Octahedral metal carbonyls
75. 'Directed' synthesis of tungsten carbonyl complexes of alkenyldiphenylphosphines*

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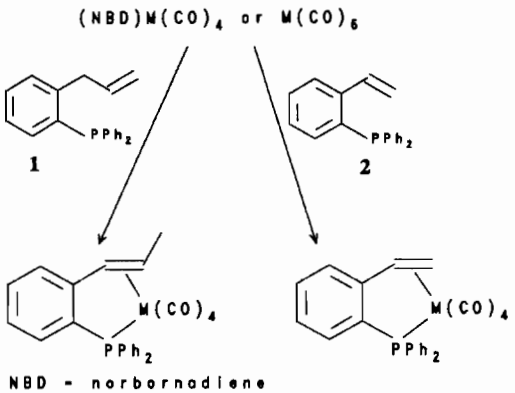
Abstract

Alkenyldiphenylphosphines, $CH_2{=}CH(CH_2)_nPPh_2$ (alkP; $n = 1$–4), react with *cis*-$(pip)_2W(CO)_4$ (pip = piperidine) to afford *cis*-(pip)(alkP)$W(CO)_4$ complexes in which alkP is coordinated through P. Two of these complexes ($n = 2, 3$) react via chelate ring closure either photochemically or thermally to afford, in high yield, (η^3-alkP)$W(CO)_4$ products in which alkP functions as a chelating ligand; for the other two ($n = 1, 4$), such products were observed in solution but could not be isolated. In contrast to observations for other complexes containing both phosphine and olefin functionalities, olefin bond migration was not observed to take place. This observation is attributed the 'direction' of the syntheses, which, for olefin bond migration to take place requires initial coordination of the alkP ligands through C=C rather than through P. The influence of the nature of the chelate ring backbone on the outcome of such reactions is also discussed.

Introduction

Synthetic studies of Group VI-B metal (=M; Cr, Mo, W) carbonyl complexes of bidentate ligands containing both phosphine and olefinic functionalities (P-ol) have shown that the identities of the products obtained are strongly influenced by the structure of the P-ol ligand and by the reaction pathway leading to chelation. Thus, where the ring backbone connecting the P and C=C functional groups contains the *o*-phenylene group, P-ol forms the most stable chelating ring, that containing 'five and a half' atoms, i.e. through a double bond involving the carbon atoms at the 3 and 4 positions relative to phosphorus, through olefinic bond migration, if required (Scheme 1) [1–4]. Similar results have been obtained for 2-alkenylpyridines [5]. However, for P-ol ligands in which the backbone connecting the olefinic and phosphine functionalities is aliphatic, complexes containing chelate rings have been produced with greater difficulty and *only* for ω-alkenylphosphines in which the olefinic linkage is located at the 3 and 4 positions (Scheme 2) [5–8].

Quite recently, the order in which the two bonds (Mo—olefin and Mo—P) were formed to afford the chelate ring was shown to influence the reactive products obtained. For the 2-propenylphenyldiphenylphosphine ligand (PP; **1**, Scheme 1), where the Mo—olefin rather than the Mo—P bond was formed upon chelate ring closure, olefin bond migration was observed *not* to take place [9]. These results prompted a study of the synthesis of Group VI-B metal carbonyl complexes of P-ol chelating ligands containing aliphatic backbones, for the series of (ω-alkenyl)diphenylphosphine ligands,



Scheme 1.

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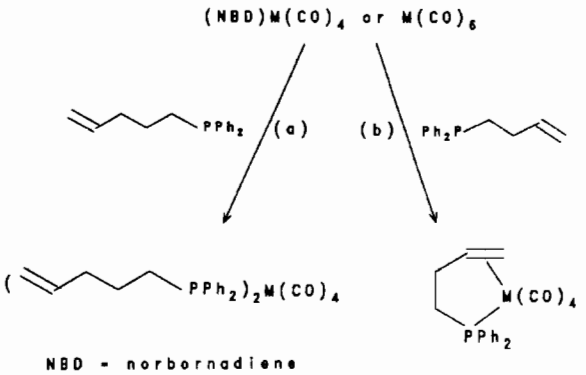


Scheme 2

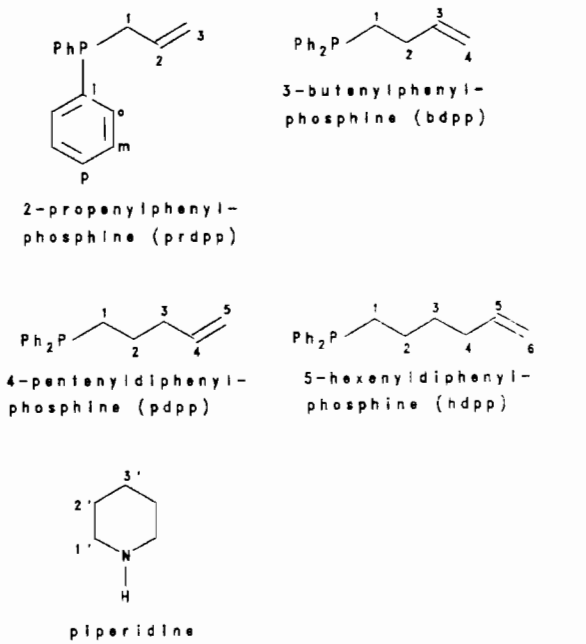


Fig. 1. The ω-alkenyldiphenylphosphines, together with their NMR labeling schemes.

$(C_6H_5)P(CH_2)_nCH{=}CH_2$ (alkP; $n = 1-4$. Fig. 1), in which the initial site of P-ol coordination to the metal atom also is 'directed'. As was the case for the PP ligand [9], this direction can be accomplished through isolation of intermediates containing the thermodynamically more stable linkage isomer, that in which alkP functions as a monodentate ligand coordinated through P rather than through C=C. Some preliminary results of this investigation have been communicated [10, 11].

Experimental

General procedures

All moisture-sensitive reactions were conducted in flame- or oven-dried apparatus under a nitrogen atmosphere. Chromatographic separations were performed on a silica gel column (160–200 mesh, Davisil Grade 62). The solvents used were dried and distilled [12] as follows: benzene and hexane from sodium; diethyl ether from sodium benzophenone ketyl; dichloromethane from calcium hybride. All solvents were stored under nitrogen; benzene was stored over type 4-A molecular sieves. All solvents were thoroughly deoxygenated prior to use. The allyl bromides (3-bromo-1-propene, 4-bromo-1-butene, 5-bromo-1-pentene and 6-bromo-1-hexene) were obtained from Wiley Organics, Inc., and were distilled before use. Piperidine (Lancaster Synthesis, Ltd.) was distilled from KOH; chloro-diphenylphosphine (Lancaster) and $W(CO)_6$ (Pressure Chemical Co.) were used as received.

Infrared spectra were recorded on a Nicolet 20 SXB FT-IR spectrometer. Mass spectra were obtained with a Hewlett Packard 5970 GCMS. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian VXR 300 spectrometer (300 MHz for ^1H, 75 MHz for ^{13}C and 120 MHz for ^{31}P) in $CDCl_3$. The 7.24 ppm resonance of residual $CHCl_3$ and the 77.0 ppm resonance of $CDCl_3$ were used as internal references for ^1H and ^{13}C, respectively, while the phosphorus chemical shifts are relative to that of external 85% H_3PO_4, with a positive value being downfield of the respective reference. All two-dimensional pulse sequences were run using standard Varian software. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

Syntheses

The general procedure used for the preparation of the alkP ligands, 2-propenyldiphenylphosphine [13] (prdpp), 3-butenyldiphenylphosphine [6] (bdpp), 4-pentenyldiphenylphosphine [14] (pdpp) and 5-hexenyldiphenylphosphine (hdpp), the latter previously not reported, is that described in the literature.

5-Hexenyldiphenylphosphine

Magnesium (0.53 g, 22 mmol), a crystal of iodine and 60 ml of diethyl ether were placed in a 100 ml round bottom flask provided with a condenser, dropping funnel and stir-bar. 6-Bromo-1-hexene (2.93 g, 18.0 mmol) dissolved in 10 ml of diethyl ether were added at such a rate so as to maintain gentle reflux. After the addition was complete, the reaction mixture was cooled to 0 °C and a solution of chlorodiphenylphosphine (4.2 g, 19.0 mmol) in 10 ml of ether was then added dropwise. After addition was complete, the solution was allowed to warm to room temperature and was stirred for 1 h. The reaction mixture was then quenched with saturated ammonium chloride and the solution was extracted with ether. The

ether solution was then washed with brine (10 ml), dried over anhydrous magnesium sulfate, filtered and evaporated under reduced pressure. The resulting residue was vacuum-distilled to afford 3.9 g (81% yield) of a colorless oil, b.p. 154–156 °C/0.5 torr. The ligand was characterized by GC-MS and through complete analysis of the ^{1}H and ^{13}C NMR spectra of its *cis*-(η^1-hdpp)(piperidine)W(CO)$_4$ derivative (*vide infra*). GC-MS, *m/e* (relative intensity) 268 (26, M^+) 267 (100) 199 ($M^+ - CH{-}CH_2$), 183 (66), 108 (87, PPh).

The ligands prdpp, bdpp and pdpp were prepared and purified similarly and were identified by GC-MS.

2-Propenyldiphenylphosphine: b.p. 98–110 °C/0.1 torr (lit. 118–28 °C/0.2 torr [14]). GC-MS (relative intensity) 226 (27, M^+), 225 (110), 108 (56, PPh).

3-Butenyldiphenylphosphine: b.p. 113–115 °C/0.1 torr (lit. 115 °C/0.1 torr [6]). GC-MS (relative intensity) 240 (29, M^+), 239 (100), 212 (33, $M^+ - CH{=}CH_2$), 183 (51) 121 (65), 108 (43, PPh).

4-Pentenyldiphenylphosphine: b.p. 120–25 °C/0.1 torr (lit. 118–121 °C/0.15 torr [15]). GC-MS (relative intensity) 253 (19, M^+), 252 (100), 108 (62, PPh).

cis-(η^1-ω-Alkenyldiphenylphosphine)-(piperidine)W(CO)$_4$ complexes

These complexes were synthesized in yields of *c.* 90% through direct reaction of *cis*-(pip)$_2$W(CO)$_4$, synthesized by the literature method [15] employing the appropriate ω-alkenyldiphenylphosphine in dichloromethane. The synthetic procedure, which was similar for each complex, is illustrated for the synthesis of *cis*-(η^1-pdpp)(pip)W(CO)$_4$. Fifteen mmol (7.0 g) of *cis*-(pip)$_2$W(CO)$_4$ and 15 mmol of pdpp (3.8 g) were refluxed under nitrogen in 50 ml of dichloromethane for 5 min. The resulting bright yellow solution was filtered through a Celite pad which had been washed with 5 ml of dichloromethane, was concentrated, and was then purified by column chromatography (silica, 3% ethyl acetate in hexanes as eluent). *Anal.* Calc. for $C_{26}H_{30}NO_4PW$: C, 49.15; H, 4.76. Found: C, 49.10; H, 4.84%. Carbonyl stretching spectrum (cyclohexane solution): 2010(s), 1903(s), 1883(vs), 1863(s) cm^{-1}.

^{1}H and ^{13}C NR data for *cis*-(η^1-pdpp)(pip)W(CO)$_4$ and its prdpp, bdpp and hdpp analogues are presented in Table 1. Chemical analyses and IR data for these complexes are as follows.

TABLE 1. ^{1}H and ^{13}C NMR data for *cis*-(pip)(η^1-alkP)W(CO)$_4$ complexes (alkP = prdpp, bdpp, pdpp, hdpp)[a]

Complex[b]	Position[c]	(^{1}H)[d]	(^{13}C)	^nJ(pc)
prdpp	1	3.38	39.15	23.2
	2	5.56	129.57	4.2
	3	4.90	120.13	10.6
	i		133.57	32.7
	o	7.58	132.74	10.5
	m	7.45	129.00	8.6
	p	7.45	130.16	
	1′	2.65	58.25	
	2′	1.24	28.65	
	3′	0.45	58.25	
	NH	0.68		
	CO[e]		209.48	32.5
	CO[f]		209.16	5.55
			204.22	7.1
bdpp	1	2.58	32.65	24.5
	2	2.12	28.11	2.3
	3	5.80	137.70	15.6
	4	4.95	115.17	
	i		134.15	33.1
	o	7.62	132.57	10.7
	m	7.48	129.17	8.6
	p	7.48	130.19	
	1′	2.7	58.23	
	2′	1.3	28.64	
	3′	0.5	22.19	
	NH	0.74		
	CO[e]		209.31	16.1
	CO[f]		209.55	9.7
			204.06	7.1
pdpp	1	2.50	32.60	25.4
	2	1.48	22.97	2.1
	3	2.10	34.80	14.6
	4	4.95	137.61	
	5	5.68	115.61	
	i		134.45	32.9
	o	7.59	132.59	10.7
	m	7.46	129.10	8.5
	p	7.46	129.17	2.1
	1′	2.7	58.19	
	2′	1.3	28.63	
	3′	0.49	22.19	
	NH	0.72		
	CO[e]		209.36	16.0
			209.61	10.5
	CO[f]		204.16	7.5
hdpp	1	2.45	33.11	25.3
	2	1.34	30.19	14.1
	3	1.35	23.35	
	4	1.92	33.13	
	5	5.64	138.31	
	6	4.82	114.59	
	i		134.47	32.6
	o	7.55	132.57	10.7
	m	7.40	129.06	8.6
	p	7.40	130.03	2.0
	1′	2.65	58.18	
	2′	1.38	28.63	
	3′	0.45	22.19	
	NH	0.69		
	CO[e]		209.33	16.4
	CO[f]		209.50	9.8
			204.19	7.4

[a]In ppm relative to internal solvent ($CDCl_3$), *J* in Hz. [b]Ligand abbreviations are defined in the text. [c]NMR labeling scheme is shown in Fig. 1. [d]All proton signals are multiplet except as noted. [e]CO *trans* to phosphine ligand. [f]CO *cis* to phosphine ligand.

cis-(prdpp)(pip)W(CO)$_4$. *Anal.* Calc. for $C_{24}H_{26}NO_4PW$: C: 47.46; H, 4.31. Found: C, 47.33; H, 4.35%. Carbonyl stretching absorptions (cyclohexane solution): 2011(s), 1904(s), 1883(vs), 1866(m) cm^{-1}.

cis-(bdpp)(pip)W(CO)$_4$. *Anal.* Calc. for $C_{25}H_{28}NO_4PW$: C: 48.33; H, 4.54. Found: C, 48.46; H, 4.71%. Carbonyl stretching absorptions (cyclohexane solution): 2011(s), 1904(s), 1884(vs), 1864(s) cm^{-1}.

cis-(hdpp)(pip)W(CO)$_4$. *Anal.* Calc. for $C_{27}H_{32}NO_4PW$: C: 48.94; H, 4.97. Found: C, 50.21; H, 5.17%. Carbonyl stretching absorptions (cyclohexane solution): 2010(s), 1903(s), 1882(s), 1863(s), cm^{-1}.

cis-(η^3-Alkenyldiphenylphosphine)W(CO)$_4$ complexes

These complexes (alkenyldiphenylphosphine = bdpp, pdpp) can be synthesized from the corresponding *cis*-(ω-alkenyldiphenylphosphine)(pip)W(CO)$_4$ complex either thermally or photochemically. Both methods will be illustrated.

cis-(η^3-bdpp)W(CO)$_4$. cis-(η^1-bdpp)(pip)W(CO)$_4$ (2.0 g, 3.2 mmol) was dissolved in 50 ml of dry benzene under nitrogen and was heated under reflux for 7 h. The reaction solution was then cooled, the solvent was removed *in vacuo*, and the residue was chromatographed on a silica gel column using 3% ethyl acetate in hexanes as eluent to afford 1.5 g (89%) of light yellow product. *Anal.* Calc. for $C_{20}H_{17}O_4PW$: C, 44.80; H, 3.19. Found: C, 44.85; H, 3.35%. Carbonyl stretching spectrum (cyclohexane solution): 2031(vs), 1939(s), 1930(m), 1914(vs), 1901(m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ7.2–7.8 (m, 10 H, Ar H), 4.80 (m, –CH=), 3.4–3.8 (m, =CH_2), 2.90 (m, 2 H), 2.10 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ209.39, 204.98, 202.08, 200.16, 129.81—136.97 (Ar C), 90.37 (–CH=), 59.14 (=CH_2), 37.35, 32.83. ^{31}P NMR ($CDCl_3$, 120 MHz): δ37.14 (J_{PW} 241.8 Hz).

cis-(η^3-pdpp)W(CO)$_4$. cis-(η^1-pdpp)(pip)W(CO)$_4$ (0.35 g, 0.55 mmol) in dried and degassed benzene (50 ml) was irradiated for 20 min employing a 400 w Hanovia medium pressure mercury lamp in a quartz immersion reactor. The reaction was monitored by IR spectroscopy. Workup identical to that employed for *cis*-(η^3-bdpp)W(CO)$_4$ afforded 0.24 g (78%) of light yellow crystals. A sample for elemental analysis was recrystallized from toluene/hexane. *Anal.* Calc. for $C_{21}H_{19}O_4PW$: C, 45.85; H, 3.38. Found: C, 45.91; H, 3.39%. Carbonyl stretching spectrum (cyclohexane solution): 2031(s), 1939(s), 1931(s), 1900(s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ7.22–7.80 (m, 10 H, Ar H), 3.34 (1 H), 3.08 (2 H), 2.68 (2 H), 2.18 (2 H) 1.78 (2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ206.03, 205.37, 199.60, 198.56, 140.02, 128.4 (Ar C), 65.18 (–CH=), 52.22 (=CH_2), 35.13, 27.68, 24.95.

cis-(η^3-prdpp)W(CO)$_4$ and cis-(η^3-hdpp)W(CO)$_4$

Both thermal and photochemical methods were employed in attempts to synthesize these complexes; they could not be isolated, but carbonyl stretching spectra taken during the reaction of the respective *cis*-(pip)(alkp)W(CO)$_4$ complexes (alkP = prdpp, hdpp) revealed traces of the (η^3-alkP)W(CO)$_4$ products (ν(CO), benzene solution: 2029, 1931, 1900, 1884 cm^{-1}).

Results

The (η^3-alkP)W(CO)$_4$ complexes were synthesized through the stepwise reaction of alkP ligands with *cis*-(pip)$_2$W(CO)$_4$ (eqn. (1)), prepared through reaction of W(CO)$_6$ with pip in decalin at 165 °C for 24 h [15].

$$\begin{aligned} W(CO)_6 + 2pip \rightarrow\ & cis\text{-}(pip)_2(W(CO)_4 + 2CO \\ & \downarrow + \text{alkP} \\ & cis\text{-}(\eta^1\text{-alk})(pip)W(CO)_4 \\ & \downarrow + pip \\ & cis\text{-}(\eta^3\text{-alkP})W(CO)_4 + pip \end{aligned} \quad (1)$$

cis-(η^1-alkP)(pip)W(CO)$_4$ intermediates

cis-(pip)$_2$W(CO)$_4$ reacts with alkP (1:1 mol ratio) in refluxing dichloromethane for 5 min to afford the *cis*-(η^1-alkP)(pip)W(CO)$_4$ intermediates in high yield (*c.* 90% [15]). The infrared spectra of these intermediates exhibit four carbonyl stretching bands, indicative of a *cis* arrangement of alkP and pip. The positions of these bands are consistent with those expected for coordination of a phosphine and a piperidine to W [15–18]. NMR spectral assignments confirm the structures of the alkP ligands as $(C_6H_5)_2P(CH_2)_nCH{=}CH_2$ ($n = 1$–4). The assignments, given in Table 1, are similar for all four (η^1-alkP)(pip)W(CO)$_4$ complexes; they are exemplified here by those for *cis*-(η^3-hdpp)(pip)W(CO)$_4$ ($n = 4$). Proton connectivities were deduced from the two-dimensional ^{1}H—^{1}H correlated spectrum (COSY) [19] (Fig. 2). H-6 appears as a multiplet at 4.82 ppm showing an allylic coupling with H-4. Thus, the resonance at 5.64 ppm is assigned to the olefinic proton H-5. Furthermore, the COSY spectrum indicates that the resonances at 1.92, 1.35, 1.34 and 2.45 ppm

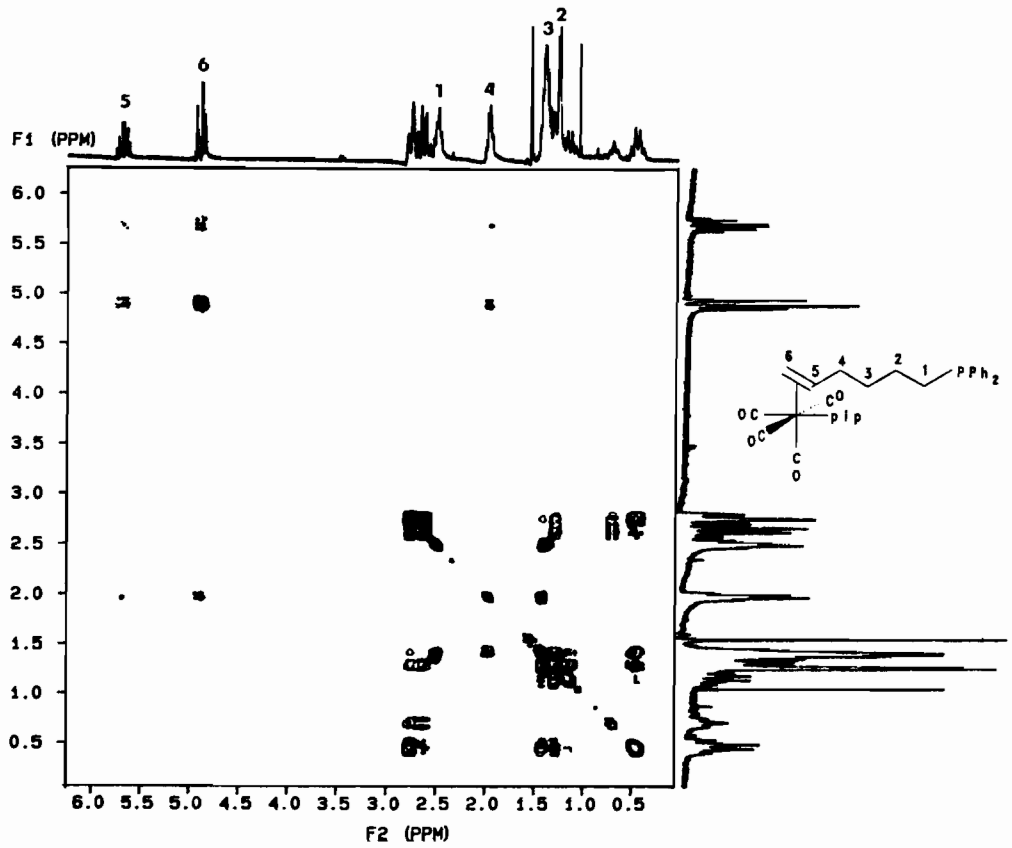


Fig. 2. Partial two-dimensional $^1H-^1H$ COSY NMR spectrum of *cis*-(pip)(η^1-hdpp)$W(CO)_4$ in $CDCl_3$.

can be attributed to a $-CH_2-CH_2-CH_2-CH_2-P$ moiety, which appears to be a connecting unit, confirming the signal at 2.45 ppm as H-1. The remaining signals correspond to those expected for coordinating pip.

The assignment of the ^{13}C chemical shifts was achieved using the attached proton test (APT) [20], the phosphorus–carbon coupling constants [21, 22], and the heteronuclear chemical shift correlated spectrum (HETCOR) [23]. The P–C couplings for the phenyl ring carbons are larger than those observed for triphenylphosphine, which reflects the differing orientations of the phenyl rings in that compound [24].

cis-(η^3-alkP)W(CO)$_4$ complexes

Thermal or photochemical reactions of *cis*-(η^1-alkP)(pip)$W(CO)_4$ in benzene afford *cis*-(η^3-alkP)$W(CO)_4$ products in high yield (>78%) for alkP = bdpp and pdpp, but for prdpp and hdpp, while the ring-closed products were observed in solution (carbonyl stretching spectra), they could not be isolated. This would suggest that bdpp and pdpp form chelate rings of optimum stabilities. The carbonyl stretching frequencies observed for (η^3-bdpp)$W(CO)_4$ and (η^3-pdpp)$W(CO)_4$, and in solution for their prdpp and hdpp analogues ('Eperimental') are observed at higher frequencies than are those for the *cis*-(η^1-alkP)(pip)$W(CO)_4$ complexes from which they are produced, indicative of the expected olefin-to-W π-backbonding. The complex (η^3-bdpp)$W(CO)_4$ exhibits five carbonyl stretching frequencies; the additional band suggests the presence of interconverting rotational isomers involving the plane of the coordinated alkene, as has been noted in other systems [7, 25].

The ^1H and ^{13}C NMR spectra for (η^3-bdpp)$W(CO)_4$ in $CDCl_3$ solution reveal expected changes in the chemical shifts attributable to coordination of the olefin [22]. The resonances corresponding to the olefinic carbons, C-3 and C-4, shift from 137.70 and 115.17 ppm, respectively, in (η^1-bdpp)$W(CO)_4$ to 90.37 and 59.14 ppm, respectively in (η^3-bdpp)$W(CO)_4$ as a result of olefin coordination to W. Examination of a typical ^{13}C NMR spectrum of (η^3-bdpp)$W(CO)_4$ shows that the number of ^{13}C phenyl ring resonances is twice that observed for *cis*-(η^1-bdpp)(pip)$W(C0)_4$, which indicates that rotation about the W–P bond does not take place after coordination. The COSY spectrum shows two upfield doublets (AX pattern)

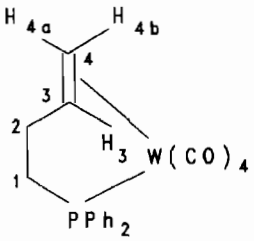


Fig. 3. Labeling scheme for (η^3-3-butenyldiphenylphosphine)-$W(CO)_4$.

with $J = 9.0$ and 14.4 Hz, respectively, also indicative of olefin coordination.

The nuclear Overhauser effect (NOE) has been used successfully to determine the relative stereochemistry of olefinic protons [26, 27]. Irradiation of the methine proton (H-3, Fig. 3) at 4.8 ppm in (η^3-bdpp)$W(CO)_4$ produced an enhancement (*c.* 9%) of the signal at 3.75 ppm (H-4b) and a small negative enhancement of the signal at 3.56 ppm (H-4a). A strong NOE correlation between H-3 and H-4b establishes a *cis* relationship between these protons.

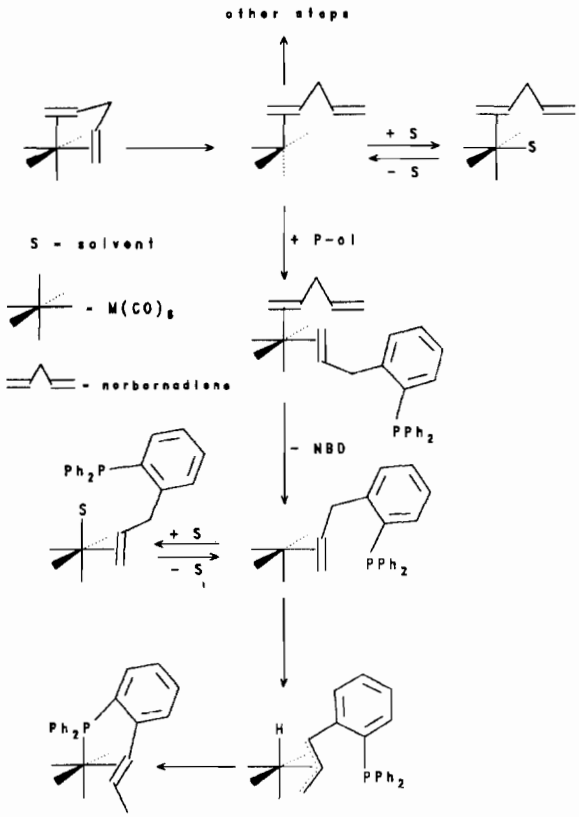
The double bond position in the ligand pdpp in *cis*-(η^3-pdpp)$W(CO)_4$ was confirmed by ^{13}C NMR and ATP experiments. The chemical shift at 52.22 ppm, assigned to the terminal olefinic carbon, indicated that no olefin bond migration had taken place.

Discussion

The synthesis of (η^3-pdpp)$W(CO)_4$ demonstrates that olefin bond migration to afford a P-ol complex in which a double bond at the 3 and 4 positions is coordinated to W does not take place. This observation is in contrast to the results of Interrante *et al.* [1] for displacement of norbornadiene (=NBD) from (NBD)$M(CO)_4$ (M = Cr, Mo, W) by PP (**1**, Scheme 1) but consistent with those of Wang and Dobson, where this synthesis took place via the intermediacy of (η^1-PP)(pip)$Mo(CO)_4$ but no olefin bond migration was observed. [10]. These seemingly contrasting results are explicable in terms of the direction of initial interaction of the P-ol ligand with the metal atom.

As first discussed by King and Fronzaglia based upon the inertness of $W(CO)_6$, tungsten carbonyl complexes containing olefinic linkages are best synthesized via displacement of weakly-bonded substituents from the tungsten carbonyl moiety [28]. A precursor commonly employed in syntheses of complexes containing P-ol ligands is (η^4-NBD)$W(CO)_4$, synthesized in turn from $(CH_3CN)_3W(CO)_3$ [28]. The displacement of NBD from (NBD)$W(CO)_4$ evidently takes place through NBD ring opening. The (η^2-NBD)$W(CO)_4$ intermediate thus produced can then react either with the olefin or the phosphine functional group of alkP.

Recent studies have indicated that for reactions under kinetic control the steric properties of the functional groups, and not the strengths of the bonds being formed, dictate the 'end' of initial coordination of the bidentate ligand; electronic factors governing the site of initial coordination are relatively unimportant [29, 30].* Thus it is reasonable to presume, given the steric congestion at the vacant coordination site in (η^2-NBD)$W(CO)_4$, that coordination of P-ol will take place predominantly at the sterically less demanding olefinic linkage despite the greater stabilities of W—P than W—olefinic bonds. Thus, upon olefin coordination, a *cis*-(η^2-P-ol)(η^2-NBD)$W(CO)_4$ intermediate, which can undergo further reaction



Scheme 3.

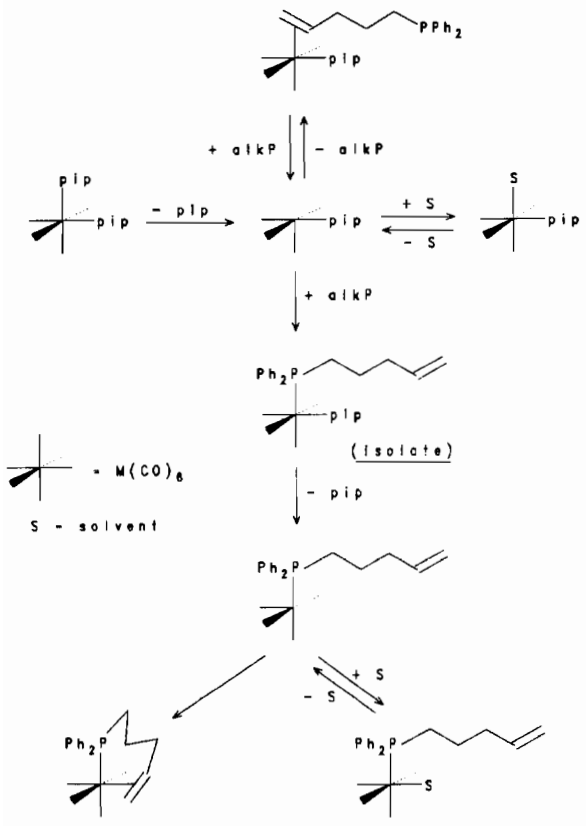
*The rate constants for reactions of N_2 and CO with $[W(CO)_5]$ in n-heptane differ by <40% despite the similar steric nature of CO and N_2 but greatly differing OC–W and N_2–W bond strengths. Displacement of n-heptane from (n-heptane)$W(CO)_5$ at the rates observed is dissociative in nature [31].

to afford coordinatively-unsaturated *cis*-(η^2-P-ol)W(CO)$_4$, will be produced. This coordinatively-unsaturated species can undergo olefin bond migration via an allylic intermediate to afford the most stable chelate ring, as has been observed for PP (Scheme 1, **1**). This reaction sequence is illustrated in Scheme 3.

If the critical requirement for olefin bond migration is the presence of a vacant coordination site adjacent to a coordinated olefin, the olefin bond migration pathway can be eliminated via 'directed' ligand displacement by alkP. Darensbourg and Kump demonstrated that displacement of pip from (pip)$_2$W(CO)$_4$ takes place in a stepwise fashion and that *cis*-(L)(pip)W(CO)$_4$ complexes, where L is a phosphine or phosphite were isolable in high yield [15]. This procedure, employed in this study, has afforded analogous complexes in which alkP is coordinated through P (the thermodynamically more stable product). Chelate ring closure in such *cis*-(pip)(η^1-alkP)W(CO)$_4$ species thus takes place without olefin isomerization (Scheme 4).

The differences in the observed reactivity of the PP versus alkP ligands (Schemes 1, 2) would appear to be related to the ease of chelate ring closure. The *o*-phenylene backbone in PP reduces the number of degrees of freedom in the chelating ring relative to an alkP ligand, facilitating chelate ring closure, and inhibiting possible competing reaction pathways such as those leading to substitution by two P-ol ligands (Scheme 2, pathway (a)). In this regard it is to be observed that ring closure through coordination of the bulky and massive PPh$_2$ moiety in alkP ligands should be especially slow.

The results obtained here provide strong additional evidence that for bidentate ligands containing two different functional groups the site of initial bond formation in the ligand may be a consideration in determining the outcome of the reaction. Where this is the case, methods of 'directed' ligand displacement to select the functional group which initially coordinates to the metal atom will be important to the achievement of synthetic objectives.



Scheme 4.

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