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The First Pan-Group VI Transition Metal Complex: Synthesis of $(OC)_5WPPh[CH_2CH_2PPh_2Mo(CO)_5][CH_2CH_2PPh_2Cr(CO)_5]$

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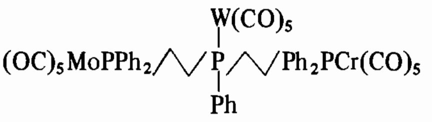
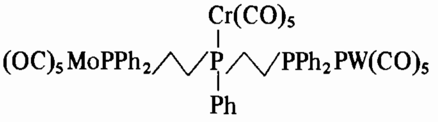
The number and kind of metal sites to which a polydentate phosphorus ligand such as $Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2$ is coordinated can be controlled by constructing the complex of interest from judiciously selected coordinated fragments, To illustrate the synthetic utility of this approach we have synthesized I and II, the first transition metal complexes to our knowledge which contain all elements of Group 6.


$(OC)_5MoPPh_2\diagup\!\diagdown\!\diagup\overset{W(CO)_5}{\underset{Ph}{P}}\diagup\!\diagdown\!\diagup Ph_2PCr(CO)_5$

I


$(OC)_5MoPPh_2\diagup\!\diagdown\!\diagup\overset{Cr(CO)_5}{\underset{Ph}{P}}\diagup\!\diagdown\!\diagup PPh_2PW(CO)_5$

II

Our synthetic procedures follow those developed by King [1], Grim [2] and their coworkers for the production of free polydentate phosphines. These methods are based upon the base-catalyzed addition of R_2P^- to unsaturated carbon–carbon bonds. In previous work we have extended the approach to reactions of coordinated phosphinoalkenes [3]. Other groups have investigated addition reactions of coordinated phosphinoalkynes [4] and of secondary phosphines [5].

The reaction of $(OC)_5WPPh(CH{=}CH_2)_2$ (2 mmol) with $(OC)_5CrPPh_2H$ [3] (1.6 mmol) in refluxing THF (50 ml) for 1.0 hour in the presence of potassium tert-butoxide (0.1 g) afforded white crystalline $(OC)_5WPPh(CH{=}CH_2)[CH_2CH_2PPh_2Cr(CO)_5]$ (66% based on $(OC)_5CrPPh_2H$) which was recrystallized from CH_2Cl_2/CH_3OH.

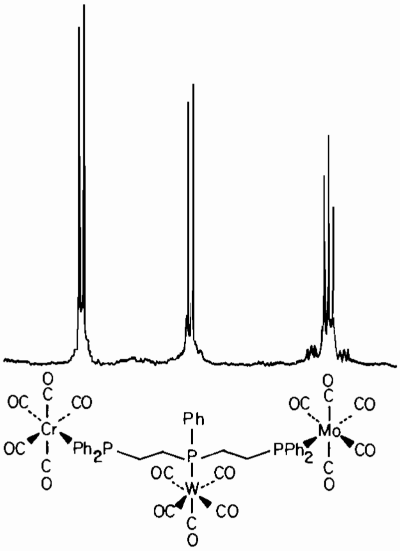


Fig. 1. $^{31}P[H]$ NMR spectrum of $(OC)_5WPPh[CH_2CH_2PPh_2Mo(CO)_5][CH_2CH_2PPh_2Cr(CO)_5]$ recorded at 40.5 MHz on a Varian XL-100 NMR spectrometer equipped with Fourier transform and a pulsed deuterium lock.

$$(OC)_5CrPPh_2H + (OC)_5WPPh(CH{=}CH_2)_2 \xrightarrow[THF]{KOBu^t}$$

$$(OC)_5WPPh(CH{=}CH_2)[CH_2CH_2PPh_2Cr(CO)_5]$$

The ^{31}P NMR spectrum ($CDCl_3$) of the intermediate showed a doublet ($^3J_{PP}$ = 32.9 Hz) at 50.1 ppm (Cr–P) and a doublet ($^3J_{PP}$ = 32.9 Hz) at 4.3 ppm (W–P) flanked by tungsten–phosphorus satellites (J_{WP} = 239.2 Hz). The carbonyl region of the IR spectrum ($CHCl_3$) showed distinct $A_1^{(2)}$ absorptions (1) at 2077 cm^{-1} for $-W(CO)_5$ and 2068 cm^{-1} for $-Cr(CO)_5$, and overlapping (E + $A_1^{(1)}$) modes centered at 1946 cm^{-1}.

Equimolar quantities (1.0 mmol) of the intermediate and $(OC)_5MoPPh_2H$ were allowed to react as described above to give I. A near stoichiometric yield of the faint yellow complex was obtained after recrystallization from CH_2Cl_2/CH_3OH.

$$(OC)_5MoPPh_2H +$$

$$+(OC)_5WPPh(CH{=}CH_2)CH_2CH_2PPh_2Cr(CO)_5 \xrightarrow[THF]{KOBu^t} I$$

The ^{31}P NMR spectrum ($CDCl_3$) of I (Fig. 1) revealed chemical shifts at 50.2 ppm (Cr–P), 31.1 (Mo–P) and 6.8 (W–P) with $^3J_{PP}$ values of 31.7 (CrP–WP) and 34.2 (MoP–WP) Hz. A value of 241.4

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Hz was recorded for $^1J_{WP}$. The carbonyl stretching E + $A_1^{(1)}$ modes of the three $-M(CO)_5$ moieties appeared as an unresolved broad absorption (1944 cm^{-1}). The $A_1^{(2)}$ modes were found at 2067 cm^{-1} (Cr) and at 2077 cm^{-1} (Mo, W).

The same reaction sequence with $(OC)_5CrPPh(CH=CH_2)_2$ (δ_P = 38.1 ppm) and $(OC)_5WPPh_2H$ [3] as starting materials was used to prepare II, a constitutional isomer of I in which Cr is bound to the central phosphorus. The ^{31}P NMR spectrum of the intermediate, $(OC)_5CrPPh(CH=CH_2)[CH_2CH_2PPh_2\text{-}W(CO)_5]$, consisted of two doublets ($^3J_{PP}$ = 32.1 Hz) at 41.5 ppm (Cr–P) and 13.0 ppm (W–P) with J_{WP} equal 242.1 Hz. The trimetallic species, II, gave chemical shifts at 44.5 (Cr–P), 30.7 (Mo–P) and 13.4 ppm (W–P) with $^3J_{PP}$ values of 32.8 (CrP–WP) and 31.8 (CrP–MoP) Hz and $^1J_{WP}$ at 243.6 Hz. Undoubtedly the third constitutional isomer in which molybdenum is attached to the central phosphorus atom could be prepared by the methods described if one so desired.

Products such as I and II could not be obtained by standard substitution reactions without many tedious separations. Addition reactions performed as described render them easily accessible.

Acknowledgement

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