Journal of Organometallic Chemistry, 206 (1981) C38—C42
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

INTERMEDIATES IN ASSOCIATIVE PHOSPHINE SUBSTITUTION REACTIONS OF $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$

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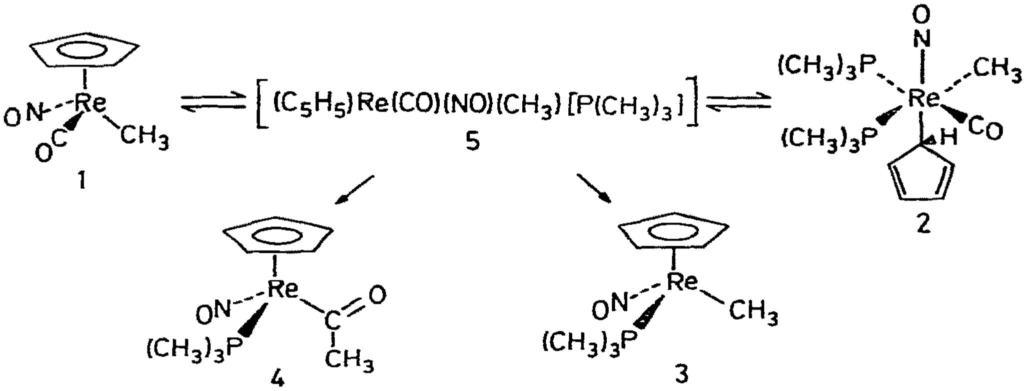
(Received November 26th, 1980)

Summary

The reaction of $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$, 6W, with $P(CH_3)_3$ proceeds rapidly at 25°C to give $(\eta^5\text{-}C_5H_5)W(CO)(NO)[P(CH_3)_3]$, 7W. The rate of formation of 7W was found to be $4.48 \times 10^{-2}\ M^{-1}\ \text{sec}^{-1}\ [6W][P(CH_3)_3]$ at 25.0°C in THF. In neat $P(CH_3)_3$ at −23°C, 6W is converted to $(\eta^1\text{-}C_5H_5)W(CO)_2(NO)[P(CH_3)_3]_2$, 8W. In dilute solution, 8W decomposes to initially give a 2:1 mixture of 6W and 7W. The mixture is then converted to 7W. The reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)$, 6Mo, with $P(CH_3)_3$ is 6.1 times faster than that of the tungsten analog.

We recently reported that $(\eta^5\text{-}C_5H_5)Re(CO)(NO)(CH_3)$, 1, reacts with two equivalents of $P(CH_3)_3$ at 25°C to produce $(\eta^1\text{-}C_5H_5)Re(CO)(NO)(CH_3)[P(CH_3)_3$ 2 [1]. Upon heating to 90°C, 1 and 2 equilibrate [1] and are converted to a mixture of phosphine-substituted methyl compound 3 and the phosphine-substituted acetyl compound 4 [2]. We believe that the interconversions of these four compounds proceed via a common intermediate 5.



To find other examples of trimethylphosphine-induced conversions of η^5-C_5H_5 compounds to bisphosphine-substituted η^1-C_5H_5 derivatives and to test for the formation of phosphine adducts as intermediates in the CO substitution reactions of cyclopentadienyl compounds, we have studied the reaction of $P(CH_3)_3$ with $(\eta^5\text{-}C_5H_5)M(CO)_2(NO)$, **6W** (M = W), **6Mo** (M = Mo). These compounds were chosen for study because of their similarity to **1** and since Brunner's observation that **6W** reacts with $P(C_6H_5)(CH_3)_2$ much faster than with $P(C_6H_5)_3$ implied that an associative substitution mechanism was likely [3].

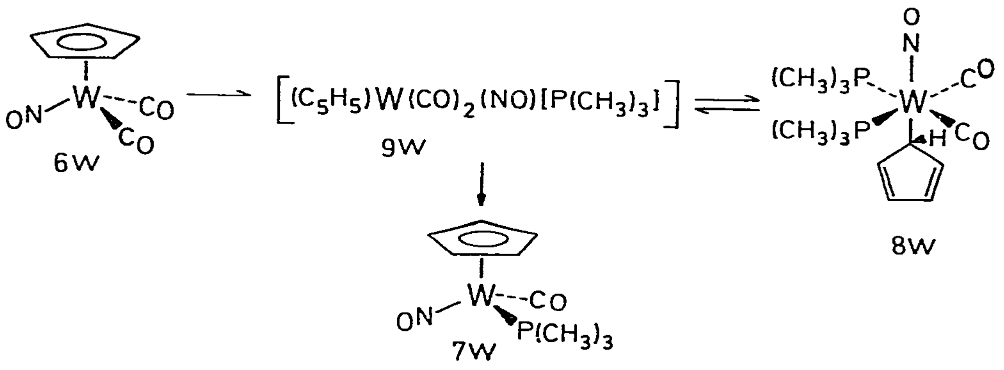
An orange acetone solution of $(\eta^5\text{-}C_5H_5)W(CO)_2(NO)$, **6W**, [4] (55 mg, 0.16 mmol, 0.16 *M*) and $P(CH_3)_3$ [5] (0.33 mmol) reacted rapidly upon warming from −78°C to room temperature to produce a red solution of $(\eta^5\text{-}C_5H_5)W(CO)(NO)[P(CH_3)_3]$, **7W**. Evaporation of solvent and sublimation (80°C, 10^{-2} mmHG) led to the isolation of analytically pure **7W** (55 mg, 88%). IR(THF): 1887, 1599 cm^{-1}; ^1H NMR(acetone-d_6): δ 5.56 (d, J = 1.3 Hz, 5H), 1.65 ppm (d, J = 9.7 Hz, 9H); ^{13}C $\{^1H\}$ NMR(acetone-d_6): δ 91.2 (s, C_5H_5), 21.9 ppm (d, J = 34.9 Hz, CH_3), CO not observed; m.p. 119—120°C. Anal. Found: C, 28.59; H, 3.82; N, 3.74. Calcd. for $C_9H_{14}NO_2PW$: C, 28.22; H, 3.68; N, 3.66%.

The reaction of **6W** with $P(CH_3)_3$ is much more rapid than its reaction with $P(C_6H_5)_3$, which required refluxing for 3 hours in benzene [3]. The rate of reaction of **6W** with $P(CH_3)_3$ in acetone was measured by monitoring the decrease in the intensity of the absorption at 465 nm (ϵ = 100 for **6W**, ϵ = 41 for **7W**). At a given $P(CH_3)_3$ concentration, the disappearance of **6W** followed pseudo first order kinetics to greater than 80% reaction. The observed first order

TABLE 1

RATE OF REACTION OF 6 WITH $P(CH_3)_3$ IN THF AT 25.0°C

	$[P(CH_3)_3]$ (*M*)	k_{obs} (sec^{-1})		k_2 ($M^{-1} sec^{-1}$)
6W	0.154	7.03×10^{-3}		4.56×10^{-2}
6W	0.103	4.53×10^{-3}		4.40×10^{-2}
6W	0.051	2.30×10^{-3}		4.47×10^{-2}
			avg. =	4.48×10^{-2}
6Mo	0.154	4.19×10^{-2}		2.72×10^{-1}
6Mo	0.077	2.06×10^{-2}		2.67×10^{-1}
6Mo	0.051	1.42×10^{-2}		2.77×10^{-1}
			avg. =	2.72×10^{-1}



rate constants depended linearly on the $P(CH_3)_3$ concentration (Table 1).

When the reaction of **6W** is carried out at low temperature in the presence of high concentrations of $P(CH_3)_3$, a bisphosphine adduct **8W** is obtained instead of phosphine substitution product **7W**. A rapid reaction of **6W** (0.18 mmol) occurre at −65°C in $P(CH_3)_3$ containing enough acetone-d_6 (10%) to deuterium lock a 270 MHz ^{1}H NMR instrument. After one hour at −65°C, the NMR spectrum showed the presence of 5% starting material **6W**, no phosphine substitution product **7W**, and 95% of a new species **8W** whose ^{1}H NMR spectrum consisted of a triplet ($J = 1.4$ Hz) of relative intensity 5 at δ 5.60 ppm assigned to a C_5H_5 unit coupled to two phosphorus atoms* and of a doublet ($J = 7.7$ Hz) of relative intensity 18 at δ 1.76 ppm assigned to two equivalent $P(CH_3)_3$ ligands.

The formation of **8W** was also observed by low temperature infrared spectroscopy. A solution of **6W** (4 mg) in 0.45 ml $P(CH_3)_3$ and 0.05 ml THF (to prevent freezing of $P(CH_3)_3$) was prepared at −78°C and transferred via a cannula packed in dry ice into an IR cell maintained at -50 ± 5°C.** The half time for disappearance of the bands at 2003, 1926, and 1660 cm^{-1} due to starting material **6W** was approximately 30 min***. After 150 min, complete conversion to **8W** with bands at 2003, 1938, and 1617 cm^{-1} had occurred. These $P(CH_3)_3$ solutions of **8W** are stable for short times at 0°C but are cleanly converted to **7W** in less than an hour at 25°C as shown by IR and ^{1}H NMR observations.

The bisphosphine adduct **8W** was isolated in 81% yield as a yellow solid by reaction of **6W** (219 mg, 0.65 mmol) with 0.5 ml of neat $P(CH_3)_3$ for 30 min at −23°C followed by removal of $P(CH_3)_3$ on a vacuum line at −23°C*. Solid **8W** is stable at room temperature for several hours and dilute solutions of **8W** are stable for short times below −20°C. The observation of two intense CO stretching frequencies requires a *cis* arrangement of the CO ligands in **8W**. As in the case of the conversion of **1** to **2**, an increase in the CO stretching frequencies and a decrease in the NO stretching frequency occurred upon conversion of **6W** to bisphosphine adduct **8W**.

There are two structures which have *cis* carbonyl ligands and equivalent $P(CH_3)_3$ ligands: that shown as **8W** and a structure with *cis* CO's and *trans* $P(CH_3)_3$'s. We favor structure **8W**** on the basis of analogous shifts of the CO and NO stretching frequencies in the IR spectra of **1**→**2** and of **6W**→**8W**.

The decomposition of a THF-d_8 solution of isolated **8W** (0.04 *M*) was followed by low temperature ^{1}H NMR. At −53°C, the sample consisted of a mixture of 95% **8W**, 3% **6W**, and 2% **7W**. Upon warming to 0°C, **8W** decomposes with a half-life of about 25 min. Initially **8W** decomposes to a ~2:1 mixture of phosphine-free **6W** and phosphine substitution product **7W**. After 16 min at 0°C, the sample consists of 72% **8W**, 18% **6W**, and 10% **7W**. In a slower reaction, **6W** reacts with liberated $P(CH_3)_3$ to give **7W**.

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*All protons of the η^1-C_5H_5 unit are NMR equivalent. Similar observations were made for 2 [1].

**A Research and Industrial Instruments Co. VLT-2 IR Cell obtained from Beckman Instruments was used in these experiments. The 90% $P(CH_3)_3$/10% THF solution has weak bands at 2102, 2057, 1985 and 1930 cm^{-1}.

***Little change is seen in the 2003 cm^{-1} peak since this band is present in the spectra of both 6W and 8W.

*Low temperature spectra of 8W were similar to those obtained at high $[P(CH_3)_3]$. ^{1}H NMR (acetone-d_6, −61°C) δ 5.58 (bs), 1.76 ppm (d, $J = 5.9$ Hz); IR(THF, −58°C): 2000, 1932, 1611 cm^{-1}.

**In addition, equivalent *trans* $P(CH_3)_3$ ligands normally give rise to a triplet in the NMR spectrum for the P—CH_3 groups due to virtual coupling to the strongly coupled P atoms.

The same sequence of reactions was also observed spectrophotometrically. When isolated **8W** is rapidly dissolved in THF at 25°C in a sealed cuvette, the initial UV-visible spectrum taken after 20 sec is different from either that of **6W** or **7W** (Fig. 1). After 145 sec, **8W** is nearly completely converted to a 2.1 : 1 mixture of **6W** : **7W** as determined from the observed absorbance at 465 nm. The subsequent slow conversion of **6W** to **7W** can be observed by monitoring the decrease in absorbance at 465 nm. An isobestic point at 506 nm is associated with the conversion of **6W** to **7W**. Therefore it was convenient to monitor the conversion of **8W** to a mixture of **6W** and **7W** by visible spectroscopy without complications arising from the conversion of **6W** to **7W**. The rate of decomposition of **8W** was independent of added $P(CH_3)_3$ (0.12 M, 0.34 M), $k = 1.3 \times 10^{-2}$ sec^{-1} ($t_{1/2} = 53$ sec) at 25°C.

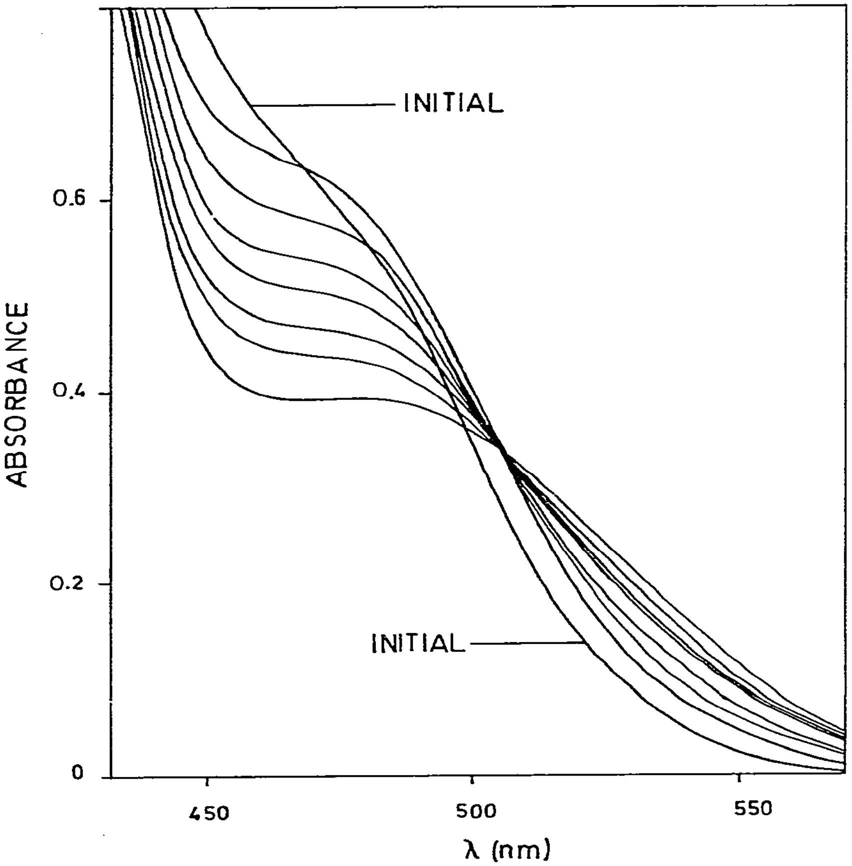

Fig. 1. Reaction of 8W (8.47×10^{-3} M) in THF at 25°C. Spectra were recorded at 20, 145, 395, 650, 950, 1260, 1620, and 2400 sec.

In contrast to reactions in neat $P(CH_3)_3$, a solution of **6W** (0.1 mmol) and 0.58 M $P(CH_3)_3$ (0.22 mmol) in acetone-d_6 was converted into a mixture of 25% **6W**, 52% **7W**, and 23% **8W** after 40 min at −37°C.

The observation of second order kinetics in the formation of **7W**, taken together with the observed dependence of the ratio of **7W** : **8W** on the $P(CH_3)_3$

concentration, implies that attack of $P(CH_3)_3$ on **6W** produces an intermediate $(C_5H_5)W(CO)_2(NO)[P(CH_3)_3]$, **9W**, which can either expel CO to give phosphine substitution product **7W** or add a second equivalent of $P(CH_3)_3$ to produce the bisphosphine adduct **8W**. When the same intermediate **9W** is generated by loss of phosphine from **8W** at low (<0.3 *M*) phosphine concentrations, readdition of phosphine is slow and loss of $P(CH_3)_3$ to give **6W** and of CO to give **7W** occurs in a 2:1 ratio. Two possible 18-electron structures for intermediate **9W** are an η^3-C_5H_5 linear nitrosyl compound or an η^5-C_5H_5 bent nitrosyl compound.

The reaction of the molybdenum compound **6Mo** [4] with $P(CH_3)_3$ is similar to that of tungsten compound **6W**. Thus reaction of **6Mo** (69 mg, 0.37 mmol) with $P(CH_3)_3$ (0.78 mmol) in acetone at room temperature gives a 93% yield of **7Mo** (103 mg, 93%): IR(THF): 1901, 1610 cm^{-1}; ^1H NMR(acetone-d_6): δ 5.45 (d, $J = 1.1$ Hz, 5H), 1.53 ppm (d, $J = 9$ Hz, 9H); ^{13}C $\{^1H\}$ NMR(acetone-d_6): δ 92.8 (s, C_5H_5), 20.9 ppm (d, $J = 28.6$ Hz, PCH_3), CO not observed; m.p. 98.5—100.5°C. Anal. Found: C, 36.85; H, 4.95; N, 4.93. Calcd. for $C_9H_{14}NO_2PMo$: C, 36.63; H, 4.78; N, 4.75%. The reaction of $P(CH_3)_3$ with **6Mo** is second order and is 5.7 times faster than the reaction of **6W**. After several min at −60°C, **6Mo** (0.24 mmol) in 85% $P(CH_3)_3$/15% acetone-d_6 reacted to form a ~2:1 mixture of 7Mo:8Mo [^1H NMR of 8Mo: δ 5.69 (t, $J = 1$ Hz, C_5H_5), 1.62 ppm (d, $J = 8$ Hz, PCH_3)]. In a separate low temperature infrared experiment, **6Mo** (5 mg) in 0.5 ml 90% $P(CH_3)_3$/10% THF at −78°C had reacted after 45 min to produce a ~1:1 mixture of phosphine substitution product **7Mo** (1900, 1606 cm^{-1}) and bisphosphine adduct **8Mo** (2014, 1956, 1621 cm^{-1}). **8Mo** is much less stable than **8W** and was converted to **7Mo** within 45 min at -57 ± 5°C, as shown by IR spectroscopy.

Acknowledgment

Support from the National Science Foundation is gratefully acknowledged.

References

1 C.P. Casey and W.D. Jones, J. Amer. Chem. Soc., 102 (1980) 6154.
2 C.P. Casey and W.D. Jones, unpublished observations.
3 H. Brunner, H.-D. Schindler, E. Schmidt and M. Vogel, J. Organometal. Chem., 24 (1970) 515; H. Brunner, J. Organometal. Chem., 16 (1969) 119.
4 J.K. Hoyano, P. Legzdins and J.T. Malito, Inorg. Synth., 18 (1978) 126.
5 R.T. Markham, E.A. Dietz, Jr. And D.R. Martin, Inorg. Synth., 16 (1976) 153.