Synthetic Equivalents of 2-Lithiophosphinines: New Routes to 2-Functional Phosphinines

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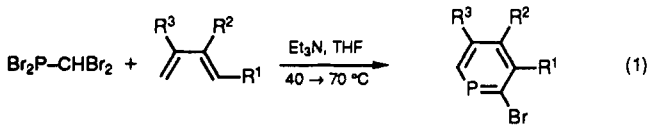
Two routes converting 2-bromophosphinines into 2-functional phosphinines are described. In the first one, a [2 + 4] cycloadduct between the 2-bromophosphinine, 2,3-dimethylbutadiene, and sulfur is first formed. On this adduct, a bromine to lithium exchange is performed by phenyllithium in THF at low temperature. This lithium derivative is converted into a functional derivative by reaction with an electrophile. Then, the 2-functional phosphinine is obtained by a combined reduction–cycloreversion using $P(CH_2CH_2CN)_3$ as the reducing agent at ca. 180 °C. A 2-(trimethylsilyl)- and a 2-(diphenylphosphino)phosphinine were thus prepared. In the second route, a bromine to lithium exchange is performed on a (2-bromophosphinine)pentacarbonyltungsten complex by phenyllithium in THF at −80 °C. The 2-functional phosphinine is recovered from its complex by heating with $Ph_2PCH_2CH_2PPh_2$ at 110 °C in toluene. A 2-iodo-, 2-(trimethylsilyl)-, and 2-[(diphenylphosphino)pentacarbonyltungsten]phosphinine were thus obtained. An intermediate [2-(ethoxycarbonyl)phosphinine]pentacarbonyltungsten complex readily adds water to give the corresponding 1-hydroxy-1,6-dihydrophosphinine complex.

Several functional phosphinines have been described in the literature since 1977.[1] However, in almost all cases, the functional group is introduced during the building of the ring. No general technique exists that would allow one to graft a functional group onto a preformed phosphinine ring. For example, Friedel–Crafts chemistry fails and no lithiophosphinine has ever been mentioned. In such a context, we wish to describe two synthetic equivalents of 2-lithiophosphinines and their use to synthesize a series of new 2-functional phosphinines.

Results and Discussion

Our starting products were the 2-bromophosphinines 1–4 that are easily obtained according to a previously described method[2] (eq 1). The yield lies ca. 40% in all cases. With

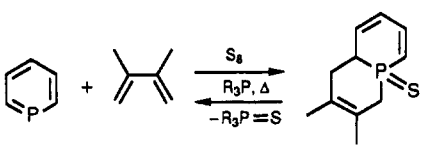


(1)

1: R^1 = Me, R^2 = R^3 = H
2: R^1 = R^2 = H, R^3 = Me
3: R^1 = R^3 = H, R^2 = Me
4: R^1 = H, R^2 = R^3 = Me

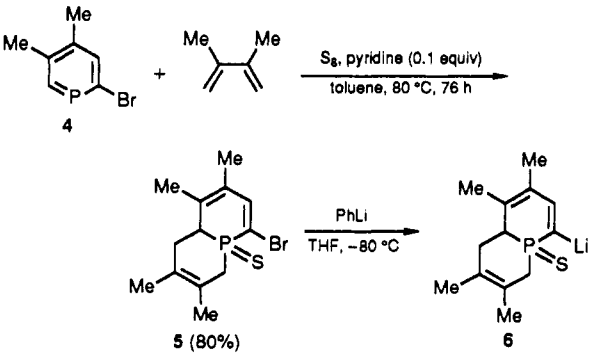
penta-1,3-diene (R^1 = Me, R^2 = R^3 = H), the regiochemistry of the cycloaddition was easily established by inspection of the ^1H NMR spectrum of phosphinine **1**. The α CH proton appears as a characteristic doublet of doublet with a huge ^2J(H–P) coupling: δ 8.40, ^2J(H–P) = 39.13 Hz, ^3J(H–H) = 9.7 Hz. With isoprene, the major compound is phosphinine **2**. The ratio **2**:**3** lies ca. 4:1. The regiochemistry was also established by inspecting the resonance of the α proton. In **2**, it appears as a doublet of doublet with a very small ^4J(H–H) coupling, δ 8.33, ^2J(H–P) = 39.94 Hz, ^4J(H–H) = 1.75 Hz, whereas in **3**, a significant ^3J(H–H) coupling is found, as in **1**, δ 8.5, ^2J(H–P) = 40 Hz, ^3J(H–H) = 10 Hz. Finally, it is interesting to note that the 4-methyl substitution induces a sizable shift to high fields of the ^{31}P resonance of these 2-bromophosphinines: ^{31}P (CH_2Cl_2) δ 210.6 (**1**), 206.4 (**2**), 190.3 (**3**), 191 (**4**).

With these 2-bromophosphinines in hand, the next step was to find how to use these halogen substituents to functionalize the ring. In our preceding work,[2] it has clearly been shown that a nucleophile tends to preferentially attack the C=P double bond rather than the C—halogen bond. Thus, the idea to reversibly mask this bond was logical. The combined reaction of a conjugated diene and sulfur was a possibility. Indeed, in the presence of a reducing agent, the phosphinine can be regenerated from its [2 + 4] cycloadduct[3] (eq 2). The experiments were



(2)

carried out with **4**. The cycloaddition with 2,3-dimethylbutadiene and sulfur gives the [2 + 4] adduct **5** in good yield. The C–Br bond of **5** displays a normal vinyl halide reactivity. Phenyllithium performs an almost instantaneous bromine–lithium exchange at low temperature in THF (eq 3). The formation of **6** and its use to prepare



(3)

(1) (a) Märkl, G.; Adolin, G.; Kees, F.; Zander, G. *Tetrahedron Lett.* **1977**, *18*, 3445. (b) Märkl, G.; Hock, K. *Tetrahedron Lett.* **1983**, *24*, 2645, 5051, and 5055. (c) Pellon, P.; Yeung Lam Ko, Y. Y. C.; Cosquer, P.; Hamelin, J.; Carrié, R. *Tetrahedron Lett.* **1986**, *27*, 4299. (d) Pellon, P.; Hamelin, J. *Tetrahedron Lett.* **1986**, *27*, 5611. (e) Blatter, K.; Rösch, W.; Vogelbacher, U.-J.; Fink, J.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 85. (f) Märkl, G.; Dorfmeister, G. *Tetrahedron Lett.* **1987**, *28*, 1093. (g) Dimroth, K.; Kaletsch, H. *Chem. Ber.* **1987**, *120*, 1245. (h) Holah, D. G.; Hughes, A. N.; Knudsen, K. L.; Perrier, R. *J. Heterocycl. Chem.* **1988**, *25*, 155. (i) Märkl, G.; Dörges, Ch.; Riedl, Th. *Tetrahedron Lett.* **1990**, *32*, 4589. (j) Holand, S.; Ricard, L.; Mathey, F. *J. Org. Chem.*, in press.

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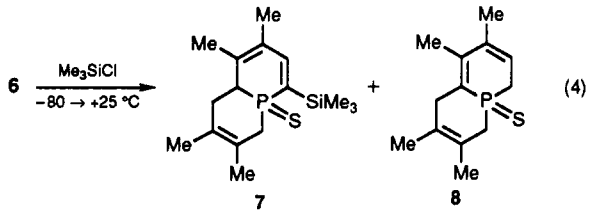
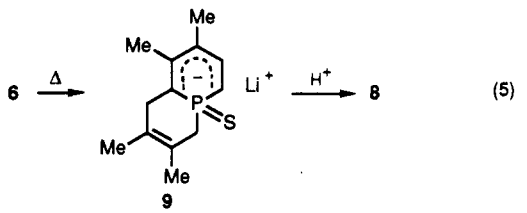
2,2′-biphosphinine has been described in a preliminary communication.[4] We wish to focus here on its use for the synthesis of 2-functional phosphinines.

Treating **6** with trimethylchlorosilane affords an inseparable mixture of sulfides **7** (^{31}P δ 24.9 in THF) and **8** (^{31}P δ 10.3) with a 7:8 ratio of ca. 2:1 (eq 4). It is impossible



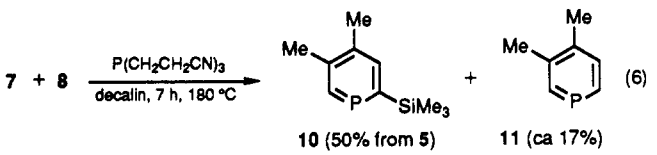
(4)

to avoid the formation of the protonation product **8**. Its formula was unambiguously established in our preliminary communication.[4] We suggest that it results from a H-shift, converting **6** into the very stable delocalized species **9**, which would be destroyed only during the aqueous workup (eq 5). The reduction of the mixture **7** + **8** by tris(β-



(5)

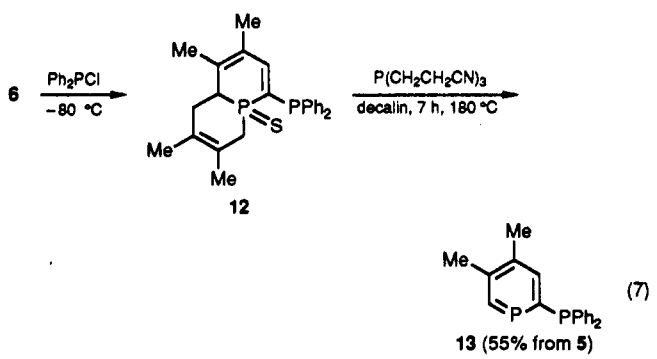
cyanoethyl)phosphine then gives 2-(trimethylsilyl)-4,5-dimethylphosphinine (**10**) in fair yield together with some 3,4-dimethylphosphinine (**11**)[5] (eq 6). The excess of P-



(6)

$(CH_2CH_2CN)_3$ and its sulfide precipitates from the reaction mixture at room temperature, and the phosphinine **11** partly evaporates with the solvent. The purification of **10** is thus quite easy. Previously, other authors[6] have just characterized **10** by ^{31}P NMR spectroscopy.

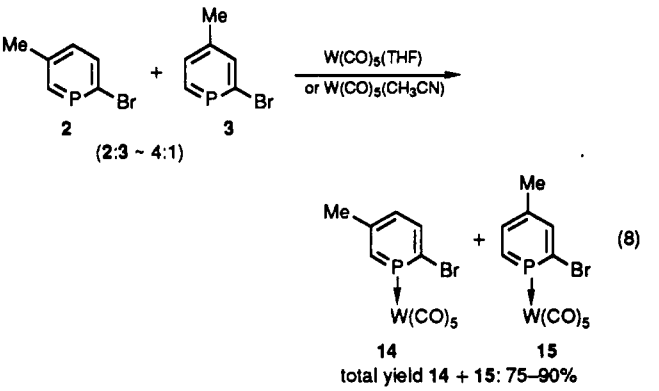
A similar scheme gave an easy access to 2-(diphenylphosphino)-4,5-dimethylphosphinine (**13**) (eq 7). In that case, no protonation product is formed because the elec-



(7)

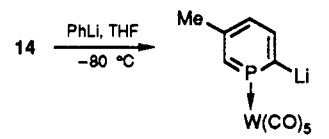
trophile rapidly reacts with **6** at −80 °C. Several other 2-(diphenylphosphino)phosphinines have recently been described in the literature.[1h,i] These molecules have some potential as chelating ligands in coordination chemistry.

While continuing our investigations on the chemistry of (2-halophosphinine)pentacarbonyltungsten complexes,[2b] we discovered that, contrary to alkyllithiums, phenyllithium does not add to the P=C double bond of the ring but performs a bromine to lithium exchange, as with **5**. As already noted,[7] it seems that the complexation of phosphorus reduces the cyclic delocalization within the ring and thus, reactivates the C—Br bond while providing some steric protection to the phosphorus atom. We performed our experiments with (2-bromo-5-methylphosphinine)-pentacarbonyltungsten (**14**). This complex was prepared from the 4:1 mixture of phosphinines **2** and **3** (eq 8). The



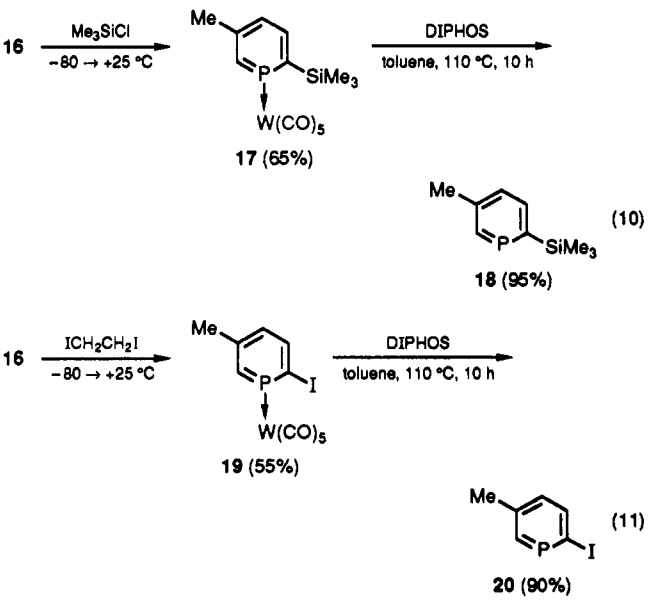
(8)

mixture of complexes **14** and **15** was treated with pentane. Complex **14** was thus obtained in 95% purity. The reaction of **14** with phenyllithium in THF at −80 °C affords the 2-lithiophosphinine complex **16** almost instantaneously (eq 9). Attacks at the P=C double bond and at the carbonyls remain negligible. Complex **16** reacts with a wide



(9)

range of electrophiles to give the expected 2-functional phosphinine complexes shown in eqs 10–13. The free



(10)
(11)

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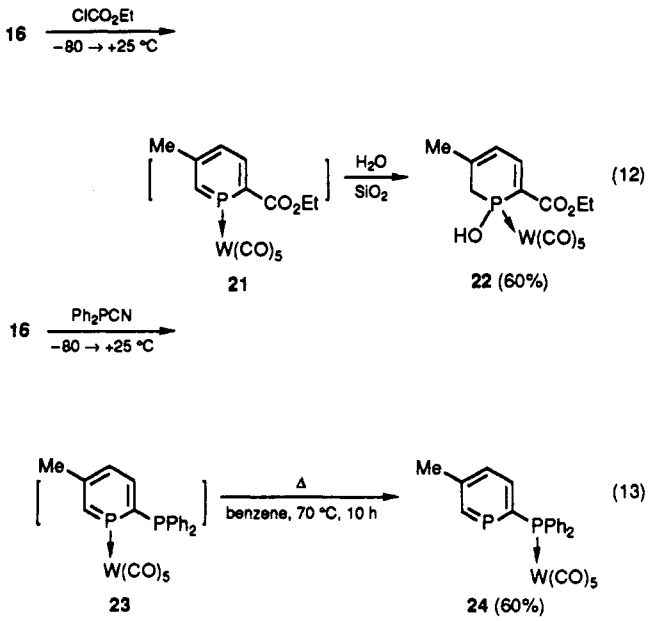

phosphinines can be recovered from their $W(CO)_5$ complexes by displacement with $Ph_2PCH_2CH_2PPh_2$ according to a technique devised in our laboratory by Philippe Le Goff.[8]

A 2-iodophosphinine has independently been synthesized by Bickelhaupt and his group from Cl_2P–CHI_2 via the route depicted in eq 1.[9] The iodine substitution induces an additional deshielding of the ^{31}P resonance: ^{31}P δ 206.4 (**2**); ^{31}P δ 229.1 (**20**) (CH_2Cl_2). On another side, the P=C double bond of the 2-ethoxycarbonyl-substituted complex **21** has a high electrophilicity and readily adds water during chromatography. The ^{31}P NMR resonance shifts from δ +188 for **21** (CH_2Cl_2) to +95 for **22**. The CH_2 resonance appears as an ABX system centered at δ 2.96 (A) and 3.60 (B) on the ^1H NMR spectrum of **22**. A similar hydration has already been observed by Venanzi and his group on the Pt^{II} and Pd^{II} complexes of a 2-(2-pyridyl)phosphinine.[10] Finally, the relatively weak σ-coordination ability of phosphinines is well-evidenced by the behavior of complex **23**. An internal displacement of the $W(CO)_5$ complexing group from the phosphinine phosphorus to the PPh_2 phosphorus takes place at 70 °C. Similar competitions between two phosphorus sites have been described in the literature.[11] Another observation concerns the great variations of the $^2J(P{=}C{-}P)$ coupling constants within the series of 2-(diphenylphosphino)phosphinine derivatives described in this work (**13**, **23**, **24**) and elsewhere[1h,i] (from 19 to 215 Hz). This variability has already been noticed on other P=C—P systems.[12] The easy access to 2-lithiophosphinine equivalents such as **6** and **16** paves the way for a systematic study of 2-functional phosphinines whose chemistry remains largely unexplored at the moment.

Experimental Section

NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^1H and 50.32 MHz for ^{13}C and a Bruker WP 80 SY spectrometer operating at 32.44 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from internal TMS (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants are expressed in hertz. Mass spectra were obtained at 70 eV with a Shimadzu GC-MS QP 1000 instrument by the direct-inlet method. Infrared spectra were recorded with a Perkin-Elmer Model 297 spectrometer. Elemental analyses were performed by the "Service d'analyse du CNRS", Gif-sur-Yvette, France. Silica gel (70–230 mesh) was used for chromatographic separations. All commercially available reagents were used as received from the suppliers. The synthesis of phosphinine **4** has been described previously.[2b] The new phosphinines described in this work are unstable upon standing. Their elemental analysis proved to be very difficult. They have been analyzed as their P–$W(CO)_5$ complexes.

3-Methyl-2-bromophosphinine (1). Dibromomethyldibromophosphine[13] (20 g, 55 mmol) was added dropwise to a solution of triethylamine (11.1 g, 100 mmol), piperylene (37.3 g, 0.55 mol), and THF (10 mL) at 40 °C. At the end of the addition, the solvent and the excess of amine and diene were evaporated. The residue was then dissolved in THF (50 mL) and triethylamine (11.1 g, 0.1 mol) and was heated at 50 °C for 3 h. After evaporation of the solvent, 500 mL of dry hexane was added and the reaction mixture was filtered. Finally, the final product was quickly chromatographed on dry silica gel with hexane as eluent. Yield: 4.15 g (40%), colorless oil. ^{31}P NMR (CH_2Cl_2): δ 210.61. ^1H NMR ($CDCl_3$): δ 2.56 (d, 3 H, ^4J(H–P) = 2.17 Hz, Me), 7.44 (dd, 1 H, ^3J(H–H) = 8.56 Hz, ^4J(H–P) = 3.4 Hz, H_4), 7.72 (dt, 1 H, ^3J(H–H) = 8.56 Hz, ^3J(H–H) = 9.7 Hz, ^3J(H–P) not estimated, H_5), 8.4 (dd, 1 H, ^2J(H–P) = 39.13 Hz, ^3J(H–H) = 9.7 Hz, H_6). ^{13}C NMR ($CDCl_3$): δ 26.08 (s, Me), 132.98 (d, J(C–P) = 13.77 Hz, C_4 or C_5), 133.44 (d, J(C–P) = 17.2 Hz, C_4 or C_5), 144.59 (d, ^2J(C–P) = 14.21 Hz, C_3), 154.0 (d, ^1J(C–P) = 66.79 Hz, C_2), 155.48 (d, ^2J(C–P) = 54.27 Hz, C_6). Mass spectrum, m/z (ion, relative intensity): 189 (M, 98), 109 (M – Br, 100).

5-Methyl-2-bromophosphinine (2) and 4-Methyl-2-bromophosphinine (3). The same procedure as for **1** was used with dibromomethyldibromophosphine (80 g, 0.22 mol), triethylamine (44.5 g, 0.44 mol), and isoprene (150 g, 2.2 mol). Yield: 16.5 g (40%), colorless oils. ^{31}P NMR (CH_2Cl_2): δ 206.4 (**2**), 190.3 (**3**). ^1H NMR ($CDCl_3$) (**2**): δ 2.42 (s, 3 H, Me), 7.25 (dq, 1 H, ^3J(H–H) = 8.92 Hz, ^4J(H–H) = 1.75 Hz, ^4J(H–P) = not measurable, H_4), 7.96 (dd, 1 H, ^3J(H–H) = 8.92 Hz, ^3J(H–P) = 4.24 Hz, H_3), 8.33 (dd, 1 H, ^2J(H–P) = 39.94 Hz, ^4J(H–H) = 1.75 Hz, H_6). ^{13}C NMR ($CDCl_3$): δ 24.42 (s, Me), 132.95 (d, J(C–P) = 15.87 Hz, C_3 or C_4), 138.4 (d, J(C–P) = 13.88 Hz, C_3 or C_4), 142.18 (d, ^2J(C–P) = 14.64 Hz, C_5), 148.94 (d, ^2J(C–P) = 66.32 Hz, C_2), 156.89 (d, ^2J(C–P) = 55.65 Hz, C_6). Mass spectrum, m/z (ion, relative intensity): 189 (M, 79), 109 (M – Br, 100).

Sulfide 5. 4,5-Dimethyl-2-bromophosphinine (10 g, 49.2 mmol), sulfur (2.36 g, 73.8 mmol), 2,3-dimethylbutadiene (40.3 g, 0.49 mol), and pyridine (0.4 g, 5 mmol) were heated in 20 mL of toluene at 80 °C for 72 h. After evaporation of the excess of diene and toluene, the crude product was purified by column chromatography with hexane to remove the excess sulfur and finally with hexane/ether (3:1) as eluent. **5** was recovered as a yellow powder. Yield: 12.47 g (80%). ^{31}P NMR ($CDCl_3$): δ 30.30. ^1H NMR ($CDCl_3$): δ 1.68–1.99 (4s, 4 × 3 H, 4 Me), 2.0–3.1 (m, 5 H, 2 × CH_2 and CH—P), 6.67 (d, ^3J(H—P) = 25.64 Hz, =C—H). ^{13}C NMR ($CDCl_3$): δ 19.86 (d, J(C—P) = 23.47 Hz, Me), 20.49 (s, Me), 20.63 (s, Me), 20.75 (s, Me), 34.63 (d, ^2J(C—P) = 5.03 Hz, CH_2), 36.89 (d, ^1J(C—P) = 53.52 Hz, CH_2—P), 46.3 (d, ^1J(C—P) = 61.28 Hz, CH—P), 112.86 (d, ^1J(C—P) = 66.75 Hz, =*C*—Br), 122.58 (d, J(C—P) = 9.22 Hz, *C*—Me), 124.84 (d, J(C—P) = 11.61 Hz, =*C*—Me), 129.94 (d, J(C—P) = 11.4 Hz, =*C*—Me), 131.7 (d, J(C—P) = 7.2, =*C*—Me), 143.49 (d, ^2J(C—P) = 4.93 Hz, =*C*—H). Mass spectrum, m/z (ion, relative intensity: 317 (M, 60), 285 (M – S, 21), 234 (M – C_6H_{10} – H, 100). Anal. Calcd for $C_{13}H_{18}PBrS$: C, 49.22; H, 5.72. Found: C, 50.06; H, 5.28.

4,5-Dimethyl-2-(trimethylsilyl)phosphinine (10). Phenyllithium (10 mmol, 2 mol/L in ether) was added at −80 °C to a solution of sulfide **5** (3.17 g, 10 mmol) in 25 mL of THF. After a few seconds, chlorotrimethylsilane (1.6 g, 15 mmol) was added and the reaction mixture was allowed to warm to room temperature. After evaporation of the solvent, decalin (20 mL) and

(8) This work will be described elsewhere.
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tris(2-cyanoethyl)phosphine (2.9 g, 15 mmol) were added and the reaction mixture was heated at 180 °C for 7 h. After cooling, the reaction mixture was quickly chromatographed with hexane as eluent. Yield: **10**, 0.98 g (50%), colorless oil. **11**, 0.22 g (17%). ^{31}P NMR (pentane): δ 219.04. ^1H NMR ($CDCl_3$): δ 0.4 (s, 9 H, Me_3Si), 2.43 (d, J(H-P) = 3.6 Hz, Me), 2.46 (s, Me), 7.93 (d, ^3J(H-P) = 10.58 Hz, H_3), 8.6 (d, ^2J(H-P) = 36.59 Hz, H_6). ^{13}C NMR ($CDCl_3$): δ 0.07 (d, ^3J(C-P) = 5.8 Hz, Me), 22.56 (s, Me), 23.69 (s, Me), 137.52 (d, J(C-P) = 23 Hz, C_4 or C_5), 141.16 (d, ^2J(C-P) = 14.13 Hz, C_3), 143.61 (d, J(C-P) = 14.49 Hz, C_4 or C_5), 154.68 (d, ^1J(C-P) = 57.4 Hz, C_6), 167.53 (d, ^1J(C-P) = 71.96 Hz, C_2) ppm. Mass spectrum, m/z (ion, relative intensity): 196 (M, 28), 181 (M - CH_3, 100).

Sulfide 12. Phenyllithium (20 mmol) was added at -80 °C to a solution of sulfide **5** (6.34 g, 20 mmol) in 50 mL of THF. After a few seconds, diphenylchlorophosphine (4.41 g, 20 mmol) was added and the reaction mixture was allowed to warm to room temperature. After evaporation of the solvent, the final product was crystallized with acetone at 0 °C. Yield: 6.33 g (75%), colorless solid. ^{31}P NMR (CH_2Cl_2), AB system: δ 25.57 (^2J(P—P) = 97.66 Hz, P=S), -18.48 (Ph_2P). ^1H NMR ($CDCl_3$): δ 1.12, 1.46, 1.62, 1.89 (4s, 12 H, 4 Me), 2.3-2.9 (m, 5 H, 2 × CH_2 and CH), 5.98 (dd, ^3J(H—P_A) = 33.7 Hz, ^3J(H—P_B) = 9.25 Hz, =C—H), 7.1-8.0 (m, 10 H, 2 × C_6H_5). ^{13}C NMR ($CDCl_3$): δ 19.31 (s, Me), 19.79 (s, Me), 20.42 (d, J(C—P) = 10.74 Hz, Me), 21.26 (d, J(C—P) = 7.03 Hz, Me), 34.77 (dd, ^1J(C—P) = 53.17 Hz, ^3J(C—P) = 4.96 Hz, CH_2—P), 36.39 (d, ^2J(C—P) = 3.27 Hz, CH_2), 42.38 (d, ^1J(C—P) = 54.96 Hz, CH—P), 121.75—135.44 (=C— and C_6H_5), 147.96 (s, =C—H). Mass spectrum, m/z (ion, relative intensity): 422 (M, 100), 390 (M - S, 19), 340 (M - C_6H_{10}, 85), 308 (340 - S, 59). Sulfide **12** was analyzed as the PPh_2 oxide. Anal. Calcd for $C_{25}H_{28}P_2OS$: C, 68.47; H, 6.43. Found: C, 68.31; H, 6.39.

4,5-Dimethyl-2-(diphenylphosphino)phosphinine (13). Sulfide **12** (6 g, 14.2 mmol) and tris(2-cyanoethyl)phosphine (4.11 g, 21.3 mmol) were heated at 180 °C for 7 h in 40 mL of decalin. After this period, the reaction mixture was allowed to cool to room temperature and 30 mL of dry hexane was added. A rapid chromatography on dry silica gel with hexane/Et_2O (1:1) as eluent gave **13**. Yield: 3.19 g (73%), yellow viscous oil. ^{31}P NMR (CH_2Cl_2), AB system: δ 209.33 (d, ^2J(C-P) = 92.77 Hz, =P-), -0.43 (d, Ph_2P). ^1H NMR ($CDCl_3$): δ 2.33 (d, 1 H, J(H-P) = 2 Hz, Me), 2.48 (s, Me), 7.37 (s, 10 H, 2 × C_6H_5), 7.63 (m, 1 H, H_3), 8.52 (d, 1 H, ^1J(H-P) = 40 Hz, H_6). ^{13}C NMR ($CDCl_3$): δ 22.37 (s, Me), 23.30 (s, Me), 128.44 (d, J(C-P) = 5.06, CH of C_6H_5), 128.83 (s, CH of C_6H_5), 131.72 (d, ^1J(C-P) = 17.5 Hz, C of C_6H_5), 132.54 (s, C_4 or C_5), 133.92 (d, ^2J(C-P) = 19.11 Hz, CH of C_6H_5), 137.66 (s, C_4 or C_5), 142.92 (dd, C_3), 155.79 (dd, ^2J(C-P) = 55.01 Hz, ^3J(C-P) = 5.47 Hz, C_6). Mass spectrum, m/z (ion, relative intensity): 308 (M, 100).

(5-Methyl-2-bromophosphinine)- and (4-Methyl-2-bromophosphinine)pentacarbonyltungsten Complexes 14 and 15. First Method. A mixture of 5-methyl- and 4-methyl-2-bromophosphinine (4:1) (1.9 g, 10 mmol) was added to W(CO)$_5$THF (10 mmol) in 200 mL of THF at room temperature. After 10 min, the solvent was evaporated and the yellow residue was chromatographed with hexane as eluent. Yield: 4.35 g (85%).

Second Method. A mixture of 5-methyl- and 4-methyl-2-bromophosphinine (4:1) (9.5 g, 50 mmol) was added to W(CO)$_5$(MeCN) (18.24 g, 50 mmol) in 300 mL of THF. The solution was heated for 3 h at 40 °C. After evaporation of the solvent, the yellow residue was chromatographed with hexane as eluent. Yield: 19.2 g (75%). A mixture of complexes **14** and **15** (21 g, 41 mmol) was washed with pentane (100 mL). Complex **14** (14 g, 27.3 mmol) was thus obtained in 95% purity as a yellow solid. ^{31}P NMR (CH_2Cl_2): δ 182.46 (^1J(^{31}P-^{183}W) = 283.2 Hz). ^1H NMR ($CDCl_3$): δ 2.44 (d, 3 H, ^4J(H-P) = 1.82 Hz, Me), 7.07 (dt, 1 H, ^3J(H-H) = 9.2 Hz, ^4J(H-P) = 9.2 Hz, ^4J(H-H) = 1.84 Hz, H_4), 8.07 (dd, 1 H, ^3J(H-H) = 9.2 Hz, ^3J(H-P) = 14.15 Hz, H_3), 8.09 (dd, 1 H, ^2J(H-P) = 25.49 Hz, ^4J(H-H) = 1.84 Hz, H_6). ^{13}C NMR ($CDCl_3$): δ 24.35 (d, ^3J(C-P) = 9.11 Hz, Me), 130.17 (d, J(C-P) = 24.28 Hz, C_3 or C_4), 140.76 (d, J(C-P) = 10.17 Hz, C_4 or C_3), 143.76 (d, J(C-P) = 16.17 Hz, C_2 or C_5), 146.73 (d, J(C-P) = 16.55 Hz, C_2 or C_5), 151.46 (d, ^2J(C-P) = 16.88 Hz, C_6), 193.93 (d, ^2J(C-P) = 9.3 Hz, CO cis), 198.17 (d, ^2J(C-P) = 32.83 Hz, CO trans). Anal. Calcd for $C_{11}H_6BrPWO_5$: C, 25.75; H, 1.17. Found: C, 25.65; H, 1.12.

[5-Methyl-2-(trimethylsilyl)phosphinine]pentacarbonyltungsten (17). Phenyllithium (12 mmol, 2 mol/L in ether) was added to a solution of complex **14** (6 g, 11.4 mmol) in 100 mL of THF at -80 °C. After a few seconds, chlorotrimethylsilane (1.32 g, 12 mmol) was added and the reaction mixture was allowed to warm to room temperature. After evaporation of the solvent, the final product was chromatographed with hexane as eluent. Yield: 3.84 g (65%), yellow solid. ^{31}P NMR ($CDCl_3$): δ 184.59 (^1J(^{31}P-^{183}W) = 258.79 Hz). ^1H NMR ($CDCl_3$): δ 0.51, 0.53, 0.55 (3s, 9 H, $SiMe_3$), 2.51 (d, 3 H, ^4J(H-P) = 1.8 Hz, Me), 7.31 (dt, 1 H, ^3J(H-H) ~ ^4J(H-P) = 8.4 Hz, ^4J(H-H) = 0.8 Hz, H_4), 8.06 (dd, 1 H, ^3J(H-P) = 28 Hz, ^3J(H-H) = 8.4 Hz, H_3), 8.38 (dd, 1 H, ^2J(H-P) = 24.6 Hz, ^4J(H-H) = 0.8 Hz, H_6). ^{13}C NMR ($CDCl_3$): δ 0.92 (s, $SiMe_3$), 24.49 (d, ^3J(C-P) = 7.59 Hz, Me), 127.96 (d, J(C-P) = 34.5 Hz, C_3 or C_4), 142.87 (d, J(C-P) = 19 Hz, C_3 or C_4), 148.05 (d, ^2J(C-P) = 15.29 Hz, C_5), 153.5 (d, ^1J(C-P) = 13.32 Hz, C_6), 158.92 (d, ^1J(C-P) = 21.31 Hz, C_2), 195.84 (d, ^2J(C-P) = 8.95 Hz, CO cis), 198.77 (d, ^2J(C-P) = 28.36 Hz, CO trans). Mass spectrum, m/z (ion, relative intensity): 506 (M, 23), 450 (M - 2CO, 40), 422 (M - 3CO, 28), 394 (M - 4CO, 36), 366 (M - 5CO, 64). Anal. Calcd for $C_{14}H_{15}PSiWO_5$: C, 33.22; H, 2.98. Found: C, 33.31; H, 3.10.

5-Methyl-2-(trimethylsilyl)phosphinine (18). Complex **17** (3 g, 5.49 mmol) was heated with DIPHOS (2.62 g, 6.6 mmol) in 30 mL of toluene at 110 °C for 18 h. After evaporation of the solvent, the crude mixture was chromatographed with hexane as eluent. Yield: 0.94 g (95%), colorless oil. ^{31}P NMR (CH_2Cl_2): δ 229.43. ^1H NMR ($CDCl_3$): δ 0.45 (s, 9 H, $SiMe_3$), 2.55 (s, 3 H, Me), 7.40 (d, 1 H, ^3J(H-H) = 8.1 Hz, H_4), 8.09 (dd, 1 H, ^3J(H-H) = 8.1 Hz, ^3J(H-P) = 10.23 Hz, H_3), 8.68 (dd, 1 H, ^2J(H-P) = 37.0 Hz, ^4J(H-H) = 0.91 Hz, H_6). ^{13}C NMR ($CDCl_3$): δ 0.14 (d, ^3J(C-P) = 5.56 Hz, Me), 25.06 (s, Me), 129.78 (d, J(C-P) = 23 Hz, C_3 or C_4), 138.91 (d, J(C-P) = 13.9 Hz, C_4 or C_3), 143.73 (d, ^2J(C-P) = 13.79 Hz, C_5), 154.24 (d, ^1J(C-P) = 59.4 Hz, C_6), 166.23 (d, ^1J(C-P) = 74.9 Hz, C_2).

(5-Methyl-2-iodophosphinine)pentacarbonyltungsten (19). Phenyllithium (12 mmol, 2 mol/L in ether) was added to a solution of complex **14** (6 g, 11.4 mmol) in 100 mL of THF at -80 °C. Then, 1,2-diodoethane (3.96 g, 13.8 mmol) was added and the reaction mixture was allowed to warm to room temperature. After evaporation of the solvent, the final product was chromatographed with hexane as eluent. Yield: 3.68 g (55%), yellow solid. ^{31}P NMR ($CDCl_3$): δ 199.02 (^1J(^{31}P-^{183}W) = 283.2 Hz). ^1H NMR ($CDCl_3$): δ 2.4 (d, 3 H, ^4J(H-P) = 0.83 Hz, Me), 6.92 (dt, 1 H, ^3J(H-H) ~ ^3J(H-P) = 8.9 Hz, ^4J(H-H) = 0.83 Hz, H_4), 8.04 (dd, 1 H, ^2J(H-P) = 25.9 Hz, ^4J(H-H) = 0.86 Hz, H_6), 8.31 (dd, 1 H, ^3J(H-P) = 17.02 Hz, ^3J(H-H) = 8.98 Hz, H_3). ^{13}C NMR ($CDCl_3$): δ 24.55 (d, ^3J(C-P) = 8.86 Hz, Me), 116.22 (s, C_2), 130.15 (d, J(C-P) = 26 Hz, C_3 or C_4), 143.73 (d, J(C-P) = 13.79 Hz, C_3 or C_4), 147.15 (d, ^2J(C-P) = 15.67 Hz, C_5), 152.59 (d, ^1J(C-P) = 13.40 Hz, C_6), 194.29 (d, ^1J(C-P) = 9.14 Hz, CO cis), 198.28 (d, ^1J(C-P) = 32.59 Hz, CO trans). Mass spectrum, m/z (ion, relative intensity): 559 (M, 32), 503 (M - 2CO, 31), 475 (M - 3CO, 19), 447 (M - 4CO, 32), 419 (M - 5CO, 91). Anal. Calcd for $C_{11}H_6IPWO_5$: C, 23.59; H, 1.08. Found: C, 23.48; H, 1.04.

5-Methyl-2-iodophosphinine (20). Complex **18** (3.5 g, 6.26 mmol) was heated with DIPHOS (3 g, 7.5 mmol) in 30 mL of toluene at 110 °C for 4 h. After evaporation of the solvent, the crude mixture was chromatographed with hexane as eluent. Yield: 1.4 g (90%), colorless oil. ^{31}P NMR (CH_2Cl_2): δ 229.13. ^1H NMR ($CDCl_3$): δ 2.41 (s, 3 H, Me), 7.04 (d, 1 H, ^3J(H-H) = 8.6 Hz, H_4), 8.18 (d, 1 H, ^2J(H-P) = 39.52 Hz, H_6), 8.21 (dd, 1 H, ^3J(H-P) = 5.64 Hz, ^3J(H-H) = 8.6 Hz, H_3). ^{13}C NMR ($CDCl_3$): δ 24.73 (s, Me), 119.90 (d, ^1J(C-P) = 74.62 Hz, C_2), 132.80 (d, J(C-P) = 17.37 Hz, C_3 or C_4), 142.26 (d, ^2J(C-P) = 13.80 Hz, C_5), 143.64 (d, J(C-P) = 14.76 Hz, C_4 or C_3), 158.89 (d, ^1J(C-P) = 58.92 Hz, C_6). Mass spectrum, m/z (ion, relative intensity): 236 (M, 100).

[1-Hydroxy-2-(ethoxycarbonyl)-5-methyl-1,6-dihydrophosphinine]pentacarbonyltungsten (22). Phenyllithium (2 mmol, 2 mol/L in ether) was added to a solution of **14** (1 g, 1.9 mmol) in 25 mL of THF at -80 °C. After a few seconds, ethyl chloroformate (0.32 g, 3 mmol) was added and the reaction mixture was allowed to warm to room temperature. After evaporation of the solvent, the final product was chromatographed with hexane/Et_2O (1:1) as eluent. Yield: 0.61 g (60%), yellow solid. ^{31}P NMR (CH_2Cl_2): δ 95.0 (^1J(^{31}P-^{183}W) = 273.38 Hz). ^1H NMR

($CDCl_3$): δ 1.37 (t, 3 H, ^3J(H-H) = 14.14 Hz, Me), 2.09 (s, 3 H, Me), 2.96 (dd, 1 H, ^2J(H-H) = 17.19 Hz, ^2J(H-P) = 2.51 Hz, H_6), 3.6 (t, 1 H, ^2J(H-H) ~ ^2J(H-P) = 17.2 Hz, H_6'), 4.34 (m, 3 H, OCH_2 and OH), 6.04 (m, 1 H, H_4), 7.21 (dd, 1 H, ^3J(H-P) = 21.62 Hz, ^3J(H-H) = 7.45 Hz, H_3). Anal. Calcd for $C_{14}H_{13}PWO_8$: C, 32.08; H, 2.5. Found: C, 32.14; H, 2.52.

5-Methyl-2-[(diphenylphosphino)pentacarbonyltungsten]phosphinine (24). Phenyllithium (8 mmol, 2 mol/L in ether) was added to a solution of complex 14 (4 g, 7.6 mmol) in 75 mL of THF at -80 °C. Then, cyanodiphenylphosphine (1.6 g, 7.6 mmol) in 5 mL of THF was added and the reaction mixture was allowed to warm to room temperature. After evaporation of the solvent, benzene (30 mL) was added and the reaction mixture was heated at 70 °C for 10 h. After evaporation of the solvent, the final product was chromatographed with hexane/CH_2Cl_2 (4:1) as eluent. Yield: 2.84 g (60%), yellow solid. ^{31}P NMR (CH_2Cl_2), AB system: δ 227.03 (d, ^2J(P—P) = 107.42 Hz, -P=), 24.65 (d, $^1J(^{31}P—^{183}W)$ = 249.02 Hz, Ph_2P). ^1H NMR ($CDCl_3$): δ 2.56 (s, 3 H, Me), 7.41-7.65 (m, 11 H, C_6H_5 and H_4), 8.07 (ddd, 1 H, ^3J(H-P_A) = 16.02 Hz, ^3J(H-P_B) = 5.2 Hz, ^3J(H-H) = 8.68 Hz, H_3), 8.63 (dd, 1 H, ^2J(H-P_A) = 41.38 Hz, ^4J(H-P_B) = 4.92 Hz, H_6). ^{13}C NMR ($CDCl_3$): δ 24.66 (s, Me), 128.71 (d, J(C-P) = 9.66 Hz, CH of C_6H_5), 130.49 (s, CH of C_6H_5), 130.93 (d, ^1J(C-P) = 10.74 Hz, C of C_6H_5), 131.27 (d, ^1J(C-P) = 10.65 Hz, C of C_6H_5), 133.21 (d, J(C-P) = 11.75 Hz, CH of C_6H_5), 136.3 (dd, J(C-P_A) = 40.05 Hz, J(C-P_B) = 4.7 Hz, C_3), 140.56 (dd, J(C-P_A) = 12.44 Hz, J(C-P_B) = 8.96 Hz, C_4), 145.25 (d, ^2J(C-P) = 11.94 Hz, C_5), 153.92 (dd, ^2J(C-P_A) = 58.02 Hz, ^3J(C-P_B) = 13.1 Hz, C_6), 161.29 (dd, ^1J(C-P_A) = 68.32 Hz, ^1J(C-P_B) = 27.25 Hz, C_2), 197.67 (d, ^2J(C-P) = 5.94 Hz, CO cis), 199.54 (d, ^2J(C-P) = 21.76 Hz, CO trans). Mass spectrum, m/z (ion, relative intensity): 590 (M - CO, 32), 534 (M - 3CO, 62), 478 (M - 5CO, 100), 294 (M - $W(CO)_5$, 60). Anal. Calcd for $C_{23}H_{16}P_2WO_5$: C, 44.68; H, 2.60. Found: C, 44.08; H, 2.42.

Sulfur-Coordinated Thiophene and Dibenzothiophene in $Cp'(CO)_2Re$(thiophene) Complexes

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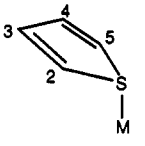
A series of stable S-bound thiophene complexes $Cp'(CO)_2Re(Th)$, Cp' = C_5H_5 or C_5Me_5, Th = thiophene (T), 2-MeT, 3-MeT, 2,5-Me_2T, Me_4T, and dibenzothiophene (DBT), are prepared by the reaction of $Cp'(CO)_2Re(THF)$ with thiophenes. The first structural determination of a simple nonchelated S-coordinated thiophene complex $Cp^*(CO)_2Re(T)$ is reported. Reactions of several of the $Cp'(CO)_2Re(Th)$ complexes

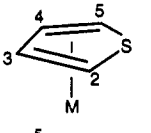
(Th = T, 2-MeT, and 3-MeT) with $Fe_2(CO)_9$ give thiophene-bridging dinuclear compounds $Cp'(CO)_2Re(\mu_2$-$\eta^4(S)$-Th)$Fe(CO)_3$ in which thiophene is coordinated to the Re via the sulfur and to the Fe through the four carbons of the diene system. This reaction is the first to demonstrate that S coordination activates thiophene to undergo further reactions.

Introduction

Thiophene and its derivatives, among the organosulfur compounds in petroleum, are the most difficult to desulfurize in the heterogeneous catalytic hydrodesulfurization (HDS) process.[2] In order to understand the mechanism(s) of HDS, it is important to know how thiophene adsorbs at metal sites on the catalyst surface. Thiophenes may coordinate through the sulfur and/or the unsaturated carbon-carbon double bonds. In its transition-metal complexes, thiophene is known[3] to bind in various ways which involve the sulfur and unsaturated carbon-carbon bonds. Of these known thiophene coordination modes, the S- and η^5-bound forms are most often suggested for initial thiophene adsorption to catalyst surfaces.[4]



S-bound



η^5-bound

In a mechanism proposed in these laboratories[4c,5] for the catalytic hydrodesulfurization (HDS) of thiophenes, the thiophene is adsorbed via the entire π-ring in the η^5-mode.[6] Thiophenes coordinated in this manner in Mn and Ru complexes[7] are susceptible to attack by hydride sources,

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