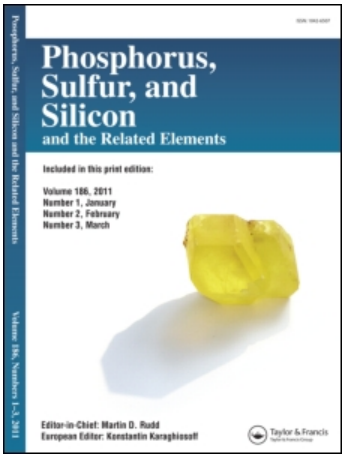

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Diphosphine Compounds, Part III: UV/Visible Spectroscopy and Novel Routes to Functionalized Diphosphine-$M(CO)_6$ Complexes (M = W, Mo, or Cr)

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Diphosphine Compounds, Part III: UV/Visible Spectroscopy and Novel Routes to Functionalized Diphosphine-M(CO)$_6$ Complexes (M = W, Mo, or Cr)

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*Reaction of coordinated (diphenylphosphino)methane and ketones or aldehydes have been characterized by $^{31}P\{H^1\}$-NMR, $^{1}H\{^{31}P\}$-NMR, and UV/vis spectroscopy in dichloromethane. Group VI metals hexacarbonyl [$M(CO)_6$ where M = Cr, Mo, and W] reacted with (diphenylphosphino)methane, [$(Ph_2P)_2CH_2$], to give [$(OC)_4M\{(Ph_2P)_2CH_2\}$] depending upon the reaction conditions. Condensation of [$(CO)_4M\{(Ph_2P)_2CH_2\}$] with different ketones or aldehydes forms [$(CO)_4M\{(Ph_2P)_2C = CR_1R_2\}$]. Complexes of the types [$(OC)_4M\{(Ph_2P)_2C = CR_1R_2\}$] reacted with hydrazine in a Michael addition to give [$(CO)_4M\{(Ph_2P)_2CHC(R_1R_2)NHNH_2\}$](**1.3a–e**), which condensed with different ketones and aldehydes to give complex of the type [$(CO)_4M\{(Ph_2P)_2CHC(R_1R_2)NHN = C(R_3)$] (**1.4a–e**). The structures of the complexes are discussed on the basis of elemental analysis (EA), IR, ^{1}H-NMR, ^{31}P-NMR spectroscopic data, and FAB mass spectra. The UV/vis spectra show two absorption bands with the low energy band moving to lower energy with increasing substitution on the (diphenylphosphino) methane (dppm) (a bathochromic effect).*

Keywords Diphosphine compounds; organometallic; transitions metal complexes; UV/visible spectroscopy

INTRODUCTION

Although tertiary phosphine ligands are important ligands in coordination and organometallic chemistry and essential components in many catalytic systems, relatively little has been reported with regard to functionalized phosphines.[1–3] This is partly due to the multistage synthesis often required, particularly in the case of bidentate ligands. Our attention has been centered on substitution reactions involving loss of

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carbon monoxide from the metal hexacarbonyl complexes [$M(CO)_6$] by the bidentate phosphine ligand (dppm). In the last two decades, there has been a great deal of interest in the preparation and characterization of transition metal carbonyl complexes stabilized with multidentate ligands.[4–15] We have reported that, although the vinylidine double bond in uncoordinated 1,1-bis(diphenylphosphino)ethene (Vdpp) is not susceptible to attack, complexation susceptible to nucleophilic attack, complexation to the fragment $M(CO)_4$ (M = Cr, Mo, or W) activates the double bond such that a variety of nucleophiles (amines, hydrazines, amino acids) can undergo conjugate or Michael addition to it under mild conditions.[1,3,4] We now report on the synthesis, characterization, and novel route to functionalized diphosphine-$M(CO)_4$ complexes (M = Cr, Mo, or W).

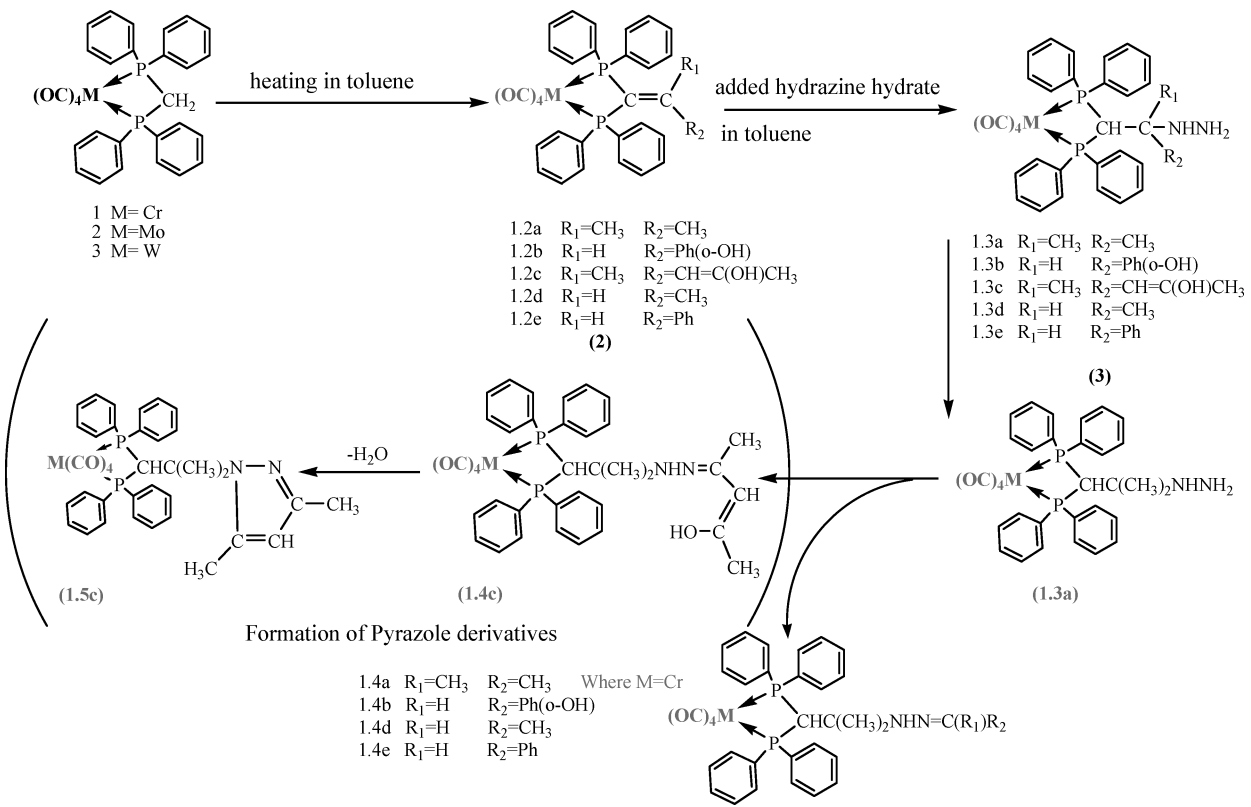
RESULTS AND DISCUSSION

The synthesis and characterization of the new derivatives of (diphenylphosphino)ethene metal complexes are illustrated in Scheme 1.

All complexes can be prepared by treatment of the chromium complexes (as an example) of the type [$(OC)_4M\{(Ph_2P)_2C{=}CH_2\}$] with acetone, salicylaldehyde, acetylacetone, acetaldehyde. and benzaldehyde (formed by condensation reaction) to give complexes of the type [$(OC)_4M\{(Ph_2P)_2C{=}CR_1R_2\}$] (**1.2a–e**) in toluene. Complexes (**1.2a**) to (**1.2e**) underwent Michael addition with hydrazine and yielded [$(CO)_4M\{(Ph_2P)_2CHC(R_1R_2)NHNH_2\}$] (**1.3a–e**). Alkyl- and arylhydrazines have a very extensive chemistry, and we found that compounds [$(OC)_4Cr(Ph_2P)_2CHCR_1R_2NHNH_2\}$](**1.3a–e**) readily undergo condensation reactions with organic carbonyl compounds; thus, condensation of complexes of the types [$(CO)_4M\{(Ph_2P)_2CHC(R_1R_2)NHNH_2\}$] (**1.3a–e**) with acetone, salicylaldehyde, acetylacetone, acetaldehyde, and benzaldehyde yielded adducts of the type [$(CO)_4M\{(Ph_2P)_2CHC(R_1R_2)NHN = C(CH_3)_2\}$] (**1.4a**), [$(CO)_4M\{(Ph_2P)_2CH\text{-}C(R_1R_2)NHN = CHPh(o\text{-}OH)\}$] (**1.4b**), [$(CO)_4M\{(Ph_2P)_2CHC(R_1R_2)NHN = C(CH_3)CH = C(OH)CH_3\}$] (**1.4c**), [$(CO)_4M\{(Ph_2P)_2CHC(R_1R_2)NHN = CHCH_3\}$] (**1.4d**), and [$(CO)_4M\{(Ph_2P)_2CH\text{-}C(R_1R_2)NHN = CHPh)\}$] (**1.4e**), whose structures were investigated by spectroscopic techniques. Complexes were formed upon treatment of complexes of (**1.4a–e**) with acetylacetone for prolonged heating (see the Experimental section).

Condensation with Acetone

Treatment of the tungsten-hydrazine adduct in toluene with a slight excess (20%) of acetone) after heating ca. 1 h under dinitrogen gave the



SCHEME 1

tungsten adduct $[(OC)_4W\{(Ph_2P)_2CH^1\ C(CH_3{}^2\ )_2NH\ {}^3N = C(CH_3{}^4)_2\}]$ (**3.4a**) in >70% yield as yellow crystals. We assigned the structure of this adduct on the basis of the following data. The elemental analysis was satisfactory. The $^{31}P\text{-}\{^1H\}$ NMR spectrum showed a singlet at δ (chemical shift) $= -1.7$ ppm with ^{183}W satellites, $^1J(WP)/Hz$ (coupling constant) $= 205$. The ^1H and $^1H\text{-}\{^{31}P\}$ NMR spectra showed four signals (excluding aromatic hydrogen). At $\delta = 3.73$ ppm, a triplet of relative intensity 1H is observed and assigned to CH^1. A singlet is centered at $\delta = 1.64$ ppm, of relative intensity 6H, assigned to $CH_3{}^2$ protons. A singlet at $\delta = 1.91$ p.p.m of relative intensity 6H is observed, assigned to $CH^4{}_3$ proton. Finally a broad signal is observed at $\delta = 1.72$ ppm of relative intensity 1H, assigned to NH^3 proton. These signals due to NH disappeared on addition of D_2O. In the ^1H NMR spectrum, coupling to phosphorus is shown by the protons CH^1, $^2J(\underline{P}C\underline{H}^1) = 10$ Hz. The infrared spectrum showed υ(NH) at 3300 cm^{-1}.

Condensation with Salicylaldehyde

Treatment of the tungsten-hydrazine adduct in toluene with a slight excess (20%) of salicylaldehyde after heating ca. 1 h under dinitrogen gave brown crystals of the tungsten adduct in >80% yield of $[(OC)_4W\{(Ph_2P)_2CH^1C(CH_3{}^2)_2NH^3N = CH^4(Ph(o\text{-}OH^5)\}]$ (**3.4b**). We assigned the structure of this adduct on the basis of the following data. The elemental analysis was satisfactory. The $^{31}P\text{-}\{^1H\}$ NMR spectrum showed a singlet at $\delta = -4.08$ ppm with ^{183}W satellites, $^1J(WP)/Hz = 203$. The ^1H and $^1H\text{-}\{^{31}P\}$ NMR spectra showed five signals (excluding aromatic hydrogen). At $\delta = 5.44$ ppm, a triplet of relative intensity 1H is observed and assigned to CH^1. A singlet is centered at $\delta = 1.66$ ppm, of relative intensity 6H, assigned to $CH_3{}^2$ protons, coupling with the CH^1 proton. A singlet at $\delta = 8.01$ ppm of relative intensity 1H is observed, assigned to CH^4 proton. Another singlet at $\delta = 10.67$ ppm of relative intensity 1H, is observed and assigned to the OH^5 proton. Finally a broad signal is observed at $\delta = 1.49$ ppm of relative intensity 1H, assigned to NH^3 proton. These signals due to OH and NH disappeared on addition of D_2O. In the ^1H NMR spectrum, coupling to phosphorus is shown by the protons CH^1, $^2J(\underline{P}C\underline{H}^1) = 10$ Hz. The infrared spectrum showed υ(OH) at 3240 cm^{-1} and υ(NH) at 3300 cm^{-1}.

Formation of a Pyrazole Derivative

Hydrazine complexes of the type $[(OC)_4W\{(Ph_2P)_2CHC(CH_3)_2NHNH_2\}]$ were reacted with acetylacetone to give a pyrazole derivates, and upon

TABLE I ^{31}P-{^{1}H} NMR[a] and Infrared[b] Data for Some Condensation Products of [$(OC)_4W\{(Ph_2P)_2CHC(CH_3)_2NHNH_2\}$] with Acetone, Acetylacetone, or Salicylaldehyde

Complex	M	δ(P)[a] ppm	^{1}J(WP) Hz	(υ(CO)/cm^{-1}) [ν(P-C)][b]	υ(NH)/cm^{-1}
3.5c	W	−4.23	205	(2005s, 1960w, 1885w, 1865sb)[715s]	—
3.4c[f]	W	−4.93	207	(2005s, 1930w, 1885w, 1865sb) [692s]	3300
3.4b	W	−4.08	203	(2005s, 1940w, 1890w, 1870sb) [721s]	3300
3.4a	W	−1.7	205	(2010s, 1984w, 11891w, 1865sb) [682s]	3250
3.4d	W	−2.6	205	(2017s, 1942w, 1893w, 1852sb) [702s]	3300
3.4e	W	−4.20	203	(2000s, 1981w, 1892w, 1860sb) [695s]	3300

(a) In $CDCl_3$ (b) In KBr discs (f) υ(OH) = 3240 cm^{-1} (s) Strong, (w) Weak, and (sb) Strong board.

heating the tungsten-hydrazine adduct with 1 mol equivalent of acetylacetone in toluene for a prolonged period (ca. 16 h), pale brown crystalline product formed, which we formulated as the pyrazole derivatives (**3.4c**) and [$(OC)_4W\{(Ph_2P)_2CH^1C(N^*N = C(CH_3)^2CH^3 = C^*CH_3{}^4)(CH_3)_2{}^5\}$] (**3.5c**). This complex was formulated on the following basis of the following data. The elemental analysis was satisfactory [Found: C, 54.40; H, 4.25; N, 3.42%]. The ^{31}P-{^{1}H} NMR spectrum showed a singlet at $\delta = -4.93$ ppm with ^{183}W satellites. ^{1}J(WP)/Hz = 207 (see Table I for data). The ^{1}H-{^{31}P} and ^{1}H NMR spectra (Figure 1) showed five signals. At $\delta = 6.35$ ppm, a triplet of relative intensity 1H is observed and is assigned to CH^1 proton. A singlet of relative intensity 1H at $\delta = 5.43$ ppm is observed and is assigned to (–N-N = C-CH^3) proton coupling with CH_3 protons, ^{4}J($\underline{CH}$-C-$\underline{CH_3}{}^4$) = 2.5 Hz. A strong single is observed at $\delta = 2.67$ ppm of relative intensity 6H, assigned to $2CH_3{}^5$ protons. Two singlets are observed at $\delta = 1.39$ ppm and $\delta = 2.17$ ppm of relative intensity 3H each, assigned to two methyl protons $CH_3{}^2$ and $CH_3{}^4$. It is difficult to distinguish between the two. It showed coupling to phosphorus by the CH^1 proton, the signal being a triplet of triplets, ^{3}J($\underline{PCH}$) = 12 Hz. The infrared spectrum was characteristic of a cis-chelated tetracarbonyl complex. The υ(N-H) band had disappeared.

The Electronic Spectra of Synthesized Diphosphine Derivative Complexes

The electronic absorption spectral data λ_{max} and ε_{max} values for the synthesized diphosphine derivatives chromium complexes as an

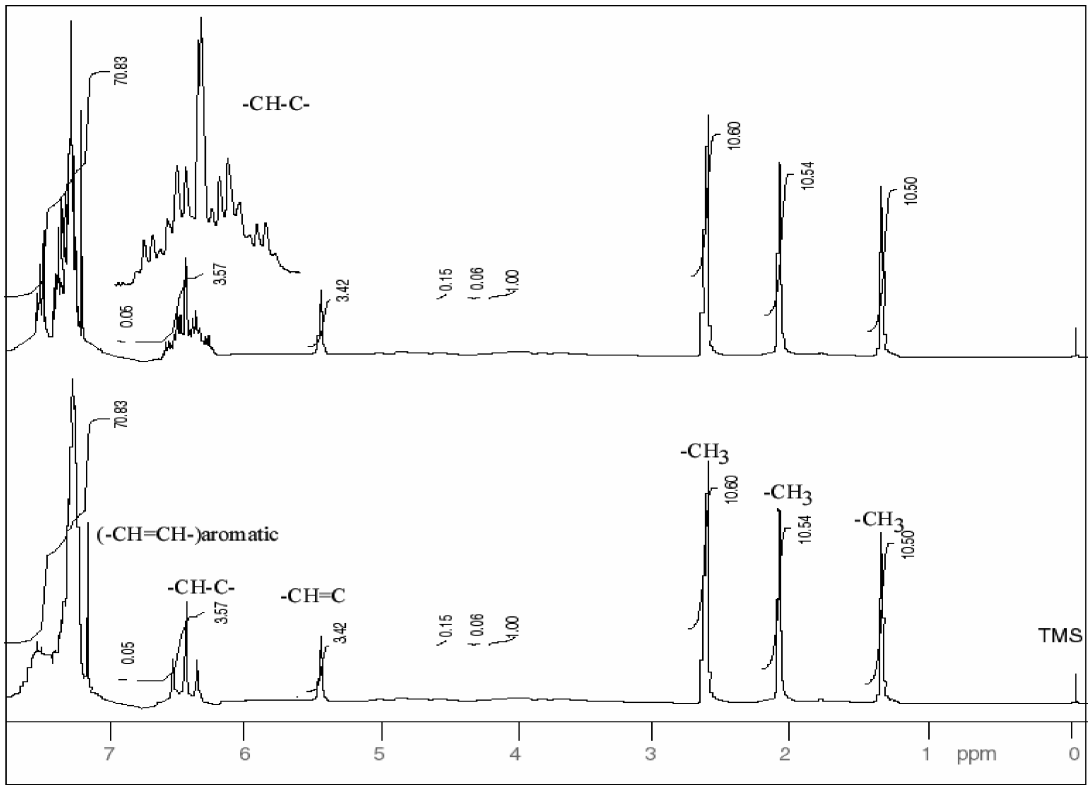


FIGURE 1 ^{1}H-{^{31}P} and ^{1}H NMR spectra for the complex $[(OC)_4W\{(Ph_2P)_2CHC(CH_3)_2N\text{-}N=C(CH_3)CH=C(CH_3)\}]$.

TABLE II UV/Vis Data for Phosphino-Substituted Hydrazine Chromium Complexes in CH_2Cl_2

Compound	λ_{max}/nm (ε/L mol^{-1}$_{Cm}$$^{-1}$)	λ_{max}/nm (ε/L mol^{-1}$_{Cm}$$^{-1}$)
$C_{29}H_{22}CrO_4P_2$ (1)	—	546 (340)
$C_{33}H_{26}CrO_4P_2$ (1.2a)	420 (655)	561 (280)
$C_{32}H_{30}CrN_2O_4P_2$ (1.3a)	440 (860)	570 (330)
$C_{37}H_{36}CrN_2O_5P_2$ (1.4c)	453 (1132)	594 (450)
$C_{37}H_{34}CrN_2O_4P_2$ (1.5c)	442 (740)	581 (350)

example (**1.2a, 1.3a, 1.4a, 1.5a**) in dichloromethane are presented in Table II. The visible absorption spectra of these chromium complexes exhibit various absorption bands within the wavelength range λ = 350–700 nm. These absorption bands depend primarily on the terminal group (hydrazine derivatives), their linkage position,[16,17] and the type of the transient metal complex. The visible absorption maxima of diphosphine derivatives chromium (dppm) complexes in CH_2Cl_2 undergo bathochromic or hypsochromic shifts, depending on the nature of the aliphatic and aromatic aldehydes and ketones (which undergo condensations reaction) gave complexes of the type $[(OC)_4Cr\{(Ph_2P)_2C{=}C(CH_3)CH_3\}]$ (**1.2a**). Thus, substituting acetonyl group in compound (**1.4c**) typically exhibits two UV/vis absorption bands (with extinction coefficients between 250 and 880 L mol^{-1}cm^{-1}), one band near 410 nm and the other near 550 nm. These bands are likely to be d–d transitions since the HOMO is largely metal-based, and the extinction coefficients are less than 1000 L mol^{-1} cm^{-1}. It has been observed that for methyl substitution, the UV/vis spectra vary by only 15 nm (546–561 nm) (a bathochromic shift).

For $[(OC)_4W\{(Ph_2P)_2CHC(NHN = C(CH_3)CH = C(OH)CH_3)(CH_3)_2\}]$, we found that the UV/vis absorption peaks change by 15–24 nm, whereas for pyrazole, all of the UV/vis absorption peaks shift to lower wavelength by 11–13 nm. Apparently, the σ^* orbitals of the tetra carbonyl transition metals groups have a significant influence on the pyrazole ring MOs, thus affecting the bands in the UV/vis spectra. Table II gives the absorptions for the phosphino derivatives illustrated in Scheme 1 and typical UV/vis spectra (hyrazine and pyrazole) are shown in Figure 2. It can be seen from Figure 2 that the hydrazine and pyrazole substituted both exhibit two bands in the UV/vis spectra and that these occur at similar energies. Although some extinction coefficients for the high energy band are over 1000 L mol^{-1} cm^{-1}, it should be noted that these absorptions

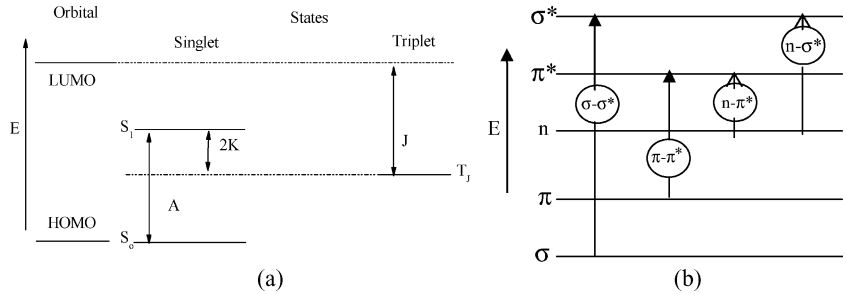


FIGURE 2 (a) Energy scheme for the electronic transition between HOMO and LUMO. (b) Molecular orbitals and electron transitions.

overlap with a charge transfer band. Unfortunately, we were unable to obtain meaningful UV/vis spectra for the satirically congested, and consequently sensitive, complex of the type $[(OC)_4Cr\{(Ph_2P)_2CH_2]$ (band at near 420 nm).

The UV/vis spectroscopy provides information on the HOMO–LUMO gap in both derivatives **1.4c** and **1.5c**. It is assigned to a ligand to metal charge transfer (LMCT) process from diphenylphosphino to a d° metal center in the complexes rather than a d–d transition of the chromium atom. One must be careful, therefore, when making comparisons between these derivates. $[(OC)_4W\{(Ph_2P)_2CHC(NHN = C(CH_3)CH = C(OH)CH_3)(CH_3)_2\}]$ typically exhibit two UV/vis

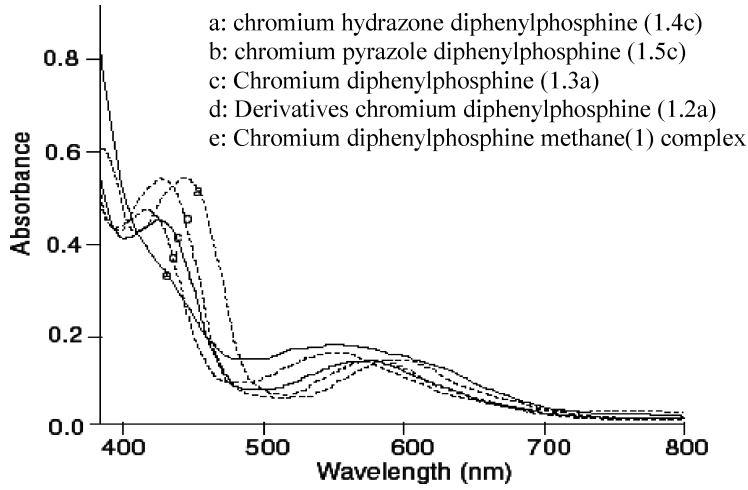


FIGURE 3 Typical UV/vis spectra of phosphino-substituted transition metals (group VI) complexes in CH_2Cl_2.

absorption bands (with extinction coefficients of between 300 and 900 L mol^{-1} cm^{-1}), one near 450 nm, and the other near 590 nm. Pyrazole derivatives (**1.5c**) exhibit two UV/vis absorption bands, one near 420 nm and the other near 550 nm. These bands are likely to be d–d transitions, since the HOMO is largely metal-based[18–25] and the extinction coefficients are less than 1000 L mol^{-1} cm^{-1}.

EXPERIMENTAL

Apparatus

Melting points were recorded on a Galenkamp melting point apparatus and are uncorrected. Elemental analyses were carried out at the Micro Analytical Center (Assiut University). The IR spectra (KBr) were determined on a Shimadzu corporation Chart 200-91527 spectrophotometer. ^{1}H NMR spectra were recorded with a Bruker AMX-250 spectrometer (40.25 MHz). Mass spectra were recorded on HPMs 6988 spectrometer and electron-impact (EI). Visible spectra (300–999 nm) were recorded on Shimadzu UV/vis160-A spectrophotometer at the Aswan Faculty of Science. All reagents and solvents were obtained from Aldrich Chemical Company (Milwaukee, WI, USA).

Preparation of Organometallic Compounds: $[(OC)_4Cr\{(Ph_2P)_2C{=}CR_1R_2\}]$(1.2a–1.2e) [Where ($R_1$ = CH_3, H, CH_3, H, H and R_2 = CH_3, Ph(o-OH), CH = $C(OH)CH_3$, CH_3, Ph)]

Acetone, salicylaldehyde, acetylacetone, acetaldehyde, and benzaldehyde in toluene (0.5 mL) were each added to a suspension of $[(OC)_4Cr\{(Ph_2P)_2CH_2\}]$ (0.15 g, 0.28 mmol). The mixture was then heated to *ca.* 80°C for 5–20 min during which period the chromium complexes dissolved and a new crystalline precipitate formed. These were filtered off, washed with Et_2O, and dried giving the required products $[(OC)_4Cr\{(Ph_2P)_2C{=}C(CH_3)_2\}]$ (brown) (**1.2a**), $[(OC)_4Cr\{(Ph_2P)_2C{=}CHPh(o\text{-}OH)\}]$ (yellow) (**1.2b**), $[(OC)_4Cr\{(Ph_2P)_2C{=}C(CH_3)CH = C(OH)CH_3\}]$ (pale brown) (**1.2c**), $[(OC)_4Cr\{(Ph_2P)_2C{=}CHCH_3\}]$ (brown) (**1.2d**), and $[(OC)_4Cr\{(Ph_2P)_2C{=}CHPh\}]$ (dark brown) (**1.2e**), respectively. The final products were recrystallized from ether-methanol. Data are listed in Table (2)

Preparation of $[(OC)_4W\{(Ph_2P)_2C{=}C(CH_3)_2\}]$ (3.2a)

Acetone in toluene (0.5 mL) was added to a suspension of $[(OC)_4W\{(Ph_2P)_2CH_2\}]$ (0.19 g, 0.28 mmol). The mixture was then heated to *ca.* 80°C for 5 min, during which period the tungsten

TABLE III Characterization Data of the Newly Synthesized (Diphenylphosphino)ethene Derivative Complexes

Compd. No	Mol. formula (mol. wt.)	Calcd.%,(Found) % C	H	N	Yield%	m.p., °C	IR (ν^{KBr} max), cm^{-1}	$^1H\{^{31}P\}$-NMR($CDCl_3$) δ, ppm, Assignment	M^+
1.2a	$C_{32}H_{26}CrO_4P_2$	65.31	4.45	—			2010s, 1980,1892w,1860sb (νCO)	1.73(s, 6H, CH_3 methyl)	588.07
	(588.49)	(64.98)	(4.50)	—	73	201–211	720s, 690s single band (ν P-C)	{7.25(s, 4H, p-CH)}, {7.11(s, 8H, o-CH)}	
				—				{7.53(s, 8H, m-CH)}aromatic ring	
1.2b	$C_{36}H_{26}CrO_5P_2$	66.26	4.02	—			2000s, 1980,1892w,1860sb (νCO)	4.68(wb, 1H, OH(o-Ph) salicylaldehyde)	652
	(652.53)	(66.32)	(4.11)	—	64	198–203	720s, 690s single band (ν P-C)	7.92(s, 1H, -C=CH- ethylene)	
				—				{6.92–7.56 (s, 5H, 10H, 9H), p-CH, o-CH and m-CH)} aromatic ring	
1.2c	$C_{34}H_{28}CrO_5P_2$	64.77	4.48	—			2000s, 1980w,1890w, 1860sb (νCO)	10.03(wb, 1enol, OH) –C=C(OH)CH_3	630
	(630.53)	(64.59)	(4.52)	—	82	223–231	725s, 685s single band (ν P-C)	1.71(s, 3H, methyl,1beta –CH=C) 2.07(s, 3H, methyl,1alpha -C=C) 3.23(w, 1H, 1-ethylene –C=C) {7.13–7.62(s, 4H, 8H, 8H)} aromatic ring	
1.2d	$C_{31}H_{24}CrO_4P_2$	64.81	4.21	—			2000s, 1985,1892w,1860sb (νCO)	1.87(s, 3H, methyl,1alpha -CH=C)	574
	(574.46)	(65.02)	(4.23)	—	81	186–192	720s, 690s single band (ν P-C)	5.73(m, 1H, 1-ethylene –C=C) {7.12–7.42(s, 4H, 8H, 8H)} aromatic ring	
1.2e	$C_{36}H_{26}CrO_4P_2$	67.93	4.12	—			2005s, 1980,1890w,1860sb (νCO)	6.69(m, 1H, 1-ethylene –C=C)	637
	(636.53)	(67.90)	(4.10)	—	75	203–210	720s, 690s single band (ν P-C)	{7.15–7.59(s, 5H, 10H, 10H)} aromatic ring	

(Continued on next page)

TABLE III Characterization Data of the Newly Synthesized (Diphenylphosphino)ethene Derivative Complexes *(Continued)*

Compd. No	Mol. formula (mol. wt.)	Calcd.%,(Found) %			Yield%	m.p., °C	IR (ν^{KBr} max), cm^{-1}	$^1H\{^{31}P\}$-NMR($CDCl_3$)	M^+
		C	H	N				δ, ppm, Assignment	
1.3a	$C_{32}H_{30}CrN_2O_4P_2$	61.94	4.87	4.51			2000s, 1985,1892w,1860sb (νCO)	2.48(w, 1NH, $2NH_2$, amine)	621
	(620.54)	(62.05)	(4.85)	(4.63)	77	211–219	720s, 690s single band (ν P-C)	3.72(w, 1H, methine, 1 beta -N)	
							3300w, (ν (NH))	1.56(s, 6H, methyl –CH)	
								{6.85–7.57(s, 4H, 8H, 8H)}aromatic ring	
								2.26(w, 1NH, $2NH_2$, amine)	
1.3b	$C_{36}H_{30}CrN_2O_5P_2$	63.16	4.42	4.09			2005, 1980,1892w,1865sb (νCO)	4.39(s, 1H, methine, 1 beta -N)	620
	(620.54)	(63.00)	(4.51)	(4.11)	82	198–203	725s, 690s single band (ν P-C)	5.23(w, 1H, methine, 1 alpha -N)	
							3400w, (ν (NH))	4.05(w, aromatic C-OH)	
								{6.85–7.57(s, 5H,10H, 9H)}aromatic ring	
								2.40(w, 1NH, $2NH_2$, amine)	
								9.04(wb, 1enol, OH)	
								-C=C(OH)CH_3	
1.3c	$C_{34}H_{32}CrN_2O_5P_2$	61.63	4.87	4.23			2000s, 1985,1890w,1860sb (νCO)	1.54(s, 3H, methyl,1beta –N)	620
	(662.57)	(62.09)	(4.93)	(4.20)	88	213–221	720s, 690s single band (ν P-C)	1.89(s, 3H, methyl,1alpha -C=C)	
							3320w, (ν (NH))	4.43(w, 1H, 1-ethylene –C=C)	
								3.41(w, 1H, methine, 1beta -N)	
								{6.80–7.60(s, 4H, 8H, 8H)} aromatic ring	
								1.05(s, 3H, methyl,1beta -N)	

1.3d	$C_{31}H_{28}CrN_2O_4P_2$	61.39	4.65	4.62			2010s, 1980,1895w,1865sb (νCO)	4.52(m, 1H,methine, 1alpha –N)	607.10
	(606.51)	(60.95)	(4.71)	(4.69)	76	225–235	720s, 690s single band (ν P-C)	3.67(s, 1H,methine, 1beta –N)	
							3350w, (ν (NH))	2.51(w, 1ÑH,2NH_2, amine)	
								{6.86–7.40(s, 4H, 8H, 8H)} aromatic ring	
1.3e	$C_{36}H_{30}CrN_2O_4P_2$	64.67	4.52	4.19			2000s, 1980,1892w,1860sb (νCO)	4.75(m, 1H,methine, 1alpha –N)	669.11
	(668.58)	(64.34)	(4.56)	(4.32)	82	198–204	720s, 690s single band (ν P-C)	4.02(s, 1H,methine, 1beta –N)	
							3300w, (ν (NH))	2.35(w, 1ÑH,2NH_2, amine)	
								{6.80–7.57(s, 4H, 8H, 8H)} aromatic ring	
								1.65(s, 6H, methyl,1alpha -N)	
1.4a	$C_{35}H_{34}CrN_2O_4P_2$	63.64	5.19	4.24			2010s, 1980,1890w,1860sb (νCO)	1.89(s, 6H, methyl,1alpha -N)	
	(660.54)	(63.60)	(5.20)	(4.29)	75	205–210	725s, 690s single band (ν P-C)	3.73(m, 1H,methine, 1beta –N)	
							3350w, (ν (NH))	1.73(w, 1ÑH, hydrazid)	
								{6.80–7.57(s, 4H, 8H, 8H)} aromatic ring	
								1.45(s, 6H, methyl,1beta -N)	
1.4b	$C_{36}H_{30}CrN_2O_5P_2$	64.64	4.73	3.87		201–207	2020, 1985,1890w,1865sb (νCO)	3.26(m, 1H,methine, 1beta –N)	724
	(724.64)	(64.53)	(4.89)	(3.90)	73		720s, 695s single band (ν P-C)	7.92(m, 1H,benzylidenimin, 1alpha –N)	
							3400w, (ν (NH))	8.85(w, 1ÑH, amine)	
								8.85(m, aromatic C-OH)	
								{6.80–7.58(s, 5H, 10H, 9H)} aromatic ring	
								1.31(s, 6H, methyl,1beta -N)	

(Continued on next page)

TABLE III Characterization Data of the Newly Synthesized (Diphenylphosphino)ethene Derivative Complexes *(Continued)*

Compd. No	Mol. formula (mol. wt.)	Calcd.%,(Found) %			Yield%	m.p., °C	IR (ν^{KBr} max), cm^{-1}	$^1H\{^{31}P\}$-NMR($CDCl_3$)	M^+
		C	H	N				δ, ppm, Assignment	
1.4c	$C_{37}H_{36}CrN_2O_5P_2$	63.25	5.16	3.99			2000s, 1980w,1890w,1860sb (νCO)	3.304(w, 1H,methine, 1beta –N)	702
	(702.15)	(62.98)	(5.15)	(4.02)	85	172–187	720s, 690s single band (ν P-C)	4.93(m, 1H, 1-ethylene, 1alpha –C=C)	
1.4d	$C_{34}H_{32}CrN_2O_4P_2$	63.16	4.99	4.33			2020s, 1980w,1890w,1865sb (νCO)	3.304(w, 1H,methine, 1beta –N)	646
	(646.57)	(63.24)	(4.85)	(4.39)	88	209–215	725s, 680s single band (ν P-C)	6.59(s, 1H, 1-hydrazid, 1alpha –N)	
							3200w, (ν (NH))	2.53(w, 1ÑH, hydrazid)	
								0.96(s, 3H, methyl, 1alpha –N)	
								{6.53–7.55(m, 4H, 8H, 8H)} aromatic ring	
1.4e	$C_{39}H_{34}CrN_2O_4P_2$	66.10	4.84	3.95			2000s, 1985,1890w,1860sb (νCO)	1.54(s, 6H, methyl,1beta -N)	709
	(708.64)	(66.05)	(4.95)	(4.08)	86	169–175	720s, 690s single band (ν P-C)	3.304(w, 1H,methine, 1beta –N)	
							3320w, (ν (NH))	8.09(s, 1H, 1-benzylidenimin, 1alpha –N)	
								2.09(w, 1ÑH, amine)	
								{6.53–7.55(m, 4H, 8H, 8H)} aromatic ring	
								1.94(s, 6H, methyl,1beta -N)	
								4.094(w, 1H,methine, 1beta –N)	

Compd. No	Mol. formula (mol. wt.)	Calcd.%,(Found) %			Yield%	m.p., °C	IR (ν^{KBr} max), cm^{-1}	$^1H\{^{31}P\}$-NMR($CDCl_3$)	M^+
		C	H	N				δ, ppm, Assignment	
1.5c	$C_{37}H_{34}CrN_2O_4P_2$	64.91	5.01	4.09			2020s, 1980,1895w,1860sb (νCO)	5.89(s, 1H, 1-pyrazole, 1alpha –N-N = C-C1)	685
	(684.62)	(65.08)	(5.12)	(4.25)	80	208–214	720s, 690s single band (ν P-C)	2.35(s, 3H, methyl, 1 alpha –N-N = C-1) 2.13(s, 3H, methyl, 1 alpha –N-N = C-CH = C-1) {6.80–7.55(m, 4H, 8H, 8H)} aromatic ring	

IR (ν^{KBr} max), cm^{-1} spectra: (s) Strong (sb) Strong board (w) Weak (wb) weak board $^1H\{^{31}P\}$-NMR($CDCl_3$) spectra: (δ) Chemical shift (m) Mediam (s) Strong (wb) Weak board (w) Weak (p-) Para Position (o-) Ortho position (m-) Meta position (ppm) Part per million (enol) Hydroxyl group.

complex dissolved and a new pale brown crystalline precipitate formed. This was filtered off, washed with Et_2O, and dried, giving a pale brown precipitate, yield 0.17 g (83%). The required product $[(OC)_4W\{(Ph_2P)_2C{=}C(CH_3)_2\}]$ was recrystallized from ether-methanol to give a pale brown crystals.

Preparation of $[(OC)_4W\{(Ph_2P)_2C{=}CHPh(o\text{-}OH)\}]$(3.2b)

Salicylaldehyde [Ph(o-OH)CHO] in toluene (0.5 mL) was added to a suspension of $[(OC)_4W\{(Ph_2P)_2CH_2\}]$ (0.19 g, 0.28 mmol). The mixture was then heated to *ca.* 80°C for 14 min, during which period the tungsten complex dissolved and a brown crystalline precipitate formed. This was filtered off, washed with Et_2O, and dried giving brown precipitate, yield 0.17 g (76%). The required product $[(OC)_4W\{(Ph_2P)_2C{=}CHPh(o\text{-}OH)\}]$, was recrystallized from ether-methanol to give brown crystals.

Preparation of $[(OC)_4W\{(Ph_2P)_2C{=}C(CH_3)CH = C(OH)CH_3\}]$ (3.2c)

Acetylacetone $[CH_3COCH = C(OH)CH_3]$ in toluene (0.5 mL) was added to a suspension of $[(OC)_4W\{(Ph_2P)_2CH_2\}]$ (0.19 g, 0.28 mmol). The mixture was then heated to *ca.* 80°C for 10 min, during which period the tungsten complex dissolved and a brown crystalline precipitate formed. This was filtered off, washed with Et_2O, and dried giving brown precipitate, yield 0.17 g (83%). The required product $[(OC)_4W\{(Ph_2P)_2C{=}C(CH_3)CH = C(OH)CH_3\}]$ was recrystallized from ether-methanol to give brown crystals.

Preparation of $[(OC)_4W\{(Ph_2P)_2C{=}CHCH_3\}]$ (3.2d)

Acetaldehyde $[(CH_3CHO]$ in toluene (0.5 mL) was added to a suspension of $[(OC)_4W\{(Ph_2P)_2CH_2\}]$ (0.19 g, 0.28 mmol). The mixture was then heated to *ca.* 80°C for 5 min, during which period the tungsten complex dissolved and a pale brown crystalline precipitate formed. This was filtered off, washed with Et_2O, and dried giving a pale brown precipitate, yield 0.16 g (79%). The required product $[(OC)_4W\{(Ph_2P)_2C{=}CHCH_3\}]$ was recrystallized from ether-methanol to give pale brown crystals.

Preparation of $[(OC)_4W\{(Ph_2P)_2C{=}CHPh\}]$ (3.2e)

Benzaldehyde [(PhCHO] in toluene (0.5 mL) was added to a suspension of $[(OC)_4W\{(Ph_2P)_2CH_2\}]$ (0.19 g, 0.28 mmol). The mixture was

TABLE IV Characterization Data of the Newly Synthesized (Diphenylphosphino)ethene Derivative Complexes

Compd. No	Mol. formula (mol. wt.)	Calcd.%,(Found) % C	H	N	Yield%	m.p., °C	IR (ν^{KBr} max), cm^{-1}	$^1H\{^{31}P\}$-NMR($CDCl_3$) δ, ppm, Assignment	M^+
2.2a	$C_{32}H_{26}MoO_4P_2$	60.77	4.14	—	76	225–233	2005s, 1980,1892w,1865sb (νCO)	1.71(s, 6H, CH_3 methyl)	634.04
	(632.43)	(60.21)	(4.25)	—			720s, 690s single band (ν P-C)	{7.20(s, 4H)}, {7.12(s, 8H)} {7.55(s, 8H)}aromatic ring	
2.2b	$C_{36}H_{26}MoO_5P_2$	62.08	3.76	—	73	214–223	2010s, 1980,1890w,1865sb (νCO)	4.65(wb, 1H, OH(o-Ph) salicylaldehyde)	696.03
	(698.48)	(62.10)	(3.83)	—			715s, 680s single band (ν P-C)	7.90(s, 1H, -C=CH- ethylene) {6.95–7.60(s, 5H, 10H, 9H) } aromatic ring	
2.2c	$C_{34}H_{28}MoO_5P_2$	60.55	4.18	—	80	198–203	2000s, 1985w,1890w,1865sb (νCO)	10.05(wb, 1enol, OH) –C=C(OH)CH_3	674.05
	(674.47)	(61.02)	(4.18)	—			720s, 690s single band (ν P-C)	1.70(s, 3H, methyl,1beta –CH = C) 2.09(s, 3H, methyl,1alpha -C=C) 3.21(w, 1H, 1-ethylene –C=C) {7.15–7.60(s, 4H, 8H, 8H)} aromatic ring	
2.2d	$C_{31}H_{24}MoO_4P_2$	60.21	3.91	—	77	216–223	2005s, 1980,1893w,1865sb (νCO)	1.88(s, 3H, methyl,1alpha -CH = C)	617.41
	(618.41)	(60.20)	(3.95)	—			720s, 690s single band (ν P-C)	5.70(m, 1H, 1-ethylene –C=C) {7.10–7.45(s, 4H, 8H, 8H)} aromatic ring	
2.2e	$C_{36}H_{26}MoO_4P_2$	63.54	3.85	—	80	193–200	2000s, 1985,1892w,1860sb (νCO)	6.65(m, 1H, 1-ethylene –C=C)	680.04
	(680.48)	(63.86)	(3.80)	—			720s, 690s single band (ν P-C)	{7.11–7.63(s, 5H, 10H, 10H)} aromatic ring	

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TABLE IV Characterization Data of the Newly Synthesized (Diphenylphosphino)ethene Derivative Complexes *(Continued)*

Compd. No	Mol. formula (mol. wt.)	Calcd.%,(Found) % C	H	N	Yield%	m.p., °C	IR (ν^{KBr} max), cm^{-1}	$^1H\{^{31}P\}$-NMR($CDCl_3$) δ, ppm, Assignment	M^+
2.3a	$C_{32}H_{30}MoN_2O_4P_2$	57.84	4.55	4.22	73	234–242	2010s, 1980,1892w,1865sb (νCO)	2.46(w, 1NH, $2NH_2$, amine)	663.07
	(664.48)	(57.80)	(4.55)	(4.20)			720s, 690s single band (ν P-C)	3.70(w, 1H, methine, 1 beta -N)	
							3310w, (ν (NH))	1.53(s, 6H, methyl –CH)	
								{6.81–7.59(s, 4H, 8H, 8H)}aromatic ring	
2.3b	$C_{36}H_{30}MoN_2O_5P_2$	59.35	4.15	3.85	72	217–223	2005, 1980,1892w,1865sb (νCO)	2.25(w, 1NH, $2NH_2$, amine)	728.07
2.3c	$C_{34}H_{32}MoN_2O_5P_2$	57.80	4.57	3.97	82	193–202	2005s, 1980,1890w,1865sb (νCO)	2.43(w, 1NH, $2NH_2$, amine)	706.08
	(708.08)	(57.76)	(4.54)	(4.00)			725s, 690s single band (ν P-C)	9.00(wb, 1enol, OH) -C=C(OH)CH_3	
							3310w, (ν (NH))	1.55(s, 3H, methyl,1beta –N)	
								1.90(s, 3H, methyl,1alpha -C=C)	
								4.41(w, 1H, 1-ethylene –C=C)	
								3.40(w, 1H, methine, 1beta -N)	
								{6.85–7.63(s, 4H, 8H, 8H)} aromatic ring	
2.3d	$C_{31}H_{28}MoN_2O_4P_2$	57.24	4.34	4.31	80	213–220	2000s, 1980,1890w,1865sb (νCO)	1.07(s, 3H, methyl,1beta -N)	650.07
	(650.45)	(57.25)	(4.32)	(4.35)			720s, 690s single band (ν P-C)	4.50(m, 1H,methine, 1alpha –N)	
							3330w, (ν (NH))	3.66(s, 1H,methine, 1beta –N)	
								2.50(w, 1ÑH,$2NH_2$, amine)	
								{6.85–7.40(s, 4H, 8H, 8H)} aromatic ring	
2.3e	$C_{36}H_{30}MoN_2O_4P_2$	60.68	4.24	3.93	79	195–201	2010s, 1985,1892w,1863sb (νCO)	4.73(m, 1H,methine, 1alpha –N)	712.07
	(712.52)	(60.60)	(4.25)	(3.90)			723s, 695s single band (ν P-C)	4.00(s, 1H,methine, 1beta –N)	
							3310w, (ν (NH))	2.30(w, 1ÑH,$2NH_2$, amine)	
								{6.85–7.53(s, 4H, 8H, 8H)} aromatic ring	
2.4a	$C_{35}H_{34}MoN_2O_4P_2$	59.67	4.86	3.98	78	213–221	2010s, 1980,1890w,1860sb (νCO)	1.60(s, 6H, methyl,1alpha -N)	703.11

	(704.54)	(59.60)	(4.85)	(4.00)			720s, 690s single band (ν P-C) 3320w, (ν (NH))	1.89(s, 6H, methyl,1alpha -N) 3.71(m, 1H,methine, 1beta –N) 1.70(w, 1N̂H, hydrazid) {6.80–7.57(s, 4H, 8H, 8H)} aromatic ring	
2.4b	$C_{39}H_{34}MoN_2O_5P_2$	60.95	4.46	3.64	77	231–240	2020, 1980,1890w,1865sb (νCO)	1.47(s, 6H, methyl,1beta -N)	768.10
	(724.64)	(60.90)	(4.43)	(3.60)			720s, 690s single band (ν P-C) 3350w, (ν (NH))	3.25(m, 1H,methine, 1beta –N) 7.90(m, 1H,benzylidenimin, 1alpha –N) 8.85(w, 1N̂H, amine) 8.70(m, aromatic C-OH) {6.80–7.58(s, 5H, 10H, 9H)} aromatic ring	
2.4c	$C_{37}H_{36}MoN_2O_5P_2$	59.52	4.86	3.75	81	217–228	2010s, 1985w,1890w,1860sb (νCO)	1.33(s, 6H, methyl,1beta -N)	745.12
	(746.58)	(59.50)	(4.90)	(3.74)			720s, 695s single band (ν P-C) 3400w, (ν (NH)) 3200wb, (ν (OH))	3.354(w, 1H,methine, 1beta –N) 4.90(m, 1H, 1-ethylene, 1alpha –C=C) 8.11(w, 1N̂H, hydrazid) 11.85(w, enol (C-OH)) 1.86(s, 3H, methyl, 1alpha –C=CH) 0.95(s, 3H, methyl, 1gama C=CH-) {6.80–7.57(m, 4H, 8H, 8H)} aromatic ring	
2.4d	$C_{34}H_{32}MoN_2O_4P_2$	59.14	4.67	4.06	83	197–204	2010s, 1980w,1890w,1860sb (νCO)	1.35(s, 6H, methyl,1beta -N)	690.09
	(690.52)	(60.00)	(4.65)	(4.05)			720s, 680s single band (ν P-C) 3200w, (ν (NH))	3.30(w, 1H,methine, 1beta –N) 6.60(s, 1H, 1-hydrazid, 1alpha –N) 2.53(w, 1N̂H, hydrazid) 0.99(s, 3H, methyl, 1alpha –N) {6.53–7.55(m, 4H, 8H, 8H)} aromatic ring	
2.4e	$C_{39}H_{34}MoN_2O_4P_2$	62.24	4.55	3.72	80	183–189	2010s, 1980,1890w,1860sb (νCO)	1.55(s, 6H, methyl,1beta -N)	751.11
	(752.59)	(62.25)	(4.55)	(3.70)			725s, 690s single band (ν P-C) 3350w, (ν (NH))	3.31(w, 1H,methine, 1beta –N) 8.10(s, 1H, 1-benzylidenimin, 1alpha –N) 2.09(w, 1N̂H, amine) {6.53–7.55(m, 4H, 8H, 8H)} aromatic ring	

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TABLE IV Characterization Data of the Newly Synthesized (Diphenylphosphino)ethene Derivative Complexes *(Continued)*

Compd. No	Mol. formula (mol. wt.)	Calcd.%,(Found) % C	H	N	Yield%	m.p., °C	IR (ν^{KBr} max), cm^{-1}	$^1H\{^{31}P\}$-NMR($CDCl_3$) δ, ppm, Assignment	M^+
2.5c	$C_{37}H_{34}MoN_2O_4P_2$	61.00	4.70	3.85	80	237–244	2010s, 1980,1890w,1860sb (νCO)	1.95(s, 6H, methyl,1beta -N)	727.11
	(728.56)	(61.08)	(4.74)	(3.91)			720s, 690s single band (ν P-C)	4.09(w, 1H,methine, 1beta –N) 5.90(s, 1H, 1-pyrazole, 1alpha –N-N = C-C1) 2.30(s, 3H, methyl, 1 alpha –N-N = C-1) 2.15(s, 3H, methyl, 1 alpha –N-N = C-CH = C-1) {6.80–7.55(m, 4H, 8H, 8H)} aromatic ring	

IR (ν^{KBr} max), cm^{-1} spectra: (s) Strong (sb) Strong board (w) Weak (wb) weak board $^1H\{^{31}P\}$-NMR($CDCl_3$) spectra: (δ) Chemical shift (m) Mediam (s) Strong (wb) Weak board (w) Weak (p-) Para Position (o-) Ortho position (m-) Meta position (ppm) Part per million (enol) Hydroxyl group.

TABLE V Characterization Data of the Newly Synthesized (Diphenylphosphino)ethene Derivative Complexes

Compd. No	Mol. formula (mol. wt.)	Calcd.%,(Found) % C	H	N	Yield%	m.p., °C	IR (ν^{KBr} max), cm^{-1}	$^1H\{^{31}P\}$-NMR($CDCl_3$) δ, ppm, Assignment	M^+
3.2a	$C_{32}H_{26}WO_4P_2$	53.36	3.64	—	75	183–188	2020s, 1980,1895w,1860sb (νCO)	1.75(s, 6H, CH_3 methyl)	722.08
	(720.33)	(53.41)	(3.62)	—			725s, 690s single band (ν P-C)	{7.23(s, 4H)}, {7.12(s, 8H)} {7.55(s, 8H)}aromatic ring	
3.2b	$C_{36}H_{26}WO_5P_2$	55.12	3.34	—	79	197–203	2010s, 1980,1890w,1860sb (νCO)	4.70(wb, 1H, OH(o-Ph) salicylaldehyde)	786.08
	(784.38)	(55.13)	(3.35)	—			720s, 690s single band (ν P-C)	7.90(s, 1H, -C=CH- ethylene) {6.92–7.56(s, 5H, 10H, 9H))} aromatic ring	
3.2c	$C_{34}H_{28}WO_5P_2$	53.56	3.70	—	73	185–189	2000s, 1980w,1890w,1865sb (νCO)	10.00(wb, 1enol, OH) –C=C(OH)CH_3	764.10
	(762.37)	(53.53)	(3.65)	—			720s, 685s single band (ν P-C)	1.75(s, 3H, methyl,1beta -CH = C) 2.05(s, 3H, methyl,1alpha -C=C) 3.20(w, 1H, 1-ethylene –C=C) {7.13–7.62(s, 4H, 8H, 8H)} aromatic ring	
3.2d	$C_{31}H_{24}WO_4P_2$	52.72	3.42	—	80	226–231	2010s, 1980,1890w,1865sb (νCO)	1.88(s, 3H, methyl,1alpha -CH = C)	708.07
	(706.31)	(52.70)	(3.47)	—			720s, 690s single band (ν P-C)	5.70(m, 1H, 1-ethylene –C=C) {7.12–7.42(s, 4H, 8H, 8H)} aromatic ring	

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TABLE V Characterization Data of the Newly Synthesized (Diphenylphosphino)ethene Derivative Complexes *(Continued)*

Compd. No	Mol. formula (mol. wt.)	Calcd.%,(Found) % C	H	N	Yield%	m.p., °C	IR (ν^{KBr} max), cm^{-1}	$^1H\{^{31}P\}$-NMR($CDCl_3$) δ, ppm, Assignment	M^+
3.2e	$C_{36}H_{26}WO_4P_2$	56.27	3.41	—	75	233–239	2020s, 1980,1890w,1865sb (νCO)	6.71(m, 1H, 1-ethylene –C=C)	770.08
	(768.38)	(56.30)	(3.49)	—			720s, 690s single band (ν P-C)	{7.15–7.59(s, 5H, 10H, 10H)} aromatic ring	
3.3a	$C_{32}H_{30}WN_2O_4P_2$	51.08	4.02	3.72	82	200–206	2000s, 1980,1892w,1860sb (νCO)	2.49(w, 1NH, $2NH_2$, amine)	754.12
	(752.38)	(51.05)	(4.11)	(3.75)			720s, 690s single band (ν P-C)	3.73(w, 1H, methine, 1 beta -N)	
							3310w, (ν (NH))	1.56(s, 6H, methyl –CH) {6.85–7.57(s, 4H, 8H, 8H)}aromatic ring	
3.3b	$C_{36}H_{30}WN_2O_5P_2$	52.96	3.70	3.43	71	199–209	2000, 1980,1890w,1865sb (νCO)	2.27(w, 1NH, $2NH_2$, amine)	816.11
	(816.42)	(52.86)	(3.75)	(3.40)			720s, 690s single band (ν P-C)	4.40(s, 1H, methine, 1 beta -N)	
							3400w, (ν (NH))	5.22(w, 1H, methine, 1 alpha -N) 4.05(w, aromatic C-OH) {6.85–7.57(s, 5H,10H, 9H)}aromatic ring	
3.3c	$C_{34}H_{32}WN_2O_5P_2$	51.40	4.06	3.53	84	182–187	2010s, 1985,1890w,1865sb (νCO)	2.43(w, 1NH, $2NH_2$, amine)	796.13
	(794.13)	(51.49)	(4.13)	(3.50)			720s, 690s single band (ν P-C)	9.05(wb, 1enol, OH) -C=C(OH)CH_3	
							3310w, (ν (NH))	1.52(s, 3H, methyl,1beta –N) 1.89(s, 3H, methyl,1alpha -C=C) 4.43(w, 1H, 1-ethylene –C=C) 3.46(w, 1H, methine, 1beta -N) {6.80–7.60(s, 4H, 8H, 8H)} aromatic ring	

3.3d	$C_{31}H_{28}WN_2O_4P_2$	50.43	3.82	3.79	86	224–231	2010s, 1980,1895w,1860sb (νCO)	1.07(s, 3H, methyl,1beta -N)	740.11
	(738.35)	(50.65)	(3.77)	(3.74)			720s, 690s single band (ν P-C)	4.50(m, 1H,methine, 1alpha –N)	
							3350w, (ν (NH))	3.67(s, 1H,methine, 1beta –N)	
								2.53(w, 1ÑH,2NH_2, amine)	
								{6.86–7.40(s, 4H, 8H, 8H)} aromatic ring	
3.3e	$C_{36}H_{30}WN_2O_4P_2$	54.02	3.78	3.50	80	200–204	2010s, 1980,1890w,1860sb (νCO)	4.75(m, 1H,methine, 1alpha –N)	802.12
	(800.42)	(54.04)	(3.72)	(3.52)			720s, 690s single band (ν P-C)	4.02(s, 1H,methine, 1beta –N)	
							3310w, (ν (NH))	2.35(w, 1ÑH,2NH_2, amine)	
								{6.80–7.57(s, 4H, 8H, 8H)} aromatic ring	
3.4a	$C_{35}H_{34}WN_2O_4P_2$	53.05	4.32	3.54	82	234–237	2010s, 1980,1890w,1865sb (νCO)	1.65(s, 6H, methyl,1alpha -N)	794.14
	(792.44)	(53.13)	(4.40)	(3.49)			720s, 690s single band (ν P-C)	1.90(s, 6H, methyl,1alpha -N)	
							3350w, (ν (NH))	3.74(m, 1H,methine, 1beta –N)	
								1.71(w, 1ÑH, hydrazid)	
								{6.80–7.57(s, 4H, 8H, 8H)} aromatic ring	
3.4b	$C_{39}H_{34}WN_2O_5P_2$	54.69	4.00	3.27	73	214–217	2020, 1980,1890w,1860sb (νCO)	1.44(s, 6H, methyl,1beta -N)	858.15
3.4c	$C_{37}H_{36}WN_2O_5P_2$	53.25	4.35	3.36	85	193–198	2020s, 1985w,1895w,1860sb (νCO)	1.30(s, 6H, methyl,1beta -N)	836.17

(Continued on next page)

TABLE V Characterization Data of the Newly Synthesized (Diphenylphosphino)ethene Derivative Complexes *(Continued)*

Compd. No	Mol. formula (mol. wt.)	Calcd.%,(Found) %			Yield%	m.p., °C	IR (ν^{KBr} max), cm^{-1}	$^1H\{^{31}P\}$-NMR($CDCl_3$)	M^+
		C	H	N				δ, ppm, Assignment	
	(834.48)	(52.98)	(4.29)	(3.40)			720s, 690s single band (ν P-C) 3410w, (ν (NH)) 3220wb, (ν (OH))	3.32(w, 1H,methine, 1beta –N) 4.90(m, 1H, 1-ethylene, 1alpha –C=C) 8.11(w, 1ÑH, hydrazid) 11.86(w, enol (C-OH)) 1.89(s, 3H, methyl, 1alpha –C=CH) 0.99(s, 3H, methyl, 1gama C=CH-) {6.80–7.57(m, 4H, 8H, 8H)} aromatic ring	
3.4d	$C_{34}H_{32}WN_2O_4P_2$	52.46	4.14	3.60	82	249–255	2010s, 1980w,1890w,1860sb (νCO)	1.35(s, 6H, methyl,1beta -N)	778.13
	(778.42)	(52.24)	(4.15)	(3.59)			725s, 680s single band (ν P-C) 3210w, (ν (NH))	3.31(w, 1H,methine, 1beta –N) 6.60(s, 1H, 1-hydrazid, 1alpha –N) 2.53(w, 1ÑH, hydrazid) 1.00(s, 3H, methyl, 1alpha –N) {6.53–7.55(m, 4H, 8H, 8H)} aromatic ring	
3.4e	$C_{39}H_{34}WN_2O_4P_2$	55.73	4.08	3.33	76	172–175	2000s, 1980,1890w,1865sb (νCO)	1.52(s, 6H, methyl,1beta -N)	842.15
	(840.49)	(55.66)	(3.95)	(3.35)			720s, 690s single band (ν P-C) 3310w, (ν (NH))	3.34(w, 1H,methine, 1beta –N) 8.13(s, 1H, 1-benzylidenimin, 1alpha –N) 2.04(w, 1ÑH, amine) {6.53–7.55(m, 4H, 8H, 8H)} aromatic ring	

3.5c	$C_{37}H_{36}WN_2O_4P_2$	54.30	4.43	3.42	84	218–220	2010s, 1985,1895w,1865sb (νCO)	1.93(s, 6H, methyl,1beta -N)	820.17
	(818.48)	(54.28)	(4.51)	(3.45)			725s, 690s single band (ν P-C)	4.14(w, 1H,methine, 1beta –N) 5.87(s, 1H, 1-pyrazole, 1alpha –N-N = C-C1) 2.33(s, 3H, methyl, 1 alpha –N-N = C-1) 2.15(s, 3H, methyl, 1 alpha –N-N = C-CH = C-1) {6.80–7.55(m, 4H, 8H, 8H)} aromatic ring	

IR (ν^{KBr} max), cm^{-1} spectra: (s) Strong (sb) Strong board (w) Weak (wb) weak board $^1H\{^{31}P\}$-NMR($CDCl_3$) spectra: (δ) Chemical shift (m) Mediam (s) Strong (wb) Weak board (w) Weak (p-) Para Position (o-) Ortho position (m-) Meta position (ppm) Part per million (enol) Hydroxyl group.

then heated to *ca.* 80°C for 5 min, during which period the tungsten complex dissolved and a new pale yellow crystalline precipitate formed. This was filtered off, washed with Et_2O, and dried giving a pale yellow precipitate, yield 0.15 g (76%). The required product $[(OC)_4W\{(Ph_2P)_2C{=}CHPh\}]$ was recrystallized from ether-methanol to give pale yellow crystals.

Preparation of $[(OC)_4W\{(Ph_2P)_2CHCNHNH_2(CH_3)_2\}]$(3.3a)

Hydrazine hydrate $[NH_2NH_2]$ (0.5 cm^3), was added to a suspension of $[(OC)_4W\{(Ph_2P)_2C{=}C(CH_3)_2\}]$ (0.2 g, 0.28 mmol) in toluene. The mixture was then heated to *ca.* 80°C for 15 min, during which period the tungsten complex dissolved and a brown crystalline precipitate formed. This was filtered off, washed with Et_2O, and dried, giving the required product $[(OC)_4W\{(Ph_2P)_2CHC(NHNH_2)(CH_3)_2\}]$, yield 0.17 g (81%). The brown precipitate $[(OC)_4W\{(Ph_2P)_2CHCNHNH_2(CH_3)_2\}]$ was recrystallized from ether-methanol to give brown crystals.

Preparation of $[(OC)_4W\{(Ph_2P)_2CHC(NHN{=}C(CH_3)CH{=}C(OH)CH_3)(CH_3)_2\}]$(3.4c)

$[(OC)_4W\{(Ph_2P)_2CHC(NHNH_2)(CH_3)_2\}]$ (0.21 g, 0.28 mmol) in toluene (1 cm^3) and acetylacetone $CH_3COCH{=}C(OH)CH_3$ (0.028 g, 0.28 mmol) was heated under reflux for 16 h to give pyrazole. The resulting yellow solution was evaporated to low volume under reduced pressure and ethanol added. The product separated $[(OC)_4W\{(Ph_2P)_2CHC(NHN{=}C(CH_3)CH{=}C(OH)CH_3)(CH_3)_2\}]$ as yellow prisms. Yield 0.15 g (63%), found: C,53.20; H, 4.36; N, 3.38% . Calc.: C, 53.25; H, 4.35; N, 3.36%. $M^+ = 834.16$ (mass spectrometry).

Preparation of $[(OC)_4W\{(Ph_2P)_2CHC(NHN{=}C((R_1)R_2)(CH_3)_2\}]$, Where $R_1{=}CH_3$, H, H, H and $R_2{=}CH_3$,Ph(o−OH), CH_3, Ph (1.4a–1.4e)

$[(OC)_4Cr\{(Ph_2P)_2CHC(NHNH_2)(CH_3)_2\}]$ (0.17 g, 0.28 mmol) was suspended in toluene (10 cm^3) for 10–25 min, during which period the chromium complex dissolved and new dark brown, brown, brown, and brown crystalline precipitates formed, respectively. These were filtered off, washed with Et_2O, and dried, giving the required products $[(OC)_4Cr\{(Ph_2P)_2CHC(NHN = C(CH_3)_2)(CH_3)_2\}]$ (dark brown) (**1.4a**), $[(OC)_4Cr\{(Ph_2P)_2CHC(NHN = CH(Ph(o\text{-}OH))(CH_3)_2\}]$ (pale brown) (**1.4b**), $[(OC)_4Cr\{(Ph_2P)_2CHC(NHN = CH(CH_3))(CH_3)_2\}]$ (brown) (**1.4d**), and $[(OC)_4Cr\{(Ph_2P)_2CHC(NHN = CH(Ph))(CH_3)_2\}]$ (**1.4e**)

(brown), respectively. The final products were recrystallied from ether-methanol. Data are listed in Table III.

Molybdenum complexes have been prepared in a similar manner to chromium and tungsten complexes; data are listed in Tables IV and V.

Formation of Pyrazole Derivative with Acetylacetone $[(OC)_4Cr\{(Ph_2P)_2CHC(N^*N = C(CH_3)\text{-}CH = C^*CH_3)(CH_3)_2\}]$ (1.5c)

A suspension of $[(OC)_4Cr\{(Ph_2P)_2CHCNHNN_2(CH_3)_2\}]$ (**1.3a**) (0.18 g, 0.28 mmol) in toluene (1 mL) and acetylacetone (0.028 g, 0.28 mmol) was heated under reflux for 15 h. The resultant pale yellow solution was evaporated to low volume under reduced pressure and ethanol was added. The product separated as yellow prism. Yield, 0.12 g (53%).

Molybdenum and tungsten pyrazol derivatives with acetylacetone compounds were synthesized in a similar fashion to chromium compounds.

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