

Octahedral metal carbonyls

LXV *. Olefin isomerization in (2-allylphenyldiphenylphosphine)tetracarbonyltungsten(0)

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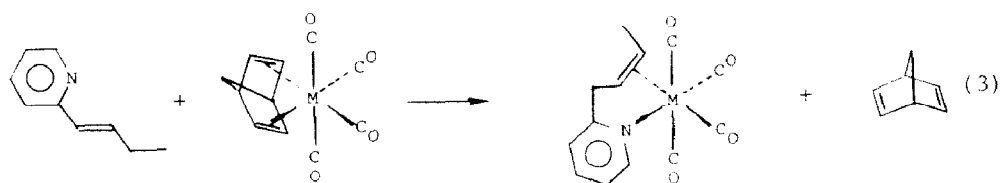
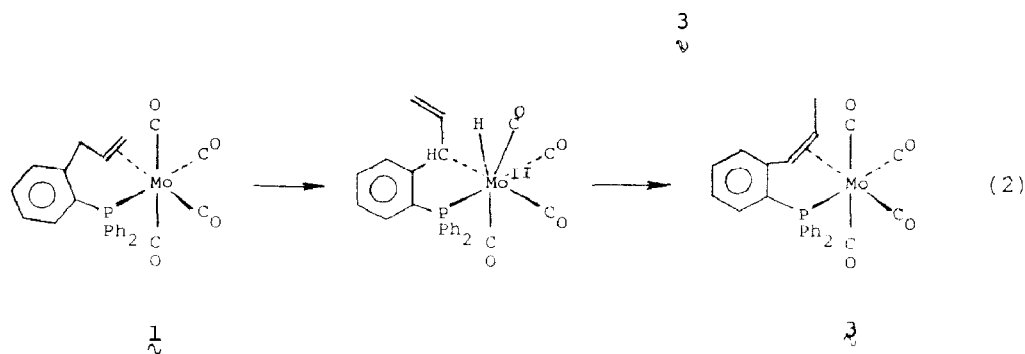
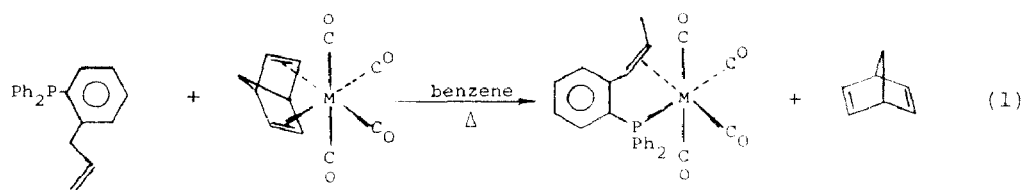
Abstract

The stepwise displacement of pip (= piperidine) from *cis*-(pip)₂W(CO)₄ by 2-allylphenyldiphenylphosphine (adpp) affords *cis*-(η^3 -adpp)W(CO)₄ (**1**) when the *cis*-(pip)(η^1 -adpp)W(CO)₄ intermediate (**2**; adpp is P-bonded) is isolated and purified; directly, this reaction affords a 85/15 ratio of **1** to *cis*-(η^3 -pdpp)W(CO)₄ (**3**; pdpp = 2-propenylphenyldiphenylphosphine). In contrast, it had been reported that displacement of norbornadiene (= NBD) from (η^4 -NBD)M(CO)₄ by adpp affords primarily **3**. It is concluded that olefin bond-migration takes place in a η^3 -allylmetal hydride intermediate produced from a [$(\eta^2$ -adpp)W(CO)₄] precursor in which adpp is coordinated *cis* to a vacant coordination site through the olefinic linkage.

Introduction

For several chelating ligands containing both nitrogen and olefin (N-ol) or phosphorus and olefin (P-ol) functional groups, olefin bond-migration has been observed to take place upon formation of their metal carbonyl complexes, (N-ol')M(CO)₄ or (P-ol')M(CO)₄ (M = Cr, Mo, W). Thus Interrante, Bennett and Nyholm [1] observed that upon displacement of norbornadiene (NBD) from (η^4 -NBD)M(CO)₄ by the P-ol ligand 2-allylphenyldiphenylphosphine (adpp) the (P-ol')M(CO)₄ complexes containing 2-propenylphenyldiphenylphosphine (pdpp) were obtained (eq. 1). The structure of the pdpp complex (M = Mo) was confirmed by an

* For part LXIV, see K.J. Asali, G.J. van Zyl and G.R. Dobson, *Inorg. Chem.*, in press.



X-ray structural determination [2]. Nyholm suggested the bond-migration in this complex to take place (eq. 2) via a seven-coordinate complex of molybdenum(II) [3]. Heaton and McCaffrey have also noted olefin bond-migration during $(N\text{-ol}')M(CO)_4$ complex formation where the $N\text{-ol'}$ were various 2-alkenylpyridines (eq. 3) [4]. They suggested that these migrations, which proceed in either direction (toward or away from the pyridine moiety) take place via an intramolecular rearrangement to afford an η^3 -allylmethylmetal hydride intermediate; in each instance the observed product is the thermodynamically more stable five-membered chelate ring. Precedents for such a reaction pathway have been noted [5,6]. An olefin isomerization taking place via an η^3 -allylmethylmetal hydride intermediate would require either internal oxidative addition through formation of a molybdenum(II) species or, for a reaction involving molybdenum(0), the presence of a vacant coordination site adjacent to the coordinated olefin. We have examined these possibilities through an investigation of the stepwise replacement by adpp of pip (= piperidine) from $cis\text{-(pip)}_2W(CO)_4$.

Experimental

General. Infrared spectra were determined employing Perkin-Elmer Model 1710 or Nicolet Model 20SXB FT-IR spectrophotometers or a Perkin-Elmer Model

621 grating spectrophotometer. NMR spectra (^{31}P , 121 MHz; ^1H , 300 MHz; ^{13}C , 75 MHz) were obtained using a Varian VXR-300 spectrometer. Chemical analyses were carried out by Midwest Microlabs Ltd., Indianapolis, IN.

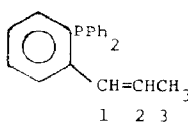
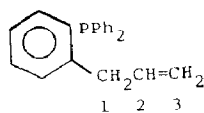
Preparation of reagents. *o*-Chloroallylbenzene. The preparation of this precursor followed the procedure of Nyholm and coworkers [1] except that the formation of the Grignard of 2-bromochlorobenzene (prepared through use of the standard procedure [7] from *o*-chloroaniline (Aldrich)) was carried out at -5 to 0°C . The reactants, Mg (4.5 g; 0.185 mol), allyl bromide (22 g; 0.16 mol) and *o*-chlorobromobenzene (35.45 g; 0.214 mol) afforded, after fractional distillation, 26.5 g (81% yield) of pure *o*-chloroallylbenzene, b.p. $70\text{--}71^\circ\text{C}/0.2$ torr.

2-Allylphenyldiphenylphosphine. This ligand (adpp) was prepared employing a modification of the method of Nyholm and coworkers [1]. Magnesium (4.2 g, 0.17 mol), *o*-chloroallylbenzene 22 g, 0.14 mol) and 300 ml of dry THF were placed in a 500 ml, three-necked round-bottom flask provided with a condenser and magnetic stir-bar under a nitrogen atmosphere and were heated to reflux. A solution of 1,2-dibromoethane (5 ml in 20 ml of dry THF), employed as an entrainment reagent [8], was injected into the reaction mixture at a rate of 1.2 ml/h over 20 h employing a syringe pump. Reflux was continued for 3 h after the addition was complete. The reaction mixture was cooled and chlorodiphenylphosphine (30 g, 0.14 mol) in 50 ml of THF was added to it dropwise over 2 h; the mixture was then stirred for two additional h. The work-up which followed was that described by Nyholm and coworkers [1]. The crude solid product was recrystallized from ether/*n*-pentane to afford 15.7 g (36% yield) of colorless crystals, *m* (uncorr.) $65\text{--}66^\circ\text{C}$ (lit. $65\text{--}68^\circ\text{C}$ [1]).

cis-(η^1 -2-Allylphenyldiphenylphosphine)(piperidine)tetracarbonyltungsten(0) (**2**). *cis*-(Pip) $_2\text{W}(\text{CO})_4$ prepared via the literature method [9] (1.48 g, 3.2 mmol) and adpp (0.8 g, 2.6 mmol) were refluxed for 5 min in 50 ml of CH_2Cl_2 under nitrogen. After solvent removal the crude product was purified by column chromatography (silica gel; 3% ethyl acetate in hexane as eluant). The eluant was removed and the product (1.5 g, 83% yield, *m* (uncorr.) $149\text{--}150^\circ\text{C}$) was obtained as bright yellow crystals after recrystallization from toluene/hexane. Anal. Found: C, 52.12; H, 4.41. $\text{C}_{30}\text{H}_{30}\text{NO}_4\text{PW}$ calcd.: C, 52.72; H, 4.42%. IR (cyclohexane solution); $\nu(\text{CO})$, 2012.7(s), 1903.9(s), 1887.3(vs) and 1864.3(s) cm^{-1} . NMR: ^1H (CDCl_3), δ 7.3–7.7 (m, 14H), 5.4 (m, 1H), 4.9 (m, 2H), 3.8 (m, 2H), 2.7 (m, 4H), 1.3 (m, 4H), 0.6 (m, 2H); ^{13}C (CDCl_3), δ 209.05, 204.7, 142.9, 126–136 (Ar C), 117.6, 58.4, 39.1, 28.6, 22.6. ^{31}P (CDCl_3 , 85% H_3PO_4 external standard), δ 48.3 (satellites, $^1J(\text{PW})$ 232 Hz). A two-dimensional $^1\text{H}\text{--}^1\text{H}$ correlation (COSY) spectrum [10] was employed in the assignment of the ^1H resonances, while an Attached Proton Test (ATP) experiment [11] assisted in the assignment of the ^{13}C NMR spectrum. These assignments for the allyl protons and carbons, together with attributions of the ^1H and ^{13}C resonances for atoms in the chelate rings for *cis*-(η^3 -adpp) $\text{W}(\text{CO})_4$ and *cis*-(η^3 -pdpp) $\text{W}(\text{CO})_4$ (pdpp = propenylphenyldiphenylphosphine, vide infra) are given in Table 1.

cis-(η^3 -2-Allylphenyldiphenylphosphine)tetracarbonyltungsten(0) (**1**). *cis*-(η^1 -Adpp)(pip) $\text{W}(\text{CO})_4$ (**2**), 0.30 g, 0.43 mmol) was refluxed in 20 ml dry benzene under nitrogen for 3 h. The solvent was removed and the residue was purified by column chromatography on silica gel (3% ethyl acetate/hexane eluant) to afford 0.24 g (92%) of light yellow crystalline (**1**), *m*. $157\text{--}158^\circ\text{C}$. Anal. Found: C, 49.97; H, 3.33. $\text{C}_{25}\text{H}_{19}\text{O}_4\text{PW}$ calcd.: C, 50.19; H, 3.20%. IR (cyclohexane solution): $\nu(\text{CO})$,

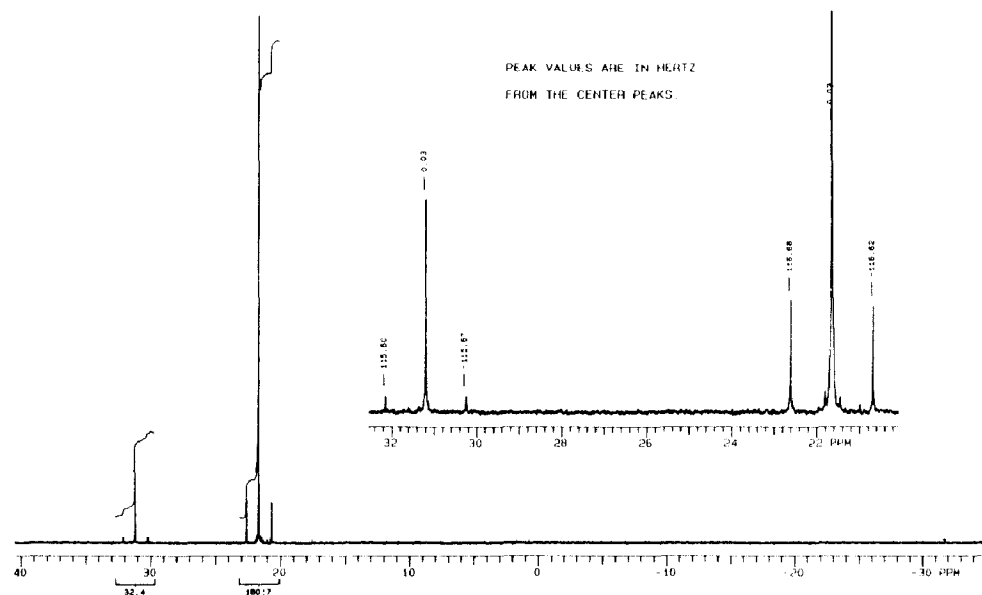
Table 1

 ^1H and ^{13}C NMR assignments for the complexes a, b adpp = 2-(allylphenyl)-
diphenylphosphinepdpp = 2-*cis*-propenyl-
phenyl)diphenylphosphine

Complex	Chemical shifts (ppm)		
	C(1)H(1)	C(2)H(2)	C(3)H(3)
$(^1\text{H})^{a,b}$			
<i>cis</i> -(η^1 -adpp)(pip)W(CO) ₄	3.8	5.4	4.4
<i>cis</i> -(η^3 -adpp)W(CO) ₄	4.2	3.7	3.2
<i>cis</i> -(η^3 -pdpp)W(CO) ₄	5.6	4.7	2.2
$(^{13}\text{C})^{a,b}$			
<i>cis</i> -(η^1 -adpp)(pip)W(CO) ₄	39.1(u) ^c	142.9(d)	117.6(u)
<i>cis</i> -(η^3 -adpp)W(CO) ₄	48.1(u)	68.6(d)	53.2(u)
<i>cis</i> -(η^3 -pdpp)W(CO) ₄	112.7(d)	85.4(d)	19.0(d)

^a CDCl₃ solvent. ^b CDCl₃ internal reference: ^1H : δ 7.24; ^{13}C : δ 77.0. ^c ^{13}C multiplicities determined employing the Attached Proton Test (APT, ref. 11), distinguishing primary and tertiary C (= down, (d)) from secondary and quaternary C (= up (u)).

2034(s), 1943(s), 1933(s) 1926(m), 1908(vs) and 1898(m) cm⁻¹. NMR: ^1H (CDCl₃), δ 6.8–7.6 (m, 14H), 4.2 (m, 1H), 3.7 (m, 2H), 3.2 (m, 2H); ^{13}C (CDCl₃), δ 208.0, 204.2, 200.2, 198.8, 126–142 (Ar C), 68.6, 53.2, 41.8; ^{31}P (CDCl₃): δ 21.8 (satellites, $^1J(\text{PW})$ 234 Hz).

Fig. 1. ^{31}P NMR spectrum of products of the reaction *cis*-(pip)₂W(CO)₄ with adpp.

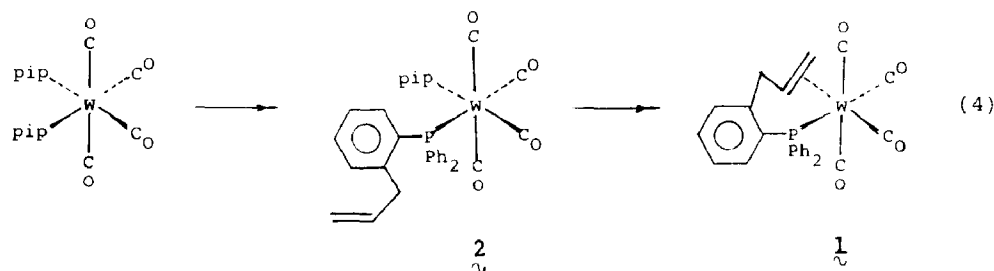
The direct reaction of 2-allylphenyldiphenylphosphine with $cis-(pip)_2W(CO)_4$ to displace two molecules of pip. 2-Allylphenyldiphenylphosphine (0.4 g; 1.3 mmol) and $cis-(pip)_2W(CO)_4$ (0.74 g, 1.6 mmol) were heated at reflux in 25 ml of CH_2Cl_2 under nitrogen. The reaction was monitored by IR and was complete in 7 h. The solution was cooled, filtered through Celite, evaporated to dryness and the residue was recrystallized from hexane to afford 0.8 g (89% yield) of yellow powder.

NMR spectra of the product showed it to be a mixture of $cis-(\eta^3\text{-adpp})W(CO)_4$ (vide supra) and $cis-(\eta^3\text{-pdpp})W(CO)_4$; the carbonyl stretching and 1H NMR spectra of the latter had been reported previously [1]. The two species were found to be present in an 85/15 ratio as determined from integration of the two peaks present in the ^{31}P NMR spectrum (Fig. 1). For $cis-(\eta^3\text{-pdpp})W(CO)_4$, the ^{31}P NMR spectrum (85% H_3PO_4 external standard) exhibits a peak at δ 32.4 (satellites, $^1J(PW)$ 232 Hz). The ^{31}P absorption for $(adpp)W(CO)_4$ at δ 21.8 indicates that the P is contained within a six-membered, rather than a five-membered chelate ring [12].

$(NBD)W(CO)_4$, prepared by the literature method [13], was allowed to react with adpp in benzene at $80^\circ C$, the conditions employed by Interrante, Bennett and Nyholm [1]. The progress of the reaction was monitored by IR; no species other than $(NBD)W(CO)_4$ and $cis-(pdpp)W(CO)_4$ were observed to be present during the reaction's course. Similarly, IR evidence for the presence of no intermediate other than **2** was observed during the reaction of $cis-(pip)_2W(CO)_4$ with adpp.

Results

The displacement of two molecules of pip from $cis-(pip)_2W(CO)_4$ takes place in a stepwise fashion (eq. 4), as is indicated by the isolation of $cis-(\eta^1\text{-adpp})(pip)W(CO)_4$



(**2**) and through the further reaction of this complex after its isolation to form $cis-(\eta^3\text{-adpp})W(CO)_4$ (**1**). However, when $cis-(pip)_2W(CO)_4$ is allowed to react directly with adpp (without isolation of intermediate (**2**)), the final reaction products are an 85/15 mixture of **1** and $cis-(\eta^3\text{-pdpp})W(CO)_4$ (**3**), the product observed by Nyholm and coworkers to be produced upon an analogous reaction of $(NBD)W(CO)_4$ with adpp [1]. The additional band observed in the carbonyl stretching spectrum for **1** is reasonably attributed to the existence of rotational isomers of **1** as has been noted in related P-ol and N-ol complexes [14,15]; as was the case in those studies, their existence on the NMR time-scale was not observed.

The mode of attachment of the bidentate adpp ligand to W in **2**, through P rather than through the olefinic linkage, was determined spectroscopically. The ^{13}C NMR spectrum for **2** exhibits a terminal olefin resonance at δ 117.8. Only two resonances (δ 209.05 and 204.7, *trans* and *cis*, respectively) are observed for the carbonyl carbons, probably a result of free rotation about the P-W and P-C (in

C₆H₄CH₂CH=CH₂) bonds. The ³¹P NMR spectrum shows a resonance at δ 48.3, accompanied by satellites due to coupling with ¹⁸³W (*I* = 1/2, 14% abundance, ¹*J*(PW) 232 Hz) attributable to coordinated P [12]. This assignment is also supported by the carbonyl stretching spectrum for **2**, the absorbances of which (2012.7, 1903.8, 1887.3, 1864.3 cm⁻¹ in cyclohexane) are nearly identical to those observed for the closely-related *cis*-(PPh₃)(pip)W(CO)₄ in the same solvent (2013, 1904, 1891, 1865 cm⁻¹) [16], but markedly different from those of *cis*-(η³-N-ol)W(CO)₄ (N-ol = CH₂=CHCH₂CH₂-N(CH₃)₂), in which N-ol is coordinated to W through an amine and an olefinic functionality, observed at 2028, 1925, 1914 and 1882 cm⁻¹ in n-heptane solution [15].

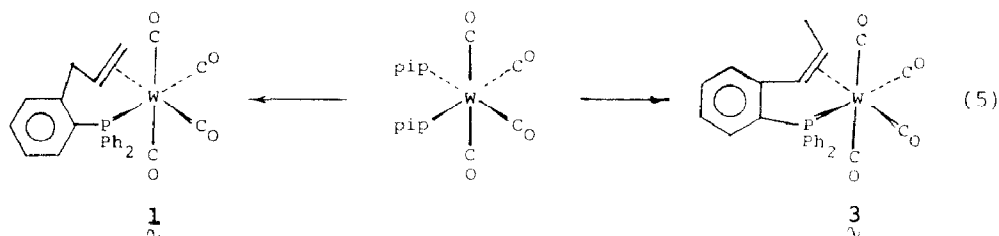
This intermediate **2**, when isolated, purified and then refluxed in benzene solution, undergoes chelate ring-closure to afford *cis*-(η^3 -adpp)W(CO)₄ exclusively. Examination of the ³¹P NMR spectrum of the crude reaction product revealed the presence of only a single resonance, attributable to this species (vide infra), which indicated that no olfin bond-migration had taken place.

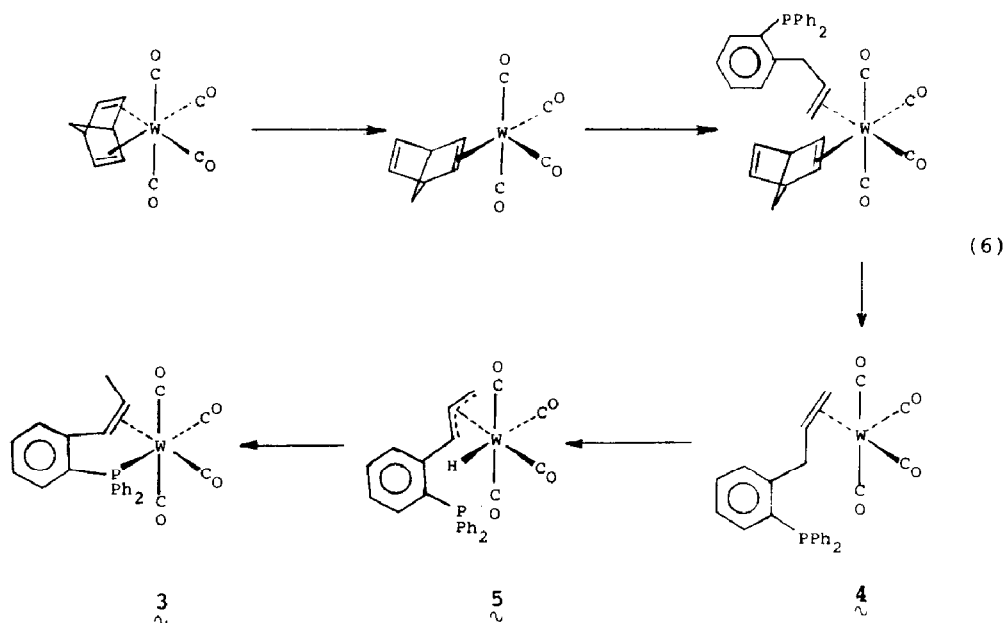
Examination of carbonyl stretching spectra obtained during the course of the reactions of $(\text{NBD})\text{W}(\text{CO})_4$ or *cis*-(pip)₂W(CO)₄ with adpp revealed no bands attributable to species other than these reactants, **1**, **2** or **3**; it thus is concluded that other possible reaction intermediates are present only in steady-state concentration.

Discussion

When pure **2** is allowed to undergo ring-closure, no olefin bond-migration is observed and **1** is the exclusive reaction product (cf. eq. 4). The mechanism proposed by Nyholm (eq. 2) thus is incorrect, since in that mechanism **1** was envisioned to be the precursor to the oxidative addition/reductive elimination processes through which the olefin bond migration takes place. Olefin bond-migration via a η^3 -allylmetal hydride intermediate [5,6] thus likely would involve a precursor containing a coordinated olefin *cis* to a vacant coordination site, a mechanism which would not require expansion of the coordination sphere about the metal. Such an arrangement is not possible during ring-closure of **2** to afford **1** since during this process the P in adpp remains coordinated to W. Ligand-exchange in *cis*-(pip)(L)W(CO)₄ complexes in which L = PPh₃, very similar to adpp, affords only *cis*-(L)(L')W(CO)₄ products upon reaction with triisopropyl phosphite (= L'): thus the P-W bond remains intact during the course of this reaction, which takes place under similar reaction conditions as were employed here [16]. The present results are also in agreement with recent work which, in contrast to the results of Nyholm and coworkers [1], demonstrates that P-ol (= Ph₂P(CH₂)₃CH=CH₂), undergoes no olefin bond-migration upon photolytically-induced chelate ring-closure in *cis*-(η^1 -P-ol)(pip)W(CO)₄ to afford (η^3 -P-ol)W(CO)₄ [17].

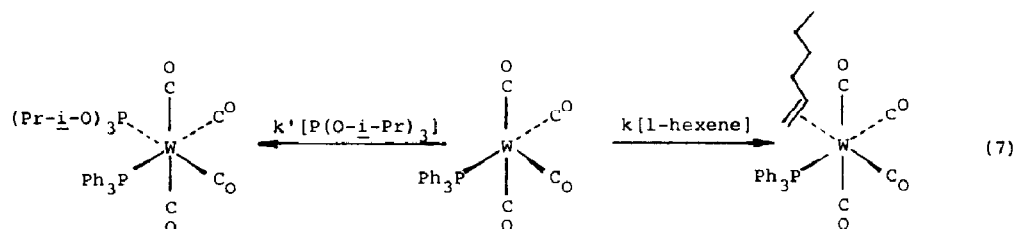
On the other hand, the reaction of *cis*-(pip)₂W(CO)₄ with adpp affords both **1** and **3** (eq. 5). Thus, olefin bond-migration must take place via a second inter-





mediate, the only reasonable candidate for which is $\text{cis}-[(\eta^2\text{-adpp})\text{W}(\text{CO})_4]$ (4), in which adpp is coordinated via the olefinic linkage rather than through P. Equation 6 outlines the series of steps through which this species could be produced during formation of 3 through displacement of NBD by adpp from $(\text{NBD})\text{W}(\text{CO})_4$. Analogous mechanisms can be envisioned for formation of 3 from $\text{cis}-(\text{pip})_2\text{W}(\text{CO})_4$ and for the olefin-migration reactions of Heaton and McCaffrey [4].

In general, P–W bonds are much stronger than olefin–W bonds in Group VIB metal carbonyl complexes. Thus, for example, while $(\eta^2\text{-propylene})\text{W}(\text{CO})_5$ decomposes slowly under nitrogen at room temperature [18], $(\text{P}(\text{OMe})_3)\text{W}(\text{CO})_5$, when heated for two days at 78°C , shows no evidence of W–P bond-fission [19]. On the other hand, rates of formation of olefin–W and P–W bonds are quite similar. Recent studies of the reactivities of $\text{cis}-(\text{solvent})(\text{L})\text{W}(\text{CO})_4$ species with various Lewis bases have shown that the species reacting with L' is the coordinatively-unsaturated $\text{cis}-(\text{L})\text{W}(\text{CO})_4$ intermediate, probably square-pyramidal with L in the equatorial plane. This species has been found to be virtually non-discriminating among attacking phosphines and olefins which pose no severe steric congestion in the transition states [16]. Estimates of the relative rates of attack at $\text{cis}-(\text{PPh}_3)\text{W}(\text{CO})_4$ by 1-hexene and $\text{P}(\text{O}-i\text{-Pr})_3$ show the ratio of rate constants, k/k' (eq. 7) to be 1.2 ± 0.2 [20]. Thus 4 should be readily produced under kinetic control



as a precursor to olefin bond-migration via an η^3 -allylmetal hydride intermediate, **5**. The failure to observe the olefin-bonded species, *cis*-(η^2 -adpp)(pip)W(CO)₄, during this olefin isomerization reaction is reasonable based on its expected kinetic and thermodynamic instability relative to its linkage isomer **1** containing a P–W bond. It is likely that coordination takes place preferentially at the olefin end of adpp in view of the steric demands imposed by its phosphine end and the dihapto NBD ligand or coordinated pip. It is reasonable to attribute the preference toward isomerization in (NBD)W(CO)₄ vs. *cis*-(pip)₂W(CO)₄ to greater steric congestion in the *cis*-(η^2 -NBD)W(CO)₄ intermediate than in its *cis*-(pip)W(CO)₄ counterpart, which would favor olefin coordination in the former.

The mechanism proposed here, involving as it does an intermediate containing a vacant coordination site and a coordinated olefin *cis* to it, is similar to that favored for photochemically-induced olefin bond migration catalyzed by M(CO)₆ complexes (M = Mo, W), in which photolysis promotes M–CO bond-fission to create the vacant coordination site, and in which olefin–M coordination must take place as a result of an absence of a second potentially-coordinating functional group [21,22].

Acknowledgments

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