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# Synthesis of Bimetallic Phosphido-Bridged Isocyanide M−Mo (M = Mo, W) Complexes

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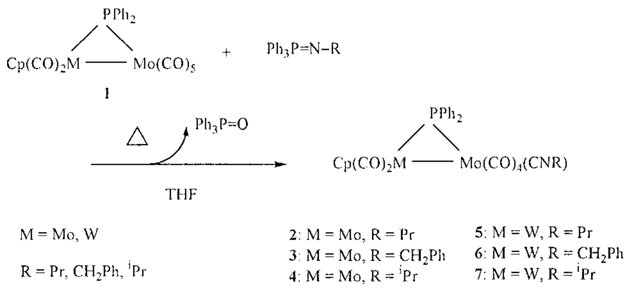
The reaction of $Cp\overline{M(CO)_2(\mu\text{-}PPh_2)Mo}(CO)_5$ (M = Mo, W) with phosphine imide was regiospecific with the isocaynide ligand regiospecifically coordinated to the Mo atom to produce bimetallic isocyanide complexes $Cp\overline{M(CO)_2(\mu\text{-}PPh_2)Mo}(CO)_4(CNR)$ (M = Mo, W; R = Pr, $CH_2Ph$, $^iPr$). A single-crystal study of cis-$Cp\overline{W(CO)_2(\mu\text{-}PPh_2)Mo}(CO)_4(CNPr)$ was performed.

Phosphine imide, a deoxygenating reagent,[1] has been used to react with metal carbonyl compounds to prepare isocyanide metal complexes.[2] Nucleophilic attack of the phosphine imide at the carbonyl carbon followed by the elimination of the triphenylphosphine oxides to generate the isocyanide ligand was proposed as the reaction mechanism.[2] This effective alternative preparation method has been successfully employed on monomeric metal complexes and homonuclear trimeric cluster compounds.[2a,b,3] However, reaction between phosphine imide and heterobimetallic carbonyl complex has not been revealed. Reported herein is the study of the regiospecific reaction between phosphine imides and phosphido-bridged bimetallic complexes $Cp\overline{M(CO)_2(\mu\text{-}PPh_2)Mo}(CO)_5$ (M = Mo, W).

The bimetallic complex $Cp\overline{M(CO)_2(\mu\text{-}PPh_2)Mo}(CO)_5$ (M = Mo, W) (**1**)[4,5] has two sets of carbonyl ligands. One set is composed of the carbonyl ligands on the $CpM(CO)_2$ (M = Mo, W) moiety; the other set is the carbonyl ligands on $Mo(CO)_5$. Complex **1** reacts with phosphine imide to produce $Cp\overline{M(CO)_2(\mu\text{-}PPh_2)Mo}(CO)_4(CNR)$ (M = Mo, W; R = Pr, $CH_2Ph$, $^iPr$) with the isocyanide ligand coordinated to the Mo as the only isolated product.



Reaction between $Cp\overline{M(CO)_2(\mu\text{-}PPh_2)Mo}(CO)_5$ (M = Mo, W) (**1**) and phosphine imides produced maroon red solids. $^{31}P$ NMR spectra of these red solids at room temperature showed a sharp singlet (for M = W, $J_{P-W}$ satellite was observed) and a broad hump. $^1H$ NMR showed signals of Cp and Ph protons with the Cp to Ph intensity ratio 1:2 in all the products. The rest of the proton signals in the spectrum indicate that there is totally one isocyanide ligand in the products. The observed $\nu$(CN) stretching frequencies of the products (2170 $cm^{-1}$ for **2** to 2162 $cm^{-1}$ for **7**) in their IR spectra further indicate the presence of a coordinated CN ligand.[6] In addition, elemental analysis of the products is consistent with the empirical formula of the isocyanide complex $Cp\overline{M(CO)_2(\mu\text{-}PPh_2)Mo}(CO)_4(CNR)$ (M = Mo, W; R = Pr, $CH_2Ph$, $^iPr$). All this indicates the product is a mixture of isomers and rules out the possibility that the product is a pure compound with two phosphorus atoms in the complex. To clarify the position of the isocyanide ligand and identify the structure of the products, single-crystal X-ray diffraction study of *cis*-$Cp\overline{W(CO)_2(\mu\text{-}PPh_2)Mo}(CO)_4(CNPr)$ (**5-cis**) obtained from the product mixture was carried out. Figure 1 shows the ORTEP structure of the complex.

The structure of **5-cis** is similar to the structure of its parent compound $Cp\overline{W(CO)_2(\mu\text{-}PPh_2)Mo}(CO)_5$ (**1-W**).[5] A W−Mo distance of 3.1894(8) Å, which is similar to the W−Mo bond length of 3.2054(16) Å in **1-W**, indicates a metal−metal bond between two metals in the complex.

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[1] Abel, E. W.; Mucklejoin, S. A. *Phosphorus Sulfur Relat. Elem.* **1981**, *9*, 235, and references therein.

[2] (a) Kiji, J.; Matsumura, A.; Haishi, T.; Okazaki, S.; Furukawa, J. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2731. (b) Alper, H.; Partis, R. A. *J. Organomet. Chem.* **1972**, *35*, c40. (c) Mirkin, C. A.; Lu, K. L.; Geoffroy, G. L.; Rheingold, A. L.; Staley, D. L. *J. Am. Chem. Soc.* **1989**, *111*, 7279.

[3] (a) Chen, L. C.; Chen, M. Y.; Chen. J. H.; Wen, Y. S.; Lu, K. L. *J. Organomet. Chem.* **1992**, *425*, 99. (b) Lin. Y. W.; Gau, H. M.; Wen, Y. S.; Lu, K. L. *Organometallics* **1992**, *11*, 1445. (c) Mirkin, C. A.; Lu, K. L.; Snead, T. W.; Young, B. A.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 3800. (d) Lu, K. L.; Chen, C. C.; Lin, Y. W.; Hong, F. E.; Gau, H. M.; Gan, L. L.; Luoh, H. D. *J. Organomet. Chem.* **1993**, *453*, 263.

[4] Shyu, S.-G. Unpublished results.

[5] Shyu, S.-G.; Hsu, J.-Y.; Lin, P.-J.; Wu, W.-J.; Peng, S.-M.; Lee, G. H.; Wen, Y.-S. *Organometallics* **1994**, *13*, 1699.

[6] Albers, M. O.; Coville, N. J.; Singleton, E. *J. Organomet. Chem.* **1987**, *323*, 37.

S0276-7333(98)00236-2 CCC: $15.00

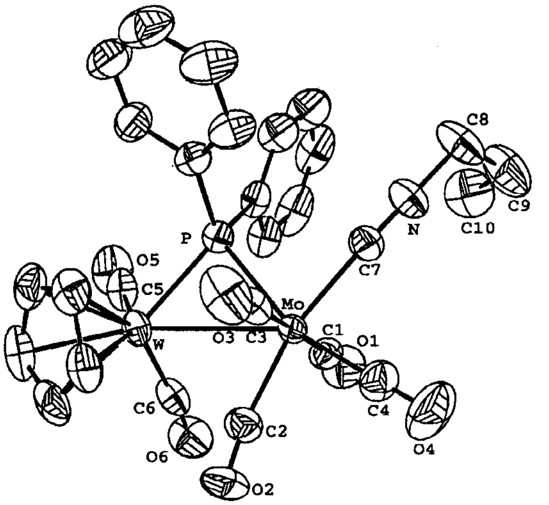

**Figure 1.** ORTEP drawing of **5**. Hydrogen atoms are omitted.

This observation is consistent with the observed downfield resonance of the phosphorus signal in its $^{31}$P NMR spectrum.[7]

The isocyanide ligand coordinates to the Mo and is cis to the phosphido bridge ligand. The observed $^{13}$C NMR tungsten carbonyl resonance signals at 229.7 ($J_{C-P}$ = 17.4 Hz) and 223.8 ppm, which are in good agreement with the W carbonyl resonance signals in **1-W** (226.7 ppm, $J_{C-P}$ = 17.5 Hz; 221.8 ppm) and the W carbonyl resonance signals of its phosphine derivative $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_4(PPh_3)$ (231.0 ppm, $J_{C-P}$ = 15.8 Hz; 223.5 ppm), are consistent with the two carbonyl ligands on the W atom.[5]

Attempts to obtain the spectroscopic data of the pure cis isomer failed. When the crystals of the cis isomers were dissolved in solution, the $^1$H and $^{31}$P NMR spectra of the solution were the same as the product mixture obtained in the first stage. This indicates that isomerization occurs when the pure cis isomer dissolves into the solvent.

The only observed $^{13}$C NMR tungsten carbonyl resonance signals at 229.7 and 223.8 ppm indicate that the other isomer also has two carbonyl ligands on the W atom. This indicates that the isocyanide ligand is coordinated to the Mo in both isomers. We propose the other isomer to be the trans isomer. Transformations between cis and trans isomers in heterobimetallic phosphido-bridged complexes have been observed in $CpFe(CO)(\mu\text{-}PPh_2)W(CO)_4(L)$ (L = $P(OMe)_3$, $PPh_3$, $PPh_2H$).[8]

The broad hump at 163 ppm in the $^{31}$P NMR indicates the possibility of the fluxional behavior of one isomer. To understand this fluxional behavior and to assign the NMR signals in the mixture spectra, variable-temperature $^{31}$P NMR of **5-cis** was obtained in toluene-$d_8$ (Figure 2a). At room temperature, there were two signals. One was a broad hump at 163 ppm. The other was a sharp singlet at 163.8 with signal to $J_{P-W}$ satellite intensity ratio 11:1. At 273 K, the sharp singlet remained unchanged; however, the hump split into two broad signals. Below 253 K, these two signals sharpened and the $J_{P-W}$ satellites could be observed. The coalescence temperature was obtained at 340 K. The broad signal sharpened (164.3 ppm), and the $J_{P-W}$ (340.2 Hz) could be clearly observed.

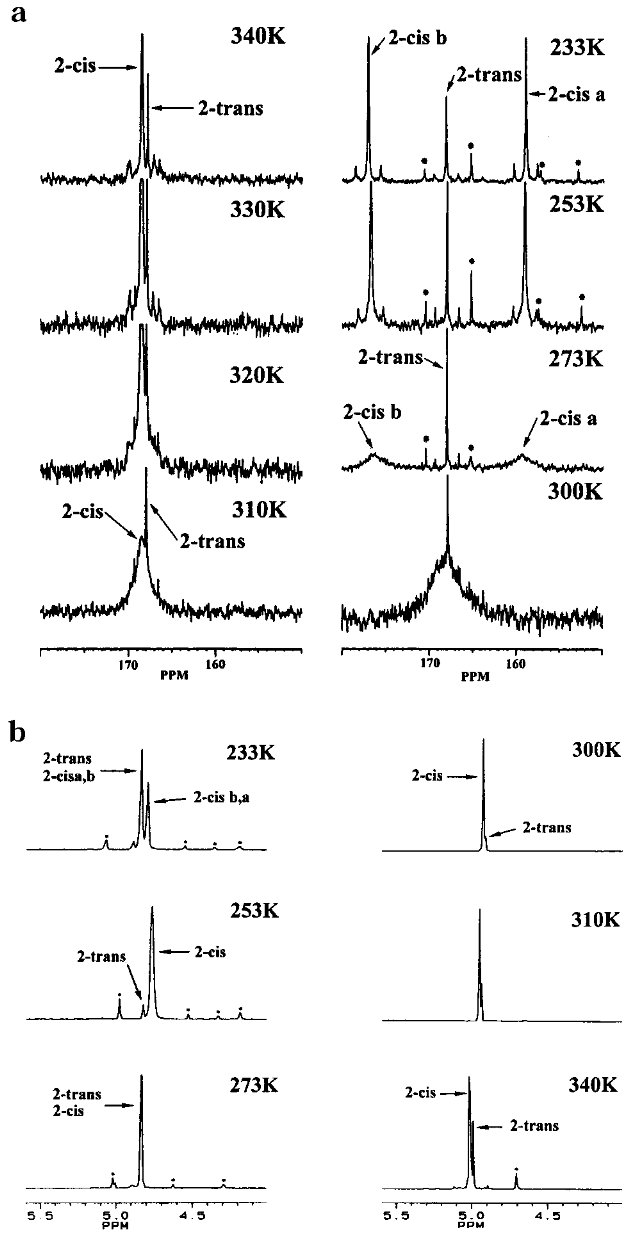

**Figure 2.** (a) Variable-temperature $^{31}$P{$^1$H} NMR and (b) $^1$H NMR spectra of **5** in toluene-$d_8$. Only the Cp region is shown in part b. **5-cis a** and **5-cis b** represent two conformational isomers of **5-cis**. Signals due to impurities are marked *.

The broad signal is assigned to the cis isomer in which the isocyanide ligand is coordinated to Mo and cis to the phosphido bridge. It has been proposed that the four ligands cis to the phosphido bridge ligand are fluxional through the rotation of the Mo−P bonding.[5,8] In addition, in $CpW(CO)_3(\mu\text{-}PPh_2)Mo(CO)_4(L)$ (L = $P(OMe)_3$, $PPh_3$, $PPh_2H$), the Mo−P bond can rotate in the solution such that two conformational isomers are

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[7] (a) Carty, A. J.; Maclaughlin, S. A.; Nucciarone, D. In *Phosphrous-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; Verkade, J. G., Quin, L. P., Eds.; VCH: New York, 1987; Chapter 16, and references cited therein. (b) Carty, A. *J. Adv. Chem. Ser.* **1982**, *No. 196*, 163. (c) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

[8] Shyu, S.-G.; Lin, P.-J.; Lin, K.-J.; Chang, M.-G.; Wen, Y.-S. *Organometallics* **1995**, *14*, 2253.

**Table 1. Spectroscopic Data for the Complexes**

| complex | $^{31}P\{^1H\}$ NMR,[a,b] $\delta$ | $^1H$ NMR,[a,b,d] $\delta$ | $^{13}C\{^1H\}$ NMR,[a,d] $\delta$ | IR,[c,f] $cm^{-1}$ |
|---|---|---|---|---|
| **1-Mo**[g] | 204.51 | 5.05 (s, 5H, $C_5H_5$) | | $\nu$ (CO), 2071 m, 1964 s, 1935 sh, 1869w |
| **2-cis**[e] | 199.59(br) | 5.01 (s, 5H, $C_5H_5$), 3.33 (t, 2H, $CNCH_2$, $J_{H-H} = 6.52$ Hz), 1.50 (m, 2H, $-CH_2-$), 0.84 (t, 3H, $-CH_3$, $J_{H-H} = 7.35$ Hz) | 92.93 (s, $C_5H_5$), 45.96 (s, $CNCH_2$), 22.50 (s, $-CH_2-$), 10.92 (s, $CH_3$) | $\nu$ (CN), 2170w; $\nu$ (CO), 2036m, 2021w, 1941s, 1853w |
| **2-trans**[e] | 202.53 | 4.95 (s, 5H, $C_5H_5$), 3.72 (t, 2H, $CNCH_2$, $J_{H-H} = 6.42$ Hz), 1.84 (m, 2H, $-CH_2-$), 1.12 (t, 3H, $-CH_3$, $J_{H-H} = 7.36$ Hz) | 92.60 (s, $C_5H_5$), 46.72 (s, $CNCH_2$), 23.12 (s, $-CH_2-$), 10.92 (s, $CH_3$) | |
| **3-cis**[e] | 200.06(br) | 5.01 (s, 5H, $C_5H_5$), 4.65 (d, 1H, $CH_aH_b$, $J_{H-H} = 16.5$ Hz), 4.55 (d, 1H, $CH_aH_b$, $J_{H-H} = 16.8$ Hz) | 155.97 (br, CN), 92.92 (s, $C_5H_5$), 48.09 (s, $CH_2$) | $\nu$ (CN), 2164w; $\nu$ (CO), 2036m, 2021w, 1941s, 1855w |
| **3-trans**[e] | 202.53 | 4.96 (s, 5H, $C_5H_5$), 4.99 (s, $CH_2$) | 92.63 (s, $C_5H_5$), 48.65 (s, $CH_2$) | |
| **4-cis**[e] | 198.52(br) | 5.02 (s, 5H, $C_5H_5$), 3.77 (m, 1H, CH), 1.18 (d, 3H, $CHCH_3$, $J_{H-H} = 6.60$ Hz), 1.21 (d, 3H, $CHCH_3$, $J_{H-H} = 6.45$ Hz) | 92.88 (s, $C_5H_5$), 48.63 (s, CH), 22.88 (s, $-CH_3$) | $\nu$ (CN), 2162w; $\nu$ (CO), 2036m, 2020w, 1939s, 1854w |
| **4-trans**[e] | 202.47 | 4.95 (s, 5H, $C_5H_5$), 4.11 (m, 1H, CH), 1.20 (d, 6H, $CH_3$, $J_{H-H} = 6.45$ Hz) | 92.55 (s, $C_5H_5$), 49.32 (s, CH), 23.55 (s, $-CH_3$) | |
| **1-W**[g] | 170.46 ($J_{P-W} = 342.6$) | 5.17 (s, 5H, $C_5H_5$) | | $\nu$ (CO), 2071m, 1961s, 1929sh, 1856w |
| **5-cis**[e] | 166.45(br) | 5.13 (s, 5H, $C_5H_5$), 3.35 (t, 2H, $CNCH_2$, $J_{H-H} = 6.60$ Hz), 1.52 (m, 2H, $-CH_2-$), 0.84 (t, 3H, $-CH_3$, $J_{H-H} = 7.20$ Hz) | 91.31 (s, $C_5H_5$), 45.92 (s, $CNCH_2$), 22.45 (s, $-CH_2$), 10.87 (s, $-CH_3$) | $\nu$ (CN), 2169w; $\nu$ (CO), 2037m, 2022w, 1935s, 1843m |
| **5-trans**[e] | 169.34 ($J_{P-W} = 329.3$) | 5.05 (s, 5H, $C_5H_5$), 3.69 (t, 2H, $CNCH_2$, $J_{H-H} = 6.60$ Hz), 1.84 (m, 2H, $-CH_2-$), 1.12 (t, 3H, $-CH_3$, $J_{H-H} = 7.50$ Hz) | 91.01 (s, $C_5H_5$), 46.73 (s, $CNCH_2$), 22.97 (s, $-CH_2$), 10.87 (s, $-CH_3$) | |
| **6-cis**[e] | 167.07(br) | 5.12 (s, 5H, $C_5H_5$), 4.58 (d, 1H, $CH_aH_b$, $J_{H-H} = 18.0$ Hz), 4.68 (d, 1H, $CH_aH_b$, $J_{H-H} = 18.0$ Hz) | 91.36 (s, $C_5H_5$), 48.05 (s, $CH_2$) | $\nu$ (CN), 2163w; $\nu$ (CO), 2038w, 2021w, 1940s, 1843w |
| **6-trans**[e] | 170.46 ($J_{P-W} = 326.8$) | 5.06 (s, 5H, $C_5H_5$) | 91.09 (s, $C_5H_5$), 48.68 (s, $CH_2$) | |
| **7-cis**[e] | 164.68(br) | 5.12 (s, 5H, $C_5H_5$), 3.78 (m, 1H, CH), 1.18 (d, 3H, $CHCH_3$, $J_{H-H} = 6.60$ Hz), 1.21 (d, 3H, $CHCH_3$, $J_{H-H} = 6.8$ Hz) | 91.31 (s, $C_5H_5$), 48.65 (s, CH), 22.92 (s, $-CH_3$) | $\nu$ (CN), 2162w; $\nu$ (CO), 2037w, 2021w, 1939s, 1843w |
| **7-trans**[e] | 169.42 ($J_{P-W} = 326.8$) | 5.05 (s, 5H, $C_5H_5$), 4.02 (m, 1H, CH), 1.50 (d, 6H, $CH_3$, $J_{H-H} = 6.6$ Hz) | 91.00 (s, $C_5H_5$), 49.37 (s, CH), 23.47 (s, $-CH_3$) | |

[a] At room temperature. [b] *J* values in Hz. [c] In $CH_2Cl_2$ solution unless otherwise indicated. Abbreviations: w, weak; m, medium; s, strong; vs, very strong. [d] In $CDCl_3$ solution unless otherwise indicated. $C_5H_5$, Pr, $^iPr$, $CH_2Ph$, and CN group only. Abbreviations: s, singlet; d, doublet; t, triplet; br, broad. [e] Not separated pure. [f] For complexes **5**, **6**, and **7** the IR of the mixture of their trans and cis isomers. [g] These data are taken from refs 4 and 5.

observed in the solution.[5] On the basis of these observations, the variable $^{31}P$ NMR can be explained as follows. At low temperature there exist two conformational isomers for the cis complex. In both isomers, the isocyanide ligands are cis to the phosphido bridge. At higher temperature, these two conformational isomers exchange through the rotation of the Mo$-$P bonding so that the phosphido bridge signal broadens. At higher temperature, the coalescence point is obtained and a sharp signal is observed. For the trans isomer, the rotation of the Mo$-$P bond does not result in any structural changes. A sharp phosphido signal in $^{31}P$ NMR should remain the same throughout the temperature change, as observed in the variable-temperature NMR study.

The cis and trans isomers can also be observed in $^1H$ NMR. Both isomers have different Cp and different isocyanide proton resonance positions and can be assigned easily (Table 1). However, at 273$-$253 K, the Cp protons of both stereoisomers have similar resonance position in the $^1H$ NMR and cannot be resolved (Figure 2b). At 233 K, signals corresponding to the conformational isomers of the cis isomer can be observed at 4.65 and 4.61 ppm. The signal of the trans isomer at that temperature still cannot be observed because it overlaps with the signal of one of the conformational isomers.

The attack of phosphine imide on the binuclear complex is regiospecific. However, whether the attack of phosphine imide on the Mo carbonyl is stereospecific cannot be clarified. Although isomerization from the cis isomer to the trans isomer is observed by dissolving the single crystals of the cis isomer in solution, the possibility of initial nucleophilic attack on the trans Mo carbonyl still cannot be ruled out completely.

From the electronic point of view, the carbon atoms on the cis carbonyl ligands are more electrophilic than the carbon on the trans carbonyl ligand. First, if we consider the metallophosphine $CpM(CO)_2PPh_2$ (M = Mo, W) as a ligand similar to a phosphine ligand, the aptitude of back-donation from the Mo to the trans carbonyl ligand should be larger than that to the cis CO ligand because phosphine is a better electron donor than carbonyl. This makes the carbon atom on the trans CO ligand less electophilic than the carbon atoms on the cis CO ligands. Second, in $CpM(CO)_2(\mu\text{-}PPh_2)Mo(CO)_5$ (M = Mo, W), the metal$-$metal bond can be considered as a dative bonding from Mo to M. The Mo metal donates two electrons from its filled $t_{2g}$ orbitals to the adjacent metal M.[5,8] Powell suggested that the net results of this donation will be a decrease in $d_{xy} \rightarrow \pi$ CO bonding to the equatorial CO's.[9] This may weaken the Mo–CO bonds of the two equatorial Mo-CO's cis to the phosphido ligand[10] and also reduces the electron density of the carbon atom on these CO ligands. The former will enhance the substitution of the carbonyl ligands toward Lewis bases, as observed in the regiospecific substitution reaction of $CpM(CO)_2(\mu\text{-}PPh_2)Mo(CO)_5$ (M = Mo, W) with phosphines.[5] The latter may further increase the electrophilic abilities of the carbon atoms on the equatorial CO's cis to the phosphido ligand toward nucleophilic reagents, as observed in this study.

## Experimental Section

All reactions were carried out under a purified nitrogen atmosphere with standard Schlenk techniques. Infrared (IR) spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. The $^1H$, $^{13}C$, and $^{31}P$ NMR spectra were recorded by using Bruker AMX-500, MSL-200, AC-200, and AC-300 spectrometers. The $^{31}P$ NMR shifts are referenced to 85% $H_3PO_4$. Except as noted, spectra were collected at room temperature. The fast atom bombardment (FAB) mass spectra were recorded on a VG70-250S or a JEOL JMS-HX 110 mass spectrometer. Microanalyses were performed by the Microanalytical Laboratory at National Cheng Kung University, Tainan, Taiwan.

**Materials.** THF was distilled from potassium and benzophenone under an atmosphere of purified nitrogen just before use. Other solvents were purified according to established procedures.[11] The complexes $CpMo(CO)_2(\mu PPh_2)Mo(CO)_5$[4] (**1-Mo**) and $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_5$5 (**1-W**) were prepared according to literature procedures. The compounds $Ph_3P{=}N{-}R$ (R = Pr, $CH_2Ph$, $^iPr$) were prepared as described in the literature.[12,13]

**Synthesis of $CpMo(CO)_2(\mu\text{-}PPh_2)Mo(CO)_4(CNPr)$ (2-cis and 2-trans).** A mixture of **1-Mo** (0.319 g, 0.50 mM) and $Ph_3P{=}N{-}Pr$ (0.319 g, 1.00 mM) in 20 mL of THF was stirred and heated at 68 °C for about 6 h. The solvent was then removed, and the residue was chromatographed on grade III alumina and eluted with a mixture of $CH_2Cl_2$/hexanes to afford two fractions. From the first band, a trace amount of the unreacted starting material was recovered on elution with 10% $CH_2Cl_2$/hexane. The second band contained a mixture of **2-cis** and **2-trans** on elution with a 20% $CH_2Cl_2$/hexane mixture. Yield: 0.260 g (76.5%). Anal. Calcd for $C_{27}H_{22}Mo_2NO_6P$: C, 47.74; H, 3.26; N, 2.06. Found: C, 47.84; H, 3.30; N, 2.11. MS (FAB): $M^+$ *m/z* 680. Spectral data are given in Table 1.

**Synthesis of $CpMo(CO)_2(\mu\text{-}PPh_2)Mo(CO)_4(CNCH_2Ph)$ (3-cis and 3-trans).** Reaction and separation conditions similar to those for **2** were applied to prepare **3**. The reaction time was 55 h, and 0.240 g (0.38 mM) of **1-Mo** and 0.276 g (0.75 mM) of $Ph_3P{=}N{-}CH_2Ph$ were used. Yield: 0.074 g (26.8%). Anal. Calcd for $C_{31}H_{22}Mo_2NO_6P$: C, 51.19; H, 3.05; N, 1.93. Found: C, 51.62; H, 3.38; N, 1.83. MS (FAB): $M^+$ *m/z* 730. Spectroscopic data indicate that the product is a mixture of two isomers. Spectral data are given in Table 1.

**Table 2. Crystal and Intensity Collection Data for 5-cis**

| | |
|---|---|
| mol formula | $C_{27}H_{22}MoNO_6PW$ |
| mol wt | 767.24 |
| space group | $P\bar{1}$ |
| $a$ (Å) | 10.542(3) |
| $b$ (Å) | 10.594(4) |
| c (Å) | 14.61(2) |
| α (deg) | 76.76(2) |
| $\beta$ (deg) | 73.15(2) |
| $\gamma$ (deg) | 62.40(3) |
| $V$ (Å$^3$) | 1375.4(7) |
| $\rho$(calcd) (Mg m$^{-3}$) | 1.853 |
| $Z$ | 2 |
| cryst dimens (mm) | 0.19 × 0.22 × 0.31 |
| temp | room temperature |
| $\lambda$(Mo Kα) (Å) | 0.710 73 |
| $2\theta$ range (deg) | 50 |
| scan type | $\omega{-}2\theta$ |
| no. of reflns | 4823 |
| no. of obsd rflns | 3935 (>2.0$\sigma(I)$) |
| variables | 334 |
| $R$ | 0.027 |
| $R_w$ | 0.029 |
| $S$ | 1.38 |
| $\Delta F_{max,min}$ (e/Å$^3$) | 0.840, −0.980 |

**Table 3. Selected Bond Lengths and Bond Angles in Complex 5-cis**

| selected bond distance (Å) | | selected bond angle (deg) | |
|---|---|---|---|
| W-Mo | 3.1894(8) | W–P–Mo | 81.72(5) |
| W–P | 2.3689(17) | P–W–C5 | 82.22(18) |
| W–C5 | 1.951(6) | P–W–C6 | 109.13(16) |
| W–C6 | 1.945(7) | P–Mo–C1 | 90.06(16) |
| Mo–P | 2.5035(15) | P–Mo–C2 | 113.44(17) |
| Mo–C1 | 2.052(6) | P–Mo–C3 | 89.94(17) |
| Mo–C2 | 2.020(6) | P–Mo–C4 | 161.79(18) |
| Mo–C3 | 2.022(6) | P–Mo–C7 | 79.87(15) |
| Mo–C4 | 2.010(6) | W–C5–O5 | 177.2(5) |
| Mo–C7 | 2.120(6) | W–C6–O6 | 176.5(5) |
| C1–O1 | 1.132(7) | Mo–C1–O1 | 178.7(5) |
| C2–O2 | 1.142(7) | Mo–C2–O2 | 169.7(5) |
| C3–O3 | 1.144(8) | Mo–C3–O3 | 176.6(7) |
| C4–O4 | 1.127(8) | Mo–C4–O4 | 179.0(6) |
| C5–O5 | 1.150(8) | Mo–C7–N | 176.9(5) |
| C6–O6 | 1.160(8) | C7–N–C8 | 173.3(6) |
| C7–N | 1.139(7) | | |
| C8–N | 1.454(8) | | |

**Synthesis of $CpMo(CO)_2(\mu\text{-}PPh_2)Mo(CO)_4(CN^iPr)$ (4-cis and 4-trans).** Reaction and separation conditions similar to those for **2** were applied to prepare **4**. The reaction time was 187 h, and 0.336 g (0.53 mM) of **1-Mo** and 0.336 g (1.06 mM) of $Ph_3P{=}N^iPr$ were used. The parent complex **1-Mo** was recovered in 0.092 g. Yield: 0.076 g (21.3% based on parent compound used and 29.2% based on the parent compound consumed in the reaction). Anal. Calcd for $C_{27}H_{22}Mo_2NO_6P$: C, 47.74; H, 3.26; N, 2.06. Found: C, 47.41; H, 3.30; N, 2.04. MS (FAB): $M^+$ *m/z* 681. Spectroscopic data indicate that the product is a mixture of two isomers. Spectral data are given in Table 1.

**Synthesis of $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_4(CNPr)$ (5-cis and 5-trans).** Reaction and separation conditions similar to those for **2** were applied to prepare **5**. The reaction time was 11 h, and 0.331 g (0.46 mM) of **1-W** and 0.324 g (1.02 mM) of $Ph_3P{=}N{-}Pr$ were used. Yield: 0.172 g (49.1%). Anal. Calcd for $C_{27}H_{22}MoNO_6PW$: C, 42.27; H, 2.89; N, 1.83. Found: C, 42.10; H, 2.89; N, 1.87. MS (FAB): $M^+$ *m/z* 769. Spectroscopic data indicate that the product is a mixture of two isomers. Spectral data are given in Table 1.

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**Synthesis of $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_4(CNCH_2Ph)$ (6-cis and 6-trans).** Reaction and separation conditions similar to those for **2** were applied to prepare **6**. The reaction time was 48 h, and 0.340 g (0.47 mM) of **1-W** and 0.349 g (0.95 mM) of $Ph_3P{=}N{-}CH_2Ph$ were used. Yield: 0.092 g (24.0%). Anal. Calcd for $C_{31}H_{22}MoNO_6PW$: C, 45.67; H, 2.72; N, 1.72. Found: C, 45.41; H, 3.06; N, 1.56. MS (FAB): $M^+$ *m/z* 818. Spectroscopic data indicate that the product is a mixture of two isomers. Spectral data are given in Table 1.

**Synthesis of $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_4(CN^iPr)$ (7-cis and 7-trans).** Reaction and separation conditions similar to those for **2** were applied to prepare **7**. The reaction time was 72 h, and 0.319 g (0.44 mM) of **1-W** and 0.280 g (0.88 mM) of $Ph_3P{=}N{-}^iPr$ were used. Yield: 0.122 g (36%). Anal. Calcd for $C_{27}H_{22}MoNO_6PW$: C, 42.27; H, 2.89; N, 1.83. Found: C, 42.07; H, 3.08; N, 1.85. MS (FAB): $M^+$ *m/z* 768. Spectroscopic data indicate that the product is a mixture of two isomers. Spectral data are given in Table 1.

**Structure Determination of *cis*-$CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_4(CNPr)$.** A crystal of **5-cis** was grown by slow diffusion of hexanes into the saturated $CH_2Cl_2$ solution of the mixture of **5-cis** and **5-trans** at 4 °C. Diffraction measurements were made using an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares using SHELXL-93. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were constrained to geometrically calculated positions.

Crystal data and details of data collection and structure analysis are summarized in Table 2. Selected interatomic distances and bond angles are given in Tables 3. The final positional and displacement parameters for all atoms are provided in the Supporting Information.

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**Supporting Information Available:** Listings of calculated atomic coordinates, anisotropic thermal parameters, and bond distances and angles of compound **5-cis** (7 pages). Ordering information is given on any current masthead page.

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