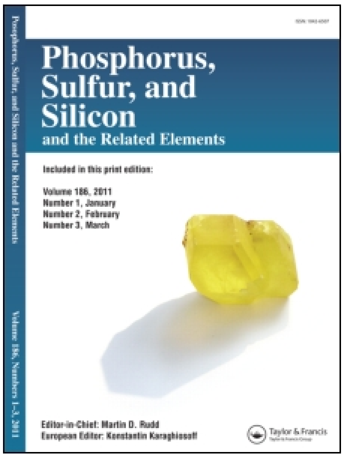

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SYNTHESIS AND STEREOCHEMISTRY OF PENTACARBONYL(PHOSPHOLE)METAL(0)- AND TETRACARBONYLBIS(PHOSPHOLE)METAL(0) COMPLEXES OF 6B ELEMENTS

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SYNTHESIS AND STEREOCHEMISTRY OF PENTACARBONYL(PHOSPHOLE)METAL(0)- AND TETRACARBONYLBIS(PHOSPHOLE)METAL(0) COMPLEXES OF 6B ELEMENTS

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Pentacarbonylphospholemetal(0) and *cis*-tetracarbonylbis(phosphole)metal(0) complexes were synthesized from the thermal reaction of $M(CO)_5(THF)$ and $M(CO)_4(COD)$ (M: Cr, Mo, W) with corresponding phosphole (1-phenyl-3,4-dimethylphosphole, 1-phenyl-3-methylphosphole, and 1-phenylphosphole). These complexes were isolated as orange crystals by column chromatography on silicagel at 253 K and crystallization from n-hexane at 223 K and characterized by means of IR and NMR (^1H, ^{13}C, and ^{31}P). Spectroscopic data shows that the phosphole is coordinated to the transition metal through its phosphorus atom rather than through the conjugated diene unit in the both types of complexes. The tetracarbonylbis(phosphole)metal(0) complexes were found to have *cis*-arrangement of two phosphole ligands. Comparing ^{13}C-NMR chemical shifts of the complexes with the free ligands, one can deduce that the involvement of the phosphorus atom in the ring π-electron delocalization is drastically reduced upon coordination. This is attributed to the stronger σ-donation but weaker π-accepting ability of the phosphorus atom in the phosphole ligands compared to the carbonyl groups.

Key words: Phosphole; chromium; molybdenum; tungsten; carbonyl.

INTRODUCTION

Although the use of the phosphole derivatives as a donor ligand is fairly new, many transition metal complexes have been synthesized in which phosphole generally donates two electrons to the transition metal.[1–8] However, only a few phosphole complexes of 6B metals are known.[1,6,9–12]

The first phosphole complexes of the 6B elements, $M(CO)_5L$ (M: Cr, Mo, W; L: 1,2,5-triphenylphosphole) have been obtained by the treatment of triphenylphosphole with $M(CO)_6$ at 150–180°C and characterized solely by the interpretation of the IR-spectra.[1]

In 1980, Mathey and his coworkers reported the synthesis of the pentacarbonyl(1-phenyl-3,4-dimethylphosphole)metal(0) complexes for all of the three members of the group 6B, from the UV-irradiation of $M(CO)_6$ in the presence of the phosphole in THF.[9] They have reported that the further irradiation of the solution leads to the [2 + 2] and [4 + 2] dimerization around the metalcarbonyl moieties. For M = Cr and Mo, they could also isolate the tetracarbonylbis(1-phenyl-3,4-dimethylphosphole)metal(0) complexes in low yield. In the case of tungsten, however, the only product obtained from the long UV irradiation has been found to be a tetracarbonyltungsten(0) complex with the dimerized phosphole. All of these complexes have been characterized by IR, ^1H and ^{31}P NMR spectroscopies.

Even though the ^{13}C NMR spectra could be rich in information about the stereochemistry and bonding relationship in these complexes, with one exception,[12] no reports have been found for their ^{13}C NMR data. In this paper we report the synthesis of pentacarbonyl(phosphole)metal(0) and tetracarbonylbis(phosphole)-metal(0) complexes of 1-phenyl-3,4-dimethylphosphole, a, and 1-phenyl-3-methylphosphole, b, for all of the group 6B elements by using new methods described in the following schemes. From the reaction of $M(CO)_5(THF)$ with 1-phenylphosphole, c, only pentacarbonyl(1-phenyl-phosphole)tungsten(0), 3c, could be isolated.

All of these complexes were isolated and purified by recrystallization from n-hexane at 223 K or by column chromotography on silicagel at 253 K and characterized by IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy.

RESULT AND DISCUSSION

The IR-spectra of the $M(CO)_5L$ complexes, 1a–3c give three absorption bands in the CO-stretching region indicating that $M(CO)_5$-moiety has a C_{4v} symmetry with $2A_1 + E$ CO-vibrational pattern. The $M(CO)_4L_2$ complexes, 4a–6b, show four absorption bands in the same region of the IR spectrum. This indicates that two phosphole ligands are *cis* to each other in the octahedral coordination sphere of the transition metal. Thus the $M(CO)_4$-unit in the complex has C_{2v}-symmetry with

$$M(CO)_6 + THF \xrightarrow[\text{1-hour}]{h\nu,\ 263\ K} M(CO)_5(THF) + CO$$

$$M(CO)_5(THF) + L \xrightarrow{\text{room tem.}} M(CO)_5L + L$$

M:	L: a	L: b	L: c
Cr	1a	1b	–
Mo	2a	2b	–
W	3a	3b	3c

Scheme I

$$M(CO)_6 + COD \xrightarrow[\text{n-pentane}]{h\nu,\ 263\ K} M(CO)_4(COD) + 2\ CO$$

$$M(CO)_4(COD) + 2\ L \xrightarrow{\text{room tem.}} M(CO)_4L_2 + COD$$

M:	L: a	L: b
Cr	4a	4b
Mo	5a	5b
W	6a	6b

Scheme II

general CO vibrational modes of $2A_1 + B_1 + B_2$. The CO force constants were calculated from the CO stretching frequencies by using the Cotton-Kraihanzel approximation.[16] The CO-stretching frequencies and C—O force constants of all the complexes are listed in Table II. The inspection of the ν(CO) frequencies gives the first clue for the σ-donation ability of the phosphole ligand in these carbonyl(phosphole)metal complexes. All of the CO-stretching absorption bands ($2A_1(1)$, $A_1(2)$ and E) appear at noticeably lower frequencies compared to those of the analogous complexes of the normal phosphines.[17] This implies that phosphole is acting as a strong σ-donor ligand in these carbonylmetal complexes.[18] Furthermore the large frequency separation between the $A_1(1)$ and $A_1(2)$ modes observed in the pentacarbonyl(phosphole)metal(0) complexes provides additional evidence for the existence of strong σ-donation from the phosphole ligand to the transition metal leading to the strengthening of the M—CO back-bond and the weakening of the C—O bond.[19] The comparison of the C—O force constants for the penta-

TABLE II

The CO stretching frequencies (cm^{-1}) and CO-force constant (k_1 refers to CO *trans* to phosphole and k_2 is for CO *cis* to phosphole) (Nm^{-1}) for the complexes

Complex	ν_{co} (cm^{-1})				co-Force Constant (Nm^{-1})			
	$A_1(1)$	$A_1(2)$	E		k_1	k_2	k_i	$\bar{k}$
1a	2062	1942	1950		1540.	1590	27	1565
2a	2060	1942	1950		1540	1539	27	1540
3a	2058	1942	1949		1540	1587	27	1564
1b	2058	1940	1950		1536	1588	26	1562
2b	2060	1944	1950		1543	1589	27	1566
3b	2066	1944	1948		1544	1590	29	1567
3c	2066	1944	1948		1545	1590	29	1568
	$A_1(1)$	$A_1(2)$	B_1	B_2				
4a	1904	2002	1922	1896	1458	1544	27	1501
5a	1904	2002	1922	1896	1453	1544	27	1499
6a	1900	2004	1920	1890	1459	1549	27	1459
4b	1906	2010	1924	1898	1461	1552	28	1506
5b	1908	2008	1928	1900	1464	1554	27	1509
6b	1910	2016	1932	1904	1467	1564	28	1515

carbonyl and tetracarbonyl complexes shows that the average force constants $\bar{k} = (k_1 + k_2)/2$ for tetracarbonylbis(phosphole)metal(0) complexes are lower than those for pentacarbonylphospholemetal(0) complexes, as expected from the strong σ-donation and weaker π-accepting ability of the phosphole ligand compared to the CO group.[20]

The ^{31}P-$\{^1H\}$-NMR spectra exhibit only one signal for both types of complexes $M(CO)_5L$ and $M(CO)_4L_2$. The ^{31}P-NMR chemical shifts and ^{183}W—^{31}P coupling constants are listed in Table III. In all of the complexes one observes a large coordination shift, which indicates that the phosphole ligand is coordinated through the phosphorus atom rather than through the conjugated diene unit.[21] The coor-

TABLE III

^{31}P-NMR chemical shift (δ ppm rel. to H_3PO_4), coordination shift ($\Delta\delta$ ppm) and ^{183}W—^{31}P coupling constants (Hz) of the complexes in $CDCl_3$

Complex	δ (ppm)	$\Delta\delta$	$J_{^{183}W-^{31}P}$
a[1]	-4.4		
b[1]	7.4		
c[1]	6.4		
1a	51.37	55.77	
2a	30.37	34.77	
3a	10.72	15.12	212
1b	53.94	46.54	
2b	42.99	35.59	
3b	13.25	5.85	211
3c	20.30	13.90	211
4a	54.74	59.14	
5a	29.32	33.72	
6a	10.82	15.22	208
4b	66.52	59.12	
5b	54.26	46.86	
6b	26.05	18.65	210

1: Data were taken from Ref. 15

dination shift decreases by passing from chromium through tungsten as observed in similar carbonyl-phosphine-metal(0) complexes.[22,23] This high field shift of the phosphorus resonance signal by about 20 ppm upon changing the transition metal from chromium to molybdenum or from molybdenum to tungsten has been explained as a neighbour anisotropy effect.[24]

The ^{13}C-{^1H}-NMR spectra of 1a–6b exhibit two signals for the CO ligands and seven, nine or six signals for the a, b or c ligands respectively (Table IV). The CO signals appear as a doublet in the case of $M(CO)_5L$ and as a triplet in the case of $M(CO)_4L_2$ becaus of the ^{31}P—^{13}C coupling to one or two phosphorus atoms. The relative intensities of the carbonyl signals of 1:4 for the former and 1:1 for the latter complexes provide additional evidence for the C_{4v} and C_{2v} symmetry for the $M(CO)_5$ and $M(CO)_4$-fragments of the complexes respectively as elucidated from the IR spectra. In line with the metal dependence of the ^{31}P-NMR chemical shift,

TABLE IV

The ^{13}C-NMR chemical shifts (δ ppm, ref. TMS) and ^{31}P—^{13}C coupling constants (Hz given in parenthesis) of the complexes

Complex	C(2)	C(3)	C(4)	C(5)	$-CH_3$	$-C_6H_5$	CO
a[2]	128.52(7.3)	148.75(8.5)	148.75(8.5)	128.52(7.3)	17.57(3.7)	132.42(12.2) 133.37(18.9) 128.78(6.1) 129.88	
b[2]	128.56(1.2)	147.38(8.8)	140.07(7.6)	136.00(5.3)	18.35(3.7)	130.62(10.5) 132.98(19.0) 127.99(8.0) 128.09	
c[2]	135.11(−5.18)	136.71(8.17)	136.71(8.17)	135.11(−5.18)		129.59 133.31 128.33 128.93	
1a	130.87(10)	128.91(9)	128.91(9)	130.87(10)	17.13(11)	150.04(8) 130.10 129.75 128.94	221.82(8) 216.32(14)
2a	131.38(12)	128.88(9)	128.88(9)	131.38(12)	17.03(11)	149.91(9) 130.72 130.22 129.97	210.02(20) 205.65(10)
3a	131.25(12)	130.25(5)	130.25(5)	131.25(12)	16.64(12)	150.91(8) 129.31 128.96 128.64	199.45(17) 196.50(5)
1b	137.36(36)	128.90(9)	141.77(8)	131.87(11)	19.53(10)	149.58(9) 131.20 129.80 128.99	222.25(8) 217.27(13)
2b	137.23(33)	128.99(9)	140.93(7)	131.53(13)	18.34(10)	148.77(9) 130.53 129.80 129.63	209.85(20) 205.46(8)
3b	137.94(39)	129.95(9)	142.29(9)	132.38(12)	19.43(11)	150.29(9) 131.66 130.58 129.70	199.80(18) 197.05(7)

TABLE IV (*Continued*)

<u>3c</u>	137.22(21)	131.62(9)	131.62(9)	137.22(21)		149.62(9) 130.81 129.19 128.95	196.32(5) 194.85(10)
<u>4a</u>	131.04(5)	128.45	128.45	131.04(5)	17.16(3)	148.59 131.34 130.56 129.27	226.44(7) 221.42(7)
<u>5a</u>	131.38(4)	130.33(37)	130.33(37)	131.38(4)	17.29(28)	148.69 131.77 131.16 131.07	226.54(9) 221.10(14)
<u>6a</u>	132.65(12)	129.80(28)	129.80(28)	132.65(12)	18.41(11)	151.90 131.03 130.51 130.03	209.37(26) 204.32(7)
<u>4b</u>	137.28(27)	131.75	141.64	130.06(17)	18.45	148.02(4) 132.03 130.28 129.64	234.27(9) 231.62(12)
<u>5b</u>	137.72(35)	131.74	140.03	129.98(19)	18.46	147.66(4) 131.27(5) 129.63 128.65	226.32(9) 220.70(14)
<u>6b</u>	133.28(15)	131.71	132.31	129.21(15)	18.42	140.45(5) 130.69 128.88 128.34	224.96(18) 222.75(10)

2: Data were taken from Ref. 27

one observes the largest downfield shift in the ^{13}C-NMR signals of the carbonyl groups for chromium upon phosphole substitution. This reflects the existence of strongest P → M σ-donation and M → CO π-bonding in the chromium complexes. It is noteworthy to mention that the carbonyl group trans to the phosphole ligand shows a larger downfield shift than those of the others in all complexes indicating that the effect of phosphorus ligand on the carbonyl group is largest if they are trans to each other.[25]

The assignment of the ^{13}C-{^{1}H}-NMR signals for the phosphole ligands was made by considering their chemical shifts, the number of the protons attached to carbon (DEPT experiments) and the magnitude of ^{31}P—^{13}C coupling constant. The high ^{13}C-NMR chemical shifts of the phosphole ring carbon atoms in the free ligands <u>a</u>, <u>b</u> and <u>c</u> have been attributed to the aromaticity of the ring, in which the phosphorus atom is involved with its p-orbital.[26] It has been shown that the delocalization is enhanced by the $(2p\text{-}3d)\pi$ interaction between the phosphorus atom and the ring butadiene moiety in the PdX_2(phosphole) complexes in which the phosphole ligand must accept π-electron density from the filled metal d-orbitals into the empty d-orbitals on the phosphorus atom.[5] This additional electron density in the phosphorus d-orbitals can be pumped into the ring through the $2p\text{-}d\pi$ interaction. This enhanced delocalization results in the downfield shifts of the ^{13}C NMR signals for the ring carbon atoms 3, 4 and upfield shifts for those of 2 and 5. Examination of Table IV shows an opposite change in the ^{13}C-NMR chemical shift in the carbonylphosphole complexes of the group 6B elements.

Upon coordination of the phosphole to a $M(CO)_4$ or $M(CO)_5$ fragment, a large upfield shift in the signals of the ring carbon atoms 3, 4 and a slight downfield shift in those of 2 and 5 is observed in the ^{13}C-NMR spectrum. These trends may very well result from the reduced π-electron delocalization in the phosphole ring after coordination. Since the carbonyl groups are very strong π-acceptors, the phosphole ligand can act almost only as a σ-donor in these complexes. That is, the phosphorus atom uses its fourth sp^3 hybrid orbital for the σ bonding to the central metal atom. This reduces the involvement of the p-orbital of the phosphorus atom in the ring π-delocalization. Furthermore, since the phosphole ligand cannot compete with the carbonyl groups for the use the metal $d(\pi)$-orbitals, the phosphorus atom will not gain any significant π-electron density from the metal into its empty d-orbitals which would be used in the ring π-delocalization. As the effect of the π-delocalization is drastically reduced upon coordination, the inductive effect of the electronegative phosphorus atom on the ^{13}C-NMR chemical shifts of the ring carbon atoms becomes predominant. Therefore the upfield shift observed for the ^{13}C-NMR signal of all the phosphole ring carbon atoms is counterbalanced for the carbons 2 and 5 by the inductive effect of the neighbouring phosphorus atom.

Support for the proposed explanation also comes from the observation of a 20 ppm downfield shift in the ^{13}C-NMR signal of the tertiary carbon in the phenyl ring upon coordination of the phosphole to a $M(CO)_4$ or $M(CO)_5$ fragment. After coordination, the involvement of the phosphorus atom to the phenyl ring π-de-

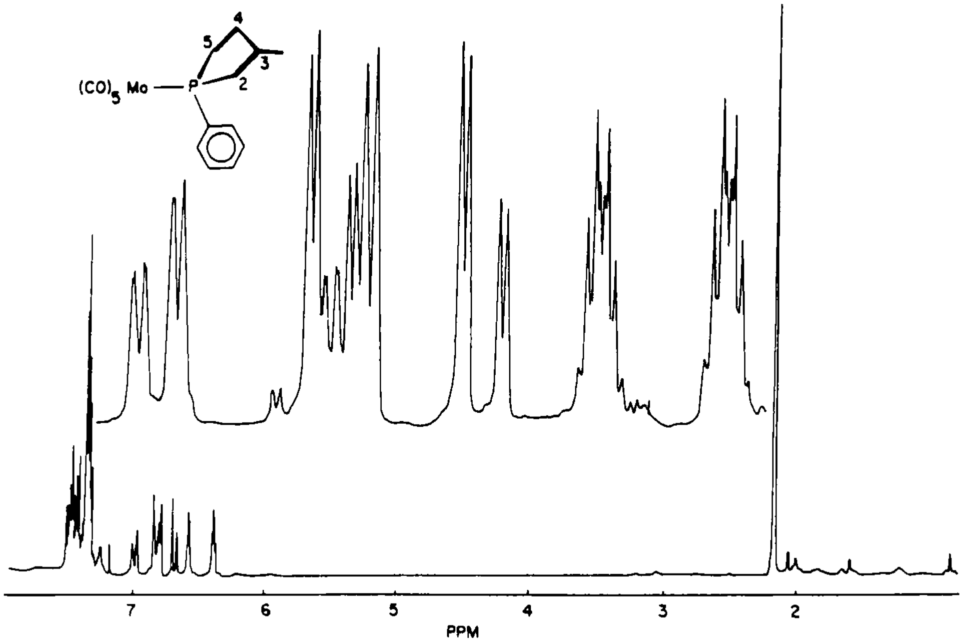

FIGURE 1 ^{1}H-NMR of 5b taken at 298 K in chloroform-d.

localization is enormously reduced. The predominant factor is then the inductive effect of the phosphorus atom. Thus, the carbon atoms which are directly bonded to the phosphorus atom show large downfield shifts.

^{1}H-NMR spectra of the complexes show two extremely complicated multiplets for the phenyl protons and a doublet for the methyl protons (due to the ^{31}P—^{1}H coupling). The olefinic protons give one simple doublet in the complexes 1a–6a. In the ^{1}H-NMR spectra of the complexes 1b–6b one observes the typical signal pattern for the *ABM* part of an *ABMX* spin system where *A*, *B*, *M* are the protons 5, 4, 2 respectively and *X* is phosphorus.[28]

Since the spin system is further perturbed by the methyl protons, further splitting is observed in the signals of the protons 2 and 4 (Figure 1). The ^{1}H-NMR chemical shifts and the ^{31}P—^{1}H coupling constants of all the complexes are given in Table V. It is noteworthy to mention the increase in the ^{31}P—^{1}H coupling constant upon coordination. This increase in the value of the ^{31}P—^{1}H coupling constant is ascribed to the strengthening of the P—CH bonds by the σ-donation from phosphorus to the metal atom. This is in line with the conclusion obtained from the ^{13}C-NMR data that the phosphole is acting mainly as a σ-donor.

TABLE V

^{1}H-NMR chemical shift values (δ, ppm) and ^{31}P—^{1}H coupling constants (Hz, given in parenthesis) of the complexes in toluene-d_8

Complex	H(2)	H(3)	H(4)	H(5)	CH_3	C_6H_5
a[3]	6.32(37)			6.32(37)	1.96(3)	7.0
b[3]	6.52(41)		6.93(12)	7.01(40)	2.31(3.3)	7.3
1a	6.64(36)			6.64(36)	2.14	7.40, 7.54
2a	6.56(37)			6.56(37)	2.16	7.38, 7.52
3a	6.54(36)			6.54(36)	2.18	7.42, 7.52
1b	6.52(38)		6.74(30)	6.94(38)	2.13	7.44, 7.34
2b	6.47(23)		6.77(29)	6.88(37)	2.18	7.48, 7.36
3b	6.48(37)		6.56(30)	6.89(37)	2.14	7.82, 7.46
4a	6.26(32)			6.26(32)	1.58	7.00, 7.42
5a	6.44(36)			6.44(36)	2.10	7.42, 7.58
6a	6.58(36)			6.58(36)	2.20	7.40, 7.58
4b	6.44(38)		6.70(30)	6.92(37)	2.14	7.44, 7.33
5b	6.38(36)		6.67(28)	6.84(37)	2.14	7.45, 7.32
6b	6.40(37)		6.64(26)	6.86(37)	2.14	7.46, 7.34

[3] Data were taken from Ref. 30

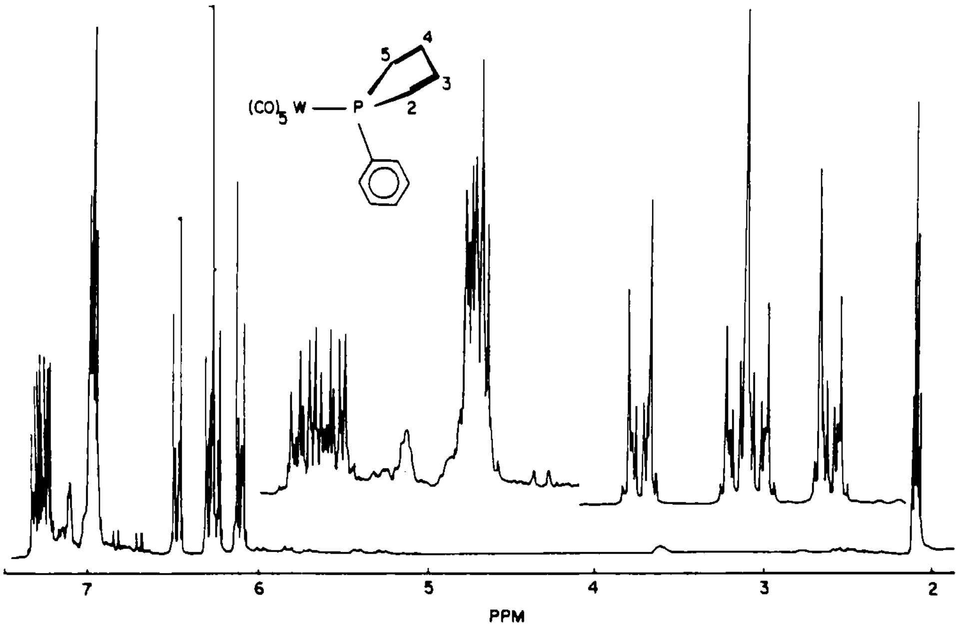

FIGURE 2 ¹H-NMR of 3c taken at 298 K in chloroform-d.

The ¹H-NMR spectrum of 3c (Figure 2) shows two multiplets for the phenyl protons. The olefinic protons give the typical signal pattern of a *AÁBB́X* system, where *X*: ^{31}P.[29] The spin system was analyzed as *AÁBB́* system after having taken the phosphorus decoupled spectrum. The ^{31}P—^{1}H and ^{1}H—^{1}H coupling constants as well as the ¹H-NMR chemical shifts are given below:

δ (ppm)	*J* (Hz)
$\delta_{2,5}$:6.39	H2-H3 = H4-H5:7.6
$\delta_{3,4}$:6.18	H2-H4 = H3-H5:1.3
$\delta_{C_6H_5}$:6.97, 7.27	H2-H5 = 1.7
	H3-H4 = 3.6
	H2-P = H5-P:38
	H3-P = H4-P:26

EXPERIMENTAL

$M(CO)_5THF$ and $M(CO)_4(COD)$ (M: Cr, Mo, W) were prepared photochemically according to the procedures described in literature.[13,14] All the reactions and manipulations were performed by using Schlenk techniques under dry and deoxygenated nitrogen gas. Solvents (Merck) were purified by refluxing over metallic sodium or phosphorus pentoxide under nitrogen for three to four days. $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$ (Ventron) have been used without further purification. Phospholes; 1-phenyl-3,4-dimethylphosphole, 1-phenyl-3-methylphosphole, and 1-phenylphosphole were prepared by using the methods described in literature.[15] The photochemical reactions and other treatment of organometallic compounds such as purification and crystallization were followed by IR spectra taken at appropriate intervals. Characterization of product: Elemental analysis, Microanalysis Laboratory of Kaiserslautern University, Germany; IR-spectra, Perkin-Elmer 1430 Instrument; NMR-spectra, Bruker WP200 instrument (¹H 200.200, ¹³C 50.28 and ³¹P 81.01 MHz).

$M(CO)_5L$ (M: Cr, Mo, W; L: a, b, c)

TABLE I
Analytical Data

Complex	Formula	Amount of Ligand(g)	%Yield	%C Calculated	%H Calculated	%C Found	%H Found
1a	$C_{17}H_{13}CrPO_5$	0.85	45.2	68.02	4.33	68.4	4.36
2a	$C_{17}H_{13}MoPO_5$	0.71	42.0	59.33	3.77	59.7	3.79
3a	$C_{17}H_{13}WPO_5$	0.47	40.1	47.26	3.00	47.4	3.02
1b	$C_{16}H_{11}CrPO_5$	0.78	38.2	47.20	3.84	67.6	3.89
2b	$C_{16}H_{11}MoPO_5$	0.66	35.0	58.26	3.33	58.8	3.38
3b	$C_{16}H_{11}WPO_5$	0.44	33.6	54.99	2.63	46.4	2.68
3c	$C_{15}H_9WPO_5$	0.40	20.1	44.50	2.22	44.8	2.26
4a	$C_{28}H_{26}CrP_2O_4$	1.38	35.6	70.61	5.45	76.9	5.49
5a	$C_{28}H_{26}MoP_2O_4$	1.18	32.1	64.64	4.99	65.0	5.03
6a	$C_{28}H_{26}WP_2O_4$	0.93	30.4	55.30	4.27	55.8	4.31
4b	$C_{26}H_{22}CrP_2O_4$	1.27	29.0	69.67	4.90	70.1	4.93
5b	$C_{26}H_{22}MoP_2O_4$	1.09	26.5	63.45	4.47	63.9	4.49
6b	$C_{26}H_{22}WP_2O_4$	0.86	23.2	53.80	3.79	53.8	3.81

The solution of metastable pentacarbonyltetrahydrofuranemetal(0), $M(CO)_5THF$ is filtered through the glass fiber to remove colloidal decomposition product. Stoichiometric amount of phosphole ligands (1:1 mol ratio, see Table I) is added to the solution under vigorous stirring. After stirring the mixture for one day at room temperature, the mixture is filtered in order to remove any residual solids. Solvent is evaporated in vacuum. The residue is dissolved in about 10 ml of n-hexane, cooled to 223 K and allowed to stand for one or two nights at this temperature. The pentacarbonylphospholemetal(0) complex is separated in the form of light orange crystals which are dried under high vacuum for one hour. The analytical data for all complexes are listed in Table I.

$M(CO)_4L_2$ (M: Cr, Mo, W; L: a and b)

1 g of $M(CO)_4(COD)$ is dissolved in 20 ml of n-hexane and stoichiometric amount of the phospholes (1:1 mol ratio, see Table I) is added to the solution. This mixture is stirred for one night at room temperature. After the evaporation of the volatiles, the residue is dissolved in a minimum amount of n-hexane and transferred to the chromatography column which is filled with silicagel and n-hexane. Elution of the column with n-hexane followed by a solution of n-hexane:benzene (5:1) gave an orange band. The orange eluate is evaporated under the vacuum. The residue is dissolved in 5 ml of n-hexane and then allowed to stand at 223 K until the crystallization is completed. Final product is recrystallized from n-hexane and dried in vacuum. Analytical data for all complexes are listed in Table I.

CONCLUSION

Both the pentacarbonyl(phosphole)metal(0) and the tetracarbonylbis(phosphole)metal(0) complexes can be synthesized in high yield from the ligand replacement reaction of $M(CO)_5(THF)$ and $M(CO)_4(COD)$ where M: Cr, Mo, W with the corresponding phosphole at ambient temperature. The IR and NMR spectroscopic data show that the phosphole ligand is coordinated to the transition metal through its phosphorus atom rather than the conjugated diene unit in both types of complexes. From the inspection of υ(CO) frequencies, ^{13}C-NMR chemical shifts and $^{31}P—^{13}C$ coupling constant, it is concluded that the phosphole ligands are acting mainly as strong σ-donor in these complexes, which contain a large number (5 or 4) of strong π-acceptor carbonyl groups. The existency of the tetracarbonylbis(phosphole)metal(0) complexes in the *cis*-isomer is also an evidence for the high σ-donation ability of the phosphole ligands.

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