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On the synthesis and $^{31}P\{^1H\}$ NMR spectrum of $(CO)_5W(\mu\text{-}PPh_2CH_2PPh_2)W(CO)_5$

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Abstract

The dimetallic complex, $(CO)_5W(\mu\text{-}PPh_2CH_2PPh_2)W(CO)_5$, is synthesized from either a 2:1 mixture of $(CO)_5W(NCMe)$ and $(CO)_5W(\eta^1\text{-}PPh_2CH_2PPh_2)$ or a 3:1 mixture of $(CO)_5W(NCMe)$ and $PPh_2CH_2PPh_2$ in toluene at 60°C. The coupling constants, $^2J_{PP'} = 22.9$ Hz, $^1J_{WP} = 246.9$ Hz and $^3J_{WP'} = 4.5$ Hz are consistent with those reported in the literature for similar complexes. The complex $(CO)_5W(\eta^1\text{-}PPh_2CH_2PPh_2)$ is stable with respect to chelation at room temperature.

Keywords: Tungsten; Bis(diphenylphosphino)methane; P-31 NMR; Ditertiary phosphines; Coupling constants; Carbonyl

1. Introduction

A recent publication describes the synthesis and characterization of a number of dimetallic compounds bridged by diphosphines, $(CO)_5M(\mu\text{-}PPh_2(CH_2)_n\text{-}PPh_2)M(CO)_5$ (M = Cr, Mo, W; $n = 1, 2, 3$) [1]. Of particular interest to our research is the formation of the dimetallic species containing one methylene unit ($n = 1$) in the diphosphine bridge. Their formation, albeit in low yields, is quite surprising as a number of research groups have attempted their synthesis and failed. Also surprising are the magnitudes of the coupling constants reported for $(CO)_5W(\mu\text{-}dppm)W(CO)_5$ (dppm = bis(diphenylphosphino)methane) from its $^{31}P\{^1H\}$ NMR spectrum: $^1J_{WP} = 332$ Hz and $^3J_{WP} = 62$ Hz. These values are significantly larger than those previously reported for complexes of the type $(CO)_5WPPh_2R$ (Table 1).

In 1972, we reported our attempt to synthesize $(CO)_5W(\mu\text{-}dppm)W(CO)_5$ by the displacement of aniline from $(CO)_5W(NH_2Ph)$ in the presence of dppm (Eq. (1)) [2]. This reaction: failed to produce the dimetallic species, giving only $(CO)_5W(\eta^1\text{-}dppm)$ even in the presence of excess $(CO)_5W(NH_2Ph)$. Likewise, Hor indicated that reaction of dppm and greater than two equivalents of $(CO)_5Mo(NCMe)$, formed in situ from $Mo(CO)_6$ and Me_3NO in acetonitrile, did not produce the diphosphine bridged species, $(CO)_5Mo(\mu\text{-}dppm)Mo(CO)_5$ (Eq. (2)) [3,4]. Alyea and co-workers were also unable to synthesize the bridged species using the identical procedure [5].

It was argued that the steric bulk of the phenyl groups, combined with the small bite angle of dppm, as a result of only one methylene unit separating the two phosphine groups, makes $(CO)_5M(\eta^1\text{-}dppm)$ too sterically crowded to coordinate another $M(CO)_5$ unit. This idea was supported by the fact that it is possible to quaternize the dangling phosphine group in $(CO)_5W(\eta^1\text{-}dppm)$ with MeI, yet no reaction occurs when the more sterically demanding alkyl halide $PhCH_2Br$ is used [2a]. It should be noted that $(CO)_5M(\mu\text{-}dppe)M(CO)_5$ (M = Cr, Mo, W; dppe = bis(diphenylphosphino)ethane), which contains two methylene units in the diphosphine bridge, forms readily at room temperature from $(CO)_5M(NH_2Ph)$ [2] or $(CO)_5M(NCMe)$ [1,6] and dppe, from a mixture of $M(CO)_6$, Me_3NO and dppe [3], and from the base catalysed addition of $(CO)_5MPPh_2H$ across the double bond of $(CO)_5MPPh_2CH{=}CH_2$ [7]. Also, $(CO)_5W(\eta^1\text{-}dppe)$ reacts with the bulky $PhCH_2Br$ to quaternize the dangling P atom [2a].

Coordination of one end of dppm also decreases the basicity of the unbound end of $(CO)_5M(\eta^1\text{-}dppm)$ (M

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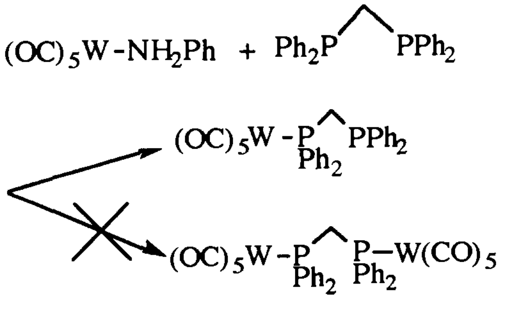
Table 1
Tungsten–phosphorus coupling constants for $(CO)_5WPPh_2R$

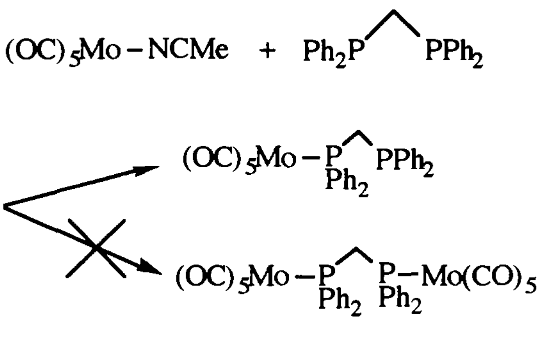
R	$^1J_{WP}$ (Hz)	$^nJ_{WP}$ (Hz, $n = 3$–8)	Ref.
$CH_2PPh_2W(CO)_5$	246.9	4.5	this work
CH_2PPh_2	245.6	6.3	13
$CH_2PPh_2Me^+$	253.2	0	13
$CH_2CH_2PPh_2$	240.0	0	13
$CH_2CH_2PPh_2Bu^+$	243.2	0	13
$CH_2CH_2P(O)Ph_2$	241.3	0	17
$CH_2CH_2PPh_2W(CO)_5$	241.6	0	7
$CH_2CH_2PPh_2Mo(CO)_5$	241.6	0	7
$CH_2CH_2PPh_2Cr(CO)_5$	241.5	0	7
$CH_2CH_2PPh_2Ni(CO)_2$	241.2	0	18
$CH_2CH_2PPh_2HgCl_2L$	243.6	0	17
$CH_2CH_2PPh_2PtCl_2L$	240.3	0	17
$C{\equiv}CPPh_2$	245.0	0	19
$C{\equiv}CPPh_2Me^+$	249.3	0	19
H	229.6	–	20
Ph	244.5	–	21
$CH{=}CH_2$	239.4	–	10
$CH{=}CHPPh_2$ (*trans*)	239.7	0	19
$CH{=}CHPPh_2Me^+$ (*trans*)	245.1	0	19
$CH{=}CHPPh_2$ (*cis*)	238.3	0	19
$CH{=}CHPPh_2Me^+$ (*cis*)	238.2	0	19
$CH_2CH_2PPh(i\text{-}Pr)$	244 ± 4	0	22
CH_2CH_2PPhMe	239 ± 3	0	22
$(CH_2)_3PPh_2W(CO)_5$	240	0	23
$(CH_2)_4PPh_2W(CO)_5$	239.0	0	6
$(CH_2)_5PPh_2W(CO)_5$	239	0	24
$(CH_2)_6PPh_2W(CO)_5$	239	0	24

= Cr, Mo, W) compared with free dppm, as shown in calorimetric studies of heats of protonation [8]. This decrease in basicity makes $(CO)_5M(\eta^1\text{-dppm})$ a poorer donor ligand for reaction with a second metal, again indicating that formation of the dppm-bridged species may not be favourable. Still, it is known that $(CO)_4Fe(\eta^1\text{-dppm})$ is a sufficiently good ligand to form a variety of bridged complexes [9].

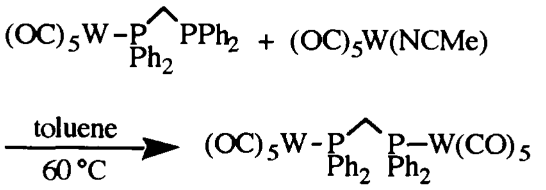


(1)

Common to all the previous attempts to synthesize $(CO)_5W(\mu\text{-dppm})W(CO)_5$ is that they have been carried out at room temperature or below, a condition that minimizes the loss of a second CO group from the metal centre, which would result in the formation of the chelated complex $(CO)_4W(\eta^2\text{-dppm})$. Higher reaction temperatures were never reported. With this in mind, we have explored the synthesis of $(CO)_5W(\mu\text{-dppm})W(CO)_5$ at 60°C from $(CO)_5W(\eta^1\text{-dppm})$ and $(CO)_5W(NCMe)$ (Eq. (3)) and from free dppm and $(CO)_5W(NCMe)$.



(2)



(3)

We have also re-examined the $^{31}P\{^1H\}$ NMR spectrum of $(CO)_5W(\mu\text{-dppm})W(CO)_5$ and have confirmed the stability of $(CO)_5W(\eta^1\text{-dppm})$ with respect to chelation at room temperature.

2. Experimental

Standard Schlenk techniques using a nitrogen atmosphere were employed for all reactions. Room temperature $^{31}P\{^1H\}$ NMR spectra, referenced to an external standard of 85% H_3PO_4, were recorded on a General Electric QE-300 NMR spectrometer using either $CDCl_3$ (Aldrich) or C_6D_6 (Cambridge) as solvents and internal locks. Low temperature $^{31}P\{^1H\}$ NMR spectra were recorded at Spectral Data Services, Champaign, Illinois on a Nicolet NT-400 NMR spectrometer using CD_2Cl_2 (Aldrich) as the solvent. Solution IR spectra of samples dissolved in CH_2Cl_2 were recorded on a Nicolet 20 DXB FT-IR spectrometer. Starting materials, $(CO)_5W(\eta^1\text{-dppm})$ [2] and $(CO)_5W(NCMe)$ [6], were prepared by literature syntheses. Toluene was dried with CaH_2 at reflux temperature and distilled under N_2 at ambient pressure. Neutral alumina, Brockmann Activity I, 150 mesh, purchased from Aldrich, was deactivated with 5% (w/w) water prior to use. All other solvents were reagent grade and used as received; dppm was purchased from Pressure Chemical Co. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, USA.

2.1. Synthesis of $(CO)_5W(\mu\text{-dppm})W(CO)_5$

Method A: acetonitrilepentacarbonyltungsten(0) (0.097 g, 0.27 mmol) and $(CO)_5W(\eta^1\text{-dppm})$ (0.111 g, 0.157 mmol) were dissolved in 10 mL of toluene. The mixture was heated at 60°C for 15 h, during which time a grey precipitate formed. The solution was cooled to room temperature and filtered via cannula. The solvent was removed from the filtrate under vacuum leaving a yellowish green residue, which was chromatographed on alumina (15 cm × 2 cm) using a 3 : 1 mixture of hexanes and CH_2Cl_2 as the eluent. One faint yellow band was collected, and the eluent was removed under vacuum. Recrystallization from CH_2Cl_2 (5 mL) and MeOH (30 mL) produced 0.116 g (71.7% yield) of $(CO)_5W(\mu\text{-dppm})W(CO)_5$ as pale yellow microcrystals. IR: ν(CO) 2071 (m), 1982 (w), 1944 (s), 1926 (s, sh) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 12.3 p.p.m. ($^2J_{PP}$ = 22.9 Hz; $^1J_{PW}$ = 246.9 Hz; $^3J_{PW}$ = 4.5 Hz). Melt. pt. = 205–207°C, decomp. Anal. Calcd. for $C_{35}H_{22}O_{10}P_2W_2$: C, 40.73; H, 2.15. Found: C, 40.71; H, 2.30.

Method B: greater than two equivalents of $(CO)_5W(NCMe)$ (0.208 g, 0.570 mmol) were mixed with dppm (0.075 g, 0.20 mmol) in 10 mL of toluene, and the solution was heated at 60°C for 18 h. The bright yellow solution darkened, and a black precipitate formed. The solution was cooled to room temperature and filtered, and the solvent was removed from the greenish filtrate under vacuum. Two pale yellow bands were collected from chromatography on alumina (15 cm × 2 cm) using a 3 : 1 mixture of hexanes and CH_2Cl_2 as the eluent. The first band was identified as $(CO)_5W(\mu\text{-dppm})W(CO)_5$, and following recrystallization from CH_2Cl_2 (2 mL) and MeOH (20 mL), 0.059 g (29% yield) was obtained as a pale yellow powder. The second band was identified as $(CO)_4W(\eta^2\text{-dppm})$ from its $^{31}P\{^1H\}$ NMR and IR spectra [6,10].

2.2. Chelation study of $(CO)_5W(\eta^1\text{-dppm})$

A saturated solution (0.75 mL) of $(CO)_5W(\eta^1\text{-dppm})$ in C_6D_6 was flame-sealed in an NMR tube at liquid nitrogen temperature under vacuum. After warming to room temperature, the tube was kept in the dark, except when it was being transported to and from the spectrometer. After 134 days, no chelated product was observed by $^{31}P\{^1H\}$ NMR spectroscopy; the only compound observed was $(CO)_5W(\eta^1\text{-dppm})$.

3. Results and discussion

The dppm-bridged dimetallic species, $(CO)_5W(\mu\text{-dppm})W(CO)_5$, is synthesized by displacement of acetonitrile from $(CO)_5W(NCMe)$ in the presence of either $(CO)_5W(\eta^1\text{-dppm})$ (Eq. (3)) or free dppm in toluene at 60°C; $(CO)_5W(\mu\text{-dppm})W(CO)_5$ is identified by IR and $^{31}P\{^1H\}$ NMR spectroscopy and elemental analysis. When $(CO)_5W(\eta^1\text{-dppm})$ is allowed to react with a slight excess of $(CO)_5W(NCMe)$, the dppm-bridged complex forms in a 3 : 1 ratio with the chelated complex $(CO)_4W(\eta^2\text{-dppm})$, as identified in the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture. When free dppm is used instead of $(CO)_5W(\eta^1\text{-dppm})$ in the reaction mixture the result is not only a reduction in yield of the bridged species (from 72% to 29%) but also a decrease in the ratio of dimetallic to chelated complex (0.4 : 1).

In the previous report of the synthesis of $(CO)_5W(\mu\text{-dppm})W(CO)_5$ [1], a 2 : 1 ratio of $(CO)_5W(NCMe)$ and dppm was stirred in toluene at −30°C (low temperature was used to prevent the chelation reaction as discussed below). Our attempts at following this procedure were unsuccessful, producing only a minute amount of $(CO)_5W(\eta^1\text{-dppm})$ after 4 days. In fact, a reaction of $(CO)_5W(NCMe)$ and dppm at −18°C in CD_2Cl_2 solvent produced no $(CO)_5W(\mu\text{-dppm})W(CO)_5$ after 9 days as determined by $^{31}P\{^1H\}$ NMR. Mixtures of either $(CO)_5W(NCMe)$ and dppm or $(CO)_5W(NCMe)$ and $(CO)_5W(\eta^1\text{-dppm})$ at room temperature produced only trace amounts of the dppm-bridged product in addition to $(CO)_5W(\eta^1\text{-dppm})$ and $(CO)_4W(\eta^2\text{-dppm})$ even after two weeks.

The $^{31}P\{^1H\}$ NMR spectrum of $(CO)_5W(\mu\text{-dppm})W(CO)_5$ is shown in Fig. 1. It consists of a singlet (δ 12.3 p.p.m.) in the centre of a second-order ABX satellite pattern, similar to that of $(CO)_5W(\mu\text{-dppe})W(CO)_5$ [1,7]. The chemical shift of δ 2.4 p.p.m. reported previously [1] appears to be in error. The satellite pattern consists of two ab subspectra indicated by lines 1, 3, 5, 7 and by lines 2, 4, 6, 8. Analysis of the

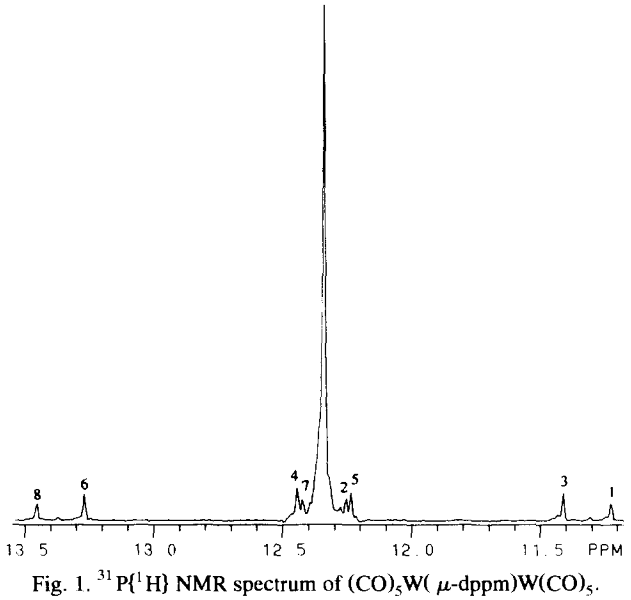
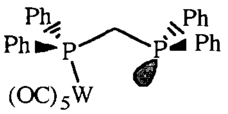


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of $(CO)_5W(\mu\text{-dppm})W(CO)_5$.

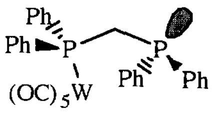
satellite pattern [11,12] gives the following coupling constants: $^2J_{PP'} = 22.9$, $^1J_{WP} = 246.9$ and $^3J_{WP'} = 4.5$ Hz. The magnitude of $^2J_{PP}$ is comparable to that found in $[(CO)_5WPPh_2CH_2PPh_2Me]^+$ (8.1 Hz) [13], another compound in which both ends of the phosphorus ligand are coordinated. The coupling is significantly smaller that that of the free ligand (125 Hz) [12] or of $(CO)_5W(\eta^1$-dppm) (106.2 Hz) [13].

The one-bond phosphorus–tungsten coupling ($^1J_{WP}$) of 246.9 Hz observed for $(CO)_5W(\mu$-dppm)$W(CO)_5$ is similar to that of $(CO)_5W(\eta^1$-dppm) (245.6 Hz) [13]. It is also in agreement with values of $^1J_{WP}$ reported for $(CO)_5W(\eta^1$-dppe) (240.0 Hz) [13] and $(CO)_5W(\mu$-dppe)$W(CO)_5$ (241.6 Hz) [6]. It is widely recognized that the magnitude of $^1J_{WP}$ increases as the electronegativities of the substituents on phosphorus increase [14]. As seen in Table 1, the range of tungsten–phosphorus coupling constants for known $(CO)_5WPPh_2R$ complexes is rather small (229.6–253.2 Hz). Our observed value for $(CO)_5W(\mu$-dppm)$W(CO)_5$ is well within this range, indicating that $R = CH_2PPh_2W(CO)_5$ does not have a significantly enhanced electronegativity over other alkyl and aryl groups. Thus, the previously reported value of 332 Hz for $(CO)_5W(\mu$-dppm)$W(CO)_5$ is doubtful, as it falls well outside the range of values observed for other compounds of this type [1]. Long-range phosphorus–tungsten coupling, $^3J_{WP}$, is also observed in the $^{31}P\{^1H\}$ NMR spectrum of $(CO)_5W(\mu$-dppm)$W(CO)_5$. This small coupling (4.5 Hz) is consistent with other values (0–6.3 Hz) reported in the literature (Table 1).

Our results show that formation of $(CO)_5W(\mu$-dppm)$W(CO)_5$ is favourable at 60°C but not at ambient or lower temperature. Two conformations of $(CO)_5W(\eta^1$-dppm), A and B, can be imagined which would reduce steric interactions between the phenyl rings on each phosphorus atom.



A



B

Conformation A would be less sterically crowded than B and preferred at room temperature. It is not, however, the ideal conformation for reaction with a second $W(CO)_5$ fragment. Conformation B, with its accessible lone pair, is sterically more suitable for the formation of the dimetallic species. Increasing the reaction temperature to 60°C would be expected to increase the availability of conformer B and enhance the formation of the ditungsten complex. Further studies are under way to explore this idea.

The mechanism for the formation of $(CO)_4W(\eta^2$-dppm) from the reactions of either dppm or $(CO)_5W(\eta^1$-dppm) with $(CO)_5W(NCMe)$ is unclear. In separate experiments, we have shown that neither $(CO)_5W(\eta^1$-dppm) nor $(CO)_5W(\mu$-dppm)$W(CO)_5$ react significantly with MeCN, and therefore neither are likely to be major precursors for the chelated complex. (Traces of $(CO)_4W(\eta^2$-dppm) were observed by ^{31}P NMR when $(CO)_5W(\eta^1$-dppm) and a 10-fold excess of MeCN were allowed to react for 4 days. Traces of $(CO)_5W(\eta^1$-dppm) were found when the same experiment was carried out with $(CO)_5W(\mu$-dppm)$W(CO)_5$.) Furthermore, we observe that $(CO)_5W(\eta^1$-dppm) is stable with respect to chelation for up to 134 days at room temperature. Although this observation is in conflict with the recent report claiming that it is necessary to perform reactions at −30°C in order to prevent chelation, it is in agreement with the kinetic studies by Connor et al. in which chelation of $(CO)_5Cr(\eta^1$-dppm) is shown to occur appreciably only at 100°C or greater [15]. (From data presented in Ref. [15], we calculate the half-life of $(CO)_5Cr(\eta^1$-dppm) with respect to chelation at 298 K to be 200 years.) A possible explanation for the formation of $(CO)_4W(\eta^2$-dppm) may lie with the tendency of $(CO)_5W(NCMe)$ to disproportionate in solution to give $W(CO)_6$ and $(CO)_4W(NCMe)_2$ [16]. If samples of $(CO)_5W(NCMe)$ became contaminated with $(CO)_4W(NCMe)_2$ during the course of the reaction with dppm, $(CO)_4W(\eta^2$-dppm) would readily form.

4. Summary

The reaction of dppm with $(CO)_5W(NCMe)$ at room temperature gives $(CO)_5W(\eta^1$-dppm), which primarily exists in a conformation unfavourable for further coordination. At higher temperatures (60°C), a more favourable conformation allows $(CO)_5W(\eta^1$-dppm) to react further to give $(CO)_5W(\mu$-dppm)$W(CO)_5$.

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