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Conjugate additions of functionalized carbanions to the vinylidene groups of $[M(CO)_4\{(Ph_2P)_2C{=}CH_2\}]$ (M = W, Mo or Cr)

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Abstract

Treatment of complexes of the type $[M(CO)_4\{(Ph_2P)_2C{=}CH_2\}]$ (M = W, Mo or Cr) with functionalized lithium reagents, LiR, followed by hydrolysis gives complexes of the type $[M(CO)_4\{PH_2P)_2CHCH_2R\}]$ in high yields; R = C_6H_4Me-4, C_6H_4OMe-2, $C_6H_3(OMe)_2$-2,6, C_6H_4OH-2, $C_6H_4(COOH)$-2, CH_2COPh or CH_2COMe. IR, and ^{31}P and ^1H NMR data are given.

We have reported previously that, although the vinylidene double bond of the diphosphine $(Ph_2P)_2C{=}CH_2$ (vdpp) is relatively inert towards Michael or conjugate addition, when complexed to a metal it becomes activated [1,2]. Thus complexes of the type $[(OC)_4M(\text{vdpp-}PP')]$ (M = W, Mo, or Cr) readily add on amines, hydrazines etc. [3] and also add LiMe or $LiBu^n$ to give after hydrolysis $[(OC)_4M\{(Ph_2P)_2CHCH_2R\}]$ (M = W, R = Me or Bu^n) [2]. We also reported that $LiC{\equiv}CPh$ alone does not add to $[(OC)_4W(\text{vdpp-}PP')]$ but in the presence of $Me_2NCH_2CH_2NMe_2$ (TMEDA), which complexes the Li and thereby increases the carbanion character of $^-C{\equiv}CPh$, smooth and rapid addition occurs, to give $[(OC)_4W\{(Ph_2P)_2CHCH_2C{\equiv}CPh\}]$ [4].

It was of interest to see if we could add (i) aryl carbanions and (ii) functionalized carbanions to the vinylidene double bond of complexes of the type $[(OC)_4M(\text{vdpp-}PP')]$, thereby synthesizing for the first time complexes of novel phosphines including functionalized phosphines which would be difficult to make in other ways. In this paper we report our results.

Treatment of $[(OC)_4W(\text{vdpp-}PP')]$ with 4-tolyllithium readily effected conjugate addition of the tolyl carbanion and after hydrolysis $[(OC)_4W\{(Ph_2P)_2CHCH_2C_6H_4Me\text{-}4\}]$ (**1a**) was isolated in 92% yield. Preparative details are in the Experimental

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Table 1

Elemental analytical, IR (cm^{-1}) and mass spectroscopic data

Complex	Analysis (Found (calcd.)(%)) C	Analysis (Found (calcd.)(%)) H	IR data (cm^{-1})[a] $\nu(C\equiv O)$	Other IR bands
1a[b]	56.8 (56.65)	3.75 (3.85)	2002, 1900, 1880, 1855	
1b[c]	63.9 (63.8)	4.4 (4.35)	2010, 1905, 1900, 1865	
1c	68.0 (68.1)	4.65 (4.65)	2000, 1907, 1895, 1865	
2a	55.6 (55.5)	3.75 (3.75)	2005, 1920, 1900, 1875	2815v (OCH_3) (KBr disc)
2b	62.15 (62.3)	4.1 (4.25)	2010, 1930, 1887	
2c	66.2 (66.45)	4.4 (4.5)	2000, 1925, 1875	
3	54.8 (54.9)	3.75 (3.9)	2005, 1915, 1900, 1875	2815s (OCH_3)
4	54.95 (55.0)	3.85 (3.6)	2007, 1920, 1900, 1870	3485v (OH)
5[d]	55.5 (55.5)	4.35 (4.3)	2008, 1930, 1910, 1882	1668s (COOH)
6	56.55 (56.2)	3.7 (3.7)	2007, 1915, 1900, 1865	1685s (C=O)
7	52.65 (52.8)	3.75 (3.75)	2008, 1925, 1920, 1890	1718s (C=O)

[a] Unless stated otherwise, the spectra of compounds **1a–2c** were determined as Nujol mulls and those of **3–7** as KBr discs. v = very strong, s = strong; all the $\nu(C\equiv O)$ bands are very strong. [b] In the mass spectrum the parent molecular ion occurred 788–782 *m/e* with good agreement between observed and calculated values. [c] In the mass spectrum the parent molecular ion occurred 702–692 *m/e* with good agreement between observed and calculated values. [d] Calculated containing 2 mols of acetone of crystallization (observed in the IR spectrum).

Table 2. ^{31}P NMR[a] and ^1H[b] NMR data

Complex	$\delta(P)$	$^1J(^{183}W^{31}P)$ (Hz)	$\delta(CH)$ (ppm)	$^2J(PCH)$ (Hz)	$\delta(CH_2)$ (ppm)	$^3J(PCH_2)$ (Hz)	$^3J(CHCH_2)$ (Hz)	Other resonances
1a	1.0	203	5.19	10.7	2.78	12.6	7.3	2.34s (CH_3)
1b	25.6		4.96	10.2	2.83	12.2	7.5	2.27s (CH_3)
1c	49.0		4.93	11	2.85	12.7	7	2.28s (CH_3)
2a	−0.1	203	5.52	11	2.79	12	7.8	3.85s (OCH_3)
2b	24.5		5.3	n.o.[c]	2.84	11.6	7.9	3.03s (OCH_3)
2c	47.9		5.44	n.o.	2.89	11.5	7.8	3.85s (OCH_3)
3	4.6	200	5.57	12.0	3.1	11.3	7.7	3.36s (OCH_3)
4	0.5	205	5.55	10.8	2.79	11.7	7.7	5.03s (OH)
5[d]	−1.6	205	6.04	10.3	3.37	12.0	8.2	
6	−1.4	205	5.33	10.4	1.92	12.7	7.4	2.56t (CH_2CO) $^3J(CH_2CH_2)$ 6.5 Hz
7	−1.0	205	5.2	10.5	1.69	12.0	7.5	1.85s ($COCH_3$) 2.05t ($COCH_2$) $^3J(CH_2CH_2)$ 6.5 Hz

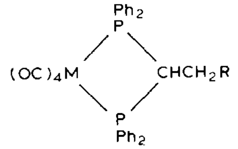
[a] Measured at 40.25 MHz. The spectra of compounds **1a–2c** were determined in CD_2Cl_2 and those of **3–7** in $CDCl_3$, unless stated otherwise. δ-values (± 0.1 ppm) relative to 85% H_3PO_4 (positive to high field). J values ± 2 Hz. [b] Compound **1a–2c** were measured in CD_2Cl_2 at 100 MHz, and compounds **3–7** in $CDCl_3$ at 400 MHz, unless stated otherwise. δ-values (± 0.01 ppm). J values ± 0.1 Hz. [c] n.o. = not observed. [d] Measured in $(CD_3)_2CO$.

section; microanalytical and IR data are given in Table 1, and ^{31}P-{^{1}H} and ^{1}H NMR data in Table 2. The corresponding molybdenum (**1b**) and chromium (**1c**) complexes were made and characterized similarly.

We then went on to study the addition of a somewhat hindered carbanion, LiC_6H_4OMe-2, to [$(OC)_4M$(vdpp-*PP*′)]. For M = W we used a reaction time of 50 min at ca. 20 °C, and isolated the hoped-for adduct (after hydrolysis) [$(OC)_4W\{(Ph_2P)_2CHCH_2C_6H_4OMe$-2} (**2a**) in 82% yield. The corresponding molybdenum (**2b**) and chromium (**2c**) complexes were made similarly in 98 and 78% yields, respectively. Preparative details are in the Experimental and characterizing data in Tables 1 and 2.

Treatment of [$(OC)_4W$(vdpp-*PP*′)] with the very sterically hindered carbanion $LiC_6H_3(OMe)_2$-2,6 [5,6] at 20 °C for 29 h gave, after hydrolysis the hoped-for adduct **3** in 66% yield.

We then went on to attempt to synthesize tungsten tetracarbonyl complexes containing functionalized diphosphines by adding functionalized carbanions to [$(OC)_4W$(vdpp-*PP*′)].



	M	R
1a	W	C_6H_4Me-4
1b	Mo	C_6H_4Me-4
1c	W	C_6H_4Me-4
2a	W	C_6H_4OMe-2
2b	Mo	C_6H_4OMe-2
2c	Cr	C_6H_4OMe-2
3	W	$C_6H_3(OMe)_2$-2,6
4	W	C_6H_4OH-2
5	W	$C_6H_4(COOH)$-2
6	W	CH_2COPh
7	W	CH_2COMe

Treatment of [$(OC)_4W$(vdpp-*PP*′)] with a solution of LiC_6H_4OLi-2, prepared by treating 2-bromophenol with LiBu^n (2 equivalents) [7] gave, after hydrolysis the hoped-for [$(OC)_4W\{(Ph_2P)_2CHCH_2C_6H_4OH$-2}] (**4**), containing a phenolic residue in 85% yield. Similar treatment however, at lower temperature with $LiC_6H_4(COOLi)$, prepared by halogen-metal exchange from 2-bromobenzoic acid, [7] gave [$(OC)_4W\{(Ph_2P)_2CHCH_2C_6H_4$(COOH-2)}] (**5**) in 67% yield.

We generated the carbanions $^-CH_2COPh$ and $^-CH_2COCH_3$ by treating, respectively, CH_3COPh and CH_3COCH_3 with $LiNPr^i_2$ and then added these carbanions to [$(OC)_4W$(vdpp-*PP*′)] at 0 °C to give [$(OC)_4W\{(Ph_2P)_2CHCH_2CH_2COR\}$] with R = Ph (**6**) or R = CH_3 (**7**) in good, 83 and 70%, yields. Preparative details are given in the Experimental section and characterization data in Tables 1 and 2.

Experimental

The experimental techniques as previously described [8].

Preparation of $[(OC)_4W\{(Ph_2P)_2CHCH_2C_6H_4Me\text{-}4\}]$ *(**1a**)*

A solution of 4-tolyllithium (0.75 cm^3, 2.6 *M*, 2 mmol) in diethyl ether was added to a solution of $[(OC)_4W(\text{vdpp-}PP')]$ (0.50 g, 0.64 mmol) in dry benzene (5 cm^3). A yellow precipitate formed immediately; the suspension was stirred for 20 min, water (2 cm^3) and then dichloromethane ($\sim$ 10 cm^3) were added and the required product was isolated from the organic layer. It formed yellow microcrystals from benzene/methanol. Yield 0.46 g, 92%.

The corresponding molybdenum (**1b**) and chromium (**1c**) complexes were made and isolated similarly in yields of 73 and 71%, respectively.

Preparation of $[(OC)_4W\{(Ph_2P)_2CHCH_2C_6H_4OMe\text{-}2\}]$ *(**2a**)*

This was made in an analogous fashion to the 4-tolyl complex **1a** above expect that a reaction time of 50 min/20 °C was used. Yield 82%.

The corresponding molybdenum (**2b**, 98% yield) and chromium (**2c**, 78% yield) complexes were made similarly both with a reaction time of 2 h.

Preparation of $[(OC)_4W\{(Ph_2P)_2CHCH_2C_6H_3(OMe)_2\text{-}2,6\}]$ *(**3**)*

A solution of n-butyllithium (1 cm^3, 2.05 mmol) in hexane was added to a solution of 1,3-dimethoxybenzene (0.27 g, 2.0 mmol) in dry tetrahydrofuran (2 cm^3) and the mixture was stirred at 40 °C for 4 h and then at 20 °C for 15 h. A solution of $[(OC)_4W(\text{vdpp-}PP')]$ (0.21 g, 0.3 mmol) in tetrahydrofuran (2 cm^3) was added and the resultant mixture was stirred at 20 °C for 29 h and then water ($\sim$ 1 cm^3) was added. This gave the required product, which formed pale yellow microcrystals from methanol. Yield 0.17 g, 66%.

Preparation of $[(OC)_4W\{(Ph_2P)_2CHCH_2C_6H_4OH\text{-}2\}]$ *(**4**)*

A solution of LiC_6H_4OLi-2 was prepared by treating a solution of 2-bromophenol (0.35 g, 2.0 mmol) in THF (2 cm^3) with a solution of $LiBu^n$ in n-hexane (2 cm^3, 4.2 mmol) and stirring the mixture for 2.5 h at 20 °C. A solution of $[W(CO)_4(\text{vdpp-}PP')]$ (0.41 g, 0.6 mmol) in THF (3.5 cm^3) was then added and the resultant mixture stirred for 20 h. Water (5 cm^3) was then added followed by sufficient dilute aqueous HCl to render the solution acid. The organic layer was evaporated to dryness and the residue treated with hexane. This gave the required product as pale yellow microcrystals. Yield 0.40 g, 85%.

Preparation of $[(OC)_4W\{(Ph_2P)_2CHCH_2C_6H_4COOH\text{-}2\}]$ *(**5**)*

2-Bromobenzoic acid (0.21 g, 1.0 mmol) was dissolved in THF (2 cm^3) and then dilithiated by treatment with $LiBu^n$ (2.05 mmol) in n-hexane (3 cm^3) at -78 °C for 1.5 h. A solution of $[W(CO)_4(\text{vdpp-}PP')]$ (0.20 g, 0.3 mmol) in dry THF (3 cm^3) was then added slowly (ca. 2 min), at -78 °C, and the resultant mixture stirred at -78 °C for 4.5 h and then at 20 °C for a further 12 h. H_2O (3 cm^3) was added, the mixture acidified with dilute hydrochloric acid, and the required product isolated from the organic layer by evaporation and treatment of the residue with n-hexane. It formed pale yellow microcrystals from acetone/n-hexane. Yield 0.17 g, 67%.

Preparation of $[(OC)_4W\{(Ph_2P)_2CHCH_2CH_2COPh\}]$ **(6)**

A solution of $LiBu^n$ in hexane (0.5 cm^3, 1.05 mmol) was added to a solution of diisopropylamine (0.10 g, 1.0 mmol) in THF (3 cm^3) and the mixture stirred for 1.5 h at 0 °C. Acetophenone (0.12 g, 1.0 mmol) was then added and the mixture stirred for a further 2 h at 0 °C. A solution of $[W(CO)_4(vdpp\text{-}PP')]$ (0.41 g, 0.6 mmol) in THF (3.5 cm^3) was then added gradually over 2 min and the mixture stirred at 0 °C for a further 6 h. The required product was then isolated by addition of H_2O (2 cm^3) and formed pale yellow microcrystals from methanol. Yield 0.41 g, 83%.

Preparation of $[(OC)_4W\{(Ph_2P)_2CHCH_2CH_2COCH_3\}]$ *(7)*

This was made in a similar manner to **6** starting from $LiCH_2COCH_3$, formed either from $LiNPr^i_2/CH_3COCH_3$ or $LiBu^n/TMEDA/CH_3COCH_3$. It formed pale yellow microcrystals from methanol. Yields 70 or 41%, respectively.

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