

Syntheses and Michael Additions to Vinylidene Diphosphine Complexes of Type $[M(CO)_4\{(Ph_2P)_2C=CH_2\}]$ ($M = Cr, Mo$ or W)

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Abstract

Treatment of $[M(CO)_4Ph_2PCHPPh_2]^-$ with CH_3OCH_2Cl at 20 °C gave the methoxymethyl derivations $[M(CO)_4\{Ph_2PCH(CH_2OCH_3)PPh_2\}]$ ($M = Cr$ or W), but a similar treatment at 80 °C gave derivatives of a vinylidene diphosphine $[M(CO)_4(Ph_2P)_2C=CH_2]$. Treatment of $[M(CO)_4Ph_2PCHPPh_2]^-$ with $CH_3CHClOCH_3$ at 20 or 80 °C gave only $[M(CO)_4(Ph_2P)_2CHCH(CH_3)OCH_3]$ ($M = Cr$ or W). The vinylidene diphosphine complexes $[M(CO)_4(Ph_2P)_2C=CH_2]$ ($M = Cr, Mo$ or W) were even more easily prepared by treating $[M(CO)_6]$ with $(Ph_2P)_2C=CH_2$ (vdpp) in hot solvents such as $CH_3OCH_2CH_2OCH_2CH_2OCH_3$.

Treatment of $[W(CO)_4vdpp]$ with $LiBu^n$ followed by methanol gave $[W(CO)_4(Ph_2P)_2CHCH_2Bu^n]$ (**1c**), i.e. conjugate addition to the $C=CH_2$ occurs. **1c** was also made by treating $[W(CO)_4(Ph_2P)_2CH]^-$ with *n*-pentyl-iodide. Similarly $LiMe$ was added to $[W(CO)_4(Ph_2P)_2C=CH_2]$. Treatment of $[M(CO)_4vdpp]$ with $NaCH(COOEt)_2$ gave $[M(CO)_4(Ph_2P)_2CHCH_2CH(COOEt)_2]$ ($M = W$ or Mo). Pyrrolidine added to the $C=CH_2$ bonds of $[M(CO)_4vdpp]$ to give $[M(CO)_4(Ph_2P)_2CHCH_2NC_4H_8]$. ^{31}P and 1H NMR and IR data are given.

Introduction

Tertiary phosphines are important ligands in chemistry, although relatively little has been done with functionalised phosphines: quite often the methods which are used to synthesise non-functionalised tertiary phosphines are not adaptable to the synthesis of functionalised tertiary phosphines. There is a great deal of interest in complexes of $Ph_2PCH_2PPh_2$ (dppm) and related ligands and we have been extending this chemistry to complexes containing ligands of type $Ph_2PCHRPPH_2$ where R = an alkyl or aryl group or particularly a functional group [1–5]. Very few such ligands are known. One problem in

their synthesis is that, although dppm can be deprotonated by strong bases such as $LiBu^n$, the resultant carbanion, $Ph_2PCHPPh_2^-$ is ambident and electrophiles attack it at both the carbon and phosphorus, giving mixtures. However, we have shown that, when complexed to a metal such as in $[(OC)_4M(dppm-PP')]^-$ ($M = Cr, Mo$ or W), dppm can be deprotonated and the resultant carbanion alkylated or acylated [1, [1, 2].

When we treated this carbanion with CH_3OCH_2Cl , in an attempt to introduce the methoxymethyl substituent, we were able to do this at 20 °C but at higher temperatures (80 °C) loss of methanol to give complexes of the then unknown ligand $(Ph_2P)_2C=CH_2$ occurred. Shortly after we submitted some of this work for publication [6], the synthesis of the free ligand, $(Ph_2P)_2C=CH_2$, was described [7]. In this paper we describe the above-mentioned work together with some Michael additions to the $C=CH_2$ moiety of the coordinated ligand.

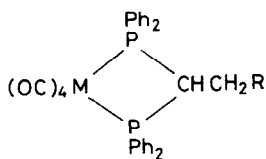
Experimental

The experimental techniques were the same as those used in other recent papers from this laboratory [8]. Complexes of the type $[M(CO)_4(dppm)]$ ($M = Cr, Mo$ or W) were made as described previously [3].

Preparation of $[Cr(CO)_4\{Ph_2PCH(CH_2OCH_3)PPh_2\}]$ (**1a**)

A solution of *n*-butyl-lithium in diethyl ether (0.72 ml, 1.04 mmol) was added to a stirred solution of $[Cr(CO)_4(dppm)]$ (0.55 g, 1.00 mmol) in dry THF (12 ml). The mixture was then stirred for 1 h, after which chloromethyl methyl ether (0.075 ml, 1.03 mmol) was added and the resultant mixture was stirred for a further 48 h. The deep yellow solution was then evaporated to dryness and the required product extracted into dichloromethane. It formed orange microcrystals from dichloromethane/methanol. Yield 0.373 g, 0.63 mmol, 63%. $[W(CO)_4\{Ph_2PCH(CH_2OCH_3)PPh_2\}]$ (**1b**) was prepared similarly. Yield 58%.

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- 1a** : M = Cr, R = OCH₃
1b : M = W, R = OCH₃
1c : M = W, R = Buⁿ
1d : M = W, R = CH₃
1e : M = W, R = CH(COOEt)₂
1f : M = Mo, R = CH(COOEt)₂
1g : M = W, R = NC₄H₈
1h : M = Cr, R = NC₄H₈

Preparation of [Cr(CO)₄[(Ph₂P)₂C=CH₂]]

(a) From [Cr(CO)₄(dppm)]

A solution of *n*-butyl-lithium in diethyl ether (1.45 ml, 2.05 mmol) was added to a solution of [Cr(CO)₄(dppm)] (0.548 g, 1.00 mmol) and Me₂NCH₂CH₂NMe₂ (TMEDA) (0.31 ml, 2.05 mmol) in dry benzene (10 ml). The mixture was stirred at *ca.* 20 °C for 1½ h, after which chloromethyl methyl ether (0.15 ml, 2.05 mmol) was added and the mixture heated to *ca.* 80 °C for 4 h. The resultant mixture was then cooled and methanol (0.5 ml) and water (10 ml) added. The required product was isolated with benzene and formed yellow needles from dichloromethane/methanol. Yield 0.38 g, 0.68 mmol, 68%.

W(CO)₄[(Ph₂P)₂C=CH₂] was made similarly from [W(CO)₄(dppm)] in 60% yield.

(b) From [Cr(CO)₆]

A mixture of [Cr(CO)₆] (0.44 g, 2.00 mmol) and (Ph₂P)₂C=CH₂ (vdpp) (0.792 g, 2.0 mmol) was refluxed in *n*-decane solution (40 ml) for 30 min. The solution was then evaporated to dryness under reduced pressure and the residue recrystallized from dichloromethane/methanol. This gave [Cr(CO)₄(Ph₂P)₂C=CH₂] in 89% yield.

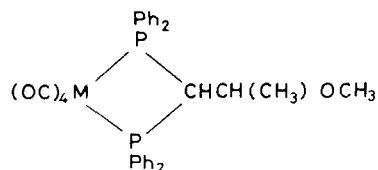
W(CO)₄[(Ph₂P)₂C=CH₂] was made similarly in 91% yield.

Preparation of [Mo(CO)₄[(Ph₂P)₂C=CH₂]]

A mixture of [Mo(CO)₆] (0.528 g, 2.00 mmol) and (Ph₂P)₂C=CH₂ (0.792 g, 2.00 mmol) was refluxed in (MeOCH₂CH₂)₂O (*ca.* 40 ml) solution for 2 h. The resultant solution was then evaporated to dryness under reduced pressure to give the required product, which formed yellow microcrystals from dichloromethane/methanol. Yield 0.91 g, 1.5 mmol, 75%. Alternatively the same reactants when heated in refluxing MeOCH₂CH₂OMe for 24 h gave [Mo(CO)₄[(Ph₂P)₂C=CH₂]] in 72% yield.

Preparation of [Cr(CO)₄[(Ph₂P)₂CHCHCH₃(OCH₃)] (2a)

A solution of *n*-butyl-lithium in diethyl ether (0.68 ml, 1.05 mmol) was added to a stirred solution of [Cr(CO)₄(dppm)] (0.548 g, 1.00 mmol) in dry THF (8 ml). The mixture was then stirred for 1 h, after which ClCH(CH₃)OCH₃ (0.20 ml, 2.09 mmol) was added. The mixture was stirred for a further 24 h and then evaporated to dryness and the residue taken up in methanol (6 ml). The required product crystallizes out as bright yellow microcrystals which were collected etc. Yield 0.33 g, 0.54 mmol, 54%.



- 2a** : M = Cr
2b : M = W

W(CO)₄[(Ph₂P)₂CHCHCH₃(OCH₃)] (**2b**) was prepared similarly in 85% yield and formed yellow microcrystals.

Michael Addition of *n*-Butyl-lithium to [W(CO)₄(vdpp)]

A solution of [W(CO)₄(vdpp)] (0.138 g, 0.2 mmol) in dry THF (5 ml) was treated with TMEDA (34 µl, 0.225 mmol) followed by *n*-butyl-lithium (0.12 ml, 0.208 mmol). The mixture was put aside at 20 °C for 16 h, then methanol (1 ml) was added and the mixture evaporated to dryness. The solid product was recrystallized from the minimum volume of hot ethanol to give [W(CO)₄[(Ph₂P)₂CH(CH₂)₄CH₃]] (**1c**) (0.137 g, 0.183 mmol, 92%).

Formation of [W(CO)₄[(Ph₂P)₂CH(CH₂)₄CH₃]] (**1c**) from [W(CO)₄(dppm)]

A solution of [W(CO)₄(dppm)] (0.68 g, 1.00 mmol) in dry THF (5 ml) was treated with *n*-butyl-lithium in hexane (1.10 mmol, 0.71 ml). The mixture was stirred at *ca.* 20 °C for 1¼ h, after which 1-iodopentane (0.15 ml, 1.14 mmol) was added. The mixture was then stirred for 2 days after which methanol was added and the end product isolated. ³¹P{¹H} NMR spectroscopy established that this product was a mixture of [W(CO)₄(dppm)] (minor component) along with a second product. Preparative t.l.c. (silica gel) separation on 75 mg of this mixture, using a solvent composed of 75% *n*-hexane and 25% dichloromethane as developer, gave two yellow bands. The front band was extracted with dichloromethane and crystallized from a minimum of ethanol. The yellow crystalline product (27 mg) was identified as [W(CO)₄[(Ph₂P)₂CH(CH₂)₄CH₃]]

TABLE I. Analytical^a and IR (cm⁻¹)^b data

Complex	Analysis (%)		$\nu(\text{C}\equiv\text{O})$	Other IR bands
	C	H		
1a	62.85 (62.85)	4.3 (4.4)	2005, 1915, 1900, 1870	2880 $\nu(\text{OCH}_3)$
1b	51.2 (51.4)	3.5 (3.6)	2020, 1930, 1915, 1855	2880 $\nu(\text{OCH}_3)$
1c	54.4 (54.3)	4.35 (4.3)	2012, 1917, 1883, 1870	
1e	51.95 (52.15)	3.85 (4.0)		
1f	58.15 (58.4)	4.2 (4.3)	2015, 1917, 1898, 1751	1725 $\nu(\text{C}=\text{O})$
1g ^c	53.5 (53.5)	4.15 (4.1)	not recorded	
1h ^d	64.45 (64.65)	4.95 (4.95)	not recorded	
2a	62.95 (63.35)	4.8 (4.65)	2008, 1918, 1905, 1895	2870 $\nu(\text{OCH}_3)$
2b	51.9 (52.1)	3.8 (3.85)	2020, 1930, 1900, 1855	2865 $\nu(\text{OCH}_3)$
[Cr(CO) ₄ vdpp]	64.1 (64.3)	4.1 (3.95)	2010, 1925, 1910, 1875	
[Mo(CO) ₄ vdpp]	59.6 (59.6)	3.9 (3.65)	2020, 1928, 1900, 1874	
[W(CO) ₄ vdpp]	51.9 (52.1)	3.15 (3.2)	2020, 1925, 1910, 1870	

^aCalculated values (%) in parentheses. ^bAs Nujol mulls. ^c%N 1.7 (1.85). ^d%N 2.05 (2.25).

(1c) by C, H analysis and by ³¹P{¹H}, ¹H{³¹P} NMR spectroscopy and by IR spectroscopy. The second band was identified as [W(CO)₄(dppm)].

Michael addition of Methyl lithium to [W(CO)₄(vdpp)]

A solution of [W(CO)₄(vdpp)] (0.138 g, 0.2 mmol) in THF (5 ml) was treated with TMEDA (31 μ l, 0.205 mmol) followed by a solution of methyl-lithium in diethyl ether (0.21 mmol, 0.175 ml). The mixture was stirred at 20 °C for 2 h, then hydrolysed and the solid product isolated and recrystallized from dichloromethane-methanol. This gave [W(CO)₄{(Ph₂P)₂CHCH₂CH₃}] (1d) (95 mg, 0.135 mmol, 68%) shown to be identical with an authentic sample [3].

Preparation of [W(CO)₄{(Ph₂P)₂CHCH₂CH(COOEt)₂}] (1e)

A solution of diethyl malonate (0.040 g, 0.25 mmol) in dry THF (2 ml) was added to a stirred suspension of sodium hydride (0.01 g, 0.25 mmol) in dry THF (5 ml). Solid [W(CO)₄(vdpp)] (0.17 g, 0.25 mmol) was added and the resultant mixture was stirred at ca. 20 °C for 16 h. The solution was then evaporated to dryness under reduced pressure and the residue was treated with methanol. This caused the required product to separate as yellow microcrystals. Yield 0.14 g, 65%, melting point (m.p. 183–187 °C).

The corresponding molybdenum complex, [Mo(CO)₄{(Ph₂P)₂CHCH₂CH(COOEt)₂}] (1f) was made similarly in 68% yield. Pale yellow microcrystals, m.p. 183–185 °C.

Addition of Pyrrolidine to [W(CO)₄(vdpp)]

Pyrrolidine (0.5 ml, ~6 mmol) was added to a solution of [W(CO)₄(vdpp)] (50 mg, 0.074 mmol)

in ethanol (5 ml). After 30 min the solution was evaporated down to ca. 2 ml under reduced pressure. This gave the addition product [W(CO)₄(PPh₂)₂CHCH₂NC₄H₈] (1g) as off-white microcrystals, m.p. 191–192 °C. Yield 51 mg, 0.069 mmol, 93%.

[Cr(CO)₄(PPh₂)₂CHCH₂NC₄H₈] (1h) was made similarly in 73% yield. Yellow microcrystals, m.p. 174–176 °C.

Results and Discussion

We now report that the carbanions, [M(CO)₄(Ph₂PCHPPh₂)]⁻, prepared by the cation of LiBuⁿ on [M(CO)₄(dppm)], when treated with ClCH₂OCH₃ in THF at 20 °C gave methoxymethyl derivatives [M(CO)₄{(Ph₂PCH(CH₂OCH₃))PPh₂}] (M = Cr, or W) (1a) or (1b) in good, ca. 60% yields, as orange crystalline solids. Characterizing elemental analytical, IR and ³¹P{¹H}, ¹H- and ¹H-³¹P} NMR data are given in the Tables I and II. Both complexes were sufficiently stable to study by mass spectrometry, the chromium complex giving a group of peaks *m/e* = 590–596 with the most intense peak occurring at *m/e* = 592 – the molecular ion. The observed isotopic distribution pattern in the region of the molecular ion is in good agreement with the calculated pattern. The IR data, Table I, are in agreement with the complexes being *cis*-chelated tetracarbonyls.

In contrast to the above results, we found that when [M(CO)₄(Ph₂PCH₂PPh₂)] (M = Cr or W) were treated with LiBuⁿ followed by two equivalents of CH₃OCH₂Cl and the resultant mixtures were heated at 80 °C, good yields of the vinylidene diphosphine (vdpp) complexes [M(CO)₄{(Ph₂P)₂C=CH₂}] M =

TABLE II. $^{31}\text{P}\{^1\text{H}\}^{\text{a}}$ and $^1\text{H}^{\text{b}}$ NMR Data

Complex	Phosphorus		Hydrogens
	$\delta(\text{P})$	$^1J(^{183}\text{W}-\text{P})$	
1a	43.6		$\delta = 4.82 (\text{CH})$; $\delta = 3.26 (\text{CH}_2)$; $\delta = 2.94 (\text{OCH}_3)$ $^3J(\text{CHCH}_2) = 8$; $^2J(\text{PCH}) = 11$; $^3J(\text{PCH}_2) = 8$
1b	-4.9	205	$\delta = 5.02 (\text{CH})$; $\delta = 3.12 (\text{CH}_2)$; $\delta = 2.92 (\text{OCH}_3)$ $^3J(\text{CHCH}_2) = 7$; $^2J(\text{PCH}) = 11$; $^3J(\text{PCH}_2) = 8$
1c	0.4	203	$\delta = 4.86 (\text{CH})$; $^3J(\text{CHCH}_2) = 6$; Complex multiplet from 1.3–0.7 ppm $(\text{CH}_2)_4\text{CH}_3$
1e	-0.7	205	$\delta = 5.21 (\text{PCH})$; $\delta = 1.94 (\text{CH}_2)$; $\delta = 2.93 (\text{CHCOOEt})$; $\delta = 4.05 (\text{CH}_2\text{CH}_3)$; $\delta = 1.15 (\text{CH}_2\text{CH}_3)$; $^3J(\text{PCHCH}_2) = 7.5$; $^3J(\text{CH}_2\text{CHCOOEt}) = 7.35$; $^3J(\text{CH}_2\text{CH}_3) = 7.2$
1f	23.8		$\delta = 4.92 (\text{PCH})$; $\delta = 1.98 (\text{CH}_2)$; $\delta = 2.94 (\text{CHCOOEt})$; $\delta = 4.05 (\text{CH}_2\text{CH}_3)$; $\delta = 1.15 (\text{CH}_2\text{CH}_3)$; $^3J(\text{PCHCH}_2) = 7.3$; $^3J(\text{CH}_2\text{CHCOOEt}) = 7.5$; $^3J(\text{CH}_2\text{CH}_3) = 7$
1g	10.9	$^1J(\text{WP}) = 205$	$\delta = 4.61 (\text{CH})$; $\delta = 2.48 (\text{CH}_2)$; Complex multiplet 2.37–1.75 ppm (NC_4H_8)
1h	48.1		$\delta = 4.63 (\text{CH})$; $\delta = 2.53 (\text{CH}_2)$; Complex multiplet 2.39–1.76 ppm $^3J(\text{CHCH}_2) = 7.1$; $^2J(\text{PCH}) = 11.4$; $^3J(\text{PCH}_2) = 11$
2a	{ 46.9 45 }	$^2J(\text{PP}) = 10$	$\delta = 4.91 (\text{CHP})$; $\delta = 3.21 (\text{CH}(\text{OMe}))$; $\delta = 0.88 (\text{CHCH}_3)$; $\delta = 2.17 (\text{OCH}_3)$; $^3J(\text{CHCH}) = 9.5$; $^3J(\text{CHCH}_3) = 6$; $^2J(\text{PCH}) = 10$; $^3J(\text{PCH}_2) = 8$
2b	{ 0.1 -2.9 }	$^1J(\text{WP}) = 205$ $^1J(\text{WP}) = 208$ $^2J(\text{PP}) = 40$	$\delta = 5.28 (\text{CHP})$; $\delta = 3.21 (\text{CH}(\text{OMe}))$; $\delta = 0.71 (\text{CHCH}_3)$; $\delta = 2.24 (\text{OCH}_3)$; $^3J(\text{CHCH}) = 9$; $^3J(\text{CHCH}_3) = 6$; $^2J(\text{PCH}) = 10.5$; $^3J(\text{PCH}_2) = 8$
$[\text{Cr}(\text{CO})_4\text{vdpp}]$	52.4		$\delta = 5.66 \text{ 'N'}^{\text{c}} = 51$
$[\text{Mo}(\text{CO})_4\text{vdpp}]$	28.6		$\delta = 5.62 \text{ 'N'} = 51$
$[\text{W}(\text{CO})_4\text{vdpp}]$	8.2	$^1J(\text{WP}) = 212$	$\delta = 5.55 \text{ 'N'} = 49.5$

^aMeasured in CDCl_3 ; δ , values ± 0.1 ppm relative to 85% H_3PO_4 ; J values ± 3 Hz. ^bIn CDCl_3 ; δ values ± 0.1 ppm; J values ± 1 Hz. The values are based on ^1H and $^1\text{H}\{^{31}\text{P}\}$ NMR spectra. Not all coupling constants could be measured. ^c'N' = [$^3J(\text{P}-\text{C}=\text{C}-\text{H})_{\text{cis}}$ + $^3J(\text{P}-\text{C}=\text{C}-\text{H})_{\text{trans}}$].

Cr (68%) $\text{M} = \text{W}$ (60%) were obtained. Characterizing data are in Tables I and II.

A similar treatment of $[\text{Mo}(\text{CO})_4\text{vdpp}]$ however, led to a complex mixture. A remarkable feature of the proton spectra of $[\text{M}(\text{CO})_4\text{vdpp}]$ was the presence of a 'virtual triplet' in the $=\text{CH}_2$ region. The $\text{P}_2\text{C}=\text{CH}_2$ AA'XX' pattern gives rise to this 'virtual triplet' with the remarkably large N-doublet separation of ca. 50 Hz. This feature probably arises because $J(\text{PP}')$ is quite large and $\text{cis-}^3J(\text{P}-\text{C}=\text{C}-\text{H})$ and $\text{trans-}^3J(\text{P}-\text{C}=\text{C}-\text{H})$ are both large and of the same (positive) sign [9, 10]. We have published a Figure showing the deceptively simple ^1H NMR methylene triplet pattern of $[\text{W}(\text{CO})_4\{(\text{Ph}_2\text{P})_2\text{C}=\text{CH}_2\}]$ in our preliminary note [6]. The IR data in the carbonyl region for these vdpp complexes are similar to those of the methoxymethyl analogues, **1a** and **1b**. Both complexes were sufficiently stable to record their mass spectra and showed groups

of peaks in the expected regions for the molecular ions with intensities in good agreement with calculated values based on isotope distributions. When we followed, by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, the formation of $[\text{W}(\text{CO})_4(\text{vdpp})]$ from $[\text{W}(\text{CO})_4\text{dppm}]$ + LiBu^{n} + $\text{CH}_3\text{OCH}_2\text{Cl}$ we found that the methoxymethyl complex was formed initially but then the vdpp complex gradually formed over a period of 6 h at ca. 80 °C. However, attempts to convert the isolated methoxymethyl complex into the vinylidene complex were unsuccessful.

Thus **1b** was, (i) heated, (ii) treated with LiBu^{n} in C_6H_6 at 80 °C, (iii) treated with $\text{LiN}(\text{SiMe}_3)_2$ or (iv) treated with dilute H_2SO_4 in THF. In no case was a significant amount of $[\text{W}(\text{CO})_4(\text{vdpp})]$ produced. Similarly, with the chromium complex, **1a**. We cannot explain this.

In view of the unexpected formation of the vinylidene diphosphine complexes we also studied the

action of α -chloroethyl methyl ether, $CH_3CHClOCH_3$, on the lithiated derivatives of $[M(CO)_4(dppm)]$. As before, with $M = Mo$, mixtures of products were obtained but treatment of $[M(CO)_4\{(Ph_2P)CHPh_2\}]^-$ ($M = Cr$ or W) in C_6H_6 or THF with $CH_3CHClOCH_3$ at $20^\circ C$ gave the hoped for methoxy-ethylidene complexes **2a** and **2b**. Characterizing data are in Tables I and II. However, attempts to convert these into complexes of the type $[M(CO)_4\{(Ph_2P)C=CHMe\}]$ were unsuccessful, i.e. by the action of heat, bases or acid. Moreover, in contrast to the behaviour with CH_3OCH_2Cl , when $[M(CO)_4(Ph_2PCHPh_2)]^-$ was treated with $CH_3OCHMeCl$ in hot benzene **2a** or **2b** were formed and none of the hoped for ethylidene complexes, $[M(CO)_4\{(Ph_2P)_2C=CHMe\}]$. We cannot explain these results.

The synthesis of the complexes $[Mo(CO)_4vdpp]$ and $[W(CO)_4vdpp]$ have been described [7]. These were characterised by elemental analysis and by ^{95}Mo or ^{183}W NMR spectroscopy but other NMR data and preparative details were not given. We have made all three complexes $[M(CO)_4vdpp]$ ($M = Cr, Mo$ or W) by treating the hexacarbonyls with $vdpp$ and give additional preparative details, and NMR and IR data, in Tables I and II.

It seemed likely that in these $vdpp$ complexes the $M(CO)_4$ moiety would be a net electron withdrawing group thus polarizing the vinylidene double bond and making it susceptible towards Michael or conjugate addition. We thus treated the tungsten complex $[W(CO)_4\{(Ph_2P)_2C=CH_2\}]$ with $LiBu^n$ in the presence of TMEDA for 16 h at $20^\circ C$, and after treatment with methanol, isolated the Michael addition product $[W(CO)_4\{(Ph_2P)_2CH(CH_2)_4CH_3\}]$ in 92% yield. We independently synthesized this complex by treating the carbanion $[W(CO)_4(Ph_2PCHPh_2)]^-$ with 1-iodopentane (see 'Experimental' for details). We also treated $[W(CO)_4vdpp]$ with methyl-lithium and isolated $[W(CO)_4\{(Ph_2P)_2CHCH_2CH_3\}]$ in 68% yield. This complex has been previously prepared by treating $[W(CO)_4\{(Ph_2P)_2CH\}]^-$ with ethyl iodide [3].

We have also added malonate ion, $^-CH(COOEt)_2$ to the vinylidene double bond of $[W(CO)_4\{(Ph_2P)_2C=CH_2\}]^-$. Treatment of this tungsten complex with $NaCH(COOEt)_2$ in THF for 16 h, followed by addition of methanol gave the hoped for adduct $[W(CO)_4\{(Ph_2P)_2CHCH_2CH(COOEt)_2\}]$ (**1e**) which was characterised by elemental analysis and by 1H and ^{31}P - $\{^1H\}$ NMR spectroscopy and IR spectroscopy (see Tables I and II). The molybdenum complex (**1f**) was made similarly. Pyrrolidine is quite a reactive nucleophile and we found that it added to the $C=CH_2$ bond of $[W(CO)_4vdpp]$ at $20^\circ C$ to give the adduct $[W(CO)_4(Ph_2P)_2CHCH_2NC_4H_8]$ (**1g**). The chromium complex (**1h**) was made similarly. Characterizing data are in Tables I and II.

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