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Thiazoline- and oxazoline-annulated (η^1-P)-1,3-azaphosphole-(pentacarbonyl)chromium, -molybdenum and -tungsten complexes

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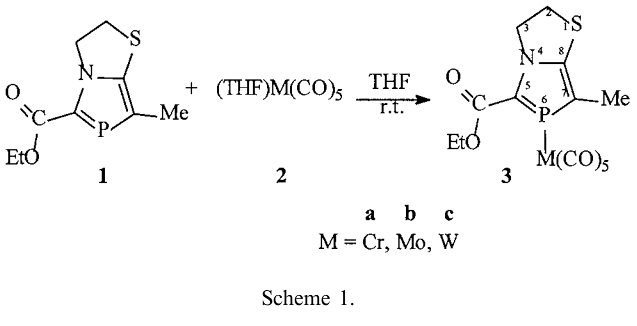
Abstract

The heterocycles 2,3-dihydro-1,3-azaphospholo[5,1-*b*]thiazole **1** and -oxazole **4** react with [(THF)M(CO)$_5$] **2** (M = Cr, Mo, W) selectively to give (η^1-P)-(2,3-dihydro-1,3-azaphospholo[5,1-*b*]thiazole and -oxazole)M(CO)$_5$ complexes **3** and **5**, respectively. The compounds are structurally characterized by NMR data which is discussed in relation to those of the free ligands. Supported by PM3 calculation of **1** and **4**, the preference to η^1-P-coordination is discussed in terms of control by d(M) → π* back-bonding.

Keywords: Annulated azaphospholes; Transition metals; Pentacarbonyl complexes; η^1-P coordination; NMR spectroscopy

1. Introduction

Recently, various 1,3-azaphospholes annulated to pyridine, pyrazine, thiazoline, oxazoline or benzothiazole rings have become available through [4 + 1]-cyclocondensation of *N*-cycloiminium salts with phosphorus trichloride [1–5]. Chemical properties of these heteroaromatic compounds incorporating a dicoordinate phosphorus are of current interest [6–8]. They have been found to show versatile reactivity towards electrophilic substitution [9,10], hydrolysis [1,5], 1,2-addition on P=C bond [10] and [1 + 4]-cycloaddition on phosphorus [11]. In view of the presence of a π-excess azaphosphole ring in these compounds, we have recently investigated the possible coordination modes of pyrido annulated derivatives, namely 2-phosphaindolizines, and observed the selective coordination through σ^2-P. (η^1-2-Phosphaindolizine)M(CO)$_5$ complexes, related to (2-phenyl-1,3-benzazaphosphole)W(CO)$_5$ [12] and some di- and triazaphosphole–M(CO)$_5$ complexes [6,7], were obtained with (THF)M(CO)$_5$ whereas with tricarbonyl(cycloheptatriene)molybdenum(0) or tricarbonyl(mesitylene)tungsten(0) a variety of σ-complexes



Scheme 1.

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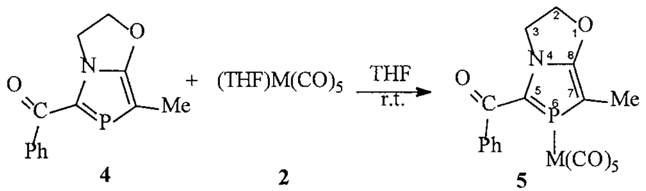

4 2 5

a b c
M = Cr, Mo, W

Scheme 2.

of the types $L_2M(CO)_4$ or $L_3M(CO)_3$ were formed, but no isolable π-complexes [13]. In 1,3-azaphospholes without aromatic annulation the preferences of σ- and π-coordination may be different. The 2,3-dihydro-1,3-azaphospholo[5,1-*b*]thiazole and -oxazole derivatives, easier accessible than 1,3-azaphospholes [14–16], may be used as model compounds if the impact of the Group 16 heteroatom is not remarkable. In this context we explored the reactions of 2,3-dihydro-1,3-azaphospholo[5,1-*b*]thiazoles and -oxazoles with (THF)$M(CO)_5$ (M = Cr, Mo, W).

2. Results and discussion

2.1. Reaction of 2,3-dihydro-1,3-azaphospholo[5,1-b]-thiazole 1 and -oxazole 4 with (THF)$M(CO)_5$

The ligand ethyl(7-methyl-2,3-dihydro-1,3-azaphospholo[5,1-*b*]thiazole)-5-carboxylate **1** reacts with an equimolar amount of (THF)$M(CO)_5$ **2** (M = Cr, Mo, W) at room temperature (r.t.) to give selectively (η^1-P)-(2,3-dihydro-1,3-azaphospholo[5,1-*b*]thiazoline)$M(CO)_5$ complexes **3** (Scheme 1).

The reaction of 5-benzoyl-7-methyl-2,3-dihydro-1,3-azaphospholo[5,1-*b*]oxazole **4** with (THF)$M(CO)_5$ at r.t. proceeds analogously and led to the formation of (η^1-P)-(2,3-dihydro-1,3-azaphospholo[5,1-*b*]oxazole)-$M(CO)_5$ complexes **5** (Scheme 2).

Extraction of the crude products **3a**, **c** and **5a**, **c** with hexane afforded analytically and spectroscopically pure, yellow crystalline or powdery complexes. In case of $Mo(CO)_5$ complexes, the reaction was not complete after 3–4 days at 20°C or even by using an excess amount (1.2 equivalents) of **2b** as revealed by ^{31}P-NMR of the reaction mixture. A mixture of the free ligand and $Mo(CO)_5$ complex (**1** + **3b** and **4** + **5b**) was obtained which could not be isolated in pure form by repeated crystallization or fractional extraction.

The results show that coordination at phosphorus is preferred to coordination at sulfur despite the reduced basicity of σ^2-phosphorus in the heteroaromatic ligand **1**. This underlines the impact of π-back-bonding in this type of complexes and a considerable acceptor strength of 1,3-azaphospholes. The heteroatom in position 1 has no marked influence on the complex chemical properties. It should be mentioned in this place that in the (thiazole)$Cr(CO)_5$ complex coordination was found to be preferred through σ^2-nitrogen instead of sulfur [17]. This implies that back bonding in this type of aromatic heterocycles is effected by $d(M) \rightarrow \pi^*$ interactions. PM3 calculations of **1** and **4** show the LUMO to be low-lying π*-orbitals (−0.97 and −0.77 eV) and to possess high coefficients at σ^2-phosphorus ($c^2 = 0.37$ and 0.34). This and the similarities of the electron systems in **1** and **3** or **4** and **5**, as seen from the ^{13}C-NMR data, suggest that the back-donation in **3** and **5** is due to strong $d(M) \rightarrow \pi^*$ rather than to $d(M) \rightarrow d(P)$ interactions. A comparison of PM3 orbital energies of unsubstituted 1H-1,3-azaphosphole with ionization potentials of this species calculated using high-level ab initio methods [18,19] shows higher deviations in the correlation with experimental ionization potentials but the general trend is the same so that the PM3 values of the higher, -M-substituted derivatives may be regarded to be sufficiently reliable.

2.2. Spectroscopic analysis of complexes 3 and 5

Pentacarbonyl metal complexes **3a**–**c** and **5a**–**c** were characterized by ^{31}P-, ^{1}H- and ^{13}C-NMR, as well as IR and mass spectroscopy. ^{31}P-NMR data for complexes **3** and **5** together with those of **1** and **4** as reference and the coordination shifts Δδ are given in Table 1. A strong upfield coordination shift of ^{31}P-NMR signal for $W(CO)_5$ complexes **3c** and **5c** (Δδ = −38 and −53) in C_6D_6 is accompanied by satellite peaks showing a large $^1J_{PW}$ coupling constant of about 260 Hz, which is in the range characteristic of $\sigma^2\lambda^3$-phosphorus-tungsten pentacarbonyl coordination [20,21]. This reveals evidence that sulfur or oxygen of the annulated hetero ring does not interfere with P-coordination. The $^1J_{PW}$ coupling in **3c** and **5c** (ca. 260 Hz) is comparable to that (253–268

Table 1
^{31}P-NMR data-chemical shifts (δ) of **1**, **3**, **4** and **5** and coordination shifts (Δδ) of **3** and **5**

Compound	M	Solvent	δ (ppm)	$^1J_{PW}$ (Hz)	Δδ
1		$CDCl_3$	174.8		
		C_6D_6	175.3		
3a	Cr	$CDCl_3$	189.7		+14.9
3b	Mo	$CDCl_3$	169.0		−5.8
3c	W	$CDCl_3$	139.8	260.9	−35.0
		C_6D_6	137.1	261.0	−38.2
4		$CDCl_3$	198.5		
		C_6D_6	193.5		
5a	Cr	C_6D_6	187.9		−5.6
5b	Mo	$CDCl_3$	177.2		−21.3
		C_6D_6	169.6		−23.9
5c	W	C_6D_6	140.4	260.0	−53.1

Table 2
^{1}H-NMR data of complexes **3** and **5**[a]

δ (ppm) J (Hz)	**3a**[b]	**3b**[b]	**3c**[b]	**5a**[c]	**5b**[c]	**5c**[c]
2-CH_2	3.72	3.73	3.73	3.68	5.01	3.70
$^3J_{HH}$	7.4	7.4	7.4	6.1	8.1	6.2
3-CH_2	4.80	4.79	4.81	3.63	4.71–4.75	3.64
$^4J_{PH}$	4.6	2.9	4.6	4.5	(m)	5.5
$^3J_{HH}$	7.4	7.4	7.4	6.1		6.2
7-CH_3	2.24	2.23	2.19	2.12	2.21	2.0
$^3J_{PH}$	15.1	15.1	15.7	15.4	15.0	15.4

[a] **5a** and **5c** in C_6D_6; others in $CDCl_3$.

[b] 5-COOEt: CH_3 ca. δ 1.39, CH_2 ca. δ 4.35, $^3J_{HH} = 7.1$ Hz.

[c] 5-COPh: *o*-H ca. δ 7.94, *m*-H ca. δ 7.15, *p*-H ca. δ 7.24.

Hz) reported for (η^1-2-phosphaindolizine)M$(CO)_5$ complexes [13] indicating similar coordination properties of σ^2-phosphorus in both cases.

Following the same trend as observed in the case of 2-phosphaindolizine complexes, the extent of coordination shift $\Delta\delta$ depends strongly on the electron withdrawing substituent in α-position to phosphorus [13], $\Delta\delta$ for complexes **5** bearing a 5-benzoyl substituent being more negative (in upfield region) as compared to those for **3** with a 5-ethoxycarbonyl substituent. Somewhat stronger coordination shifts ($\Delta\delta$ 8–10) in the higher field region for **3** and **5** than in the 2-phosphaindolizine complexes having identical α-substituents may be attributed to the stronger π-acceptor properties in the former complexes.

In ^{1}H-NMR spectra ($CDCl_3$) of **3a**–**c** (Table 2) all the protons exhibit a slight downfield shift ($\Delta\delta = 0.03$–0.24) with respect to the free ligand **1**. A marked feature in the proton NMR spectra of both the complexes, **3** and **5**, is the increase in J_{PH} coupling constants with respect to free ligands: $^3J_{PH}$ for 7-methyl protons by ca. 4.5 Hz and $^4J_{PH}$ for 3-CH_2 protons by ca. 2 Hz.

A comparison of the ^{13}C-NMR data of **3** and **5** (Table 3) and 2-phosphaindolizine complexes [13] reveals that variation in the nature of the hetero-ring annulated to the azaphosphole ring does not effect greatly the chemical shifts and the coupling constants of metal carbonyl carbons. Chemical shift values of *para*-CO are observed at lower field ($\delta = 198$–221) than the *cis*-CO ($\delta = 194$–215); also both carbonyls are most deshielded in chromium and least in tungsten complexes. The two-bond PC coupling constant is minimal (4 Hz) for *para*-CO in chromium complexes which increases in the order Cr, Mo, W (ca. 4, 30, 32 Hz) and decreases for *cis*-CO (ca. 16, 11, 9 Hz). While a slight upfield shift is observed for C-7 and C-5 carbon, their one-bond coupling constant with phosphorus decreases strongly from 46–47 to 13–23 Hz for C-7 and from 52–59 to 12–28 Hz for C-5. Moreover, in the case of **5a** and **5b** the signal observed for C-5 is unresolved.

In the mass spectra of **3a**, **3c** and **5a** the molecular ion peaks were observed. $[M\text{-}5CO]^{+\bullet}$ or $[M-(Cr/W)5CO]^{+\bullet}$ forms the base peak. The appearance of $[M-CO]^{+\bullet}$, $[M-2CO]^{+\bullet}$, $[M\text{-}3CO]^{+\bullet}$, $[M-4CO]^{+\bullet}$ and $[M-5CO]^{+\bullet}$ peaks indicates the primary decomposition by successive loss of carbon monoxide molecules. Further fragmentation involves loss of metal atom and five-substituents.

3. Experimental details

Hexane, ether, THF and toluene were dried under argon with sodium/benzophenone and freshly distilled before use. All reactions were carried out under an atmosphere of purified argon using standard Schlenk techniques. Melting points were determined in closed capillaries in inert atmosphere and were uncorrected. NMR data were recorded on a multinuclear FT-NMR spectrometer Bruker ARX-300; ^{1}H- at 300.1 MHz, ^{13}C- at 75.5 MHz and ^{31}P- at 121.5 MHz with reference to TMS (internal) and 85% H_3PO_4 (external), respectively. $CDCl_3$ was used as solvent unless otherwise indicated. Mass spectra (EI, 70 eV) were measured on a Intectra AMD-40 single focusing sector-field mass spectrometer, IR spectra on a Perkin-Elmer 2000 FT-IR spectrometer system. (THF)M$(CO)_5$ was freshly prepared before use by photolysis of metal hexacarbonyl in THF [22].

*3.1. Synthesis of 2,3-dihydro-1,3-azaphospholo[5,1-b]thiazole (**1**) and -oxazole (**4**)*

The ligands ethyl(7-methyl-2,3-dihydro-1,3-azaphospholo[5,1-*b*]thiazole)-5-carboxylate **1** and 5-benzoyl-7-methyl-2,3-dihydro-1,3-azaphospholo[5,1-*b*]oxazole **4** were prepared according to methods reported previously [4,5].

*3.2. Synthesis of (η^1-P)-(ethyl{7-methyl-2,3-dihydro-1,3-azaphospholo[5,1-b]thiazole}-5-carboxylate)-pentacarbonyl metal^{VI} complexes (**3a**–**c**) and (η^1-P(5-benzoyl-7-methyl-2,3-dihydro-1,3-azaphospholo[5,1-b]oxazole)pentacarbonyl metal^{VI} complexes (**5a**–**c**)*

3.2.1. General procedure

Metal hexacarbonyl (4 mmol) (0.88 g of $Cr(CO)_6$; 1.056 g of $Mo(CO)_6$; 1.408 g of $W(CO)_6$) was dissolved in THF (300 ml) and irradiated with an UV medium pressure lamp until 89.6 ml of CO was collected. The resulting yellow to orange solution was added to a solution of 4 mmol of **1** (0.916 g) or **4** (0.981 g) in THF (10–20 ml). After stirring 1–2 days the mixture was filtered, solvent removed in vacuo and the residue extracted with hexane (2 × 50 ml). On leaving the hexane

Table 3
^{13}C-NMR data of compounds **1, 3, 4** and **5**[a]

δ (ppm) J (Hz)	**1**	**3a**	**3c**	**4**[b]	**5a**	**5b**	**5c**
C-2	35.2	33.9	33.9	74.7	72.9	73.7	72.9
C-3	51.9	53.9	53.7	48.3	48.9	49.1	48.7
$^{3}J_{CP}$	3.2	2.2	2.0	4.3	2.9	2.9	2.2
C-5	146.3	143.8	140.8	143.9	146.6	143.8	141.8
$^{1}J_{CP}$	52.1	18.9	27.9	58.8	[c]	[c]	12.0
C-7	132.8	129.8	128.2	114.9	112.4	112.5	111.1
$^{1}J_{CP}$	46.0	13.6	20.4	47.4	15.2	13.4	23.0
C-8	144.7	146.3	146.2	159.6	158.5	158.8	158.5
$^{2}J_{CP}$	12.1	5.8	4.2	9.5			2.0
5-CO	162.9	162.1	161.9	185.9	185.1	185.8	184.9
$^{2}J_{CP}$	20.4	17.9	17.4	22.8	18.7	19.3	18.3
CH$_3$	14.4	14.2	14.3				
CH$_2$	60.4	60.9	61.0				
7-CH$_3$	14.1	12.6	12.8	10.3	9.5	9.7	9.6
$^{2}J_{CP}$	23.5	14.6	15.1	22.3	12.1	14.0	12.5
C$_6$H$_5$							
C-*i*				139.4	139.6	138.6	139.3
$^{3}J_{CP}$				1.4	2.4	2.3	3.0
C-*o*				129.1	130.0	130.1	130.4
$^{4}J_{CP}$				8.5	3.0	4.1	3.0
C-*m*				127.9	129.1	128.8	129.0
C-*p*				131.4	132.5	132.5	132.6
M(CO)$_5$							
CO(*cis*)		214.6	194.3		214.6	203.1	195.1
$^{1}J_{CW}$			125.3				125.2
$^{2}J_{CP}$		17.4	9.4		16.0	10.6	9.4
CO(*para*)		221.2	199.0		220.9	209.2	198.0
$^{1}J_{CW}$			150.4				[d]
$^{2}J_{CP}$		4.1	31.9		4.1	29.5	31.6

[a] **5a** and **5c** in C_6D_6; others in $CDCl_3$.

[b] Ref. [5].

[c] Unresolved.

[d] Not observed due to low intensity.

solution in refrigerator yellow–orange needles deposited. Alternatively, the solvent was removed completely to afford a yellow powdery complex. In case of **3b** and **5b**, the isolated product was found to be a mixture of complex and a smaller amount of the free ligand which could not be purified by repeated extraction or recrystallization with hexane.

3a: Yield 1.156 g (69%); yellow crystalline needles; m.p. 142–143°C. IR (in nujol): ν 2072m, 1985sh, 1956vst, 1937vst, 1929vst; 1275m, 671st, 647st cm^{-1}. MS (EI, 70 eV): m/z (%) 422.1 (12) [M$^+$], 394.1 (2), 366.0 (1), 337.8 (4), 309.8 (19), 281.7 (100), 230 (26), 209.5 (31), 184.4 (17), 52 (46). Anal. Found: C, 40.00; H, 3.07; N 3.22%. $C_{14}H_{12}NO_7PSCr$ (421.29) calc.: C, 39.91; H, 2.87; N, 3.32%.

3c: Yield 2.27 g (95%); yellow powder; m.p. 123–124°C. (DTA minimum: 142°C at 10 K min^{-1}). IR (in nujol): ν 2078m, 1980vst, 1954vst, 1927vst; 1276st, 593st, 572st cm^{-1}. MS (EI, 70 eV): m/z (%) 556.7 (1), 553.9 (35, M$^+$[^{184}W]), 500 (27), 497.6 (54), 470.5 (6), 442.4 (7), 416.2 (39), 414.2 (48), 412 (36), 229.6 (30), 184 (100), 156.4 (23), 71.2 (56), 29 (92). Anal. Found: C, 29.37; H, 2.11; N, 2.10%. $C_{14}H_{12}NO_7PSW$ (553.13) calc.: C, 30.40; H, 2.19; N, 2.53%.

5a: Yield 1.22 g (70%); yellow powder; m.p. 101–102°C. IR (in nujol): ν 2070m, 1996vst, 1983vst, 1971vst, 1954vst, 1931vst, 669st, 646st cm^{-1}. MS (EI, 70 eV): m/z (%) 438.4 (1) [M$^+$], 410 (1), 382.1 (1), 354.2 (2), 325.9 (11), 298 (63), 245.9 (100), 230.7 (17), 220.6 (26), 168.5 (12), 77.3 (81), 52 (51). Anal. Found: C, 50.36; H, 3.08; N, 2.99%. $C_{18}H_{12}NO_7PCr$ (437.3) calc.: C, 49.44; H, 2.76; N, 3.20%.

5c: Yield 1.36 g (60%); yellow crystalline solid; m.p. 110–112°C. IR (in nujol): ν 2076st, 1979vst, 1950vst, 1930vst, 594st, 572st cm^{-1}. Anal. Found: C, 38.4; H, 2.47; N, 2.26%. $C_{18}H_{12}NO_7PW$ (569.1) calc.: C, 37.98; H, 2.13; N, 2.46%.

PM3 calculation [23]	**1**	**4**
Total charge on phosphorus	+0.461	+0.425
π-Charge on phosphorus	−0.069	−0.097
HOMO [π] (eV)	−8.45	−8.41

n Orbital (eV); lone pair on phosphorus	−10.03	−9.88
LUMO [π*] (eV)	−0.97	−0.77
Coefficient on phosphorus in LUMO (c^2)	0.37	0.34

Selected PM3 eigenvalues of unsubstituted 1H-1,3-azaphosphole: −0.06 (π*, LUMO), −8.43 (π, HOMO), −9.77 (π), −9.76 (n), −12.01 (σ), −13.80 (π); for ab initio and experimental ionization potentials see ref. [18].

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