendency toward chelation.[11] We then turned to the synthesis of a potentially tridentate ligand, 2,5-bis(2-(diphenylphosphino)ethyl)thiophene, in the hope of forcing the binding of the sulfur atom to the metal. In this paper, we relate its synthesis and the first results concerning the evaluation of its bonding to metals which adopt various geometries: Mo(0), Co(I), and Rh(I).

## Results and Discussion

**(a) Synthesis of 2,5-Bis(2-(diphenylphosphino)ethyl)thiophene (1).** The ligand is synthesized in four steps from thiophene according to the Scheme I. In the first step, the 2,5-dilithio salt of thiophene is synthesized by the action of BuLi·TMEDA in refluxing hexane.[12] The second step is an adaptation of the synthesis of 2-(2-thienyl)ethanol.[13] The dilithium salt is reacted with ethylene oxide, and after hydrolysis and distillation, the diol

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(1) Meek, D. W.; Mazanec, T. J. *Acc. Chem. Res.* **1981**, *14*, 266.

(2) Cotton, F. A.; Hong, B. *Prog. Inorg. Chem.* **1992**, *40*, 179.

(3) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27.

(4) Miller, E. M.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 480.

(5) Keim, W. *Chem.-Ing.-Tech.* **1984**, *56*, 850.

(6) (a) Lindner, E.; Reber, J. P.; Wegner, P. *Z. Naturforsch.* **1988**, *43B*, 1268. (b) Lindner, E.; Sickinger, A.; Wegner, P. *J. Organomet. Chem.* **1988**, *349*, 75.

(7) Horner, L.; Simons, G. *Z. Naturforsch.* **1984**, *39B*, 497.

(8) For recent references, see for instance: (a) Fuchita, Y.; Ohta, Y.; Hiraki, K.; Kawatani, M.; Nishiyama, N. *J. Chem. Soc., Dalton Trans.* **1990**, 3767. (b) Fuchita, Y.; Hardcastle, K. I.; Hiraki, K.; Kawatani, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1961. (c) Al-Dulaymmi, M. F. M.; Hills, A.; Hitchcock, P. B.; Hughes, D. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1992**, 241. (d) Abel, E. W.; Dormer, J. C.; Ellis, D.; Orrell, K. G.; Sik, V.; Hursthouse, M. B.; Mazid, M. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1073.

(9) (a) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387. (b) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 27.

(10) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259.

(11) Brody, N.; Soulié, J. M.; Mathieu, R. Unpublished results.

(12) Brandsma, L.; Verkruijsse, H. *Preparative Polar Organometallic Chemistry 1*; Springer-Verlag: Berlin, 1987; p 164.

(13) Reference 12, p 125.

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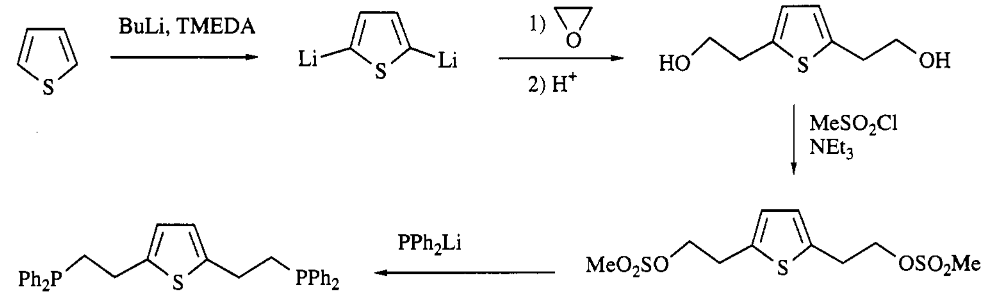
**Scheme I**



2,5-bis(2-hydroxyethyl)thiophene is isolated in 44% yield, the major byproduct being 2-(2-thienyl)ethanol. Subsequent reactions with methanesulfonyl chloride and PPh$_2$Li lead to the synthesis of **1** as white crystals in 44% yield from the diol after crystallization in methanol. Compound **1** is air stable in the solid state and moderately air stable in solution.

**Reaction of 1 with Mo(CO)$_3$(cycloheptatriene).** To evaluate the bonding properties of **1**, we have examined its reaction with Mo(CO)$_3$(cycloheptatriene), offering possibilities of meridional or facial coordination.

The addition of 1 equiv of **1** dissolved in hexane to a solution of Mo(CO)$_3$(cycloheptatriene) in the same solvent leads to the slow precipitation of a pale yellow solid **2**. The infrared spectrum of this compound in the $\nu$(CO) stretching region shows, in dichloromethane solution, two bands at 1947 and 1845 cm$^{-1}$, in agreement with a *fac* geometry for the Mo(CO)$_3$ group.[14] $^1$H NMR of a freshly prepared deuteriated chloroform solution of **2** shows, in addition to phenyl resonances, a singlet at 6.3 ppm for the protons of the thiophene ring and two multiplets at 3.37 and 2.6 ppm for the methylene groups in the ratio 2/6/2, respectively (in deuteriated benzene the methylene groups appear as two multiplets in a 1/1 ratio at 3.02 and 2.74 ppm). After a few minutes, new signals appear: a singlet at 6.59 ppm and two multiplets 3.04 and 2.78 ppm in a 1/2/2 ratio. In the $^{31}$P NMR, the same phenomenom is observed: initially a single resonance is observed at 16.6 ppm; than a new resonance slowly appears at 30.3 ppm, the 16.6 ppm signal intensity decreasing during the same time. On a larger scale, we were able to isolate the new complex **3** as yellow-brown crystals. Its infrared spectrum consists of three bands in the $\nu$(CO) stretching region at 1963 (w), 1862 (s), and 1845 (sh) cm$^{-1}$, in agreement with a *mer* configuration for the Mo(CO)$_3$ group.[14]

These results show that ligand **1** is tridentate and that it can accommodate the *fac* and *mer* geometries in an octahedral complex. The *mer* geometry is the thermodynamically stable configuration.

Nevertheless, single crystals of **2** were the ones which could be obtained. An X-ray structure determination was undertaken. A perspective view of the molecule is given in Figure 1 along with the labeling scheme. Bond lengths and angles of interest are gathered in Table I.

The *fac* structure of the complex is confirmed by this determination. The overall geometry of the molecule is a slightly distorted octahedron, this being the consequence of the strains resulting from the bonding of ligand **1**, particularly evident for the P(1)–Mo–P(2) angle (106.04(4)°). Nevertheless the Mo, P(1), P(2), C(1), and C(3) atoms are in a plane and the S atom is *trans* to the C(2) atom. The metal–phosphorus distances are normal for a (trisubstituted-phosphine)molybdenum complex[15] and the Mo–S(1) distance is in a normal range for an Mo(0)–sulfur bond.[16] As expected, the shorter metal–carbon bond is Mo–C(2) *trans* to the sulfur atom. The geometry of the thiophene ring is as is generally observed for an $\eta^1$-S-bound ring.[17-19] The geometry around S is pyramidal: at the midpoint of C(52)–C(53), the sulfur and molybdenum atoms define an angle of 125.3(6)°. The C–S distances are slightly elongated compared to those in free thiophene,[20] but the other distances and angles are similar within experimental error.

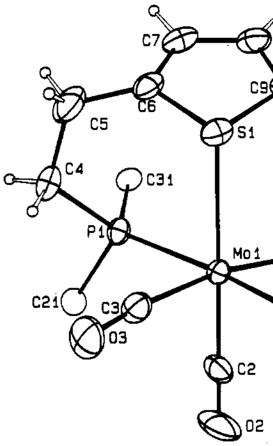


**Figure 1.** Perspective view *fac*-Mo(CO)$_3$(**1**). Thermal ellipsoids are shown at the 30% probability level.

The stability of the Mo–S bond was tested by reacting **2** and **3** with carbon monoxide: in both cases, no reaction occurred at atmospheric pressure.

**Reactivity of 1 toward Dicobalt Octacarbonyl.** Compound **1** reacts at room temperature with a solution of dicobalt octacarbonyl in hexane to give immediate precipitation of an oil. Its infrared spectrum in the $\nu$(CO) stretching region is consistent with the formation of [Co(CO)$_3$(**1**)][Co(CO)$_4$].[21] Anion exchange with sodium tetraphenylborate leads to the isolation of [Co(CO)$_3$(**1**)][BPh$_4$] (**4**) as a yellow solid whose infrared spectrum shows two strong bands at 2007–1997 cm$^{-1}$ and a very weak band at 2067 cm$^{-1}$. This spectrum is consistent with a trigonal bipyramidal structure in which the asymmetry of the ligand induces the splitting of the E$'$ mode expected for a $D_{3h}$ symmetry group for the molecule and a weak activity for the normally infrared-inactive A$'_1$ mode of vibration.[22] A single resonance is observed in the $^{31}$P{$^1$H} NMR.

We propose for [Co(CO)$_3$(**1**)]$^+$ the structure shown in Figure 2, in which ligand **1** is bound through the two phosphorus atoms

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(14) Poilblanc, R.; Bigorgne, M. *Bull. Soc. Chim. Fr.* **1962**, 1301.

(15) Favas, M. C.; Kepert, D. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1980**, 447.

(16) Adams, R. D.; Blankenship, C.; Segmuller, B. E.; Shiralian, M. *J. Am. Chem. Soc.* **1983**, *105*, 4319.

(17) Bucknor, S. M.; Draganjac, M.; Rauchfuss, T. B.; Ruffing, C. J.; Fulz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 5379.

(18) Draganjac, M.; Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 1909.

(19) Goodrich, J. D.; Nickias, P. N.; Selegue, J. P. *Inorg. Chem.* **1987**, *26*, 3426.

(20) Bak, B.; Christensen, D.; Hansen-Nygaard, L.; Rastrup-Andersen, J. *J. Mol. Spectrosc.*, **1961**, *6*, 61.

(21) Hieber, W.; Freyer, W. *Chem. Ber.* **1958**, *91*, 1230.

(22) Adams, D. M. *Metal-Ligand and Related Vibrations*; Edward Arnold Ltd.: London, 1967; p 105.

**Table I.** Selected Bond Lengths (Å) and Angles (deg) for *fac*-Mo(CO)$_3$(**1**) (**2**)

| | | | |
|---|---|---|---|
| Mo(1)–P(1) | 2.567(1) | Mo(1)–P(2) | 2.555(1) |
| Mo(1)–C(1) | 1.966(5) | Mo(1)–S(1) | 2.569(1) |
| Mo(1)–C(2) | 1.928(6) | Mo(1)–C(3) | 1.968(5) |
| P(1)–C(21) | 1.831(5) | P(1)–C(31) | 1.835(5) |
| P(1)–C(4) | 1.844(5) | P(2)–C(41) | 1.833(5) |
| P(2)–C(51) | 1.842(5) | P(2)–C(11) | 1.848(6) |
| S(1)–C(9) | 1.734(6) | S(1)–C(6) | 1.741(5) |
| C(1)–O(1) | 1.146(7) | C(2)–O(2) | 1.153(8) |
| C(3)–O(3) | 1.156(7) | C(4)–C(5) | 1.540(9) |
| C(5)–C(6) | 1.485(8) | C(6)–C(7) | 1.341(9) |
| C(7)–C(8) | 1.402(8) | C(8)–C(9) | 1.349(8) |
| C(9)–C(10) | 1.494(8) | C(10)–C(11) | 1.535(8) |
| C(2)–Mo(1)–C(1) | 86.4(2) | C(2)–Mo(1)–C(3) | 85.0(2) |
| C(1)–Mo(1)–C(3) | 83.8(2) | P(2)–Mo(1)–P(1) | 106.04(4) |
| S(1)–Mo(1)–P(1) | 82.20(4) | S(1)–Mo(1)–P(2) | 90.85(4) |
| C(21)–P(1)–C(31) | 102.0(2) | Mo(1)–P(1)–C(4) | 108.1(2) |
| Mo(1)–P(2)–C(11) | 118.4(2) | C(41)–P(2)–C(51) | 100.5(2) |
| C(9)–S(1)–C(6) | 92.4(3) | O(1)–C(1)–Mo(1) | 174.5(5) |
| O(2)–C(2)–Mo(1) | 177.4(6) | O(3)–C(3)–Mo(1) | 173.6(5) |
| C(5)–C(4)–P(1) | 114.8(4) | C(6)–C(5)–C(4) | 118.1(5) |
| C(5)–C(6)–S(1) | 121.7(5) | C(6)–C(7)–C(8) | 114.6(5) |
| C(9)–C(8)–C(7) | 113.9(5) | C(8)–C(9)–S(1) | 109.6(4) |
| C(10)–C(9)–S(1) | 119.8(4) | C(9)–C(10)–C(11) | 110.0(5) |
| C(10)–C(11)–P(2) | 115.6(4) | | |

in axial positions. Similar structures have been proposed for [Co(CO)$_3$(Me$_2$As(CH$_2$)$_n$AsMe$_2$)]$^+$ complexes ($n$ = 3–5, 6, 8).[23]

The bonding of the thiophene ring through the sulfur atom was induced by refluxing complex **4** dissolved in 2-butanone at 80 °C. The new complex **5** isolated exhibits two absorptions in the $\nu$(CO) stretching region at 2013 and 1954 cm$^{-1}$. On the basis of the ratio of intensities of the CO bands, a calculated C–Co–C angle of ca. 115° has been determined,[24] consistent with a trigonal bipyramidal structure [Co(CO)$_2$L$_3$]$^+$.[25] A single resonance is observed in the $^{31}$P{$^1$H} NMR which has shifted to higher field compared to that for **4**. In the $^1$H NMR, the hydrogens on the thiophene are shifted to lower field, and in the $^{13}$C NMR, the resonances of the 2,5-carbons shift from 140.5 ppm in **4** to 147.2 ppm. This is consistent with an S-bound thiophene ring. So we propose for **5** the structure shown in Figure 3, in which the sulfur atom of the thiophene ring is in the equatorial plane of the trigonal bipyramid and the ligand is in a planar configuration with the two phosphorus atoms in axial positions.

The reaction could not be reversed under CO up to 10 atm pressure, showing that the sulfur atom is tightly bound to cobalt. Considering these results, we have extended our study to the case of Rh(I) to see if a more labile metal–sulfur bond could be observed.

**Reactivity of 1 toward Rh(I) Complexes.** We have chosen the case of the family of cationic complexes [Rh(COD)L$_2$][ClO$_4$], which are easily obtained from (COD)Rh(acac) in the presence of perchloric acid and a ligand L. In small amounts, such compounds are good starting materials for the synthesis of carbonyl derivatives[26] (see safety note below).

When (COD)Rh(acac) is treated in THF with a slight excess of perchloric acid and then with 1 equiv of **1**, the complex [Rh(COD)(**1**)][ClO$_4$] (**6**) is isolated. The $^{31}$P{$^1$H} NMR shows a broad doublet at 17.9 ppm with $J$(Rh–P) = 142.5 Hz, a typical value for [Rh(COD)(PR$_3$)$_2$][ClO$_4$] complexes.[27] The presence of a chelating 1,5-cyclooctadiene ligand is supported by the $^1$H NMR spectrum, which shows two broad resonances at 4.52 and 2.36 ppm. The resonance of the hydrogens on the thiophene ring is observed at 6.47 ppm. These data are in agreement with a structure for **6** in which **1** would be a bidentate ligand bonding through the two phosphorus atoms.

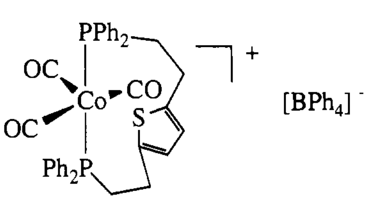

**Figure 2.** Proposed structure for [Co(CO)$_3$(**1**)][BPh$_4$].

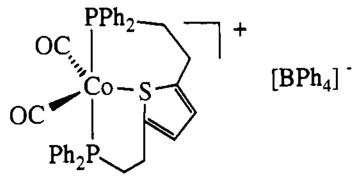

**Figure 3.** Proposed structure for [Co(CO)$_2$(**1**)[BPh$_4$].

This complex is not very stable in solution, and new resonances slowly appear in the thiophene hydrogen region with the simultaneous appearance of free 1,5-cyclooctadiene (5.58 and 2.36 ppm) and other broad resonances between 3 and 2 ppm. During the same time in the $^{31}$P{$^1$H} NMR, several doublets appear between 10 and 30 ppm. The reaction is too complex to be fully analyzed, but due to the presence of free 1,5-cyclooctadiene and the appearance of new resonances for the thiophene ring, we may propose the complexation of the thiophene part of **1**.

When a solution of **6** is saturated with carbon monoxide, a rapid color change occurs; monitoring the reaction by infrared spectroscopy shows the presence of a weak band at 2045 cm$^{-1}$ and a strong band at 1992 cm$^{-1}$. Attempts to isolate this complex lead after evaporation of the solvent to the formation of a new compound characterized by a $\nu$(CO) at 2020 cm$^{-1}$. The reaction can be reversed by bubbling carbon monoxide. These observations closely resemble those reported for the cationic complexes of the tridentate ligand PhP(CH$_2$CH$_2$PPh$_2$)$_2$ (L$_1$), for which the equilibrium

$$[\mathrm{RhL_1(CO)}][\mathrm{PF_6}] \underset{-\mathrm{CO}}{\overset{+\mathrm{CO}}{\rightleftarrows}} [\mathrm{RhL_1(CO)_2}][\mathrm{PF_6}]$$

has been observed, but in this case the dicarbonyl species is stable only under a 80 psi atmosphere of CO.[28]

The complex [Rh(**1**)(CO)$_2$][ClO$_4$] (**7**) has been isolated by crystallization in solvents saturated with carbon monoxide. Infrared spectroscopy shows for the carbonyl groups the weak band at 2045 cm$^{-1}$ and the strong band at 1992 cm$^{-1}$ previously observed for the reaction medium. In the $^{31}$P{$^1$H} NMR spectrum, one doublet is observed at 13.4 ppm ($J$(Rh–P) = 90.3 Hz), and in the $^1$H NMR spectrum, one observes one singlet at 6.96 ppm for the hydrogens of the thiophene ring and a multiplet centered at 3.09 ppm for the methylene groups.

The complex [Rh(**1**)(CO)][ClO$_4$] (**8**) is characterized by a $\nu$(CO) at 2020 cm$^{-1}$ and a doublet at 8.3 ppm ($J$(Rh–P) = 111.6 Hz) in the $^{31}$P{$^1$H} NMR spectrum. In the $^1$H NMR spectrum, the hydrogens of the thiophene ring appear as a singlet at 6.88 ppm, and a multiplet centered at 3.16 ppm is observed for the methylene groups.

To firmly establish the geometry of the ligand in these complexes, an X-ray structure determination of the most stable compound, **8**, was undertaken. A perspective view of the molecule is given in Figure 4 along with the labeling scheme. Bond lengths and angles of interest are gathered in Table II. In this molecule, **1** is a planar tridentate ligand and the two phosphorus atoms are

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(23) Thornhill, D. J.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2086.

(24) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Interscience: New York, 1980; p 1074.

(25) DuBois, D. L.; Meek, D. W. *Inorg. Chem.* **1976**, *15*, 3076.

(26) Schrock, R. R.; Osborn, A. J. *J. Am. Chem. Soc.* **1971**, *93*, 2397.

(27) (a) Thewissen, D. H. M. W.; Timmer, K.; Noltes, J. G.; Marsman, J. W.; Laine, R. M. *Inorg. Chim. Acta* **1985**, *97*, 143. (b) Del Zotto, A.; Costella, L.; Mezzetti, A.; Rigo, P. *J. Organomet. Chem.* **1991**, *414*, 109.

(28) Nappier, T. E., Jr.; Meek, D. W.; Kirchner, R. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 4194.

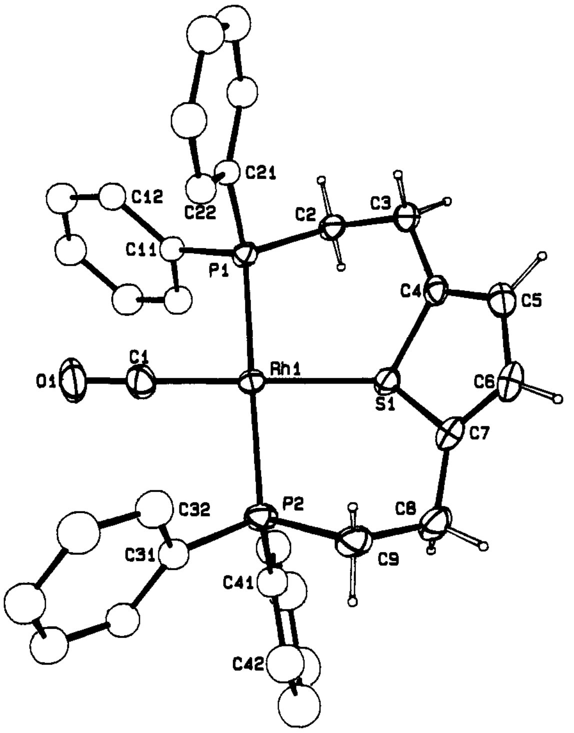

**Figure 4.** Perspective view of [Rh(CO)(**1**)][$ClO_4$]. Thermal ellipsoids are shown at the 30% probability level.

**Table II.** Selected Bond Lengths (Å) and Angles (deg) for [Rh(CO)(**1**)][$ClO_4$] (**8**)

| | | | |
|---|---|---|---|
| Rh(1)–P(1) | 2.310(1) | Rh(1)–P(2) | 2.325(2) |
| Rh(1)–S(1) | 2.318(1) | Rh(1)–C(1) | 1.833(7) |
| S(1)–C(4) | 1.748(5) | S(1)–C(7) | 1.752(6) |
| P(1)–C(11) | 1.810(4) | P(1)–C(21) | 1.812(3) |
| P(1)–C(2) | 1.834(5) | P(2)–C(41) | 1.804(4) |
| P(2)–C(31) | 1.814(3) | P(2)–C(9) | 1.836(7) |
| C(1)–O(1) | 1.133(9) | C(2)–C(3) | 1.529(8) |
| C(3)–C(4) | 1.508(8) | C(4)–C(5) | 1.345(9) |
| C(5)–C(6) | 1.427(8) | C(6)–C(7) | 1.338(8) |
| C(7)–C(8) | 1.496(8) | C(8)–C(9) | 1.531(8) |
| C(1)–Rh(1)–P(1) | 88.9(2) | C(1)–Rh(1)–S(1) | 174.5(2) |
| C(1)–Rh(1)–P(2) | 92.1(2) | P(1)–Rh(1)–S(1) | 89.32(5) |
| P(1)–Rh(1)–P(2) | 178.37(4) | S(1)–Rh(1)–P(2) | 89.52(5) |
| C(4)–S(1)–C(7) | 93.2(3) | C(4)–S(1)–Rh(1) | 114.7(2) |
| C(7)–S(1)–Rh(1) | 113.9(2) | C(2)–P(1)–Rh(1) | 113.2(2) |
| C(9)–P(2)–Rh(1) | 113.5(2) | O(1)–C(1)–Rh(1) | 177.9(7) |
| C(3)–C(2)–P(1) | 114.1(3) | C(4)–C(3)–C(2) | 115.9(4) |
| C(5)–C(4)–S(1) | 108.8(4) | C(4)–C(5)–C(6) | 114.2(5) |
| C(7)–C(6)–C(5) | 114.9(6) | C(6)–C(7)–S(1) | 108.5(4) |
| C(7)–C(8)–C(9) | 113.6(5) | C(8)–C(9)–P(2) | 114.1(4) |

*trans*. The geometry of the coordination polyhedron around the rhodium is approximately square planar, the carbonyl group being in a *trans* position relative to the sulfur atom. This structure confirms that **1** is very well adapted for adopting this mode of bonding without heavy constraints. The metal–phosphorus distances are similar to the distances found for triphenylphosphine derivatives.[28] The Rh–S(1) distance is in the range of distances observed for Rh(I) thioether complexes.[29] Compared to that of complex **2**, the geometry of the thiophene ring is not significantly different. The geometry around S is highly pyramidal: at the midpoint of C(5)–C(6), the sulfur and rhodium atoms define an angle of 129.87(5)°.

Having obtained the structure of **8**, it is possible to propose a structure for **7**. Indeed, in comparison with compounds **4** and **5**, the small differences between the two compounds **7** and **8** in the $^{31}P$ chemical shifts, the $^{13}C$ NMR resonance values for the 2,5-carbons on the thiophene ring, and the $^{1}H$ chemical shifts of the hydrogens on the thiophene ring are in favor of a similar planar tridentate mode of bonding for **1** in **7**. Furthermore, on the basis of the ratio of intensities of the CO bands in the infrared spectrum, a calculated value of the C–Rh–C angle of ca. 140° has been determined,[24] which suggests for **7** a distorted trigonal bipyramidal structure. So, with ligand **1** remaining tripodal, we observe for **7** and **8** the classical equilibrium for rhodium(I) between the 16- and 18-valence-electron complexes in the presence of CO.

In conclusion, the new ligand 2,5-bis(2-(diphenylphosphino)-ethyl)thiophene has not fulfilled our requirement of forming a labile metal–sulfur bond. This is certainly the consequence of the constraints imposed by the short ethylene chain between the phosphorus atom and the thiophene ring (recent results obtained in the case of 2,5-bis(3-(diphenylphosphino)propyl)thiophene, for which a labile Rh–S bond has been observed, confirm this hypothesis[30]). Nevertheless its tendency to coordinate in a meridional position opens a field of investigation to evaluate the influence of the substitution of a phosphorus atom by a sulfur atom by comparison with the well-developed chemistry of complexes containing tritertiary phosphine ligands with the same bonding capability.[31]

## Experimental Section

All reactions were performed under a nitrogen atmosphere with use of standard Schlenk techniques. IR spectra were recorded on a Perkin-Elmer 225 spectrometer. NMR spectra were recorded on Bruker AC 80 ($^{31}P$) and AC 200 ($^{1}H$) instruments. Elemental analyses were performed in our laboratory for the C, H, and S. $Mo(CO)_3(C_7H_8)$,[32] $PPh_2H$,[33] and (COD)Rh(acac)[34] were prepared according to published procedures.

**Safety Note!** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

**Synthesis of the 2,5-Bis(2-(diphenylphosphino)ethyl)thiophene Ligand (1).** This compound was synthesized in three steps from thiophene.

**(a) Synthesis of 2,5-Bis(2-hydroxyethyl)thiophene.** To a stirred solution of 4 mL (49.9 mmol) of thiophene and 18.9 mL (125 mmol) of tetramethylethylenediamine at 0 °C was slowly added 78 mL (125 mmol) of a solution of BuLi 1.6 M in hexane. The solution was then refluxed for 1 h. After this mixture was cooled to –5 °C, a solution of 300 mmol of ethylene oxide in 20 mL of THF was added. The solution was stirred for 10 min at this temperature, and the temperature was then slowly increased with caution as an exothermic reaction occurred. The reaction was completed by stirring the solution at 40 °C during 30 min. The solvents were evaporated under vacuum, and the residue was dissolved in 100 mL of dichloromethane. This solution was washed three times with 100 mL of water, and the dichloromethane solution was dried on sodium sulfate. After filtration and elimination of dichloromethane under vacuum, the residue was distilled under vacuum ($10^{-1}$ Torr) to give 3.77 g of 2,5-bis(2-hydroxyethyl)thiophene (bp = 140 °C; 44%). $^{1}H$ NMR ($CDCl_3$): 6.64 (2H), 3.73 (t, $J = 6.3$ Hz, 4H), 2.93 (t, $J = 6.3$ Hz, 4H), 2.37 ppm (2(OH)).

**(b) Synthesis of the Bis(methanesulfonate) of 2,5-Bis(2-hydroxyethyl)-thiophene.** To 3 g of 2,5-bis(2-hydroxyethyl)thiophene (17.4 mmol) and 5.8 mL of $NEt_3$ (41.8 mmol) in 150 mL of dichloromethane was added 2.68 mL of $MeSO_2Cl$ (34.8 mmol). The solution was stirred for 4 h, after which it was washed two times with 150 mL of water and the dichloromethane was removed under vacuum, leaving 5.5 g of the mesylate (95%). $^{1}H$ NMR ($CDCl_3$): 6.74 (2H), 4.38 (t, $J = 6.5$ Hz, 4H), 3.20 (t, $J = 6.5$ Hz, 4H), 2.95 ppm (6H).

**(c) Synthesis of 1.** The 5.5-g sample of the mesylate (16.75 mmol) was dissolved in 100 mL of THF, and the solution as cooled to 0 °C. To this solution was slowly added 33.5 mmol of $PPh_2Li$ in 100 mL of THF (synthesized from $PPh_2H$ and BuLi). The solution was stirred for 3 h at room temperature, after which the THF was eliminated under vacuum.

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(29) Cheng, C. H.; Eisenberg, R. *Inorg. Chem.* **1979**, *18*, 2438.

(30) Alvarez, M.; Mathieu, R. Unpublished results.

(31) See for instance: (a) Socol, S. M.; Yang, C.; Meek, D. W.; Glaser, R. *Can. J. Chem.* **1992**, *70*, 2424 and references therein. (b) Barbaro, P.; Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 2227.

(32) Cotton, F. A.; McCleverty, J. A.; White, J. E. *Inorg. Synth.* **1967**, *9*, 121.

(33) Gee, W.; Shaw, R. A.; Smith, B. C. *Inorg. Synth.* **1967**, *9*, 19.

(34) Sinou, D.; Kagan, H. B. *J. Organomet. Chem.* **1976**, *114*, 325.

**Table III.** Experimental Data for the X-ray Study of Compounds **2** and **8**

| | **2** | **8** |
|---|---|---|
| formula | $C_{35}H_{30}MoO_3P_2S$ | $C_{33}H_{30}ClO_5P_2RhS$ |
| molar mass, g mol$^{-1}$ | 688.58 | 738.97 |
| cryst syst | monoclinic | triclinic |
| space group | $C_{2h}^5$-$P2_1/n$ | $C_i^1$-$P\bar{1}$ |
| temp, °C | 22 | 22 |
| $a$, Å | 10.294(1) | 10.940(3) |
| $b$, Å | 16.470(1) | 16.215(3) |
| $c$, Å | 18.878(2) | 9.548(2) |
| $\alpha$, deg | | 97.93(2) |
| $\beta$, deg | 93.62(1) | 107.76(2) |
| $\gamma$, deg | | 89.29(2) |
| $Z$ | 4 | 2 |
| $V$, Å$^3$ | 3194 | 1613 |
| $\rho_{calcd}$, g cm$^3$ | 1.432 | 1.496 |
| $\lambda$(Mo K$\alpha_1$), Å | 0.7093 | 0.7093 |
| abs coeff, cm$^{-1}$ | 5.94 | 7.28 |
| transm coeff[a] | 0.96–0.99 | 0.89–0.99 |
| $R$, % (on $F_o$, $F_o^2 > 3\sigma(F_o^2)$)[b] | 0.032 | 0.040 |
| $R_w$, % (on $F_o$, $F_o^2 > 3\sigma(F_o^2)$)[c] | 0.043 | 0.042 |

[a] $\psi$-scan method. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum_w = [\sum w(|F_o| - |F_c|)^2/(\sum w|F_o|^2)]^{1/2}$, unit weights.

**Table IV.** Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (Å$^2$ × 10$^2$) with Esd's in Parentheses for Compound **2** ($U_{eq} = {}^1/_3$ Trace U)

| atom | $x/a$ | $y/b$ | $z/c$ | $U_{eq/Uiso}$ |
|---|---|---|---|---|
| Mo(1) | 0.18039(4) | 0.42420(2) | 0.19155(2) | 3.17(6) |
| P(1) | 0.3241(1) | 0.44742(8) | 0.30590(7) | 3.8(2) |
| P(2) | −0.0229(1) | 0.51105(8) | 0.20310(7) | 3.5(2) |
| S(1) | 0.3067(1) | 0.54801(8) | 0.14972(7) | 4.5(2) |
| C(1) | 0.1033(5) | 0.3954(3) | 0.0970(3) | 4.5(9) |
| O(1) | 0.0617(4) | 0.3724(3) | 0.0429(2) | 7.7(9) |
| C(2) | 0.0858(6) | 0.3329(3) | 0.2263(3) | 5(1) |
| O(2) | 0.0287(5) | 0.2772(3) | 0.2444(4) | 11(1) |
| C(3) | 0.3127(5) | 0.3432(3) | 0.1699(3) | 5(1) |
| O(3) | 0.3808(4) | 0.2906(3) | 0.1557(3) | 7.7(9) |
| C(4) | 0.4948(5) | 0.4536(4) | 0.2820(3) | 5(1) |
| C(5) | 0.5301(6) | 0.5319(5) | 0.2431(4) | 8(1) |
| C(6) | 0.4223(5) | 0.5841(4) | 0.2134(3) | 5(1) |
| C(7) | 0.3925(6) | 0.6605(4) | 0.2306(3) | 6(1) |
| C(8) | 0.2766(6) | 0.6900(4) | 0.1970(3) | 6(1) |
| C(9) | 0.2149(5) | 0.6361(3) | 0.1529(3) | 4.8(9) |
| C(10) | 0.0798(5) | 0.6379(4) | 0.1190(3) | 6(1) |
| C(11) | −0.0189(5) | 0.6181(3) | 0.1741(3) | 5(1) |
| C(21) | 0.3255(5) | 0.3598(3) | 0.3657(2) | 4.2(9) |
| C(22) | 0.2299(6) | 0.3531(4) | 0.4141(3) | 5(1) |
| C(23) | 0.2225(6) | 0.2868(4) | 0.4578(3) | 6(1) |
| C(24) | 0.3135(7) | 0.2261(4) | 0.4548(3) | 7(1) |
| C(25) | 0.4081(8) | 0.2308(4) | 0.4073(4) | 8(1) |
| C(26) | 0.4136(7) | 0.2966(4) | 0.3631(3) | 7(1) |
| C(31) | 0.3149(5) | 0.5327(3) | 0.3680(3) | 4.1(9) |
| C(32) | 0.4144(6) | 0.5491(4) | 0.4191(3) | 6(1) |
| C(33) | 0.4088(8) | 0.6158(5) | 0.4630(3) | 8(2) |
| C(34) | 0.3030(8) | 0.6662(4) | 0.4573(3) | 7(1) |
| C(35) | 0.2033(7) | 0.6512(4) | 0.4078(4) | 7(1) |
| C(36) | 0.2096(5) | 0.5853(4) | 0.3632(3) | 6(1) |
| C(41) | −0.1608(4) | 0.4692(3) | 0.1488(3) | 3.8(8) |
| C(42) | −0.2079(6) | 0.5060(4) | 0.0862(3) | 6(1) |
| C(43) | −0.3113(7) | 0.4712(5) | 0.0461(3) | 8(2) |
| C(44) | −0.3685(7) | 0.4010(5) | 0.0672(4) | 8(2) |
| C(45) | −0.3206(6) | 0.3641(4) | 0.1282(4) | 7(1) |
| C(46) | −0.2181(5) | 0.3973(3) | 0.1685(3) | 5(1) |
| C(51) | −0.0946(5) | 0.5185(4) | 0.2898(3) | 4.5(9) |
| C(52) | −0.1608(5) | 0.5876(4) | 0.3111(3) | 6(1) |
| C(53) | −0.2114(6) | 0.5896(6) | 0.3777(4) | 9(2) |
| C(54) | −0.1981(7) | 0.5255(7) | 0.4216(4) | 10(2) |
| C(55) | −0.1335(7) | 0.4568(6) | 0.4021(4) | 9(2) |
| C(56) | −0.0806(6) | 0.4539(4) | 0.3364(3) | 7(1) |

The residue was dissolved in 150 mL of dichloromethane, and the solution was washed with 2 × 150 mL of water. After elimination of the solvent, crystallization of the residue from methanol gave 3.83 g (45%) of **1** as white crystals. $^1$H NMR ($CDCl_3$): 7.41 (m, 20H), 6.55 (2H), 2.83 (dt, $J_1$ = 7 Hz, $J_2$ = 8.4 Hz, 4H), 2.39 ppm (t, $J$ = 7 Hz, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 142.7 (d, $J$ = 14.3 Hz, C(2) in $C_4H_2S$), 137.6 (d, $J$ = 12.7 Hz), 132.1 (d, $J$ = 18.5 Hz) ($C_6H_5$), 128.1 (C(3) in $C_4H_2S$), 127.7, 123.1 ($C_6H_5$), 29.7 (d, $J$ = 13.2 Hz) ($CH_2\mathit{C}H_2P$), 26.1 ppm (d, $J$ = 19.8 Hz) ($\mathit{C}H_2CH_2P$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −16.6 ppm. Anal. Calcd for $C_{32}H_{30}P_2S$: C, 75.59; H, 5.90; S, 6.30. Found: C, 75.37; H, 6.00; S, 6.44.

**Synthesis of *fac*-Mo(CO)$_3$(1) (2).** To a stirred solution of 0.2 g of $Mo(CO)_3(C_7H_8)$ (0.735 mmol) in 10 mL of hexane was added 0.374 g (0.735 mmol) of **1** dissolved in 10 mL of hexane. The solution was stirred for 30 min, and a yellow precipitate appeared. The mixture was filtered, and the precipitate was washed with a small amount of hexane. It was then redissolved in 5 mL of dichloromethane, and hexane was added. Cooling the mixture to −20 °C gave 0.4 g of **2** as yellow crystals (90%). IR, $\nu$(CO)($CH_2Cl_2$): 1947 (s), 1845 (s) cm$^{-1}$. $^1$H NMR ($CDCl_3$): 7.17 (m, 20H), 6.31 (2H), 3.37 (m, 6H), 2.61 ppm (m, 2H). $^1$H NMR ($C_6D_6$): 7.80–6.67 (m, 20H), 5.80 (2H), 3.02 (m, 4H), 2.74 ppm (m, 4H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 16.6 ppm. Anal. Calcd for $C_{35}H_{30}MoO_3P_2S$: C, 61.05, H, 4.39; S, 4.66. Found: C, 60.92; H, 4.52; S, 4.42.

**Synthesis of mer-Mo(CO)$_3$(1) (3).** A 0.2-g sample of **2** was dissolved in 5 mL of dichloromethane, and the solution was stirred for 24 h. Addition of hexane and cooling to −20 °C led to 0.15 g (75%) of **3** as brown crystals. IR, $\nu$(CO)($CH_2Cl_2$): 1963 (w), 1862 (s), 1845 (sh) cm$^{-1}$. $^1$H NMR ($CDCl_3$): 7.34 (m, 20H), 6.59 (2H), 3.04 (m, 4H), 2.78 ppm (m, 4H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 30.3 ppm. Anal. Calcd for $C_{35}H_{30}MoO_3P_2S$: C, 61.05; H, 4.39; S, 4.66. Found: C, 61.22; H, 4.42; S, 4.55.

**Synthesis of [Co(CO)$_3$(1)][BPh$_4$] (4).** To a stirred solution of 0.2 g of $Co_2(CO)_8$ (0.585 mmol) in 10 mL of hexane cooled to 0 °C was added 0.297 g (0.585 mmol) of **1** dissolved in hexane. A brown precipitate appeared, which was isolated. It was then redissolved in 7 mL of methanol, and 0.4 g (1.17 mmol) of $NaBPh_4$ in methanol was added. A brown precipitate appeared, which was filtered off, washed with water, and recrystallized in a dichloromethane/ethanol mixture to give 0.3 g (60%) of **4** as yellow crystals. IR, $\nu$(CO)($CH_2Cl_2$): 2067 (w), 2007, 1997 (s) cm$^{-1}$. $^1$H NMR ($CDCl_3$) except phenyl resonances: 6.57 (2H), 3.06 (m, 2H), 2.93 ppm (m, 6H). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): 194.0 (t, $J$ = 25 Hz), 140.5 (d, $J$ = 8.3 Hz) (C(2) in $C_4H_2S$), 136.3 ($B(C_6H_5)_4$), 133.6 (C(3) in $C_4H_2S$), 132.1 (unresolved triplet, $P(C_6H_5)_2$), 130.5 (unresolved triplet, $P(C_6H_5)_2$), 125.9 ($B(C_6H_5)_4$), 121.9 ($B(C_6H_5)_4$), 34.6 (t, $J$ = 14.3 Hz) ($CH_2CH_2P$), 25.3 ppm ($CH_2CH_2P$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 49.9 ppm. Anal. Calcd for $C_{59}H_{50}BCoO_3P_2S$: C, 73.0; H, 5.19; S, 3.30. Found: C, 72.72; H, 5.19; S, 3.34.

**Synthesis of [Co(CO)$_2$(1)][BPh$_4$] (5).** A solution of 0.284 g (0.292 mmol) of **4** in 15 mL of butanone was refluxed for 3 h. After cooling, the solvent was evaporated under vacuum and the residue was recrystallized in a dichloromethane/methanol mixture, giving 0.15 g (60%) of **5** as red crystals. IR, $\nu$(CO)($CH_2Cl_2$): 2013 (w), 1954 (s) cm$^{-1}$. $^1$H NMR ($CDCl_3$) except phenyl resonances: 6.78 (2H), 2.96 (m, 4H), 2.84 ppm (m, 4H). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): 193.9 (t, $J$ = 24.6 Hz), 147.2 (unresolved triplet, C(2) in $C_4H_2S$), 136.3 ($B(C_6H_5)_4$), 133.6 (C(3) in $C_4H_2S$), 132.1 (unresolved triplet, $P(C_6H_5)_2$), 130.5 (unresolved triplet, $P(C_6H_5)_2$), 125.9 ($B(C_6H_4)$), 121.9 ($B(C_6H_5)_4$), 34.6 (t, $J$ = 14.3 Hz) ($CH_2CH_2P$), 25.3 ppm ($CH_2CH_2P$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 33.5 ppm. Anal. Calcd for **5**·$CH_2Cl_2$, $C_{59}H_{52}BCl_2CoO_2P_2S$: C, 68.95; H, 5.10; S, 3.12. Found: C, 68.92; H, 4.94; S, 2.94.

**Synthesis of [(COD)Rh(1)][ClO$_4$] (6).** *See safety note above.* To 0.3 g (1 mmol) of (COD)Rh(acac) dissolved in 3.5 mL of THF was added 0.99 mmol of $HClO_4$. After 15 min of stirring, 0.94 mmol of **1** dissolved in 6 mL of THF was added, and the solution was stirred for 2 h. The solution was then evaporated to dryness, and the residue was dissolved in acetone. Adding diethyl ether induced the precpipitation of 0.6 g of **6** as yellow crystals (80%). $^1$H NMR ($CDCl_3$) except phenyl resonances: 6.47 (2H), 4.52 (4H), 3.02 (m, 8H), 2.36 ppm (m, 8H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 17.9 ppm (d, $J$(Rh–P) = 142.5 Hz). Anal. Calcd for $C_{40}H_{42}ClO_4P_2RhS$: C, 58.65; H, 5.17; S, 3.91. Found: C, 58.57; H, 5.55; S, 3.94.

**Synthesis of [(CO)$_2$Rh(1)][ClO$_4$] (7).** *See safety note above.* Carbon monoxide was bubbled for 30 min through a solution of 0.25 g of **6** in 10 mL of dichloromethane. Addition of 10 mL of hexane saturated with carbon monoxide induced the crystallization of 0.18 g of **7** as yellow crystals (75%). IR, $\nu$(CO)($CH_2Cl_2$): 2045 (w), 1992 (s) cm$^{-1}$. $^1$H NMR ($CDCl_3$) except phenyl resonances: 6.96 (2H), 3.09 ppm (m, 8H). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): 145.4 (unresolved triplet, C(2) in $C_4H_2S$), 132.8 (t, $J$ = 6.2 Hz, $P(C_6H_5)_3$), 132.5 (C(3) in $C_4H_2S$), 129.8 (t, $J$ = 5.3 Hz, $P(C_6H_5)_3$), 127.4 ($P(C_6H_5)_2$), 37.3 (t, $J$ = 16.8 Hz) ($CH_2CH_2P$), 24 ppm ($CH_2CH_2P$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 13.4 ppm (d, $J$(Rh–P) = 90.3

**Table V.** Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (Å$^2$ × 10$^2$) with Esd's in Parentheses for Compound **8** ($U_{eq} = {}^1/_3$ Trace U)

| atom | $x/a$ | $y/b$ | $z/c$ | $U_{eq/Uiso}$ |
|---|---|---|---|---|
| Rh(1) | 0.27589(4) | 0.23537(2) | −0.21791(4) | 3.66(2) |
| S(1) | 0.3268(1) | 0.16132(8) | −0.0197(1) | 4.11(7) |
| P(1) | 0.3549(1) | 0.12924(8) | −0.3488(1) | 3.28(7) |
| P(2) | 0.2015(1) | 0.34201(8) | −0.0804(2) | 4.44(8) |
| C(1) | 0.2522(6) | 0.2957(4) | −0.3708(7) | 6.4(4) |
| O(1) | 0.2406(6) | 0.3320(3) | −0.4661(6) | 10.7(4) |
| C(2) | 0.4489(5) | 0.0555(3) | −0.2335(5) | 3.7(3) |
| C(3) | 0.3704(5) | 0.0043(3) | −0.1672(5) | 4.0(3) |
| C(4) | 0.3052(5) | 0.0533(3) | −0.0668(5) | 3.7(3) |
| C(5) | 0.2256(5) | 0.0262(3) | 0.0008(6) | 4.9(3) |
| C(6) | 0.1744(5) | 0.0911(4) | 0.0806(6) | 5.4(3) |
| C(7) | 0.2135(5) | 0.1682(3) | 0.0761(5) | 4.7(3) |
| C(8) | 0.1783(6) | 0.2509(4) | 0.1409(6) | 6.0(4) |
| C(9) | 0.1051(6) | 0.3047(4) | 0.0258(6) | 5.8(4) |
| C(12) | 0.4549(3) | 0.1556(2) | −0.5776(3) | 4.2(1) |
| C(13) | 0.5449(3) | 0.1902(2) | −0.6307(3) | 5.6(2) |
| C(14) | 0.6483(3) | 0.2387(2) | −0.5338(3) | 6.0(2) |
| C(15) | 0.6617(3) | 0.2526(2) | −0.3838(3) | 6.0(2) |
| C(16) | 0.5717(3) | 0.2180(2) | −0.3308(3) | 4.9(1) |
| C(11) | 0.4683(3) | 0.1695(2) | −0.4277(3) | 3.5(1) |
| C(22) | 0.1102(3) | 0.0934(2) | −0.5418(4) | 4.4(1) |
| C(23) | 0.0148(3) | 0.0436(2) | −0.6494(4) | 5.5(1) |
| C(24) | 0.0448(3) | −0.0339(2) | −0.7113(4) | 6.1(2) |
| C(25) | 0.1701(3) | −0.0616(2) | −0.6657(4) | 6.1(2) |
| C(26) | 0.2654(3) | −0.0118(2) | −0.5581(4) | 4.9(1) |
| C(21) | 0.2355(3) | 0.0657(2) | −0.4961(4) | 3.4(1) |
| C(32) | −0.0149(4) | 0.3721(2) | −0.2985(4) | 6.0(2) |
| C(33) | −0.1005(4) | 0.4197(2) | −0.3920(4) | 6.9(2) |
| C(34) | −0.0786(4) | 0.5055(2) | −0.3775(4) | 6.8(2) |
| C(35) | 0.0291(4) | 0.5437(2) | −0.2696(4) | 6.2(2) |
| C(36) | 0.1147(4) | 0.4961(2) | −0.1762(4) | 5.3(1) |
| C(31) | 0.0928(4) | 0.4103(2) | −0.1906(4) | 4.3(1) |
| C(42) | 0.3018(3) | 0.4677(3) | 0.1567(5) | 7.3(2) |
| C(43) | 0.4022(3) | 0.5105(3) | 0.2689(5) | 9.5(2) |
| C(44) | 0.5291(3) | 0.4906(3) | 0.2806(5) | 9.9(3) |
| C(45) | 0.5555(3) | 0.4279(3) | 0.1802(5) | 8.9(2) |
| C(46) | 0.4550(3) | 0.3852(3) | 0.0681(5) | 6.5(2) |
| C(41) | 0.3282(3) | 0.4051(3) | 0.0563(5) | 5.2(1) |
| Cl(1) | 0.2170(1) | 0.77129(9) | −0.0858(2) | 5.66(9) |
| O(2) | 0.2351(6) | 0.6970(3) | −0.0232(7) | 11.8(5) |
| O(3) | 0.1447(6) | 0.8223(4) | −0.0123(8) | 14.1(5) |
| O(4) | 0.1496(7) | 0.7529(5) | −0.2318(7) | 13.9(6) |
| O(5) | 0.3369(5) | 0.8114(4) | −0.0608(6) | 10.4(4) |

Hz). Anal. Calcd for $C_{34}H_{30}ClO_6P_2RhS$: C, 53.25; H, 3.94; S, 4.18. Found: C, 52.74; H, 3.93; S, 4.04.

**Synthesis of [(CO)Rh(1)][ClO$_4$] (8).** *See safety note above.* The reaction was conducted in the same way as for **6** except than at the end of the reaction the solution was evaporated to dryness. Recrystallization of the residue in a dichloromethane/hexane mixture led to 0.18 g of **8** as yellow crystals (80%). Bubbling CO through a solution of **8** immediately regenerated 7. IR, $\nu$(CO)($CH_2Cl_2$): 2020 cm$^{-1}$. $^1$H NMR ($CDCl_3$) except phenyl resonances: 6.88 (2H), 3.16 ppm (m, 8H). $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): 143.5 (t, $J$ = 5 Hz, C(2) in $C_4H_2S$), 133.3 (t, $J$ = 6 Hz, $P(C_6H_5)_2$), 132.1 (C(3) in $C_4H_2S$), 129.7 (t, $J$ = 5.3 Hz, $P(C_6H_5)_3$), 128.9 ($P(C_6H_5)_2$), 31.5 (t, $J$ = 14.6 Hz) ($CH_2CH_2P$), 25.1 ppm ($CH_2CH_2P$). $^{31}$P{$^1$H} NMR ($CDCl_3$): 8.3 ppm (d, $J$(Rh–P) = 111.6 Hz). Anal. Calcd for $C_{33}H_{30}ClO_5P_2RhS$: C, 53.64; H, 4.09; S, 4.34. Found: C, 53.42; H, 4.16; S, 4.24.

**Crystallographic Studies.** Crystals of **2** suitable for X-ray diffraction were obtained through recrystallization from a dichloromethane/hexane mixture at room temperature. Crystals of **2** suitable for X-ray diffraction were obtained through recrystallization from a dichloromethane/hexane mixture at room temperature. Crystals of **8** were grown from a dichloromethane/hexane mixture at room temperature. Data were collected on an Enraf-Nonius CAD4 diffractometer at 22 °C. For both compounds, cell constants were obtained by the least-squares refinement of the setting angles of 25 reflections in the range 24° < 2$\theta$(Mo K$\alpha_1$) < 28°. The space group for **2** was determined by careful examination of systematic extinctions in the listing of the measured reflections. All calculations were performed on a MicroVax 3400. Data reductions were carried out using the SDP crystallographic computing package.[35] The intensities were corrected for absorption by using the empirical $\Psi$-scan method.[36] Table III presents further crystallographic information.

The structures were solved by using the SHELXS-86 program[37] and refined by using the SHELX-76 program.[38] The positions of Mo (for **2**) or Rh (for **8**) and P atoms were determined by direct methods. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses. Atomic scattering factors were taken from the usual tabulations.[39] Anomalous dispersion terms for Mo, Rh, and P were included in $F_c$.[40] All non-hydrogen atoms were allowed to vibrate anisotropically, except the carbon atoms of the phenyl rings in **8**, which were refined as isotropic rigid groups ($C_6H_5$ ring: imposed $D_{6h}$ symmetry, C–C = 1.395 Å, C–H = 0.97 Å). Hydrogen atoms were entered in idealized positions (C–H = 0.97 Å) and held fixed during refinements. Scattering factors for the hydrogen atoms were taken from Stewart el al.[41]

Final atomic coordinates and $U_{eq}$ × 100 (or $U_{iso}$ × 100) for non-hydrogen atoms in compounds **2** and **8** are given in Tables IV and V, respectively. Thermal parameters for atoms which were refined anisotropically and hydrogen positions are available as supplementary material.

**Supplementary Material Available:** Tables S1–S4, listing anisotropic thermal parameters and hydrogen positions for **2** and **8** (4 pages). Ordering information is given on any current masthead page.

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(35) Enraf-Nonius Structure Determination Package, B. A. Frenz & Associates, Inc., College Station, TX, and Enraf-Nonius, Delft, The Netherlands (4th ed., 1981).

(36) North, A. C. T.; Phillips, D. C.; Mathew, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(37) Sheldrick, G. M. *SHELXS-86, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1986.

(38) Sheldrick, G. M. *SHELX-76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

(39) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, Table 2.2B.

(40) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, Table 2.3.1.

(41) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.