*Journal of Organometallic Chemistry*, 331 (1987) 341–346
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# Tetracarbonyl group 6 complexes containing secondary and tertiary phosphines *

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(Received February 27th, 1987)

## Abstract

The mixed ligand tetracarbonyl derivatives, *cis*-$M(CO)_4(PPh_2H)(PPh_3)$ (M = Cr, Mo, W) and *cis*-$W(CO)_4(PPh_2H)(L)$ (L = $PEt_3$, $PEt_2Ph$, $PEtPh_2$) have been prepared from the reaction of $M(CO)_5PPh_2H$ with L in THF in the presence of potassium t-butoxide. These reactions are accompanied in most instances by the formation of $[W(CO)_5PPh_2]^-$, $[(OC)_5M(\mu\text{-}PPh_2)M(CO)_5]^-$, $[(OC)_5M(\mu\text{-}PPh_2)\text{-}M(CO)_4(PPh_2H)]^-$, $[(OC)_4M(\mu\text{-}PPh_2)_2M(CO)_4]^{2-}$, $(OC)_4M(\mu\text{-}PPh_2)_2M(CO)_4$, and *cis*-$M(CO)_4(PPh_2H)_2$.

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## Introduction

The preparation of $M(CO)_4LL'$ complexes in which L and L′ are different phosphine ligands has been of interest for a number of years [1]. Typically $M(CO)_6$ is converted to the final product by three substitution reactions. In these reactions, intermediates such as $[M(CO)_5XL]^-$ (X = halide), $M(CO)_4(CH_3CN)(L)$, and $M(CO)_4(py)(L)$ lose $X^-$, $CH_3CN$, and py respectively in the presence of L′ to form $M(CO)_4LL'$ (Scheme 1) [2,3]. Conditions are mild for the final step of these reactions and as a result ligand scrambling is minimized. The distribution of *cis* and *trans* isomers appears to be determined primarily by the steric requirements of the phosphine ligands [3]. Sterically demanding phosphines prefer trans arrangements while those with small cone angles favor *cis* configurations [4].

In the course of our studies of the reactions of diphenylphosphine complexes of group 6 metal carbonyls, we observed that $W(CO)_5PPh_2H$ reacts with potassium t-butoxide and $PPh_3$ to give *cis*-$W(CO)_4(PPh_2H)(PPh_3)$ [5]:

$$W(CO)_5(PPh_2H) + PPh_3 \xrightarrow{-OBu^t} cis\text{-}W(CO)_4(PPh_2H)(PPh_3) + CO$$

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* Dedicated to the memory of our friend and colleague, Edward O. Sherman.

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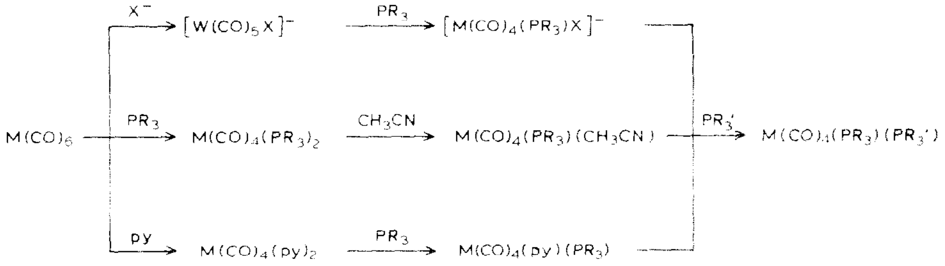

Scheme 1

It appeared that this reaction might represent a useful method for the synthesis of mixed ligand complexes which contain both secondary and tertiary phosphines. We report here an investigation of the synthesis of *cis*-$M(CO)_4(PPh_2H)(PPh_3)$ (M = Cr, Mo, W) and *cis*-$W(CO)_4(PPh_2H)(L)$ (L = $PEt_3$, $PEt_2Ph$, $PEtPh_2$) by this method.

## Results and discussion

The reaction of $W(CO)_5PPh_2H$ with $Ph_3P$, $Ph_2EtP$, $PhEt_2P$, or $Et_3P$ in THF with $KOBu^t$ for 2.5 h gave isolated yields of *cis*-$W(CO)_4(PPh_2H)(PR_3)$ of approximately 40% when a 1/1/1 mole ratio of reactants was employed. Similar results were obtained from the reactions of $Cr(CO)_5PPh_2H$ and $Mo(CO)_5PPh_2H$ with $PPh_3$. *Trans* isomers were not observed, consistent with the small cone angle of $PPh_2H$. No improvement in reaction yield was noted when reaction times were extended to as long as 72 h. Changing the mole ratio of $W(CO)_5(PPh_2H)/L/KOBu^t$ to 1/5/1 gave improvements of about 8% but the necessity of separating excess phosphine from the product offset any advantage gained. Reducing the quantity of base (ratios of 1/1/0.5 and 1/1/0.25) had essentially no effect on product yield. At temperatures below 55 °C no reaction was noted within the time frame examined. Infrared data for the new complexes are listed in Table 1. $^{31}P$ NMR data are given in Table 2.

The reaction of $M(CO)_5PPh_2H$ with $KOBu^t$ generates the reactive $[M(CO)_5\text{-}ycliPPh_2]^-$ ($\delta$ −50.9 ppm, $J(WP)$ 90 Hz) which can undergo a variety of reactions

Table 1

Infrared data for *cis*-$M(CO)_4(PPh_2H)(L)$ and $M_2(CO)_8(\mu\text{-}L)_2$ complexes ($CHCl_3$)

| M | L | $\nu(CO)(cm^{-1})$ | | |
|---|---|---|---|---|
| W | $PEt_3$ | 2016(m) | 1911(s) | 1891(s) |
| W | $PPhEt_2$ | 2018(m) | 1916(s) | 1896(s) |
| W | $PPh_2Et$ | 2023(m) | 1922(s) | 1903(s) |
| W | $PPh_3$ | 2024(m) | 1920(s) | 1903(s) |
| Mo | $PPh_3$ | 2028(m) | 1914(s) | 1888(s) |
| Cr | $PPh_3$ | 2018(m) | 1920(s) | 1905(s) |
| W (Dimer) | $PPh_2$ | 2034(s) | 1957(vs) | |
| Mo (Dimer) | $PPh_2$ | 2035(s) | 1963(s) | |
| Cr (Dimer) | $PPh_2$ | 2020(s) | 1961(vs) | |

Table 2

$^{31}P$ NMR data for *cis*-$M(CO)_4(PPh_2H)(L)$ and $M_2(CO)_8(\mu\text{-}L)_2$ complexes ($CHCl_3$) [a]

| M | L | $\delta$ ($PPh_2H$) | $\delta$ (L) | $^1J$ (WP-($PPh_2H$)) | $^1J$ (WP(L)) | $^2J$ (PP) | $^1J$ (PH) | $^3J$ (PH) |
|---|---|---|---|---|---|---|---|---|
| W | $PEt_3$ | −4.8 | −1.8 | 226 | 221 | 20 | 333 | 7.3 |
| W | $PPhEt_2$ | 0.9 | 5.0 | 230 | 221 | 18 | 332 | 8.6 |
| W | $PPh_2Et$ | 1.4 | 14.1 | 230 | 226 | 17 | 335 | 7.9 |
| W | $PPh_3$ | 3.1 | 24.0 | 230 | 231 | 17 | 334 | 8.0 |
| Mo | $PPh_3$ | 21.1 | 41.8 | | | 22 | 323 | 7.5 |
| Cr | $PPh_3$ | 46.7 | 61.9 | | | 30 | 322 | 8.3 |
| W (Dimer) | $PPh_2$ | | 180.0 | | 162 | | | |
| Mo (Dimer) | $PPh_2$ | | 232.8 | | | | | |
| Cr (Dimer) | $PPh_2$ | | 272.0 | | | | | |

[a] Chemical shifts (ppm) are relative to 85% $H_3PO_4$. Downfield shifts are defined as positive. Coupling constants are recorded in Hz.

[6]. The ease with which CO is displaced from $[M(CO)_5X]^-$ (X = halide) is well known, and one would expect $[M(CO)_5PPh_2]^-$ likewise to lose CO in the presence of phosphines [7]. We have previously reported that $W(CO)_5PPh_2H$ reacts with $PPh_2CH{=}CH_2$ in the presence of base to give chelated $W(CO)_4(PPh_2CH_2CH_2PPh_2)$ which apparently results from the cyclization of *cis*-$[W(CO)_4(PPh_2CH{=}CH_2)(PPh_2)]^-$ further supporting $[W(CO)_5PPh_2]^-$ formation and subsequent CO labilization [5].

The high reactivity of $[M(CO)_5PPh_2]^-$ leads to other reactions which are competitive with the formation of *cis*-$M(CO)_4(PPh_2H)(PR_3)$ (Scheme 2). Earlier investigations have shown that $W(CO)_5PPh_2H$ reacts with $KOBu^t$ in THF to give three anions, $[(CO)_5W(\mu\text{-}PPh_2)W(CO)_5]^-$, $[(CO)_5W(\mu\text{-}PPh_2)W(CO)_4(PPh_2H)]^-$, and $[(CO)_4W(\mu\text{-}PPh_2)_2W(CO)_4]^{2-}$ [8]. The dianion is air-sensitive and reacts with oxygen to give $(CO)_4\overline{W(\mu\text{-}PPh_2)_2W}(CO)_4$ [9*]. Examination with $^{31}P$ NMR of crude reaction mixtures prepared in sealed tubes from the reaction of $W(CO)_5PPh_2H$ with $PPh_3$ and $KOBu^t$ revealed strong absorptions for *cis*-$W(CO)_4(PPh_3)(PPh_2H)$ and minor signals for the three anions cited above. In addition a signal at −3.0 ppm ($J$(WP) 224 Hz) assigned to *cis*-$W(CO)_4(PPh_2H)_2$ was observed [10*]. When the contents of the sealed tube were exposed to air, a red color developed due to the formation of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2W}(CO)_4$, which was verified with $^{31}P$ NMR ($\delta$ 180 ppm; J(WP) 162 Hz) and IR spectroscopy ($\nu$(CO) 2035 and 1957 $cm^{-1}$) [8,9*].

Bridged metal–metal bonded complexes, $(OC)_4M(\mu\text{-}PPh_2)_2M(CO)_4$, for chromium, molybdenum, and tungsten were isolated in approximately 10% yield from all of the reactions except those involving $PEt_3$. The bimetallic products were obtained from the crude reaction mixtures by column chromatography.

Phosphorus-31 NMR studies of $M(CO)_4(PR_3)_2$ complexes have been reported, and Schenk has observed that, in general, the chemical shift for $PR_3$ shifts upfield when a *trans* carbonyl group is displaced by a phosphine from $W(CO)_5PR_3$ [11]. The effect is most significant when the incoming ligand or $PR_3$ is sterically demanding. Downfield shifts for $PR_3$ are usually observed when a carbonyl group

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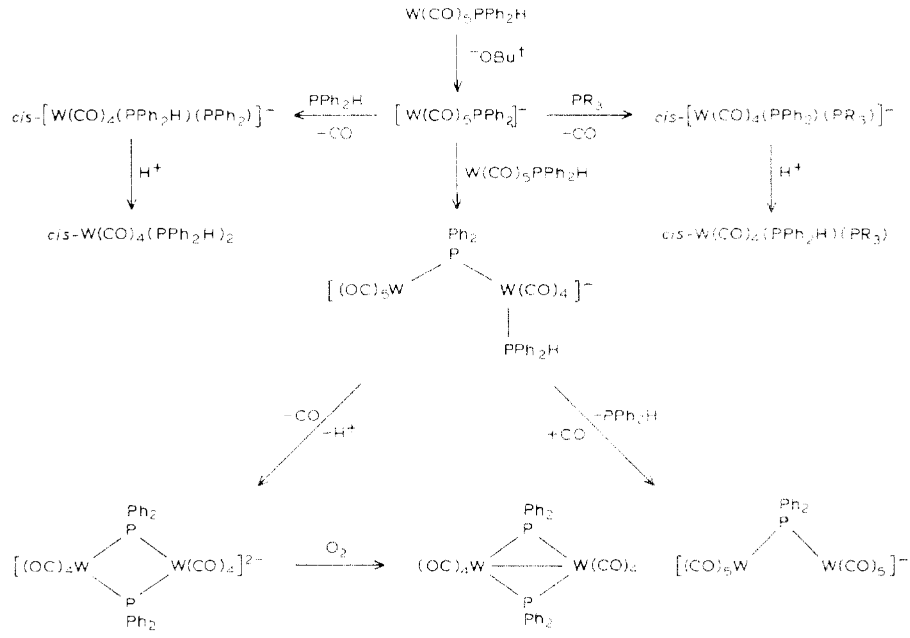
* This and other references marked with asterisks indicate notes occurring in the list of references.



Scheme 2

*trans* to $PR_3$ is displaced. For our complexes in which a carbonyl group *cis* to $PPh_2H$ is displaced, significant downfield shifts for $PPh_2H$ were seen in contrast to Schenk's observations. For example, whereas the $^{31}P$ chemical shift of $W(CO)_5PPh_2H$ is $-13.7$ ppm, the chemical shift of $PPh_2H$ is 3.1 ppm in *cis*-$W(CO)_4(PPh_2H)(PPh_3)$ [5]. Similar shifts were noted for the other tungsten complexes and for the chromium ($\delta$ 32.9 ppm for $PPh_2H$ in $Cr(CO)_5PPh_2H$ and 46.7 ppm in *cis*-$Cr(CO)_4(PPh_2H)(PPh_3)$) and molybdenum ($\delta$ 6.7 ppm for $PPh_2H$ in $Mo(CO)_5PPh_2H$ and 21.1 ppm in *cis*-$Mo(CO)_4(PPh_2H)(PPh_3)$) complexes. Modest downfield chemical shifts were observed for the incoming ligands compared to the corresponding $W(CO)_5PR_3$ complexes (e.g., $\delta$ 20.9 ppm for $W(CO)_5PPh_3$, compared to 24.0 ppm for $PPh_3$ in *cis*-$W(CO)_4(PPh_3)(PPh_2H)$) [11]. These results are in agreement with the view that upfield chemical shifts result when steric interaction is significant but downfield chemical shifts, in both *cis* and *trans* isomers, occur when steric demands are minimal.

As expected, tungsten–phosphorus coupling constants generally increase in the disubstituted complexes in the order $PEt_3$, $PPhEt_2$, $PPh_2Et$, $PPh_3$ as ethyl groups are systematically replaced by the more electronegative Ph groups [12]. Values of $J(WP)$ for $PPh_2H$ are constant in the series (except for *cis*-$W(CO)_4(PPh_2H)(PEt_3)$) and are the same as $J(WP)$ in $W(CO)_5PPh_2H$ [5]. In addition, $J(WP)$ values for $PPh_2H$ and $PPh_3$ in *cis*-$W(CO)_4(PPh_3)(PPh_2H)$ are of nearly the same magnitude. Furthermore, $J(WP)$ for $PPh_3$ in *cis*-$W(CO)_4(PPh_3)(PPh_2H)$ is 12 Hz less than in the parent $W(CO)_5PPh_3$ complex, showing that $PPh_3$ is more sensitive to its *cis* neighbor than is $PPh_2H$ [2].

Narrow ranges of $^2J(PP)$ (17–20 Hz) and $^3J(PH)$ (7.3–8.0 Hz) values were observed for the tungsten complexes. Similarly, values of $^1J(PH)$ (332–335 Hz) were essentially independent of $PR_3$.

In this work we have shown that *cis*-$M(CO)_4(PPh_2H)(PR_3)$ can be prepared in modest yields from $W(CO)_5PPh_2H$, $PR_3$, and base. Although a variety of minor products are also formed, the principal product is easily separated and purified. Thus the method should be given consideration when tetracarbonyl group 6 complexes containing secondary and tertiary phosphines are desired.

## Experimental

The phosphines and metal carbonyls were purchased from Pressure Chemical Company and used without further purification. The complexes $W(CO)_5PPh_2H$, $Mo(CO)_5PPh_2H$, and $Cr(CO)_5PPh_2H$ were synthesized as described previously [13]. All reactions were carried out under a nitrogen atmosphere.

Microanalyses were performed by Galbraith Laboratories. Infrared spectra in the carbonyl region were recorded with a Perkin–Elmer 337 infrared spectrometer and expanded with an E-H Sargent recorder. $^{31}P$ NMR spectra were recorded with a Varian XL-100 NMR spectrometer. $^{31}P$ NMR chemical shifts, relative to 85% phosphoric acid, are reported with positive values downfield from the reference.

*Synthesis of $M(CO)_4LL'$ complexes.* The following description for the preparation of *cis*-$W(CO)_4(PPh_2H)(PEtPh_2)$ was also followed for the preparation of *cis*-$W(CO)_4(PPh_2H)(PEt_2Ph)$, *cis*-$W(CO)_4(PPh_2H)(PPh_3)$, *cis*-$Mo(CO)_4(PPh_2H)(PPh_3)$, and *cis*-$Cr(CO)_4(PPh_2H)(PPh_3)$. The chromatography step was eliminated for the preparation of *cis*-$W(CO)_4(PPh_2H)(PEt_3)$ because $W_2(CO)_8(\mu\text{-}PPh_2)_2$ was not observed.

To a refluxing solution of dry THF (25 ml) containing $PEtPh_2$ (0.50 ml; 2.3 mmol) and potassium t-butoxide (0.20 g; 1.8 mmol) was added dropwise $W(CO)_5PPh_2H$ (1.0 g; 1.96 mmol) in THF over a period of 1 h. A yellow color developed immediately in the reaction pot. After addition of the tungsten reactant, the solution was heated under reflux for 1.5 h. The yellow reaction mixture was cooled to room temperature and filtered. Upon exposure to air the filtrate devel-

Table 3

Analytical data, melting points, and percentage yields for *cis*-$M(CO)_4(PPh_2H)(L)$

| M | L | Analysis (found (calcd.)(%)) C | H | P | M.p. (°C) | Yield (%) |
|---|---|---|---|---|---|---|
| W | $PEt_3$ | 44.00<br>(44.00) | 4.40<br>(4.37) | 10.30<br>(10.30) | 124–125 | 47.6 |
| W | $PEt_2Ph$ | 48.34<br>(48.17) | 4.16<br>(4.04) | 9.69<br>(9.56) | 114–115 | 38.6 |
| W | $PEtPh_2$ | 51.53<br>(51.78) | 3.92<br>(3.77) | 8.92<br>(9.19) | 128–129 | 40.2 |
| W | $PPh_3$ | | | | dec.166<br>(lit. [3]<br>dec. 166) | 37.9 |
| Mo | $PPh_3$ | 62.10<br>(62.21) | 4.06<br>(3.99) | 9.50<br>(9.44) | 147–148 | 36.2 |
| Cr | $PPh_3$ | 65.07<br>(66.70) | 4.06<br>(4.28) | 10.04<br>(10.11) | 149–150 | 17.4 |

oped a light red color. The solvent was removed and the mixture was separated on a 60-cm silica gel column which was eluted with a mixture of 90% petroleum ether and 10% ethyl acetate. A red band was eluted first which, after solvent removal and recrystallization from dichloromethane/methanol, yielded $W_2(CO)_8(\mu\text{-}PPh_2)_2$ (0.1 g; 11%). Further elution of the column gave a fraction which, after solvent removal and recrystallization from dichloromethane/methanol, produced *cis*-$W(CO)_4(PPh_2H)(PEt_2PH(PEt_2Ph))$. Elemental analyses, melting points, and percentage yields are presented in Table 3.

## Acknowledgement

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The authors are grateful to the University of Illinois and to David Vander Velde for assistance in obtaining $^{31}P$ NMR spectra. We thank Ellen A. Keiter for helpful discussions.

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