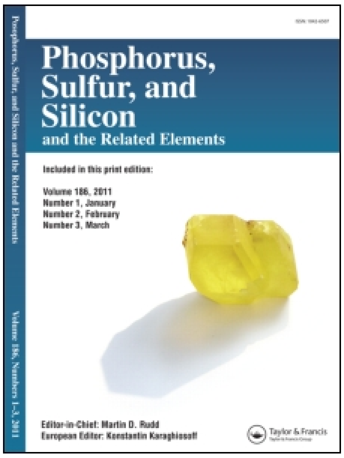

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PHOSPHOLE SULFIDES AS 6-ELECTRON η^4-C_4, η^1-S CHELATING LIGANDS*

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The reaction of 1-phenyl-3,4-dimethylphosphole sulfide with $[M(CO)_3]$ sources (M=Cr, Mo) yields the corresponding η^4-C_4, η^1-S-$M(CO)_3$ complexes. The X-ray crystal structure analysis of the Cr-complex reveals an original type of complexation of the P=S unit which lies half-way between a η^1-S and a η^2-P=S bonding mode.

INTRODUCTION

Electrophilic substitution reactions are of prime importance in the chemistry of aromatic heterocycles. They provide a ready access to a huge variety of functional derivatives. Due to the high inversion barrier of phosphorus, phospholes have pyramidal ground states and weak aromaticity.[1] As a result, any electrophile tends to attack phospholes at phosphorus, thus preventing possible functionalisation at carbon. In order to develop the chemistry of functional phospholes, one possibility is to block the lone pair at phosphorus while avoiding destruction of delocalisation within the diene subunit. Following this idea, it was shown that acylation of phosphole P-$Mo(CO)_5$ complexes by acyl chlorides is a viable route to δ 2- and 3-acylphospholes.[2] Other classical electrophilic substitution reactions such as formylation, carboxylation however fail. In order to explore this approach further, we thought that it might be possible to block the phosphole lone pair by sulfurization, thus preventing any adverse effect of steric hindrance at P. The electron withdrawing effect of the P=S could be offset by appropriate η^4-complexation of the diene. It is indeed well known that conjugated diene η^4-complexes are prone to electrophilic substitution reactions.[3] With

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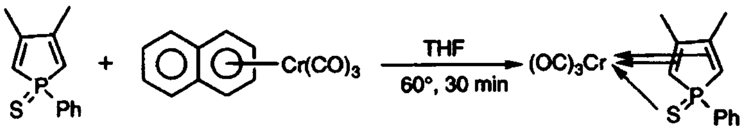
* Dedicated to Professor Robert Wolf, a pioneer of modern organophosphorus chemistry in France.

these ideas in mind, we started to study the η^4-complexation of the representative 1-phenyl-3,4-dimethylphosphole sulfide **1**. This led to the unexpected discovery of a new η^4-C_4, η^1-S 6-electron complexation mode.

RESULTS AND DISCUSSION

As a preliminary series of experiments, we started to investigate the reactions of **1** with Cr(0) and Mo(0) complexes. While $Cr(CO)_6$ gives an intractable mixture, the more reactive $Mo(CO)_6$ gives a clean desulfurization yielding $[Mo(CO)_5L]$, L=1-phenyl-3,4-dimethylphosphole, as the main product. In order to provide several free coordination sites at once, we replaced $Cr(CO)_6$ by the very reactive naphthalene-$Cr(CO)_3$ complex.[4] As expected, the diene subunit of **1** entered the coordination sphere of chromium, but the final product was the unexpected 6-electron chelate **2** (eq. 1).



1

2 (87%)

(1)

It was immediately obvious that the diene subunit is η^4-complexed in **2** upon examination of the ^1H and ^{13}C NMR spectra. The α-CH resonances appear at 3.45 (^1H) and 59.89 (^{13}C) *vs* 6.02 and 125.28 for **1**. Whereas the η^4-complexation of **1** by $Fe(CO)_3$ induces a low-field shift of the ^{31}P resonance,[5] the ^{31}P resonance of **2** occurs at high field (δ 3.0 *vs* 46.3 for **1**). Thus, complexation of sulfur appeared possible. This η^4-C_4, η^1-S complexing mode was fully demonstrated by a X-ray crystal structure analysis of **2** (Fig. 1). At 2.599 Å, the Cr-S separation clearly demonstrates the complexation of sulfur. The bond is somewhat elongated compared with $[Me_3PS\text{-}Cr(CO)_5]$ where the separation is only 2.500 Å.[6] In fact, the situation in **2** more resembles that found in the η^2-Me_2PS - molybdenum complex described by Alper *et al.*[7] The P-S-metal angle is 64.2 in **2** *vs* 112.6 in $Me_3PS\text{-}Cr(CO)_5$ [6] and 61.1 deg. in $Me_2PS\text{-}Mo(Cp)(CO)_2$.[7] The P...Cr separation is short at 2.4948(5) *vs* 2.422(1) Å in $Ph_3P\text{-}Cr(CO)_5$.[8] Finally, the P=S bond is somewhat lengthened at 1.9964(6) *vs* 1.946(1) Å in a non-complexed phosphole sulfide.[9] Thus, the complexation of sulfur lies between a η^1-S and a η^2-(P=S) bonding mode. The phosphole ring is bent away from chromium around the C_2-C_5 axis. This bending is relatively small at 9.25 ± 0.38 deg. Whereas a free phosphole sulfide is planar,[9] η^4-complexes of phosphole oxides display much stronger bending at *ca* 30°.[10] The η^4-complexation of the diene sub-unit induces an equalization of the C_α-C_β and C_β-$C_{\beta'}$ bonds which is compatible with a higher delocalization in **2** than in a free phosphole sulfide. Indeed, Δ [(C_β -$C_{\beta'}$)-(C_α- C_β)] lies around 0.04 in **2** *vs* 0.15 Å in a free species.[9]

Under identical conditions, the reaction of **1** with (cycloheptatriene)tricarbonylmolybdenum affords the analogous η^4-C_4, η^1-S complex **3** in 73% yield. The chemistry of this new type of phosphole complexes has not yet been investigated.

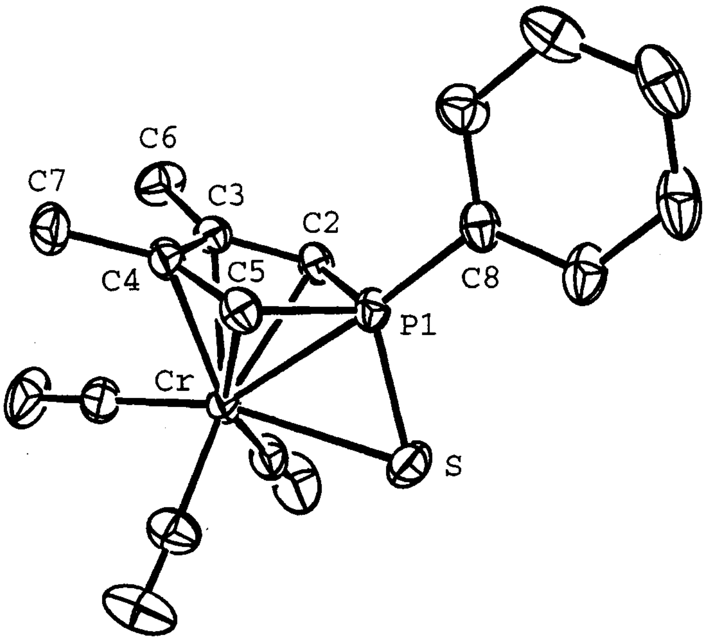


FIGURE 1 ORTEP drawing of one molecule of **2**, as determined by a single crystal X-ray diffraction study. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg.): Cr-S 2.5990(5), Cr...P(1) 2.4948(5), Cr-C(2) 2.211(2), Cr-C(3) 2.210(2), Cr-C(4) 2.225(2), Cr-C(5) 2.223(2), Cr-C(14) 1.838(2), Cr-C(16) 1.873(2), Cr-C(18) 1.869(2), S-P(1) 1.9964(6), P(1)-C(2) 1.767(2), P(1)-C(5) 1.769(2), P(1)-C(8) 1.799(2), C(2)-C(3) 1.402(2), C(3)-C(4) 1.448(2), C(4)-C(5) 1.404(2); Cr-S-P(1) 64.20(2), Cr-P(1)-S 69.71(2), S-P(1)-C(2) 107.13(6), S-P(1)-C(5) 106.48(6), S-P(1)-C(8) 115.03(6), C(2)-P(1)-C(5) 90.37(7), C(2)-P(1)-C(8) 117.23(8), C(5)-P(1)-C(8) 117.55(8), Cr-C(2)-P(1) 76.76(6), Cr-C(5)-P(1) 76.41(6)

EXPERIMENTAL

All reactions were performed under nitrogen; the solvents were purified, dried and degassed by standard techniques. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13, 50.32 and

81.01 MHz, respectively. All chemical shifts are reported in ppm downfield from internal TMS (^1H and ^{13}C) and external 85% H_3PO_4(^{31}P).

(η^4-C_4,η^1-S-1-phenyl-3, 4-dimethylphosphole sulfide) tricarbonylchromium 2

The phosphole sulfide **1** (1.66g, 7.5 mmol) in 20 mL of THF was heated at 60°C for 30 min with (naphthalene)tricarbonylchromium (2.0g, 7.5 mmol). Solvent was removed and the residue was chromatographed on silicagel with toluene.Yield of **2**: 3.2g (87%).

^1H NMR ($CDCl_3$): $\delta = 2.13$ (s, CH_3), 3.45 (d, $^2J_{HP} = 23.4$ Hz, =CH).

^{13}C NMR ($CDCl_3$): $\delta = 14.73$ (d, $^3J_{CP} = 9.9$ Hz, CH_3), 59.89 (d, $^1J_{CP} = 79.5$ Hz, C_α), 109.48 (d, $^2J_{CP} = 19.4$ Hz, C_β), 234.06 (s, CO), 242.12 (s, CO).

^{31}P NMR ($CDCl_3$): $\delta = 2.93$ ppm.

IR (decalin): ν (CO) : 2004, 1934, 1912 cm^{-1}

X-ray Structure Determination for 2

Crystals of **2**, $C_{15}H_{13}CrO_3PS$ were grown from a dichloromethane-hexane solution of the compound. Data were collected at -150 ± 0.5°C on an Enraf Nonius CAD4 diffractometer using Mo Kα radiation (λ = 0.71073Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf Nonius MOLEN package. The compound crystallises in space group $P2_1/n$ (14), a = 7.678(1)Å, b = 15.244(1)Å, c = 14.259(1)Å, β = 104.23(1)°; V = 1617.77(50)$Å^3$; Z = 4 ; dcalc = 1.463g/cm^3; $\mu = 9.2cm^{-1}$; F(000) = 728. A total of 5191 unique reflexions were recorded in the range $2° \leq 2\theta \leq 60.0°$ of which 1301 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 3890 for solution and refinement. Direct methods yielded a solution for all atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A nonPoisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were R = 0.033, Rω = 0.057, G.O.F. = 1.24.

(η^4-C_4,η^1-S-1-phenyl-3, 4-dimethylphosphole sulfide) tricarbonylmolybdenum 3

The phosphole sulfide **1** (1.0g, 4.6 mmol) in 15 mL of THF was heated at 60°C for 30 min with (cycloheptatriene)tricarbonylmolybdenum (1.2g, 4.6 mmol). Solvent was removed and the residue chromatographed on silicagel with toluene. Yield of **3**: 1.6g (73%).

^1H NMR ($CDCl_3$): $\delta = 2.21$ (s, CH_3), 3.87 (d, $^2J_{HP} = 24.6$ Hz, =CH).

^{13}C NMR ($CDCl_3$): $\delta = 15.13$ (d, $^3J_{CP}= 9.9$ Hz, CH_3), 62.81 (d, $^1J_{CP}= 77.9$ Hz, C_α), 111.89 (d, $^2J_{CP} = 18.39$ Hz, C_β), 224.13 (s, CO), 227.11 (s, CO).

^{31}P NMR (THF): $\delta = 9.9$ ppm.

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