Complexes of Azaphospholes: Synthesis and Structure of Pentacarbonyl-(η^1)-2-phosphaindolizine)chromium(0), -molybdenum(0), and -tungsten(0)

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The complex chemical behaviour of 2-phosphaindolizines **1** (1,3-azaphospholo[1,5-*a*]pyridines) towards metal carbonyl compounds was studied. (η^1-2-Phosphaindolizine)M(CO)$_5$ complexes **2–4** (M = Cr, Mo, W) were formed from **1** and [(THF)M(CO)$_5$], the *cis*-L$_2$Cr(CO)$_4$ complex **5f** from **1f** and tetracarbonyl(norbornadiene) chromium(0). The reaction of 2-phosphaindolizines **1e**, **1f**, or **1g** with tricarbonyl(cycloheptatriene)molybdenum(0) or tricarbonyl(mesitylene)tungsten(0) yielded σ-complexes of the types L$_2$M(CO)$_4$ or L$_3$M(CO)$_3$ rather than isolable π-complexes. In one case a strong upfield signal (δ^{31}P = 6.1) was observed with a coordination shift of $\Delta\delta$ = –161.7, which is typical for π-coordination. Prolonged reaction or work-up led, however, to dismutation yielding **1g** and the *fac*-L$_3$Mo(CO)$_3$ complex **6g**. X-ray structure analysis of **2a** indicates an increased 10π-delocalization compared with **1a** and a changed conformation of the acyl substituent. The influence of substituents and metals on the ^{31}P and ^{13}C complexation chemical shifts and coupling constants is discussed.

Introduction

The coordination behaviour of five-membered π-excess heterocycles has found considerable interest[1][2][3][4][5]. Mono-, di-, and triphosphole anions exhibit different coordination modes but, like cyclopentadienyl anions, they preferably form η^5-complexes[1][2][6] emphasizing the similarities of P=C and C=C structural units[7]. Pyrroles and pyrrole anions also form various types of complexes with π- and σ-coordination. Simple sandwich or η^5-coordinate (tricarbonyl)transition metal(0) complexes of pyrroles or pyrrole anions, however, need sterical stabilization by suitable substituents[4]. Thus, tricarbonyl(η^5-pyrrole)chromium(0) complexes belong to the most labile π-complexes with benzene-like ligands, reacting even with THF or benzene by ligand substitution[8], in sharp contrast to the η^5-phosphole or η^5-arsole complexes. 1*H*-1,3-azaphospholes and their anions, contain both two-coordinate phosphorus and three-coordinate nitrogen; they are aromatic 6π-systems even in the neutral state and, according to the P=C/C=C-similarity principle, should resemble the pyrroles[9][10]. There are several studies on azaphospholes and annelated azaphospholes[10][11][12] but very little is known about their behaviour in complex formation. Only two η^1-LCr(CO)$_5$ complexes with the ligands 2-phenyl-1,3-benzazaphosphole[13] and 2-phosphaindolizine[14] have been reported, which exhibit even lower ^{31}P-coordination shifts than related η^1-di- and -triazaphosphole[11][15] and η^1-phosphabenzene complexes[16] with sp^2(p$_\pi$) hybridized phosphorus. This may be viewed in association with the reduced σ- and the increased π-charge density at phosphorus[10][14] in these π-excess heterocycles. These various aspects prompted us to investigate complexation reactions of neutral and anionic 1,3-azaphospholes or more easily accessible annelated representatives thereof and to study the preferred coordination mode and possible alternatives. We report here on reactions of 2-phosphaindolizines[14][17][18] with group VI metal carbonyl complexes and the characterization of the complexes by NMR and, for **2a**, by X-ray structural analysis.

Results and Discussion

Synthesis of Phosphaindolizine Carbonyl Complexes

Various substituted 2-phosphaindolizines **1** bearing an electron-withdrawing substituent R^2 such as acyl, carbalk-

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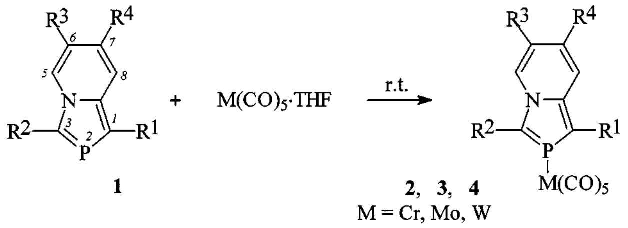
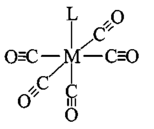
oxy or *p*-nitrophenyl in 3-position and a further substituent (Me, *n*Bu or Ph) in position 1, 6, or 7 were treated at room temperature with [(THF)M(CO)$_5$] (M = Cr, Mo, W). This led to selective formation of (η^1-2-phosphaindolizine)M(CO)$_5$ complexes **2−4**. The carbonyl or nitro groups did not interfere. Extractive purification or recrystallization of the crude products with hexane afforded powdery or crystalline, analytically pure, pale to dark yellow complexes. They were characterized by ^{31}P (Table 1), ^{1}H (Table 2), and ^{13}C NMR (Table 3) as well as by infrared spectroscopy (Table 4) and (for **2a**) by X-ray structural analysis (Figure 1). The spectroscopic data and structure are discussed below.

The reaction of **1e** with [(THF)Cr(CO)$_5$] to **2e** (δ^{31}P = 190.6) was accompanied by formation of a smaller amount of the tetracarbonyl bis(phosphaindolizine) complex **5e** (δ^{31}P = 201.5). Recrystallization of the crude product afforded, however, only pure **2e**. The synthesis of tetracarbonyl bis(phosphaindolizine) complexes can be achieved by refluxing **1** with tetracarbonyl(norbornadiene)chromium(0) in petroleum ether. In this way, **1f** gave an orange-yellow mixture of two complexes, **2f** (δ^{31}P = 190.8) and **5f** (δ^{31}P = 202.3). Recrystallization from hexane gave **5f**. Structure elucidation is based on ^{13}C and ^{1}H NMR investigations. The appearance of two triplets of equal intensity in the ^{13}C-NMR spectrum at δ = 217.0 [$^2J(^{31}\text{P}-^{13}\text{C})$ = 17.2 Hz, *cis* CO] and δ = 224.0 ($J_{\text{AX}} + J_{\text{A'X}}$ = 20.2 Hz, *trans* CO) besides the signals for the ligand indicates the presence of two equally populated types of carbonyl groups and thus proves **5f** to be the tetracarbonyl-*cis*-bis(η^1-2-phosphaindolizine)chromium(0) complex. It should be mentioned that the *cis*-L$_2$M(CO)$_4$ isomers were also formed preferentially in the reaction of triphenylphosphabenzene with tetracarbonyl(norbornadiene) complexes of group VI[16a] whereas thermal reactions of phosphanes and the metal hexacarbonyls provide mixtures of *cis* and *trans* complexes[19].

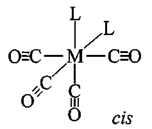
Scheme 1



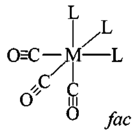
In view of the existence of σ- and π-coordination modes in carbonyl complexes of phosphabenzene[16][20][21], phosphole anions[1][2], and π-excess heterocycles such as pyrrole[3][4][5], we tried to obtain η^5-2-phosphaindolizine π-complexes. However, isolable π-complexes were obtained neither on prolonged irradiation by a high-pressure mercury lamp, e.g. of **4b** in hexane, nor on heating, nor from the reactions of 2-phosphaindolizines **1e**, **1f**, or **1g** with tricarbonyl(cycloheptatriene)molybdenum(0) or tricarbonyl(mesitylene)tungsten(0). Instead, a variety of σ-complexes of the types L$_2$M(CO)$_4$ or L$_3$M(CO)$_3$ were formed.



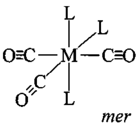
2, 3, 4



5e, f (M = Cr)



6e (M = W)
6f, g (M = Mo)

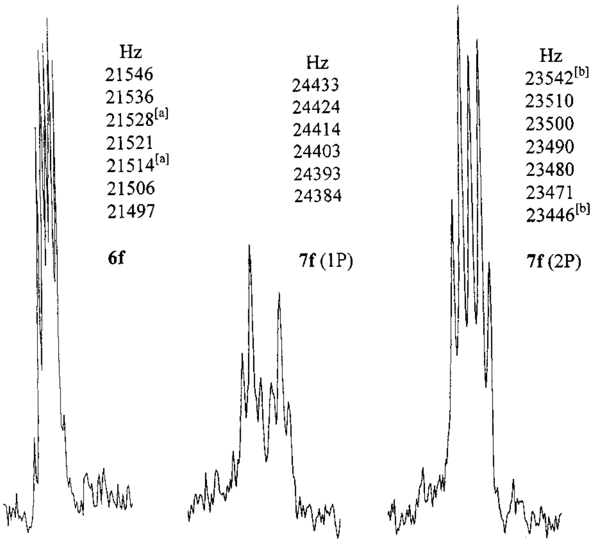


7g (M = Mo)

Solely during the reaction of excess **1g** with tricarbonyl(cycloheptatriene)molybdenum(0) in tetrahydrofuran at room temperature could a strong upfield signal at δ^{31}P = 6.1 with a coordination shift of $\Delta\delta$ = −161.7 be observed, which is close to the phosphorus resonance δ^{31}P = 4.3 and $\Delta\delta$ = −173.9 of tricarbonyl-η^3-(2,4,6-triphenylphosphabenzene)chromium(0)[20]. On prolonged reaction or attempted isolation this signal disappeared, however, and only **1g** and the *fac*-L$_3$Mo(CO)$_3$ complex **6g** (δ^{31}P = 181.2) were detected. This suggests formation of a little stable π-complex that underwent dismutation. Curiously, if the reaction was performed in a 1:1 ratio using the same solvent and reaction conditions, the isomeric *mer*-L$_3$Mo(CO)$_3$ complex **7g** [δ^{31}P = 196.3, d, 2 P$_{trans}$; 203.8, t, 1 P$_{cis}$; $^2J(^{31}\text{P}-^{31}\text{P}_{cis})$ = 9.3 Hz] was obtained. Formation of **7g** was also observed if CDCl$_3$ was used as solvent. Attempts at extractive purification or reaction in refluxing ether/hexane furnished a mixture of **6g** and **7g**. The structure assignment is supported by proton-coupled phosphorus spectra. In **6g** the proton coupling with the initial phosphorus singlet led to a symmetric multiplet with seven resolved lines, lines 1 and 7 being weak, lines 3 and 5 broad. A calculated spectrum[22] with δ^{31}P = 173.13, $^2J(^{31}\text{P}-^{31}\text{P})$ = 30 Hz and ^2J(PH1) = 30.8 Hz is in good accordance with the experimental coupling pattern. It consists of 9 inner lines, two pairs of which lie close together to form the experimental lines 3 and 5. Weak outer lines are hinted at in the spectrum by a raised base line. In **7g** the P$_c$ triplet becomes a double triplet by coupling with the H-1 proton within the ligand, while the doublet corresponding to the P$_{trans}$ ligands is split into a multiplet with five strong lines. A simulation using δ^{31}P(C$_6$D$_6$) = 193.34, 200.90, $^2J(^{31}\text{P}-^{31}\text{P}_{cis})$ = 9.3 Hz, $^2J(^{31}\text{P}-^{31}\text{P}_{trans})$ = 41 Hz and ^2J(PH1) = 30.8 Hz (δ_{H1} = 6.38) fits with the experimental spectrum (Figure 1). Since ^2J(PH1) is similar to the respective coupling in **3g** (31.5 Hz) and $^2J(^{31}\text{P}-^{31}\text{P})$ generally larger in *trans* than in *cis* complexes these values seem reasonable.

In the reaction of **1f** with tricarbonyl(cycloheptatriene)molybdenum(0), initial formation of probably **6f** was observed by a singlet at δ^{31}P = 178.9 and a line form of the proton-coupled phosphorus multiplet resembling rather a *fac*-L$_3$Mo(CO)$_3$ than a *trans*-L$_2$Mo(CO)$_4$ coupling pattern. However, this complex proved to be unstable in extractive work-up and subsequently underwent dismutation yielding the LMo(CO)$_5$ complex **3f** (δ^{31}P = 169.3), which could be isolated in spectroscopically and analytically pure form (Tables 1−4). Prolonged heating of **1e** with tricarbonyl(mesitylene)tungsten(0) in THF afforded a mixture of **6e** [δ^{31}P = 149.6, $^1J(^{31}\text{P}-^{183}\text{W})$ = 265 Hz, multiplet with five

Figure 1. Proton-coupled phosphorus spectra of **6f** (left) and **7f** (middle and right)



[a]Each two unresolved lines (calculated 21528, 21530; 21514, 21512), of which only the stronger one is seen. − [b] Small lines (calculated 23541, 23532; 23440, 23449) are superimposed by noise.

broad lines by ^{31}P-^{1}H coupling] and **4e** (δ = 140.2, quartet by ^{31}P-^{1}H coupling).

The phosphaindolizine carbonyl complexes are less stable than phosphane carbonyl complexes and are attacked by water and by air, slowly in the solid state and more rapidly in solution. In a moist CDCl$_3$ solution of **4a** we observed the phosphorus resonance of **1a**. After four days, signals of **1a** and an addition product (δ^{31}P = 128.5) are exhibited (intensity 1:2) and after a further day all of **1a** and a part of the addition product was decomposed to give a hydrolysis product with δ^{31}P = 21.8. The volatility is low but sufficient to record EI mass spectra of the complexes LM(CO)$_5$. For **2f**, **3f**, **4e** and **4h** the molecular ion peaks M^+ were observed. The appearance of $[M - \mathrm{CO}]^{+\cdot}$, $[M - 2\ \mathrm{CO}]^{+\cdot}$, $[M - 3\ \mathrm{CO}]^{+\cdot}$, $[M - 4\ \mathrm{CO}]^{+\cdot}$ and $[M - 5\ \mathrm{CO}]^{+\cdot}$ peaks indicates primary decomposition by the successive loss of carbon monoxide molecules from the LM(CO)$_5$ moieties. Further fragmentation follows similar pathways as for the free ligand[18].

Spectra of Phosphaindolizine M(CO)$_5$ Complexes and Structural Aspects

Phosphorus NMR: Preliminary reports of two Cr(CO)$_5$ complexes of annelated 1,3-azaphospholes, 2-phenyl-1,3-benzazaphosphole[13], and a 2-phosphaindolizine[14], had indicated small ^{31}P-coordination shifts of Δδ = 4.4 and 7.5, respectively. The larger body of data for **2−4** (Table 1) now reveals a much broader range of Δδ^{31}P and allows a comparison with LM$^{\mathrm{VI}}$(CO)$_5$ complexes of phosphane and heterocyclic σ^2-phosphorus ligands. The coordination shift in complexes R$_3$PM$^{\mathrm{VI}}$(CO)$_5$ becomes smaller with increasing group electronegativity of R, for Hal$_3$PM$^{\mathrm{VI}}$(CO)$_5$ even negative[23][24][25][26]. η^1-Complexes of σ^2-phosphorus compounds possessing a higher s-character at phosphorus (sp^2 hybridization) may be compared with complexes of electron-poor phosphanes, which are weak σ-donor but more efficient π-acceptor ligands. In fact, Δδ^{31}P of the 2-phosphaindolizine complexes **2−4** is somewhat lower than Δδ^{31}P of (MeO)$_3$PM$^{\mathrm{VI}}$(CO)$_5$[26][27] and similar to the η^1-phosphabenzene complexes 2,4,6-Ph$_3$C$_5$H$_2$PM$^{\mathrm{VI}}$(CO)$_5$[16]. The electron-withdrawing effect of nitrogen and -M groups in α-position to phosphorus is partly compensated by the π-excess character of the 1,3-azaphosphole ring. The stronger upfield coordination shifts of the pivaloyl and phenacyl derivatives **a-d** may be attributed to the changed conformations with increased anisotropy and reduced −M effects on phosphorus as compared to the free ligand. The one-bond ^{31}P-^{183}W couplings of **4** (253−268 Hz) are larger than those in (triorganophosphane)W(CO)$_5$ complexes which, however, increase with the group electronegativity of R in R$_3$PW(CO)$_5$[23][24][25][26].

Proton NMR: The chemical shifts and almost all coupling constants of free ligands **1a−h**[14][17][18] and their complexes (Table 2) in CDCl$_3$ are very similar. Thus the differences of respective δ values of the complex **2e** and the ligand **1e** in CDCl$_3$ are less than 0.13. However, a strong influence on the proton resonance is exerted by deuterobenzene. Almost all signals of phosphaindolizine protons in **2−4** are upfield shifted by Δδ = 0.6 to 1.1 in C$_6$D$_6$ as compared to the ligands in CDCl$_3$. Methyl groups in position 7 and 1 are also affected, but to a lower extent. Phenyl groups are at most slightly influenced, indicating stacking interactions between C$_6$D$_6$ and the phosphaindolizine ring. The lack of an upfield shift of H-5 in the 3-carbalkoxy derivatives **3e**, **4e**, **2f**, and **3f** can be attributed to a superimposed deshielding anisotropy effect of the carbonyl group of COOR (R = Me, Et). Another exception, the extreme increase of δ(H-5) in **2a** (Δδ = 2.75), **4a** (Δδ = 2.34), and **5a** (Δδ = 2.58) compared to **1a** in CDCl$_3$, is associated with a change in conformation of the 3-pivaloyl substituent which is also found for the solid state. In crystalline **1a**, the acyl group is arranged nearly coplanar to the ring system (torsion angle P−C1−C=O 178°) with the *tert*-butyl group at the P-side, whereas in the chromium complex **2a** the latter is oriented to the N-side of the azaphosphole ring, adopting a staggered conformation (see below). This arrangement shields the proton in position 5. Concerning proton couplings, the only marked changes between **1** and **2−4** are the solvent-independent increase of the magnitude of ^3J(PH) involving the 1-methyl protons by ΔJ = 3.7 to 5.3 Hz, slightly increasing from chromium to tungsten and from the 3-pivaloyl to the 3-carbalkoxy derivatives, and the decrease of the magnitude of ^2J(^{31}P-^{1}H) of the protons in 1-position of **2b**, **4b**, **4d**, and **3g** relative to the respective ligands by 7−8 Hz.

Carbon NMR: In contrast to organometallic compounds, phosphane complexes have not been extensively investigated with respect to the impact of coordination on carbon chemical shifts and couplings in the ligands[23][24][25]. In the ^{13}C NMR spectra of **2−4** (Table 3) we observed *trans* ^{13}CO (δ = 197-225) at lower field than *cis* carbonyls (δ = 194−215) and for both an increasing shielding in the series

Table 1. ^{31}P-NMR chemical shifts (δ) of **1−4** and coordination shifts (Δδ)

	R^1	R^2	R^3	R^4	δ **1**	δ **2** M = Cr	Δδ (**2−1**)	δ **3** M = Mo	Δδ (**3−1**)	δ **4** ($^1J_{PW}$, Hz) M = W	Δδ (**4−1**)
a	CH_3	$COC(CH_3)_3$	H	H	172.1	155.4	−16.7	135.3	−36.8	108.2 (258.2)	−63.9
b	H	COC_6H_5	*n*Bu	H	179.9	184.6	+4.7			133.4 (253.7)	−46.4
c	CH_3	COC_6H_5	H	H	183.6			164.3	−19.3		
d	H	COC_6H_5	H	CH_3	182.5					137.1 (264.2)	−45.4
e	CH_3	$COOC_2H_5$	H	H	165.5	190.6	+25.1	167.5	+2.0	140.2 (268.1)	−25.3
f	CH_3	$COOCH_3$	H	H	165.8	190.8	+25.0	169.3	+3.5		
g	H	CN	H	CH_3	164.5			169.9	+5.4		
h	C_6H_5	C_6H_4-NO_2(*p*)	H	H	130.6					105.2 (262.4)	−25.4

Table 2. ^{1}H-NMR data of the complexes **2−4**[a]

δ *J* [Hz]	**2a**	**2b**	**2e**	**2f**	**3a**	**3c**	**3e**	**3f**	**3g**	**4a**	**4b**	**4d**	**4e**	**4h**	**5e**	**5f**
1-H		7.09							6.38		6.95	6.85				
^2J(P,H)		28.3							31.5		27.8	28.3				
5-H	7.49	9.51	9.95	9.80	7.90	9.48	9.87	9.81	7.48	7.66	9.57	9.55	9.86	7.21	9.91	9.90
^4J(P,H)						1.8	1.9	1.9		1.6	1.5		1.9	1.4		
^3J(5-H,6-H)	7.1		7.3	7.3	7.3	7.2	7.3	7.3	7.2	7.3		7.4	7.3	6.8	7.3	7.2
^4J(5-H,7-H)			0.9	0.8		0.9	1.1	0.9		1.3	0.8		0.9	1.1		
6-H	5.87	[b]	6.89	6.12	5.98	6.05	6.16	6.14	5.70	5.91	[c]	5.96	6.14	5.95	6.82	6.09
^5J(P,H)	1.1		1.3	1.2		1.4	1.3	1.3	1.2	1.3		1.5	1.3	0.6		
^3J(6-H,7-H)	7.0		7.0	7.1	7.0	6.4	6.7	6.9		7.0			6.8	6.6	6.9	6.8
^4J(6-H,8-H)	1.1		1.4			1.3	1.3	1.0		1.3		1.0	1.5			
7-H	6.24	6.71	7.22	6.41	6.30	6.41	6.43	6.40	[d]	6.27	6.45	[e]	6.41	6.30	7.15	6.36
^5J(P,H)	1.2		1.4	1.4		1.3	1.5	1.5		1.3	1.3		1.6	1.3		
^3J(7-H,8-H)	9.1	9.0	8.9	8.9	9.1	9.3	8.9	8.9		9.0	9.0		8.9	9.1	8.9	8.9
8-H	6.58	6.47	7.43	6.54	6.66	6.63	6.60	6.57	6.29	6.58	6.70	6.41	6.55	7.08	7.32	6.53
^4J(P,H)	1.1		2.5			2.5	2.5	2.5	1.2	2.4		1.9	2.6	1.1		
R^1:																
CH_3	2.21		2.58	2.12	2.25	2.22	2.13	2.10		2.15			2.07	[f]	2.35	2.15
^3J(P,H)	16.0		16.7	16.7	16.2	16.8	16.9	16.9		16.6			17.3		(m)	(m)
R^2:																
OCH_2/OCH_3			4.47	3.65			4.28	3.64					4.28		4.26	3.61
CH_3			1.46				1.26						1.25		1.22	
^3J(H,H)			7.1				7.1						7.1		7.0	
$COC(CH_3)_3$	1.19				1.30					1.23						
o-H		7.83				7.82					7.86			7.43		
m-, *p*-H		7.17−7.19				7.20					7.16−7.21			7.94		

[a] **2e** and **5e** in $CDCl_3$, others in C_6D_6. − [b] 6-Bu: α-CH_2: δ = 2.12; β-CH_2: δ = 1.35; γ-CH_2: δ = 1.30; δ-CH_3: δ = 0.83. − [c] 6-Bu: α-CH_2: δ = 2.11; β-CH_2: δ = 1.28; γ-CH_2: δ = 1.14; δ-CH_3: δ = 0.80. − [d] 7-CH_3: δ = 1.66. − [e] 7-CH_3: δ = 1.74. − [f] 1-C_6H_5: *o*-H: δ = 6.88; *m*-H: δ = 7.37; *p*-H: δ = 7.18.

Cr, Mo, W. This can be seen e.g. for the series **2e**, **3e**, **4e** where each Δδ is about 10. The magnitude of the two-bond coupling with the phosphorus decreases for *cis* carbonyls in the order Cr, Mo, W pentacarbonyl (ca. 17, 12, 9 Hz, respectively) and increases with the metal radii for the respective *trans* carbonyls (ca. 4 << 32 , 32 Hz), causing small *trans* couplings in chromium carbonyl P-complexes. Marked differences in some carbon chemical shifts and coupling constants occur also between free and coordinate phosphaindolizines and can be attributed to steric and electronic effects. The solvent influence, in contrast to proton NMR data, is essentially negligible as can be seen, e.g., by the very small differences of δ^{13}C (< 0.6) and $J(^{31}P\text{-}^{13}C)$ (≤1) of **4b** in $CDCl_3$ and C_6D_6. The upfield coordination shift for C-5 and the opposite change for C-3 and the 3-carbonyl groups in **2a** and **4a**, not observed in other derivatives, are attributed to the distortion of the 3-pivaloyl group, causing enhanced shielding of C-5 by the *tert*-butyl group and reduced π-charge density at C-CO by loss of delocalization compared to the coplanar free ligand. Marked coordination shifts for C-5 are found in the phenacyl derivatives, nearly no effect for **3c**, shielding for **4b** and deshielding for **4d**, whereas δ(3-CO) is slightly influenced by the coordination, suggesting a torsion of the phenyl ring around the C−C(O) axis to give the minimum energy arrangement. A general upfield shift on coordination for C-1 and, except for **2a** and **4a**, also for C-3, with a slight increase from chromium to tungsten, may be assigned to electronic as well as steric influences, viz. the change in hybridization of phosphorus, back-bonding and steric shielding by the $M(CO)_5$ group. The same holds to an reduced extent for the α-C atoms of the substituents at C1 and C3, reflecting inductive effects. The lack of noticeable shift differences for C6 to C9 in free and coordinated ligands suggests that back donation, ascribed to $(d_M\text{-}\pi^*)\pi$ bonding[25], has a rather localized effect. Indeed, according to PM3 calculations[28] phosphorus has the highest coefficient in the LUMO (π*-orbital) of 2-phosphaindolizine ($\varepsilon = -0.77$ eV, $c^2 = 0.50$) and is separated by nodal planes from C1 and C3.

A strong decrease in $^1J(^{31}P\text{-}^{13}C)$ coupling constants is observed by complexation. For C1 and C3 one-bond $^{31}P\text{-}^{13}C$ coupling constants are in the range 18−30 Hz and 10−37 Hz as compared to 38−44 and 45−59 Hz, respectively, in the free ligands[14][17][18]. The absolute magnitude of $^1J(^{31}P\text{-}^{13}C3)$ increases with the electron-withdrawing effect of the 3-substituent R^2 in the order C_6H_4-4-NO_2 << COOEt < COOMe ≈ or < COPh ≈ CO*t*Bu. The much lower one-bond couplings in the complexes may be attributed to the participation of the s-orbital in the hydridization of phosphorus. The smaller differences between $^1J(^{31}P\text{-}^{13}C1)$ and $^1J(^{31}P\text{-}^{13}C3)$ in the complexes reflect a higher degree of delocalization and aromaticity than in the ligands themselves. This is consistent with nearly equal P−C bond lengths in **2a**, whereas they differ in **1a**. In rounding off this section it should be mentioned that two-bond couplings are also reduced on complexation, $^2J(^{31}P\text{-}1\text{-}^{13}CH_3)$ larger than $^2J(^{31}P\text{-}^{13}C9)$ and $^2J(^{31}P\text{-}3\text{-}^{13}CO)$, whereas $^3J(^{31}P\text{-}^{13}C8)$ are usually increased.

X-ray Analysis of 2a

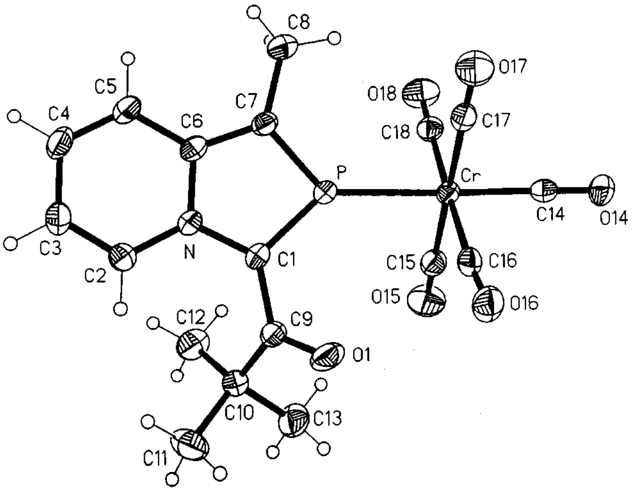
X-ray structure analysis of the $Cr(CO)_5$ complex **2a** (Figure 2) shows a planar ring system (mean deviation 3 pm) with trigonal planar coordination at phosphorus; the metal lies only slightly outside the plane (12 pm). The endocyclic angle at phosphorus in the rigid five-membered ring is not greatly affected by the steric requirements and thus only slightly opened, from 91.9(2)° in **1a**[18] to 93.5(1)° in **2a**. The P−C bond lengths become more equal [172.4, 171.7(2) pm] on complexation than in the free ligand [174.7(3), 170.8(4) pm] and on average shorter (172.1 versus 172.8 pm) indicating more effective delocalization. The rotation of the pivaloyl group from a coplanar arrangement (dihedral angle P−C1−C=O 178°) in **1a** to a staggered conformation with ϑ(P−C1−C9−O1) = 45.5° in **2a** prevents the strong -M interactions possible in **1a** and is certainly an important factor in the increase in aromaticity. Another factor may be the change in hybridization from p^2 to sp^2

Table 3. ^{13}C-NMR data of the complexes **2**−**4**[a]

δ *J* in Hz	**2a**	**2e**	**2f**	**3c**	**3e**	**3f**	**3g**	**4a**	**4b**	**4d**	**4e**	**4h**	**5f**[b]
C-1	130.3	132.5	132.2	[c]	131.7	132.4	129.7	128.6	121.6	120.3	130.8	134.4	132.0
^1J(CP)	18.3	22.9	23.0		22.2	22.3	22.5	25.1	28.3	28.6	29.4	25.5	23.3
C-3	147.0	130.0	130.1	133.2	129.5	129.6	145.4	143.4	139.7	139.4	127.4	145.1	129.3
^1J(CP)	10.0	18.3	18.4	19.3	19.1	19.7	14.7	17.0	12.7	13.5	28.2	36.9	12.1
C-5	126.7	129.6	129.1	130.0	129.6	130.1	127.2	127.1	128.2	137.1	129.8	123.8	128.3
^3J(CP)	−	2.3	−	2.0	2.4	2.3	−	−	1.7	2.3	7.8	−	8.0
C-6	112.0	113.2	113.3	113.3	113.7	113.8	116.8	112.6	125.7	116.2	113.7	112.9	112.7
^4J(CP)	4.0	4.8	4.7	−	4.7	4.9	4.7	4.4	−	4.5	5.1	3.8	<1.0
C-7	120.7	124.1	124.2	124.7	123.4	124.0	122.5	121.2	127.9	129.5	124.3	121.3	123.9
^4J(CP)	3.0	3.2	3.0	3.2	2.9	3.0	2.9	2.6	2.0	−	3.0	1.8	<1.0
C-8	116.2	115.3	115.3	115.9	115.7	116.4	117.9	116.8	118.0	117.1	116.0	118.0	115.1
^3J(CP)	17.0	11.3	11.3	−	11.7	11.2	11.8	11.2	12.4	12.4	11.7	9.5	11.4
C-9	140.6	143.6	143.7	143.7	143.3	144.0	147.6	140.6	145.6	147.0	143.6	140.3	143.6
^2J(CP)	4.0	5.7	5.7	5.8	5.7	5.7	−	2.9	8.4	8.3	4.6	−	7.3
R^1: CH_3	10.9	11.3	11.3	11.8	11.4	11.9	[d]	11.3	[e]	[f]	11.6	[g]	11.5
^2J(CP)	14.9	14.4	14.5	15.3	15.6	16.0		15.3			14.9		14.4
R^2: CO/CN	204.9	163.0	163.1	186.8	162.8	163.6	117.5	204.9	186.6	186.3	163.0		163.6
^2J(CP)	12.0	17.7	17.4	20.5	16.8	17.0	19.7	12.1	20.6	20.6	17.4		19.6
OCH_2/OCH_3		60.7	50.6		60.6	51.3					60.8		50.9
CH_3	27.5	14.4	14.4		14.4			27.1			14.5		
^4J(CP)								1.6					
$C(CH_3)_3$	45.7							45.7					
C-*i*				140.8					140.5	140.6		137.4	
$^{2/3}J$(CP)				1.8					1.8	1.8		13.6	
C-*o*				130.8					131.3	131.3		137.3	
$^{3/4}J$(CP)				2.9					2.9	3.0		7.4	
C-*m*				129.0					129.0	129.0		129.4	
C-*p*				132.5					132.7	132.6		148.2	
^5J(CP)												1.6	
$M(CO)_5$:													
CO(*cis*)	215.2	214.6	214.6	203.6	204.3	204.9	208.8	194.9	194.5	194.6	194.4	194.2	217.0
^1J(CW)								125.2	125.7	125.6	125.5	128.9	
^2J(CP)	16.0	17.2	17.3	10.7	11.7	11.8	11.9	8.7	8.7	8.8	9.4	8.7	17.2
CO(*para*)	221.1	220.9	220.9	209.6	210.0	210.6	225.1	198.4	198.2	198.3	198.7	197.8	224.0
^1J(CW)								151.4	148.8	[h]	151.6	145.2	
^2J(CP)	5.0	3.9	3.8	[i]	31.9	31.9	33.0	30.7	32.2	32.2	32.0	31.0	20.2

[a] **4e** in $CDCl_3$, others in C_6D_6. − [b] Coupling constants are not *J* values but $N = |J_{AX} - J_{A'X}|$ values. − [c] Merged in C_6D_6 peak. − [d] 7-CH_3: δ = 20.9. − [e] α-C: δ = 32.7; β-C: δ = 32.5; γ-C: δ = 22.4; δ−C: δ = 13.9. − [f] 7-CH_3: δ = 20.4. − [g] 1-C_6H_5: *i*-C: δ = 133.6 (J_{PC} = 12.8); *o*-C: δ = 130.9 (J_{PC} = 6.9); *m*-C: δ = 124.5; *p*-C: δ = 129.2. − [h] Not observed due to small intensity of signal. − [i] Not resolved.

Figure 2. Structure of **2a** in the crystal. Ellipsoids represent 50% probability levels. H atom radii are arbitrary[a]



[a] Selected bond lengths [pm] and angles: Cr−C(14) 187.0(3), Cr−C(16) 189.8(3), Cr−C(15) 190.0(3), Cr−C(18) 190.3(3), Cr−C(17) 190.6(3), Cr−P 232.50(14), P−C(7) 171.7(2), P−C(1) 172.4 (2), C(1)−N 138.2(3), N−C(6) 140.4(3), C(6)−C(7) 138.7(3); C(1)−P−Cr 135.95(8), C(7)−P−Cr 130.47(8), C(7)−P−C(1) 93.51(11), N−C(1)−P 109.6(2), C(1)−N−C(6) 113.7(2), C(7)−C(6)−N 113.2(2), C(6)−C(7)−P 109.9(2).

which makes the phosphorus more similar to carbon. In **2a** the Cr−P bond [232.50(14) pm] is slightly shortened compared to a variety of $R_3PCr(CO)_5$ and phosphaalkene $Cr(CO)_5$ complexes (235-245 pm)[29] and also the Cr−C bond of *trans*-CO [187.0(3) pm] is shorter (*trans* effect) by 3 pm than those of *cis*-CO (average 190.2 pm). Finally, it should be mentioned that the averaged P−Cr−C angles of *cis*-and *trans*-carbonyls are 90.2° and 178.4°, respectively, corresponding closely to ideal octahedral geometry around chromium.

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Experimental Section

General Comments: All reactions were carried out under a dry argon atmosphere using the Schlenk technique. − NMR spectra were recorded on Bruker ARX 300 (^{31}P-NMR at 121.5 MHz, ^{1}H-NMR at 300.1 MHz and ^{13}C-NMR at 75.5 MHz). The chemical shifts refer to 85% H_3PO_4 (external) or TMS (internal). − Mass spectra were recorded on AMD 40(intectra), IR spectra on System 2000 of Perkin-Elmer. − The synthesis of the 2-phosphaindolizines **1a-h** was recently reported[14][17][18]. [(THF)M(CO)$_5$] were freshly prepared before use[30], tetracarbonyl(norbornadiene)chromium(0) was synthesized by refluxing chromium hexacarbonyl with norbornadiene in light petroleum[31]. Tricarbonyl(cycloheptatriene)molybdenum(0) and tricarbonyl(mesitylene)tungsten(0) were commercially available and used without further treatment. Melting points of complexes are uncorrected and were determined in a capillary under argon.

Reaction of 2-Phosphaindolizines **1** *with THF·M(CO)$_5$* (**2**, **3**, **4**) − *General Procedure:* A solution of 2.0 mmol of metal hexacarbonyl [440 mg of $Cr(CO)_6$; 704 mg of $W(CO)_6$ or 528 mg of $Mo(CO)_6$] in 200 ml of oxygen-free THF was irradiated using a high-pressure mercury photo lamp with continuous stirring and monitoring of the volume of CO evolved. [If with $Mo(CO)_6$ the reaction became slower, the irradiation was interrupted and argon was bubbled through the solution to diminish the CO concentration, using a separate outlet.] After evolution of 2 mmol (44.8 ml) of CO the irradiation was stopped. The [(THF)M(CO)$_5$] solution was added to a solution of the respective 2-phosphaindolizine **1** (2.0 mmol) in THF and stirred overnight at room temperature. The solvent was removed in vacuo and the residue extracted with hexane (2 × 50 ml). Shining crystals were obtained on leaving the concentrated hexane extract (10−15 ml) in a refrigerator (−20°C). If no crystals separated, the solvent was removed completely to obtain yellow to orange powdery complexes. **2a**, **b**, **e**, **3a**, **c**, **e**, **g**, **4a**, **b**, **d**, **e** and **h** were synthesized in this manner. In case of the reaction of **1e** with [(THF)Cr(CO)$_5$], formation of some **5e** was observed in addition to **2e**. On recrystallization from hexane pure **2e** was obtained. NMR-spectroscopic data are given in Tables 1-3, substance and IR data in Table 4.

Reaction of **1f** *with Tetracarbonyl(norbornadiene)chromium(0)* (**2f** *and* **5f**): 207 mg (1.0 mmol) of **1f** was refluxed with 256 mg (1.0 mmol) of tetracarbonyl(norbornadiene)chromium(0) in petroleum ether (50 ml, b.p. 100−120°C) for three hours. The colour of the solution changed from yellow to orange. The reaction mixture was filtered, and the filtrate placed in a refrigerator (ca. −20°C). Yellow-orange crystals consisting of **2f** ($\delta^{31}P = 190.8$) and **5f** ($\delta^{31}P = 202.3$) precipitated. For ^{1}H- and ^{13}C-NMR data see Tables 2 and 3. Extraction of the mixture with hexane afforded spectroscopically pure **5f**, yield 18%, m.p. 135−137°C.

Reactions of **1g** *with Tricarbonyl(cycloheptatriene)molybdenum(0)* (**6g** *and* **7g**) − *A*: 236 mg of **1g** (1.35 mmol) and 123 mg (0.45 mmol) of (cycloheptatriene)Mo(CO)$_3$ were dissolved in THF. ^{31}P NMR (THF/[D$_8$]THF) spectra were recorded (i) after 18 hours and (ii) after 2 days at room temperature. In the first case we observed signals at δ (rel.int.) = 6.1 (65), 11.4 (12), 167.8 (85) **1g** and 181 (8) **6g**, in the second case only at δ (rel.int.) = 167.8 (110) and 181.2 (20).

B: 130 mg (0.75 mmol) of **1g** was stirred for 2 days with 203 mg (0.75 mmol) of (cycloheptatriene)Mo(CO)$_3$ in THF (40 ml) at room temperature. ^{31}P NMR (THF/[D$_8$]THF) control showed only signals of **7g**, δ = 196.3, d; 203.8, t; $^{2}J(^{31}P\text{-}^{31}P) = 9$ Hz, intensity ratio 2:1. Similarly, **7g** is formed preferentially in $CDCl_3$.

C: 120 mg (0.69 mmol) of **1g** was refluxed for 2 days with 188 mg (0.69 mmol) of (cycloheptatriene)Mo(CO)$_3$ in ether/hexane (1:2). The precipitate was separated and washed with little hexane. The ^{31}P-NMR spectra of the solid, dissolved in C_6D_6, showed it to be a mixture of **7g** (δ = 193.3, d; δ = 200.9, t; $^{2}J(^{31}P\text{-}^{31}P) = 9.3$ Hz) and **6g** (δ = 177.1, s); proton-coupled ^{31}P-NMR: **7g** δ = 193.3, dt, $^{2}J(^{31}P\text{-}^{1}H) = 30.5$ Hz, δ = 200.8, multiplet; **6g** δ = 177.1, multiplet.

Reaction of **3f** *with Tricarbonyl(cycloheptatriene)molybdenum(0)* (**3f** *and* **6f**): 207 mg (1.0 mmol) of **1f** and 272 mg of (cycloheptatriene)Mo(CO)$_3$ was stirred in THF (50 ml) for two days. ^{31}P-NMR of the reaction mixture indicated **6f** (δ = 178.9) as major product, along with **3f** (δ = 169.3). THF was removed and the residue extracted with hexane. On concentrating the filtrate, analytically and spectroscopically pure **3f** was obtained as a yellow solid. For ^{1}H- and ^{13}C-NMR see Table 2 and 3, for substance data see Table 4.

Reaction of **1e** *with Tricarbonyl(mesitylene)tungsten(0)* (**4e** *and* **6e**): 111 mg (0.5 mmol) of **1e** was heated with 194 mg (0.5 mmol)

Table 4. Substance and IR data of the complexes **2–4**

	IR ν (CO) [cm^{-1}]	mp [°C]	yield [%]	mol. formula [m. wt.]	analysis found / calc. (%) C	H	N
2a	2071 m, 2004 w,	90–92	77	$C_{18}H_{16}O_6NPCr$	50.93	4.02	3.34
	1954 s, 1940 s, 1915 sh			(425.29)	50.83	3.79	3.29
2b	–	68–69	78	$C_{23}H_{18}O_6NPCr$	56.21	3.44	2.61
				(487.35)	56.68	3.72	2.87
2e	2069 m, 1995 sh,	164–65	82	$C_{16}H_{12}O_7NPCr$	46.15	2.67	3.29
	1956 s, 1929 s,			(413.24)	46.50	2.93	3.39
3a	–	89–90	72	$C_{18}H_{16}O_6NPMo$	46.26	3.28	2.75
				(469.23)	46.07	3.44	2.99
3c	2079 w, 1987 s,	124–25	65	$C_{20}H_{12}O_6NPMo$	49.34	2.73	2.93
	1964 m, 1953 s, 1936 s			(489.22)	49.09	2.47	2.86
3e	2075 m, 2035 w,	146–47	77	$C_{16}H_{12}O_7NPMo$	42.53	2.72	3.04
	1986 m, 1961s, 1926 s			(457.18)	42.03	2.65	3.06
3f	2075 m, 1987 m,	115–16	51	$C_{15}H_{10}O_7NPMo$	40.49	2.43	3.28
	1961 s, 1948 s, 1926 s			(443.15)	40.65	2.28	3.16
3g	2072 w,	135–38	64	$C_{14}H_7O_5N_2PMo$	40.16	1.81	6.98
	986 s, 1950 s			(410.1)	40.99	1.72	6.83
4a	2077 m, 1995 w,	74–76	68	$C_{18}H_{16}O_6NPW$	39.08	2.83	2.37
	1970 sh, 1953 s, 1920 s			(557.14)	38.80	2.90	2.51
4b	2078 m, 1999 w,	66–67	75	$C_{23}H_{18}O_6NPW$	45.61	3.14	2.23
	1952 s, 1920 sh			(619.20)	44.61	2.93	2.26
4d	2079 m, 2007 m,	166–68	70	$C_{20}H_{12}O_6NPW$	42.13	2.13	2.39
	1970 s,1943 s, 1908 s			(577.13)	41.62	2.10	2.43
4e	2074 m, 1993 m,	179–81	81	$C_{16}H_{12}O_7NPW$	36.16	2.54	2.24
	1954 s, 1935 s, 1917 s			(545.09)	35.25	2.22	2.57
4h	2075 m, 1994 w,	170–71	66	$C_{24}H_{13}O_7N_2PW$	43.12	2.16	4.32
	1961 s, 1930 s, 1918 sh			(656.18)	43.93	2.00	4.27

of tricarbonyl(mesitylene)tungsten(0) in THF (40 ml) for 20 hours at 45–50°C. ^{31}P NMR presents signals of **1e**, **4e**, and **6e** in an intensity ratio of 14:8:78. After removal of THF, the residue was extracted with hexane and filtered. Removal of the solvent in vacuo afforded a yellow solid that proved to be a mixture (m.p. 110–118°C) of **6e** as major product with some **4e**. Proton-coupled ^{31}P NMR: **6e** $\delta = 149.6$, multiplet, $^{1}J(^{31}\text{P-}^{183}\text{W}) = 263$ Hz; **4e** $\delta = 140.2$, q, $^{3}J(^{31}\text{P-}^{1}\text{H}) = 17$ Hz.

X-ray Structure Analysis of **2a** *– Crystal Data*: $C_{18}H_{16}CrNO_6P$, triclinic, $P1$, $a = 905.9(3)$, $b = 977.8(4)$, $c = 1238.0(4)$ pm, $\alpha = 94.13(3)$, $\beta = 97.52(3)$, $\gamma = 116.72(3)°$, $V = 0.9604$ nm^3, $Z = 2$, $\mu = 0.71$ mm^{-1}, $D_x = 1.471$ Mg m^{-3}, λ(Mo-$K\alpha$) = 71.073 pm, $T = -130$°C. *Data Collection*: Yellow tablet 0.7 × 0.5 × 0.15 mm, Stoe STADI-4 diffractometer, $2\theta_{max}$ 50°; 3622 intensities, absorption correction with ψ-scans (transmissions 0.82–0.96), 3387 unique reflections (R_{int} 0.021). *Structure Solution and Refinement*: Direct methods, refined on F^2 using SHELXL-93[32]. Hydrogen atoms: riding model or rigid methyls. Final $wR(F^2)$ 0.077 for all reflections, conventional $R(F)$ 0.032 for 248 parameters; S 1.06, max. $\Delta\rho$ 295 e nm^{-3}.

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the number CSD 101226. Copies may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax internat.: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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