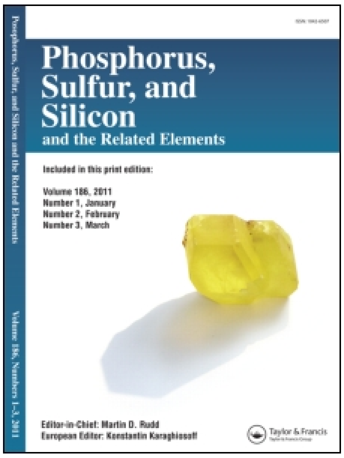

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DIPHOSPHINE COMPOUNDS: PART I. NOVEL BIOLOGICALLY ACTIVE 1,1'*bis*-AND/OR 1,2-*cis*-(DIPHENYLPHOSPHINO-)ETHENE AND THEIR COMPLEXES $[M(CO)_n\{Ph_2P(CH_n)_nPPh_2\}]$ & $[Cu(Cl)_2\{Ph_2P(CH_n)_nPPh_2\}]$, (M = W, Mo, Crn = 1,2....n)

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DIPHOSPHINE COMPOUNDS: PART I. NOVEL BIOLOGICALLY ACTIVE 1,1′*bis*-AND/OR 1,2-*cis*-(DIPHENYLPHOSPHINO-)ETHENE AND THEIR COMPLEXES $[M(CO)_n\{Ph_2P(CH_n)_nPPh_2\}]$ & $[Cu(Cl)_2\{Ph_2P(CH_n)_nPPh_2\}]$, (M = W, Mo, Crn = 1,2 . . . . n)

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Interaction of $[Ph_2PC({=}CH_2)PPh_2]$ *(A)*$^{1-3}$ *and/or* $[Ph_2P\,(CH{=}CH)\,PPh_2]$*(**B**) ligands in different molar ratio with hexacarbonyl metals* $M(CO)_6$ *gives* $[M(CO)_nPh_2PC({=}CH_2)PPh_2]$ *and/or* $[M(CO)_nPh_2P\,(CH{=}CH)PPh_2$ *where M=Cr, Mo or W, n = 2 and/or 4]. The carbon diphosphine complexes of type (**A**) which form four heteromemebered rings and/or type (B) form five heteromembered rings which reacts (addition reaction) with some different amines (methyl amine, dimethyl amine), phenyl hydrazine and/or some of amino acids (glycine, alanine, aspartic acid, serene). The structures of A and/or B complexes and their amino derivatives have been characterized by using elemental analysis, IR spectra,* ^{1}*HNMR,*^{1}*H-{*^{31}*P}-NMR, and mass spectra. Ligands and their complexes were screened in vitro to investigate the biological activities (antibacterial and antifungi). Interestingly, complexes are having strong and remarkable activities increases than the free ligands.*

Keywords: Antimicrobial screening; carbon diphenyl-phosphine derivatives; organometallic; transitions metal complexes

There is great interest in the coordination or organometallic chemistry generated by the anion $[Ph_2PCHPPh_2]^-$, these ligands form bimetallic complexes with or without metal-metal bonds, A-frames, and many other types of complexes.$^{4-6}$ In recent years there has been growing

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interest in the chemistry of hydrazides and hydrazones owing to their biological activity. In contrast there very little has been done with substituted (DPPMS) of type $Ph_2PCHRPPh_2$ (R = alkyl and/or, aryl or another functional group) although one might anticipate interesting electronic and stereochemical effects due to the presence of the R group(s). The benzoyl derivative $[\{W(CO)_4\{Ph_2PCH(COPh)PPh_2\}\dot{]}$ has a photochemically induced chelate ring expansion (four of six-membered rings)[7] and the corresponding hydrazone undergoes a thermal ring expansion, four- to seven-membered rings.[8] The synthesis of the new and reactive igand tetraphenyl carbon or carbonyl group diphosphine $[Ph_2P(CH_n)_nPPh_2]$ and their complexes have been studied. In this work A and B have been synthesized as free ligands and their complexes to improve and enhances in the biological activity.

EXPERIMENTAL

Apparatus

Infrared spectra (IR) was carried out by Shimadzu corporation Chart 200-91527, in KBr pellets. ^{1}HNMR spectra were recorded on a Varian Em-390-90MH$_z$NMR spectrometer using $CDCl_3$ as solvent and TMS as internal standard (chemical shifts in δ ppm). Microanalysis were performed on a perkin-Elmer240 E microanalysis. Mass spectra were recorded on JEOL mass spectrometer JMS600.

Preparation of Organometallic Compounds

Synthesis of Olefinic Diphosphine Ligands

The olefinic diphosphines, 1,1-*Bis*-(diphenylphosphino)ethene (A) and/or 1,2-*cis*-(diphenylphosphino)ethene(B), were prepared according to the following procedure:[16] Triphenylphosphine (86.8 g, 0.33 mmol) and lithium (4.6 g, 0.66 mmol) in thf (750 cm^3) were stirred overnight under dinitrogen. The solution was treated with 2-chloro-2-methylpropane (36.5 cm^3, 0.33 mmol) to remove phenyl-lithium and was then decanted, under dinitrogen, into a large dropping funnel. The resulting solution of $LiPPh_2$, was slowly added to 1,1-dichloro-ethene and/or 1,2-*cis*-dichloro-ethene(16.1 g, 0.165 mmol) in dry benzene (60 cm^3). Then dilute HCl (250 cm^3) was added, most of the thf solvent was removed by rotary evaporator, the organic was extracted and separated using dry ether. After removal of the solvents oil remained which crystallized on addition of absolute methanol. (A) and/or (B) ligands (colorless, air-stable crystals) were recrystallized from dry ethanol. Yield 35 g (31%); m.p. (114°C and/or 85°C).

Synthesis of Olefinic Diphosphine Complexes

The hot ethanolic solution of the vinylidene diphosphine ligand (**A**) and/or 1,2-cis-(diphenylphosphino-)ethene (**B**) (0.396 g) was added dropwise under stirring to a solution of the respective metal (0.22, 0.266, and 0.351 g) $M(CO)_6$ (M = Cr, Mo and W) and/or (0.132 g) $CuCl_2$ in decane solvent (20 ml); stirring at 70–80°C was continued for 40 min. The reaction mixture was cooled and the precipitated product was filtered, washed thoroughly with distilled water, dried, and recrystallized from ethanol/water (3/1).

Synthesis of Functionalized Diphosphine Complexes of Amines

The free diphosphine ligands (**A**) and/or (**B**) does not react with amines or hydrazine but complexation, even to a relatively weakly electron withdrawing group, $(OC)_4M$ (M = W, Mo, or Cr), is sufficient to render ($-C{=}CH_2$ and *cis*-$CH{=}CH-$) reactive toward Michael type additions. A toluene solution of the tungsten complexes I(1a) and/or II(1a) when heated and shaken with an excess of different amines: [aspartic acid I(2a), sereneI(3a) and/or alanineI(4a)] to give amino complexes derivatives after 12, 18, and/or 16 h (80°C), yield ranged from (74–85%). The corresponding Mo and Cr complexes reacted similarly.

PHYSIOLOGICAL ACTIVITY

Antibacterial and Antifungal Activity

All the newly synthesized ligands and their chelates were tested in vitro for antibacterial and antifungal activities, which were measured by using the disc-diffusion method.[9,10] The tested compounds were dissolved in sterile N,N,-dimethyl formamide (reagent grade) and added at a concentration of 0.5 mg/disc. (Whatman No, 3 filter paper, 0.5 cm diameter). The antibacterial spectrum was tested with six strains of bacteria, namely: *Serratia marcescems* (DSM/608), *Bacillus cereus* (DSM 345), *Pseudomonas aerginosa* (DSM/1299), *Micrococcus roseus* (DSM348), *Klebsiella pneumoniae* (DSM 581), and *Staphylococcus aureus* (DSM 346). Also, the antifungal effect was tested with three species of fungi, namely: *Aspergillus flavus* (Link Aucc 164), *Penicillium chrysogenum* (thom Aucc 530), and *Alternaria alternata* (Fries Keissler Aucc1110), *Fusarium equisioti* (DSM62203), *Alternaria tenussima* (DSM63360), *Aspergillus tammarii* (ATCC10836), *Penicillium digirtatum* (DSM62840), and *Penicillium paxilli* (CBS28047). The culture medium for bacteria was normal nutrient agar (NA) (composed of beef extract, 3 g peptone, 5 g agar, 15 g/l and adjusted to PH = 7 before sterilization at 121°C for 30 min). Glucose-Czapek's agar medium, ($NaNO_3$, 2 g; KH_2PO_4, 1 g; $MgSO_4{\cdot}7H_2O$, 0.5 g; KCl/0.5 g glucose. 10 g; agar, 15 g/L of distilled water) was used for fungi. The inoculated plates were incubated plates at 37 ± 1°C for 24–48 h in the case of bacteria and at 28°C for 7–8 days in the case of fungi. The inhibition zones of microbial growth produced by different compounds were measured.[11]

RESULTS AND DISCUSSION

Interaction of free ligand type $[(Ph_2P)_2C{=}CH_2]$ with some transition metals such as ($M = Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, and $CuCl_2$) by the anion $[Ph_2P(CH)PPh_2]^-$ reacts with electrophiles to give mixtures.[12] When complexed to a group VI metal carbonyl $[M(CO)_4\{Ph_2PCHPPh_2\}]^-$,[13] it reacts as a carbonion ion. The data for elemental analysis and infrared spectra tabulated in Table I. The formation of the $[(CO)_4M(Ph_2P)_2C{=}CH_2]$ was obtained by heating $M(CO)_6$ with 1,1 bis-(diphenyl phosphino) ethene in decane solvent under reflux (M=Cr, Mo, and W).

The formation of the $[(CuCl_2)(Ph_2P)_2C{=}CH_2]$ was precipitated by heating $CuCl_2$ solution with 1,1 bis-(diphenyl-phosphino) ethene in methyl alcohol at room temperature or in decane solvent under reflux at least 5 h, the ^1H NMR spectral data are useful in characterizing their complexes.

Interaction of free ligand type $[Ph_2PCH{=}CHPPh_2]$ with some transition metals such as ($M = Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, and $CuCl_2$)

TABLE I Elemental Analysis of $[(CO)_4M\{(Ph_2P)_2C{=}CH_2\}]$ (A) and Their ($M = Cr^{+6}$, Mo^{+6}, and W^{+6}) Complexes

	% Elemental analysis calculated/(found)			IR spectra in cm^{-1}		Physical properties	
Compounds	C%	H%	N%	$\nu(CO)$	$\nu({=}CH_2^-)$ Vinylidene	Yield%	m.p.°C
				Four-member rings			
$C_{26}H_{22}P_2$ (**A**)	78.78 (A)	5.59	—	—	1651	31	114°C
Mol. Wt = 396.40	78.69 (B)	5.54			894	White	
$C_{30}H_{22}CrO_4P_2$	64.29 (A)	3.96	—	2000s, 1980w,	1652 m	82%	195°C
Mol. Wt = 560.44	63.87 (B)	3.99		1890w, 1860sb	890s	White	
$C_{30}H_{22}WO_4P_2$	52.05 (A)	3.02	—	2000s, 1980w,	1656 m	77%	215°C
Mol. Wt = 692.05	52.11 (B)	3.00		1891w, 1860b	887s	Yellow	
$C_{30}H_{22}MoO_4P_2$	59.62 (A)	3.67	—	2020, 1942,	1650 m	89%	201°C
Mol. Wt = 606.38	59.17 (B)	3.71		1850, 1850	892 s	White	

IR spectra: strong (s), weak (w), board (b).

TABLE II Elemental Analysis, IR Spectra of $[(CO)_4M\{(Ph_2P\text{–}CH{=}CH\text{—}PPh_2\}](B)$ and Their ($M = Cr^{+6}$, Mo^{+6}, W^{+6}, and Cu^{+2}) Complexes

	% Elemental analysis calculated/(found)			IR spectra in cm^{-1}		Physical properties		
Complexes	C%	H%	N%	ν(CO)	(CH=CH) *cis*	Yield%	Color	m.p.°C
				Six-member rings				
$C_{26}H_{22}P_2$(**B**)	78.78	5.59	—	—	—	31	White	85°C
Mol. Wt = 396.40	(78.75)	(5.57)		—	—		crystals	
$C_{30}H_{22}CrO_4P_2$	64.21	3.92	—	2000s, 1980w,	1673(v)	87	White	198°C
Mol. Wt = 560.44	(63.87)	(3.99)		1890w, 1860sb	974(s)			
$C_{30}H_{22}WO_4P_2$	52.25	3.02	—	2000s, 1980w,	1670(v)	74	White	230°C
Mol. Wt = 692.05	(52.11)	(3.00)		1890w, 1860b	978(s)			
$C_{30}H_{22}MoO_4P_2$	59.22	3.69	—	2020, 1942,	1669(v)	68	White	209°C
Mol. Wt = 606.38	(59.17)	(3.71)	—	1850, 1850	968(s)			
$C_{26}H_{22}Cl_2CuP_2$	58.98	4.21	—	2000s, 1980w,	1672(v)	94	Blue	187°C
Mol. Wt = 529.00	(58.83)	(4.18)	—	1890w, 1860b	978(s)			

IR spectra: strong (s), weak (w), board (b), variable (v).

by heating $M(CO)_6$ with 1,2-bis(diphenyl-phosphino) ethene in decane solvent under reflux (M = Cr, Mo, and W). The data for elemental analysis and infrared spectra tabulated in Table II. The formation of the $[(CuCl_2)Ph_2PCH{=}CHPPh_2]$ was precipitated by heating $CuCl_2$ solution with 1,2 bis-(diphenyl-phosphino) ethene in methyl alcohol at room temperature or in decane solvent under reflux at least 5 h, the ^{1}H NMR spectral data are useful in characterizing this complex.

^{1}H NMR, ^{1}H-{^{31}P} NMR Spectrum (400 MHz) and Mass Spectrum

A remarkable feature of the ^{1}H NMR and ^{1}H-{^{31}P} NMR spectrum of $[Ph_2\mathbf{P}C({=}CH_2)\mathbf{P}Ph_2]$ this complex was established by the presence of a "virtual triplet" with the extremely large splitting of ca. 60 and 400 Hz. Splitting equal to $[^3\underline{J}(\underline{P}\text{—C=C—}\underline{H})(\underline{cis}) + {}^3\underline{J}(\underline{P}\text{—C=C—}\underline{H})(\underline{trans})]$.[14,15]

Cis-1,2-ethylene diphosphine complexes $[(CO)_4M\{(Ph_2P)CH{=}CH(PPh_2)\}]$ is prepared by treatment of *cis*-1,2 diphenyl phosphino ethylene with hexacarbonyl metal in n-decane under reflux in oil bath at 250°C, (M = Cr and W), in 73% yield. A remarkable feature of the ^{1}H NMR spectrum of these complexes was confirmed by the presence of a single band at $\delta = 4.83$ ppm. This separation is equal to $[^3\underline{J}(\underline{P}\text{—CH=C—}\underline{H})(\underline{cis}) + {}^3\underline{J}(\text{—CH=C}\underline{\text{H—P}})(\underline{trans})]$ ^{3}J(PCCP) Coupling.[16] Studies of vicinal P—H[17] and P—C[18] coupling make it reasonable to expect a Karplus type of dependence of $^3J(^{31}PCC^{31}P)$

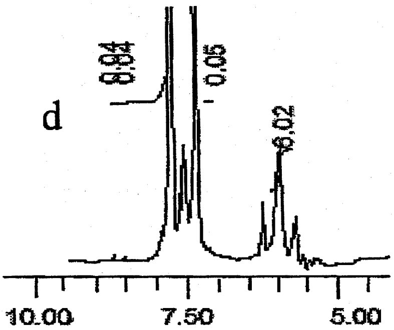
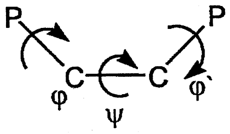


FIGURE 1 $^{1}H\text{-}\{^{31}P\}$ NMR of $[Ph_2PC(=CH_2)PPh_2]$.

coupling on dihedral angle ψ, defined as in V, and this is indeed so for the $^{3}J(^{31}P^{v}CC^{31}P)$ coupling, for example, for the ethylenic derivatives it is found that $J_{trans} > J_{cis}$. For the ethane derivative the value of ^{3}J $(^{31}P\text{-}^{31}P)$ is even greater than in the trans ethylene compound.

This is rather surprising if the observed coupling constant is a result of averaging over different conformation [cf. vicinal (H, H) coupling in ethane and ethylene[19] and suggests that there is a preponderance of



V

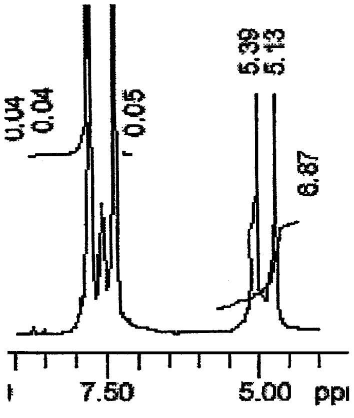


FIGURE 2 $^{1}H\text{-}\{^{31}P\}$ NMR of $[Ph_2PCH{=}CHPPh_2]$.

the conformer with phosphorus atoms mutually trans. In the diphosphines the conventional dependence of coupling constant on dihedral angle[20] does not hold, as demonstrated by the result $J_{cis} \gg J_{trans}$. This can be accounted for in terms of Ion-pair (I.p) orientation effects (i.e., the Ione pair —P—C—C dihedral angle φ and φ') and has previously been obtained[21,22] experimental for the coupling $^3J(^{31}PCCH)$. By analogy with these results it is to be expected that large positive values of $^3J(^{31}P—^{31}P)$. When the angles φ and φ' are both small. Therefore a conformation equal ($^3J = 105$ Hz). Molecular models suggest that the need to minimize interactions between the phenyl group is responsible for the adoption of this conformation, but in the trans isomer, the two diphenylphosphino-groups are sufficiently far apart to allow essentially free rotation about the two olefin C—P bounds. The mass spectra of these complexes showed a molecular ion peak, the isotopic distribution patterns of which were in agreement with the assigned molecular formula. In addition to the molecular ion, intense patterns were observed consistent with the consecutive loss of up three carbonyl ligands.

Addition of Amines and/or Amino Acids to the Complexes of Type (A)$[(CO)_4M\{(Ph_2P)_2C{=}CH_2\}]$ and Type (B)$[(Cl)_2Cu\{(Ph_2P)_2C{=}CH_2\}]$(M = Cr, Mo, W)

We have reported previously that the complex $[(OC)_4M\{Ph_2P)_2C{=}CH_2\}]$ undergoes Michael type addition with a variety of amines, hydrazine and amino acids to give functionalized phosphine complexes whereas the free ligand $(Ph_2P)_2C{=}CH_2$ (vdpp) is inactive toward these addition.[23] For example aniline to give $[(CO)_4M\{Ph_2P)_2CH—CH_2N—C_6H_5\}]$ and now report that such additions are extensive and can be used as the basis for the synthesis of a wide range of complexes containing functionalist diphosphines. A preliminary communication on this work has been published. We find that the free diphosphine $(Ph_2P)_2C{=}CH_2$, does not react with hydrazine either after prolonged heating 72 h with or without addition of hydrazine hydrochloride, or with amine after prolonged heated (48 h) with or without addition of concentrated hydrochloric acid but complexation, even to a relatively weakly electron withdrawing group, $M(CO)_4$ (M = Cr, Mo, and W) is sufficient to render the double bond $(C{=}CH_2)$ reactive toward Michael type addition. A toluene solution of the vinylidene tungsten complex $[(CO)_4W\{(Ph_2P)_2C{=}CH_2\}]$[24] when warmed and shaken with an excess of glycine (as amino acids) at room temperature or heated 8 h gave after 1 h a white solution and pale yellow crystalline adducts $[(CO)_4M\{(Ph_2P)_2CH—CH_2NH—CH_2COOH\}$

TABLE III Elemental Analysis of [$(CO)_4M\{(Ph_2P)_2CHCH_2NH{-}CH_3\}$] (M = Cr^{+6}, Mo^{+6}, and W^{+6}) Amino Complexes

Complexes	% Elemental analysis calculated/(found) C%	H%	N%	IR spectra in cm^{-1} ν(CO)	(NH)	Physical properties Yield%	Color	m.p.°C
$C_{31}H_{27}NO_4P_2W$ Mol. Wt = 723.34	51.09 (51.47)	3.80 (3.76)	1.95 (1.94)	2000s, 1980w, 1890w, 1860sb	3300s	87	White	255°C
$C_{31}H_{27}NO_4P_2Cr$ Mol. Wt = 591.49	62.75 (62.95)	4.71 (4.60)	2.37 (2.35)	2000s, 1980w, 1890w, 1860b	3290s	63	Yellow	225°C
$C_{31}H_{27}NO_4P_2Mo$ Mol. Wt = 635.44	57.98 (58.59)	4.12 (4.28)	2.20 (2.19)	2020, 1942, 1850, 1850	3305s	75	White	204°C

IR spectra: strong (s), weak (w), board (b).

(M = Cr or W)] in excellent (80%) yield Table III. The corresponding molybdenum and chromium complexes reacted similarly.

^{1}H NMR, ^{1}H-{^{31}P} NMR Spectrum (400 MHz)

The tungsten complex [$(CO)_4W\{(Ph_2P)_2CH^1{-}CH^2_2NH^3CH^4_3$] Figure 3 showed four multiples all showing first order coupling to one or more groups of protons. At $\delta = 1.97$ p.p.m, a triplet of relative intensity 1H was observed and assigned to CH^1 proton, coupling with two equivalent protons CH^2_2, J(CH^1 CH^2_2) = 7.1 Hz. A well resolved and sharp doublet is observed at $\delta = 2.86$ p.p.m. Assigned to CH^4_3 protons at $\delta = 2.73$ p.p.m, relative intensity 3H each. Finally a broad signal is observed at

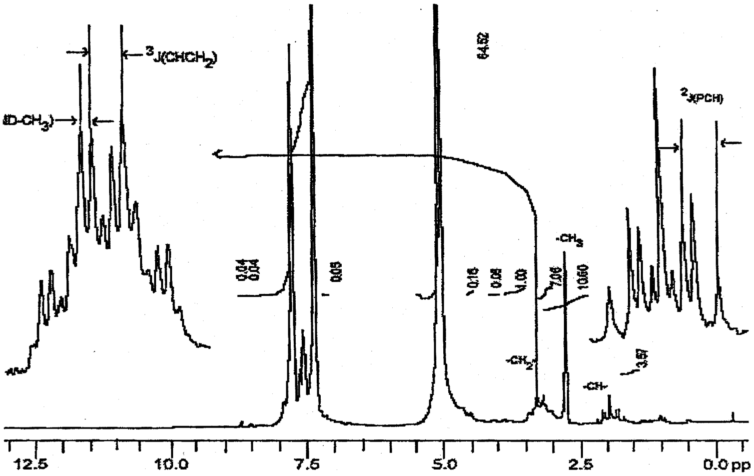


FIGURE 3 $^1H\{^{31}P\}$ NMR [$(CO)_4W\{(Ph_2P)_2CH^1{-}CH^2_2NH^3CH^4_3$].

$\delta = 0.85$ p.p.m, of relative intensity 1H assigned to the NH^3 proton which disappeared on addition of D_2O.

The ^1H-$\{^{31}P\}$ NMR spectrum of complex $[(CO)_4W\{(Ph_2P)_2CHCH_2NH{-}CH_3\}]$ is reproduced in Figure 3 and showed a triplet, adoublet of quartets and another triplet, of relative intensities corresponding to 1H, 2H, and 3H respectively. The triplet of relative intensity 1H is assigned to CH, coupling with two equivalent protons CH_2,^3J–(CH–CH_2) = 7.3 Hz. The doublet of quartets of relative intensity 2H is assigned to the CH_2, coupling to the methyl protons, $^5J(CH_2CH_3) = 2.5$ Hz and the triplet of relative intensity 3H is assigned to methyl protons coupling to the CH_2 protons. In the ^1H NMR spectrum, cupling to phosphorus was shown by the CH proton, the signal being a triplet of triplets, $^2J(PCH) = 10.0$ Hz and by the CH_2 protons, the signal become a triplet of quartets of quartets, $^3J(PCH_2) = 11$ Hz, these date and infrared data are tabulated in the following Tables IV and V.

Addition of Amines and Amino Acids to the Complexes of Type (B) $[(CO)_4M\{(Ph_2PCH{=}CH{-}PPh_2\}]$ and Type $[(Cl)_2Cu\{Ph_2PCH{=}CHPPh_2\}]$ (M = Cr, Mo and W)

Although tertiary phosphines are important ligands in chemistry, relatively little has been done with functionalist phosphines, partly because of difficulties in synthesis. The complex $[(OC)_4M\{(Ph_2PCH{=}CH(PPh_2)\}]$ undergoes Michael type addition with aniline to give

TABLE IV Infrared Spectra of Characteristic Complexes of Type (**A**) $[(CO)_4M\{(Ph_2P)_2CHCH_2\text{-}R\}]$ (M = Cr^{+6}, Mo^{+6}, and W^{+6})

Complex	R	M	ν(CO)/Cm^{-1}	ν(NH)Cm^{-1}
I(2c)	$-NHCH(COOH)CH_2(COOH)$	Cr	2020, 1960, 1890, 1855	3300
I(2a)	$-NHCH(COOH)CH_2(COOH)$	W	2025, 1940, 1858, 1850	3300
I(2b)	$-NHCH(COOH)CH_2(COOH)$	Mo	2020, 1945, 1890, 1840	3200
I(3c)	$-NHCH(COOH)CH_2(OH)$	Cr	2002, 1920, 1885, 1855	3300
I(3a)	$-NHCH(COOH)CH_2(OH)$	W	2002, 1930, 1890, 1860	3100
I(3b)	$-NHCH(COOH)CH_2(OH)$	Mo	2002, 1925, 1890, 1860	3200
I(4c)	$-NHCH(COOH)(CH_3)$	Cr	—	3300
I(4a)	$-NHCH(COOH)(CH_3)$	W	—	3300
I(4b)	$-NHCH(COOH)(CH_3)$	Mo	—	3100
I(5c)	$-NHCH_2(COOH)$	Cr	2250, 1920, 1860, 1810	3200
I(5a)	$-NHCH_2(COOH)$	W	2250, 1910, 1855, 1815	3100
I(5b)	$-NHCH_2(COOH)$	Mo	2250, 1900, 1860, 1810	3300
I(6c)	$-N(CH_3)_2$	W	2020, 1940, 1850, 1820	—
I(6a)	$-N(CH_3)_2$	Cr	2021, 1940, 1840, 1810	—
I(6b)	$-N(CH_3)_2$	Mo	2020, 1945, 1845, 1815	—

TABLE V ^{1}H-{^{31}P} NMR and Mass Spectral Data for Some Complexes of the Type **(A)** $[(CO)_4M\{(Ph_2P)_2CHCH_2–R\}](M = Cr^{+6}, Mo^{+6}, \text{and } W^{+6})$

Complex	M	R	$\frac{\delta(p)}{p.p.m}$	M$^+$
I(2c)	Cr	$–NHCH^a(COOH)CH_2{}^b(COOH)$	3.82^a, 2.58^b	693.08
I(3b)	Mo	$–NHCH^a(COOH)CH_2{}^b(OH)$	3.58^a, 3.88^b	711.05
I(4a)	W	$–NHCH^a(COOH)(CH_3{}^b)$	3.67^a, 1.23^b	781.37
I(7c)	Cr	$–NH\text{-}NH\text{-}Ph^{(o,m,p)}$	6.66^o, 7.18^m, 6.71^p	668.34
I(5a)	W	$–NHCH_2{}^a(COOH)$	3.49^a	767.25
I(6c)	Cr	$–N(CH_3)_2$	2.27^a	605.32

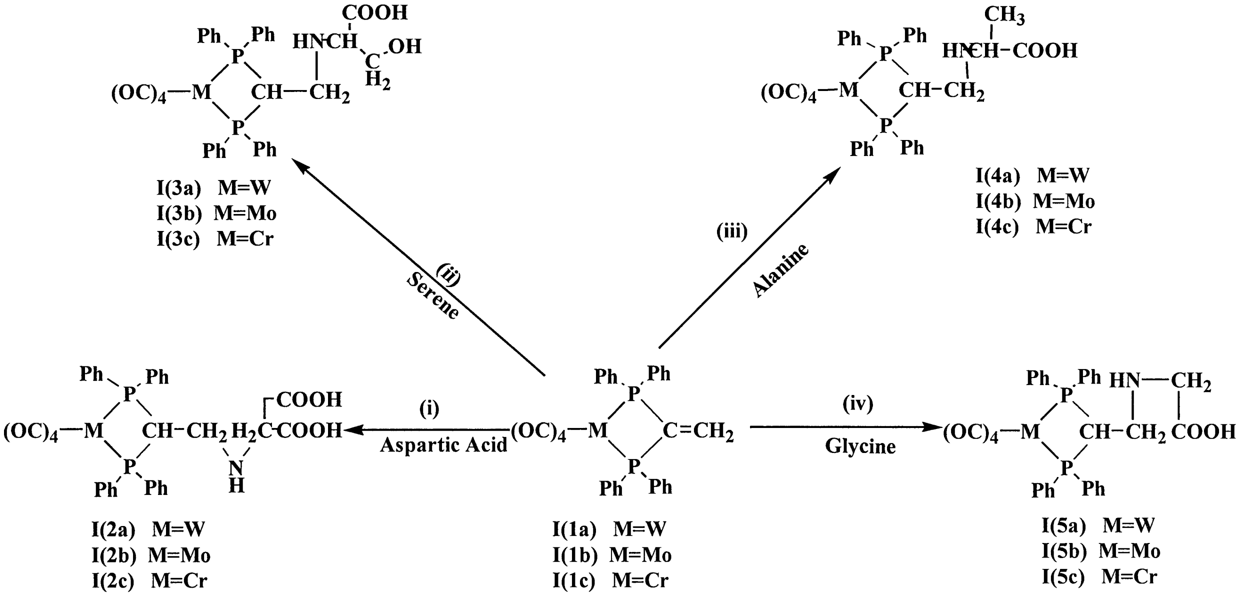
In $CDCl_3$, Chemical shifts, δ, at high frequency of TMS.
a = CH; b = CH_2; o, m, p = ortho, meta, para.

$[(CO)_4M\{Ph_2PCH–CH_2(PPh_2)N–C_6H_5\}]$ and now report that such additions are extensive and can be used as the basis for the synthesis of a wide range of complexes containing functionalist diphosphines (Scheme 1). We find that the free diphosphine $(Ph_2P)CH{=}CH(PPh_2)$, does not react with hydrazine either after prolonged heating (72 h) with or without addition of hydrazine hydrochloride, or with amine after prolonged heated (48 h) with or without addition of concentrated hydrochloric acid but complexation, even to a relatively weakly electron withdrawing group, $M(CO)_4$ (M = Cr, Mo, or W) is sufficient to render the double bond (–CH=CH–) reactive towards Michael type addition. Treatment of the trans complex $[(CO)_4M\{Ph_2PCH–CH_2(PPh_2)N–C_6H_5\}]$ with an excess of methyl amine at room temperature gave after one hour a white solution and pale yellow crystalline adducts, $[(CO)_4M\{(Ph_2P)_2CH–CH_2NHCH_3\}$ (M = Cr or W)] in excellent (87%) yield. The molybdenum complex was prepared in a similar fashion in >89% yield.

^{1}H NMR Spectrum (400 MHz)

The tungsten complex $[(CO)_4W\{Ph_2PCH^1–CH_2^2PPh_2NH^3CH_2^4COOH]$ showed four multiples all showing first order coupling to one or more groups of protons. At $\delta = 1.97$ p.p.m, a triplet of relative intensity 1H was observed and assigned to CH^1 proton, coupling with two equivalent protons CH_2^2, $^3J(CH^1\ CH_2^2) = 7.1$ Hz. A well resolved and sharp doublet is observed at $\delta = 2.86$ p.p.m. Assigned to CH_3^4 protons at $\delta =$ 3.99 p.p.m^1, relative intensity 3H each. Finally a 1H assigned to the NH^3 and COOH^5 proton which disappeared on addition of D_2O.

Methods of determining $J^3(^{31}P–^{31}P)$ in symmetrical compounds using ^{1}H-{^{31}P} double resonance experiments were some years age.[25] The ^{1}H-{^{31}P} NMR spectrum of complex $[(CO)_4W$



SCHEME 1 Chemistry related to the reactions of Vinylidine(diphenyl phosphino)ethene complexes $[\{(Ph_2P)_2\text{-}C{=}CH_2\}M^{n+}(CO)_4]$(M = W, Mo, and Cr).

{$Ph_2PCHCH_2PPh_2NH$—CH_3}] is reproduced and showed a triplet, a doublet of quartets, and another triplet, of relative intensities corresponding to 1H, 2H, and 3H, respectively. The triplet of relative intensity 1H is assigned to CH, coupling with two equivalent protons CH_2, $^3J(CH\text{—}CH_2) = 6.4$ Hz. The doublet of quartets of relative intensity 2H is assigned to the CH_2, coupling to the methyl protons, $^5J(CH_2CH_3) = 2.3$ Hz and the triplet of relative intensity 3H is assigned to methyl protons coupling to the CH_2 protons. In the H n.m.r. spectrum, Fig. (4), coupling to phosphorus was shown by the CH proton, the signal being a triplet of triplets, $^2J(PCH) = 9.8$ Hz and by the CH_2 protons, the signal become a triplet of quartets of quartets, $^3J(PCH_2) = 10$ Hz, these date and infrared data are shown in Table VI.

BIOLOGICAL EVALUATION

Antibacterial Activity

Data from the inhibition zones of various bacteria used Table VII revealed that these ligands and their chelates exhibited variable and pronounced activities against all bacteria (inhibition zones ranged from 0.80–10.00 mm). All compounds are potent effects against *Staphylococcus aurous*, *Serratia marcescens* expect B, II(7c), I(1a), I(1b), and II(1b). On the other hand, compounds, A, I(1c), I(3c), I(4c), A + Cu(II), II(1c), II(7c), and (B) are active against *Micrococcus roseus* (inhibition zones ranged from 0.75–11.5 mm) only.

TABLE VI Infrared Spectra of Characteristic Complexes Type (**B**) [$(CO)_4M$ {$(Ph_2P)_2CHCH_2$-R}]($M = Cr^{+6}, Mo^{+6}, W^{+6}$)

Complex	R	M	$\nu(CO)/Cm^{-1}$	$\nu(NH)Cm^{-1}$
II(8c)	$-NHCH(COOH)CH_2(COOH)$	Cr	2020, 1960, 1890, 1855	3300
II(8a)	$-NHCH(COOH)CH_2(COOH)$	W	2025, 1940, 1858, 1850	3300
II(8b)	$-NHCH(COOH)CH_2(COOH)$	Mo	2020, 1945, 1890, 1840	3200
II(7c)	$-NHCH(COOH)CH_2(OH)$	Cr	2002, 1920, 1885, 1855	3300
II(7a)	$-NHCH(COOH)CH_2(OH)$	W	2002, 1930, 1890, 1860	3100
II(7b)	$-NHCH(COOH)CH_2(OH)$	Mo	2002, 1925, 1890, 1860	3200
II(6c)	$-NHCH(COOH)(CH_3)$	Cr	—	3300
II(6a)	$-NHCH(COOH)(CH_3)$	W	—	3300
II(6b)	$-NHCH(COOH)(CH_3)$	Mo	—	3100
II(4c)	$-NHCH_2(COOH)$	Cr	2250, 1920, 1860, 1810	3200
II(4a)	$-NHCH_2(COOH)$	W	2250, 1910, 1855, 1815	3100
II(4b)	$-NHCH_2(COOH)$	Mo	2250, 1900, 1860, 1810	3300
II(3c)	$-N(CH_3)_2$	W	2020, 1940, 1850, 1820	—
II(3a)	$-N(CH_3)_2$	Cr	2021, 1940, 1840, 1810	—
II(3b)	$-N(CH_3)_2$	Mo	2020, 1945, 1845, 1815	—

TABLE VII Antimicrobial Screening of Some Diphenyl Phosphine Ligands and Their Cu(II), W(VI), Cr(VI), and Mo(VI) Chelates (Inhibition Zones in mm)

	Antibacterial activity						Antifungal activity								
Compd	Serratia Marce-scens DSM 1608[a]	Bacillus cereus DSM 345	Pseudo-monas aeruginosa DSM 1299	Micro-coccus roseus DSM 348	Klebsiella Pneumoniae DSM 581	Staphyl-lococcus aureus DSM 346	Asper-gillus Flavus Link AUCC[B] 164	Penicill-ium Chryso-genum Thom AUCC530	Alternaria alternata (Fries) Keissler AUCC 1110	Fusarium equisioti DSM 62203	Alternaria tenussima DSM 63360	Aspergillu stammarii ATCC[d] 10836	Penicillium digirtatum DSM 62840	Penicill-ium paxilli CBS[e] 28047
A	1.00	3.50	−*ve*[c]	0.75	−*ve*	3.00	−*ve*	8.50	5.00	0.95	6.00	10.0	−*ve*	−*ve*
I(1c)	2.10	5.00	−*ve*	1.90	2.80	4.50	−*ve*	2.50	−*ve*	4.50	4.10	6.00	1.80	−*ve*
I(3c)	8.20	7.00	5.00	7.60	−*ve*	9.50	−*ve*	4.00	2.50	6.00	6.50	6.10	−*ve*	−*ve*
I(4c)	3.00	3.80	5.80	6.80	−*ve*	4.00	3.00	2.80	1.50	9.50	−*ve*	4.00	3.80	−*ve*
B	−*ve*	−*ve*	−*ve*	−*ve*	−*ve*	2.50	−*ve*	1.00	3.00	1.80	4.00	−*ve*	−*ve*	−*ve*
II(1c)	5.10	1.80	−*ve*	4.80	3.00	5.00	1.00	4.00	−*ve*	6.50	6.70	−*ve*	−*ve*	6.00
II(7c)	−*ve*	−*ve*	−*ve*	1.50	-	7.50	7.80	−*ve*	−*ve*	−*ve*	2.00	−*ve*	−*ve*	4.10
II(6c)	7.80	8.50	7.90	7.00	3.80	6.85	4.50	3.80	−*ve*	8.02	−*ve*	4.50	−*ve*	4.00
I(1a)	3.20	−*ve*	−*ve*	−*ve*	2.00	3.00	−*ve*	−*ve*	2.00	−*ve*	−*ve*	−*ve*	1.50	−*ve*
I(1b)	5.50	−*ve*	−*ve*	−*ve*	3.40	7.50	4.90	1.80	−*ve*	−*ve*	−*ve*	−*ve*	−*ve*	−*ve*
II(1a)	−*ve*	0.80	−*ve*	−*ve*	−*ve*	1.50	1.70	2.90	−*ve*	1.01	−*ve*	−*ve*	−*ve*	−*ve*
II(lb)	0.80	−*ve*	1.80	−*ve*	−*ve*	1.10	1.20	3.00	1.10	0.61	−*ve*	−*ve*	8.80	−*ve*
A + Cu(II)	8.00	9.50	−*ve*	11.5	8.10	10.0	6.70	11.0	9.80	11.50	8.80	10.0	−*ve*	2.00
B + Cu(II)	1.80	3.00	−*ve*	−*ve*	−*ve*	5.20	−*ve*	−*ve*	−*ve*	1.00	−*ve*	5.80	2.00	−*ve*

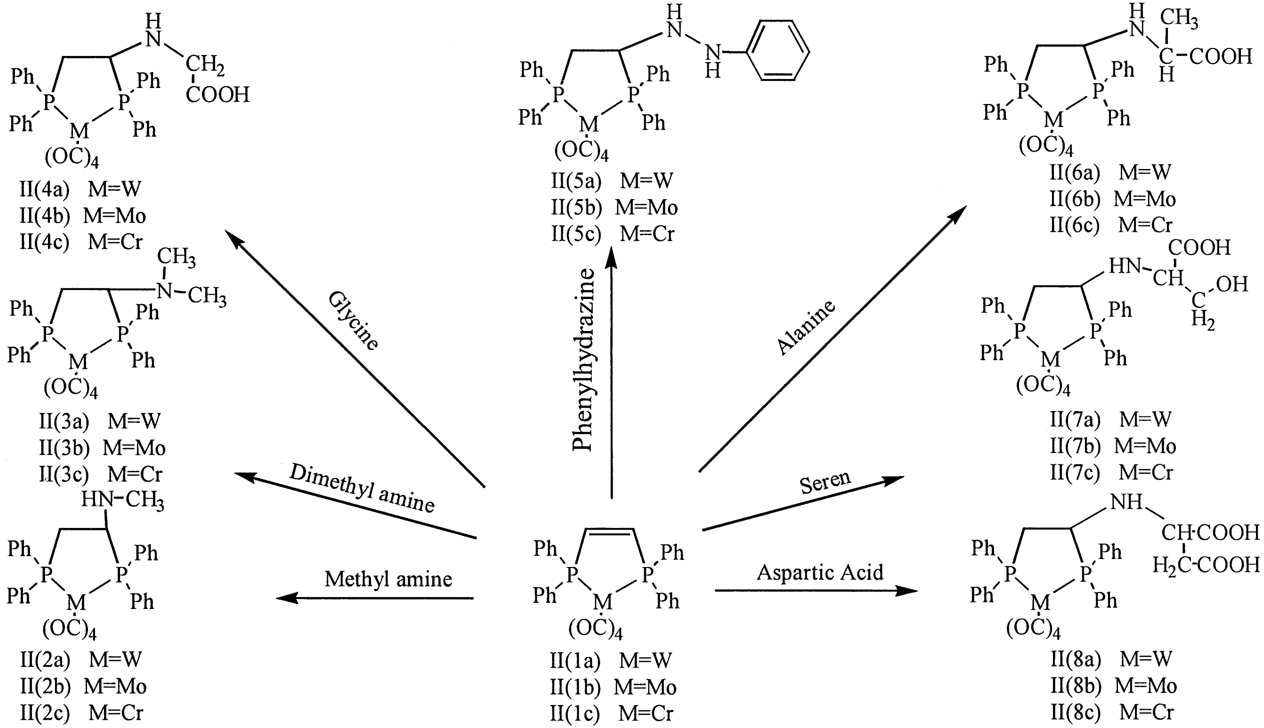
[a] DSM = Deutsche Semmlungvos Microorgamifman (German Collection of microorganisms).

[b] AUCC = Assiut University Culture Collection.

[c] (−*ve*) = Compound not active biological.

[d] ATCC = America Culture Collection.

[e] CBS = Holland culture collection.



SCHEME 2 Chemistry related to the reactions of *cis*-1,2 bis(diphenyl phosphino)ethene complexes $[\{(Ph)_2P{-}CH{=}CH{-}P(Ph)_2)\}M^{n+}(CO)_4]$(M = W, Mo, and Cr).

Antifungal Activity

The antifungal results table clearly show that all compounds are highly effective against *Penicilliu chrysogenum*, *Aspergillus fiavus* (link), and/or *Alternaria alternata* (Fries) expect A, I(3c), II(1c), II(7c), B, A + Cu(II), I(1b), and II(1a) derivatives (inhibition zones ranged from (1.00–9.80 mm). Interestingly, the synthesized compounds showed good and more antifungal than antibacterial activities.

Furthermore, compound I (3C) type of (A) with serene (amino acid) chromium and compound A-Cu(II) vinyl copper complexes are highly biologically active against all bacteria and fungi used (inhibition zones) ranged from (1.90–9.50 mm) for bacteria and (2.00–11.00 mmm) for fungi. Also compound II(6c) type of (B) with alanine (amino acid) chromium are potent active against *all bacteria* used (inhibition zones ranged from 3.80–8.5 mm).

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