Regiospecific Reaction between Dimetallic Phosphido-Bridged W−W Complexes and Phosphane Imide − Electrophilic Site Switching by Metal−Metal Bond Formation

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Reaction between $CpW(CO)_2(\mu\text{-}PPh_2)W(CO)_5$(*W–W*) (**2**) and $Ph_3P{=}NR$ (R = Pr, CH_2Ph, *i*Pr) in THF at refluxing temperature is regiospecific with the CNR ligand coordinated to the $W(CO)_4$ unit to produce $CpW(CO)_2(\mu\text{-}PPh_2)W(CO)_4(CNR)$(*W–W*) (**4**). Spectroscopic data indicate that the complex exists in two stereoisomeric forms in solution. The structure of the *cis* isomer was determined by a single-crystal X-ray diffraction study which indicates that the CNR ligand is coordinated to the W atom of the $W(CO)_4$ unit and *cis* to the phosphido bridge. Reaction between $CpW(CO)_3(\mu\text{-}PPh_2)W(CO)_5$ (**1**) and $Ph_3P{=}NR$ (R = Pr, CH_2Ph, *i*Pr) in THF under similar condition is also regiospecific. However, the CNR ligand is coordinated to the CpW site to produce $CpW(CO)_2(CNR)(\mu\text{-}PPh_2)W(CO)_5$ (**3**). There are also two stereoisomers of the complex, which were separated by column chromatography. Structures of both isomers were determined by single-crystal X-ray diffraction studies.

Introduction

It is now evident that the formation of a metal−metal bond can influence the chemistry at adjacent metal centers in dinuclear complexes and clusters.[1] Recent studies of phosphido-bridged dimetallic complexes have revealed two interesting observations. First, one metal atom can promote substitution reactions at the adjacent metal carbonyl ligand upon the formation of the metal−metal bond.[2] Second, switching of the substitution site can occur when the metal−metal bond is formed.[2b] Apparently, the formation of the metal−metal bond can result in the donation of electron density from one metal atom to the other.[2a−2e] This electron density redistribution may alter the electrophilicity of the carbon atom of the carbonyl ligands attached to the metal atoms. Thus, the electrophilic site may switch from the carbonyl ligands on one metal atom to the carbonyl ligands on the other metal atom in heterodimetallic complexes upon the formation of the metal−metal bond.

Phosphane imides, deoxygenating reagents,[3] react with carbonylmetal compounds to produce (isocyanide)metal complexes.[4] Nucleophilic attack of a phosphane imide at the carbonyl carbon atom followed by the elimination of the triphenylphosphane oxides to generate the isocyanide ligand has been proposed as the reaction mechanism.[4a−4c] Here, we report a study of the regiospecific reactions between phosphane imides and phosphido-bridged dimetallic complexes $Cp(CO)_3W(\mu\text{-}PPh_2)W(CO)_5$ (**1**)[2d] and $Cp(CO)_2W(\mu\text{-}PPh_2)W(CO)_5]$(*W−W*) (**2**)[2d] to produce $Cp(CO)_2(CNR)W(\mu\text{-}PPh_2)W(CO)_5$ (**3**) and $Cp(CO)_2W(\mu\text{-}PPh_2)W(CO)_4(CNR)$(*W−W*) (**4**), respectively. Thus, there is electrophilic site switching in these phosphido-bridged dimetallic complexes upon metal−metal bond formation.

Results and Discussion

Regiospecific Reaction of 1 with Phosphane Imides and Molecular Structures of 3a and 3a′

Reaction of **1** with $Ph_3P{=}NR$ (R = Pr, CH_2Ph, *i*Pr) produced two yellow solids **3** and **3′** in good yields (41% and 55%, Scheme 1). The ν(CN) stretching frequencies in their IR spectra indicate the terminal involvement of CNR in the coordination.[5] Signals corresponding to the protons of one isocyanide ligand were observed in their ^1H NMR spectra. Both complexes exhibited $^{31}P\{^1H\}$ NMR signals with two sets of J_{P-W} satellites at $\delta = -62.26$ (**3a**) and -61.55 (**3a′**), respectively, indicative of a bridging phosphido group and the absence of a metal−metal bond.[6] The structures of **3a** and **3a′** were determined by single-crystal X-ray diffraction studies. Their structures are shown in Figures 1 and 2.

In complex **3a**, the diphenylphosphido ligand bridges two tungsten atoms with a W−W distance of 4.454(5) Å. This indicates that there is no metal−metal bond between the tungsten atoms. This is consistent with the observed upfield position of the phosphido signal in its $^{31}P\{^1H\}$ NMR spectrum. The isocyanide ligand CNPr is terminally coordin-

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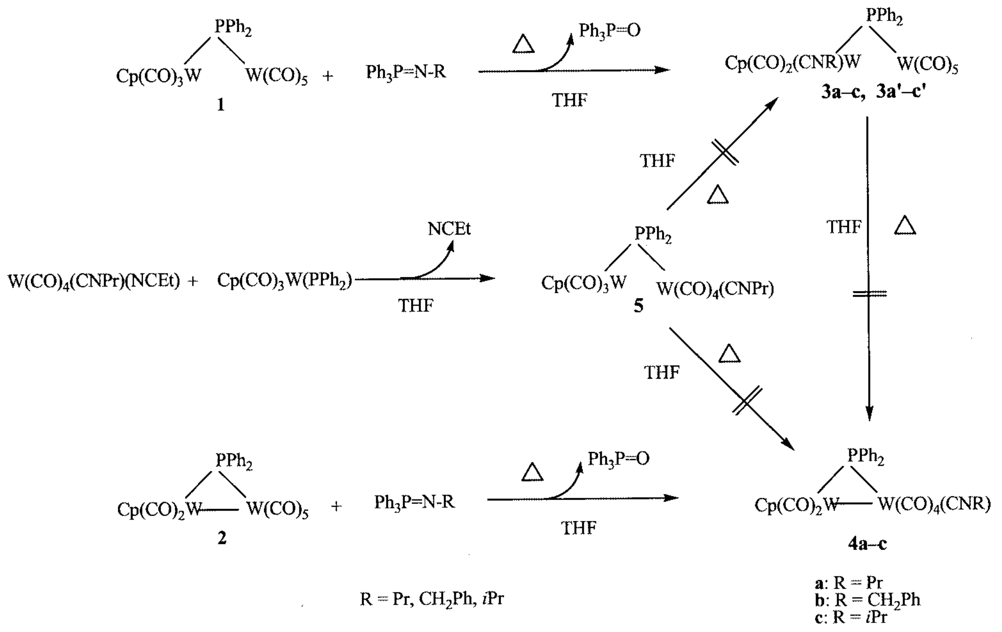

Scheme 1

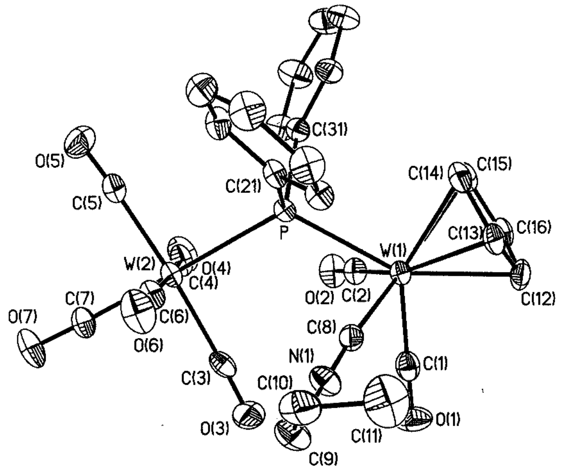

Figure 1. ORTEP drawing of **3a**, hydrogen atoms are omitted

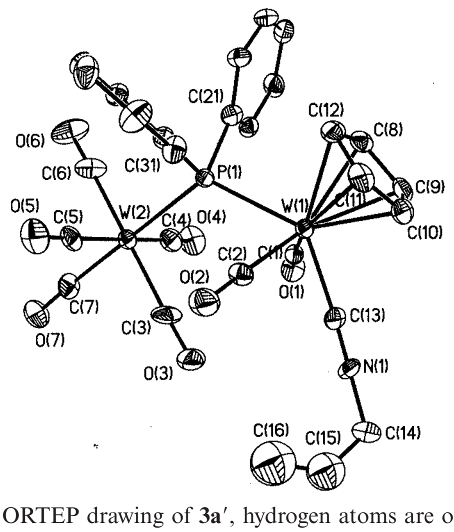

Figure 2. ORTEP drawing of **3a′**, hydrogen atoms are omitted

ated to W(1) of the CpW moiety. Thus, five CO ligands and $CpW(CO)_2(CNPr)PPh_2$ are coordinated to the W(2) atom to form a distorted octahedron around the W(2) atom. The doublet at δ = 200.44 (J_{P-C} =4.3 Hz, J_{C-W} = 123.8 Hz) in the $^{13}C\{^1H\}$ NMR spectrum is assigned to the four CO ligands on W(2) *cis* to the phosphido bridge. These four CO ligands are equivalent in the NMR spectrum because of the rotating of P−W(2) bond. Similar phenomena were observed in the $^{13}C\{^1H\}$ NMR spectra of complexes $CpFe(CO)_2(\mu\text{-}PPh_2)M(CO)_5$ (M = Cr, Mo, W).[10] The assignment is also based on the comparison of the resonance position of the *cis*-CO signal to the position of the *cis*-W(CO) signal [δ = 199.04 (d, J_{P-C} = 5.58 Hz, J_{W-C} = 121.29 Hz)] in $CpFe(CO)_2(\mu\text{-}PPh_2)W(CO)_5$.[7] The small doublet at δ = 201.62 (J_{P-C} = 18.12 Hz) is assigned to the *trans*-CO ligand based on a similar comparison with the resonance position [δ = 201.48 (d, J_{P-C} = 20.18 Hz)] of the *trans*-CO ligand of $CpFe(CO)_2(\mu\text{-}PPh_2)W(CO)_5$.[7] Also, the *trans*-CO ligand always has a lower field resonance than the resonance of the four *cis*-CO ligands as observed in $CpFe(CO)_2(\mu\text{-}PPh_2)M(CO)_5$ (M = Cr, Mo, W). The two carbonyl ligands on W(1) are non-equivalent and correspond to two broad humps (δ = 223 and 228) in the $^{13}C\{^1H\}$ NMR spectrum.

The structure of **3a′** is similar to the structure of complex **3a**. The isocyanide ligand is cordinated to the W(1) atom. The primary difference between them is that the two carbonyl ligands on W(1) are equivalent in **3a′** (cf. Figures 1 and 2). The doublet at δ = 223.40 (J_{P-C} = 15.10 Hz) in the ^{13}C NMR spectrum is assigned to the two equivalent carbonyl ligands based on the comparison of the resonance position of the CpW carbonyl ligands in $CpW(CO)_2(\mu\text{-}PPh_2)W(CO)_5(W\text{−}W)$ [δ = 226.56 (d, J_{P-C} = 17.19 Hz)][2d] and $CpW(CO)_2(\mu\text{-}PPh_2)Mo(CO)_5(W\text{−}W)$ [δ = 226.73 (d, J_{P-C} = 7.51 Hz)].[2e] Thus, the reaction between **1** and a phosphane imide is regiospecific with the isocyanide ligand coordinated to the CpW moiety.

Regiospecific Reaction of CpW(CO)$_2$(μ-PPh$_2$)W(CO)$_5$-(*W−W*) with Ph$_3$P=NR (R= Pr, CH$_2$Ph, *i*Pr) and the Structure of *cis*-CpW(CO)$_2$(μ-PPh$_2$)W(CO)$_4$(CN-Pr)-(*W−W*)

Interestingly, the reaction between **2** and a phosphane imide is also regiospecific. However, the attack is on a carbonyl ligand of the W(CO)$_5$ moiety (Scheme 1). Complex **2** reacted with a phosphane imide to produce a maroon red solid. Spectroscopic data (IR, variable-temperature ^{1}H and ^{31}P{^{1}H} NMR) and elemental analyses indicate that the product is a mixture of *cis* and *trans* isomers of **4**. We have based this conclusion on the comparison of these spectroscopic data to those of Cp(CO)$_2$M(μ-PPh$_2$)Mo-(CO)$_4$(CNR)(*M−Mo*) (M = Mo, W).[8] In addition the structure of *cis*-CpW(CO)$_2$(μ-PPh$_2$)W(CO)$_4$(CNPr)(*W−W*) (**4a-*cis***) was determined by a single-crystal X-ray study (Figure 3).

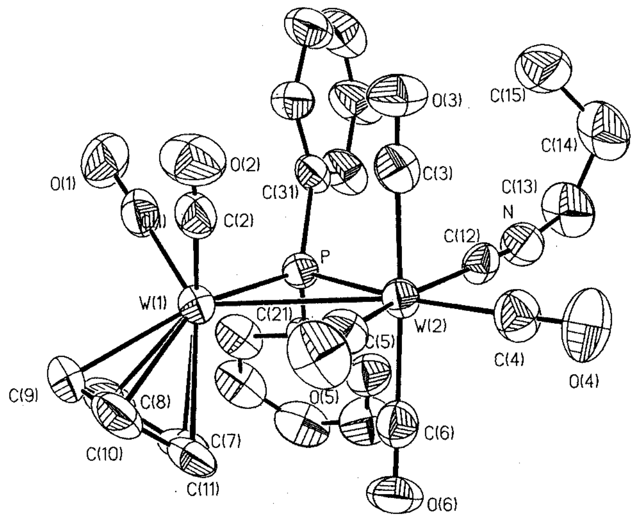

Figure 3. ORTEP drawing of **4a-*cis***, hydrogen atoms are omitted

The structure of **4a-*cis*** is similar to the structure of its W−Mo analogue Cp(CO)$_2$W(μ−PPh$_2$)Mo(CO)$_4$(CNPr)-(*W−Mo*) where the isocyanide ligand coordinates to W in the *cis* position to the phosphido bridge.[8] A W−W distance of 3.1849(9) Å, which is similar to the W−Mo bond lengths of 3.1894(8) Å in Cp(CO)$_2$W(μ-PPh$_2$)Mo(CO)$_4$(CNPr)(*W−Mo*) and 3.1942(12) Å in its parent compound **1**,[2d] indicates a metal−metal bond in the complex. This observation is consistent with the observed downfield resonance of the phosphorus signal in its ^{31}P{^{1}H} NMR spectrum.

Similar to Cp(CO)$_2$Mo(μ-PPh$_2$)M(CO)$_4$(CNR)(*W−Mo*) (M = Mo, W), attempts to spectroscopically characterize the pure isomer failed.[8] When the crystals of the *cis* isomers were dissolved in solution, the ^{1}H and ^{31}P{^{1}H} NMR spectra of the solution were the same as that of the product mixture initially obtained. This indicates that isomerization occurs rapidly when the pure *cis* isomer is dissolved in the solvent.

Synthesis and Structure of Cp(CO)$_3$W(μ-PPh$_2$)W(CO)$_4$-(CN*i*Pr) (5) − Possible Intramolecular Migration of the Isocyanide Ligand between W Atoms in Dimetallic Complex

In complex **1**, there are two sets of carbonyl ligands, one located on the CpW(CO)$_3$, and the other one on the W(CO)$_5$ unit. In principle, both sets of carbonyl ligands can be attacked by phosphane imides because there is no steric hindrance to protect the carbonyl ligands from the reaction. Intramolecular ligand exchanges have been observed in dimetallic complexes.[9] Thus, phosphane imides may attack the carbonyl ligand on the W(CO)$_5$ moiety followed by intramolecular ligand migration of the isocyanide ligand from W(2) to CpW(1). In order to evaluate the possibility of an intramolecular ligand exchange by an intermediate such as Cp(CO)$_3$W(μ-PPh$_2$)W(CO)$_4$(CNR), Cp(CO)$_3$W(μ-PPh$_2$)W-(CO)$_4$(CN*i*Pr) (**5**) was synthesized by the reaction between CpW(CO)$_3$(PPh$_2$) and W(CO)$_4$(CN*i*Pr)(NCEt). In addition to spectroscopic characterizations, the structure of the complex was determined by a single-crystal X-ray study (Figure 4).

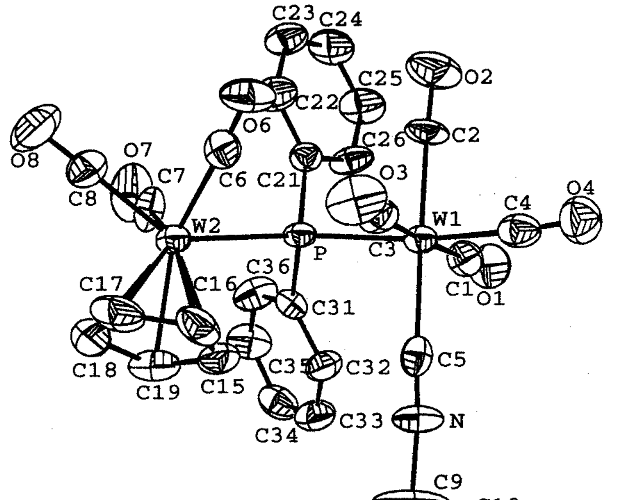

Figure 4. ORTEP drawing of **5**, hydrogen atoms are omitted

A W−W distance of 4.4548(7) Å indicates that there is no bonding between the two metal atoms in the complex. This observation is consistent with the observed upfield resonance of the phosphorus signal in its ^{31}P{^{1}H} NMR spectrum. The isocyanide ligand is coordinated to W(1) and is *cis* to the phosphido bridge ligand. The W−W distance of 4.4548(7) Å and the W(1)−P−W(2) angle of 116.71(9)° in **5** are similar to the W−W distance of 4.5096(11) Å and the W−P−W angle of 118.38(13)° in **1**.[2d] This indicates that the steric hindrance of the isocyanide ligand at the *cis* position in **5** is only slightly greater than the steric hindrance of the corresponding CO ligand in **1**.

Heating of **5** in THF to simulate the conditions of the reaction between **1** and phosphane imides does not produce **3** (Scheme 1). This observation excludes the possibility of an intramolecular exchange of the CNR ligand in an intermediate such as $Cp(CO)_3W(\mu\text{-}PPh_2)W(CO)_4(CNR)$ to form complex **3**. The regiospecific reaction between **1** and a phosphane imide is thus due to some electronic factor. The preferred attack on the carbonyl ligand of $CpW(CO)_3$ indicates that these carbonyl ligands must be more electrophilic than the carbonyl ligands of the $W(CO)_5$ unit.

Electrophilic Site Switching by Metal−Metal Bond Formation

The formation of a metal−metal bond may alter the regiospecificity of the reaction in two ways. First, it brings the two W atoms closer together, introducing steric crowding around the W(1) atom and rendering the attack of a phosphane imide at the CO ligands of the $CpW(CO)_2$ unit difficult. Second, the formation of the metal−metal bond can alter the electronic properties of the complex such that the CO ligands of the $W(CO)_5$ unit in **2** are more electrophilic than the CO ligands of the $CpW(CO)_2$ unit.

The CO ligands of the $CpW(CO)_2$ unit in **2** could still be attacked by a phosphane imide. Accordingly, one cannot exclude the steric hindrance argument completely. On the other hand, two considerations enable us to conclude that the electronic factor is dominant. First, in complex **1**, the carbonyl ligands of the $W(CO)_5$ unit are inert. Even under excess phosphane imide, no isocyanide ligand was observed to replace one of the CO ligands on the $W(CO)_5$ site. This observation indicates that the carbonyl ligand of the $W(CO)_5$ unit is not electrophilic enough to react with the nucleophilic phosphane imide under the reaction conditions. Second, one can consider the W−W bonding in **2** as a dative bond [donor−acceptor bond from W(2) to W(1)]. We may treat W(2) as a ligand of CpW(1) when one of the W(1) carbonyl ligands is removed from **1** by photolysis to form **2**.[2d,2e] Electron donation from the filled t_{2g} orbital of the W(2) atom to the W(1) atom upon formation of the metal−metal dative bond can reduce the electron density on W(2). The net result of this electron redistribution will be a decrease in $d_{xy}[W(2)] \rightarrow \pi^*(CO)$ bonding to the equatorial CO ligands.[2c−2e,2k] This will result in the reduction of the electron density on the carbon atoms of these equatorial CO ligands such that they become sufficiently electrophilic to react with the nucleophilic phosphane imides. In addition, when the electron-withdrawing CO ligand of the CpW(1) unit in **1** is replaced with the dative metal−metal bond to form **2**, electron back donation from W(1) to the two carbonyl ligands of W(1) becomes enhanced. The result is an increase in electron density of the carbon atoms of these CpW(1) carbonyl ligands. Thus, electronically, they are less reactive towards a nucleophile than the corresponding CpW(1) carbonyl ligands in **1**. We can consider that the formation of the metal−metal dative bond in **2** acts as a switch and triggers the nucleophilic attack on the $W(CO)_5$ carbonyl ligands by the activation of the equatorial CO ligands by W−W interactions. This switching of electrophilic site from the carbonyl ligands of the CpW unit in **1** to the carbonyl ligands of the $W(CO)_5$ unit in **2** in the heterodimetallic complexes by the formation of a metal−metal bond can be considered as a cooperative effect of the adjacent metal atom in dimetallic complexes.

Conclusions

Reaction between $CpW(CO)_2(\mu\text{-}PPh_2)W(CO)_5$(*W−W*) and $Ph_3P{=}NR$ (R = Pr, CH_2Ph, *i*Pr) in THF is regiospecific with the CNR ligand coordinated to the $W(CO)_4$ unit to produce $CpW(CO)_2(\mu\text{-}PPh_2)W(CO)_4(CNR)$ (*W−W*). Reaction between $CpW(CO)_3(\mu\text{-}PPh_2)W(CO)_5$ and $Ph_3P{=}NR$ (R = Pr, CH_2Ph, *i*Pr) under similar conditions is also regiospecific with the CNR ligand coordinated to the CpW site to produce $CpW(CO)_2(CNR)(\mu\text{-}PPh_2)W(CO)_5$. The switching of the electrophilic site from the carbonyl ligands of the CpW unit in **1** to the carbonyl ligands of the $W(CO)_5$ unit in **2** in the heterodimetallic complexes is considered as a cooperative effect of the adjacent metal atom in the dimetallic complexes. The redistribution of the electron density from W of the CpW moiety to the other W of the $W(CO)_5$ unit in **2** by the formation of a metal−metal bond is proposed as the reason for this switching.

Experimental Section

General Procedures: All reactions were carried out under purified nitrogen with standard Schlenk techniques. TLC and chromatographic work were performed in air. Infrared (IR) spectra were recorded with a Perkin−Elmer 882 infrared spectrophotometer. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded with Bruker AMX-500, AMX-400, AC-200 and AC-300 spectrometers. The ^{31}P NMR shifts are referenced to 85% H_3PO_4 with downfield chemical shifts as positive. Except as noted, NMR spectra were collected at room temperature. FAB mass spectra were recorded with 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 and Academia Sinica.

Materials: THF was distilled from potassium and benzophenone under purified nitrogen just before use. The complexes $CpW(CO)_3(\mu\text{-}PPh_2)W(CO)_5$ (**1**) and $CpW(CO)_2(\mu\text{-}PPh_2)W(CO)_5$(*W−W*) (**2**) were prepared according to literature procedures.[2d] The compounds $Ph_3P{=}NR$ (R = Pr, CH_2Ph, *i*Pr) were prepared as described in the literature.[10]

$CpW(CO)_2(CNPr)(\mu\text{-}PPh_2)W(CO)_5$ (3a and 3a′): A mixture of **2** (0.120 g, 0.143 mmol) and $Ph_3P{=}NPr$ (0.094 g, 0.286 mmol) was dissolved in THF (20 mL) and the resulting solution was refluxed with stirring at 68 °C for about 70 h. The solvent was then removed under vacuum and the residue was chromatographed on grade III alumina and eluted with CH_2Cl_2/hexane to afford two fractions. The first yellow band was eluted with CH_2Cl_2/hexane (20:80) to obtain yellow solid compound **3a** after removing the solvent. Yield 0.052 g (41%). $C_{28}H_{22}NO_7PW_2$(883): calcd. C 38.08, H 2.51, N 1.59; found C 37.80, H 2.53, N 1.60. MS (FAB): m/z = 884 $[M + 1]^+$. The second band was eluted with CH_2Cl_2/hexane (25:75) to produce compound **3a′** as a yellow solid after removing the solvent. Yield 0.070 g (55%). $C_{28}H_{22}NO_7PW_2$(883): calcd. C 38.08, H 2.51, N 1.59; found C 37.95, H 2.57, N 1.70. MS (FAB): *m*/*z* = 884 [M + 1]$^+$. Spectroscopic data of the complexes are presented in Table 1 of the Supporting Information (see also footnote on the first page of this article); for comparison, the spectroscopic data of the parent complexes **1** and **2** are also given there.

CpW(CO)$_2$(CNCH$_2$Ph)(μ-PPh$_2$)W(CO)$_5$ (3b and 3b′): Reaction and separation conditions similar to those for **3a** and **3a′** were applied to prepare **3b** and **3b′**. The reaction time was 70 h and 0.324 g (0.39 mmol) of **1** and 0.286 g (0.77 mmol) of Ph$_3$P=NCH$_2$Ph were used. **3b**: Yield: 0.168 g (46%). $C_{32}H_{22}NO_7PW_2$ (931): calcd. C 41.28, H 2.38, N 1.50; found C 41.13, H 2.45, N 1.43. MS (FAB): *m*/*z* = 932 [M + 1]$^+$. **3b′**: Yield: 0.166 g (46%). $C_{32}H_{22}NO_7PW_2$ (931): calcd. C 41.28, H 2.38, N 1.50; found C 41.34, H 2.47, N 1.47. MS (FAB): *m*/*z* = 932 [M + 1]$^+$. Spectroscopic data of the complexes are presented in Table 1 of the Supporting Information.

CpW(CO)$_2$(CN*i*Pr)(μ-PPh$_2$)W(CO)$_5$ (3c and 3c′): Reaction and separation conditions similar to those for **3a** and **3a′** were applied to prepare **3c** and **3c′**. The reaction time was 144 h and 0.380 g (0.45 mmol) of **1** and 0.288 g (0.90 mmol) of Ph$_3$P=N*i*Pr were used. 0.070 g of the parent complex **1** was recovered. **3c**: Yield: 0.036 g (11%). $C_{28}H_{22}NO_7PW_2$ (883): calcd. C 38.08, H 2.51, N 1.59; found C 37.87, H 2.55, N 1.56. MS (FAB): *m*/*z* = 884 [M + 1]$^+$. **3c′**: Yield: 0.070 g (22%). $C_{28}H_{22}NO_7PW_2$: (883) calcd. C 38.08, H 2.51, N 1.59; found C 37.70, H 2.55, N 1.61. MS (FAB): *m*/*z* = 856 [M − CO + 1]$^+$. Yields are based on the parent compound consumed in the reactions. Spectroscopic data of the complexes are presented in Table 1 in the Supporting Information.

CpW(CO)$_2$(μ-PPh$_2$)W(CO)$_4$(CNPr)(*W*−*W*) (4a-*cis* and 4a-*trans*): A mixture of **2** (0.306 g, 0.376 mmol) and Ph$_3$P=NPr (0.240 g, 0.752 mmol) was dissolved in THF (20 mL) and refluxed with stirring at 68 °C for about 12 h. The solvent was then removed under vacuum and the residue was chromatographed on grade III alumina and eluted with CH$_2$Cl$_2$/hexane to afford three fractions. A small amount of unchanged starting material was recovered from the first band on elution with 8% of dichloromethane in hexane. A small amount (0.011 g) of green compound was obtained from the second band on elution with 12% of dichloromethane in hexane and was not identified. A mixture of maroon red colored compounds CpW(CO)$_2$(μ-PPh$_2$)W(CO)$_4$(CNPr)(*W*−*W*) (**4a-*cis*** and **4a-*trans***) was obtained from the third band on elution with 16% of CH$_2$Cl$_2$/hexane. Combined yield of **4a-*cis*** and **4a-*trans***: 0.233 g (73%). $C_{27}H_{22}NO_6PW_2$ (855): calcd. C 37.92, H 2.59,N, 1.64; found C 38.02, H 2.74, N 1.65. Spectroscopic data indicate that the mixture consists of two isomers, which could not be separated by chromatography. Spectroscopic data are given in Table 1 of the Supporting Information.

CpW(CO)$_2$(μ-PPh$_2$)W(CO)$_4$(CNCH$_2$Ph)(*W*−*W*) (4b-*cis* and 4b-*trans*): Reaction and separation conditions similar to those for **4a-*cis*** and **4a-*trans*** were applied to prepare **4b-*cis*** and **4b-*trans***. The reaction time was 35 h and 0.354 g (0.440 mmol) of **2** and 0.324 g (0.870 mmol) of Ph$_3$P=NCH$_2$Ph were used. Combined yield of **4b-*cis*** and **4b-*trans***: 0.243 g (61%). $C_{31}H_{22}NO_6PW_2$ (903): calcd. C 41.23, H 2.46, N 1.55; found C 41.64, H 2.64, N 1.66. MS (FAB): *m*/*z* = 904 [M + 1]$^+$. Spectroscopic data indicate that the mixture consists of two isomers that could not be separated by chromatography. Spectroscopic data are given in Table 1 of the Supporting Information.

CpW(CO)$_2$(μ-PPh$_2$)W(CO)$_4$(CN*i*Pr)(*W*−*W*) (4c-*cis* and 4c-*trans*): Reaction and separation conditions similar to those for **4a-*cis*** and **4a-*trans*** were applied to prepare **4c-*cis*** and **4c-*trans***. The reaction time was 96 h and 0.407 g (0.500 mmol) of **2** and 0.319 g (1.000 mmol) of Ph$_3$P=N*i*Pr were used. Combined yield of **4c-*cis*** and **4c-*trans***: 0.180 g (42%). $C_{27}H_{22}NO_6PW_2$ (855): calcd. C 37.92, H 2.59,

Table 1. Crystal and intensity collection data for **3a**, **3a′**, **4a-*cis*** and **5**

	3a	**3a′**	**4a-*cis***	**5**
Empirical formula	$C_{28}H_{22}NO_7PW_2$	$C_{28}H_{22}NO_7PW_2$	$C_{27}H_{22}NO_6PW_2$	$C_{28}H_{22}NO_7PW_2$
Formula mass	883.14	883.14	855.13	883.16
Space group	$P\bar{1}$	Cc	$P\bar{1}$	$P2_1/c$
a [Å]	9.172(2)	12.759(3)	10.545(3)	16.2397(19)
b [Å]	10.414(2)	13.920(3)	10.588(3)	9.7464(17)
c [Å]	16.595(3)	16.038(3)	14.570(2)	18.132(3)
α [°]	82.40(3)	90	76.80(2)	90
β [°]	87.42(3)	91.70(3)	73.21(3)	102.165(12)
γ [°]	67.41(3)	90	62.42(2)	90
V [Å^3]	1450.6(5)	2847.2(11)	1371.5(6)	2805.5(8)
ρ(calcd.) [Mg m^{-3}]	2.022	2.060	2.070	2.091
Z	2	4	2	4
Cryst. size [mm]	0.2250.2450.34	0.2650.2850.32	0.2850.2450.18	0.1950.3850.38
Absorpt. coeff. μ(Mo-$K_α$) [mm^{-1}]	8.023	8.176	8.478	8.47
Temperature	room temp	room temp	room temp	room temp
Radiation	0.71069 Å	0.71069 Å	0.71069 Å	0.71069 Å
2θ range [°]	45	45	45	50
Scan type	2θ-ω	2θ-ω	2θ-ω	θ/2θ
No. of reflections	4072	1952	3817	4930
No. of observed reflections	3779	1897	3576	3447
Variables	352	342	335	353
R	0.0288	0.0271	0.0327	0.033
$wR(F^2)$	0.0787	0.0705	0.0849	0.034
S	1.091	1.067	1.050	1.45
$\Delta F_{\text{max,min.}}$ [e/Å^3]	1.727, −1.311	1.083, −1.226	2.354, −1.632	2.120, −1.020

N 1.64; found C 38.01, H 2.62, N 1.72. MS (FAB): m/z = 856 [M + 1]$^+$. Spectroscopic data indicate that the mixture consists of two isomers, which could not be separated by chromatography. Spectroscopic data are given in Table 1 of the Supporting Information.

CpW(CO)$_3$(μ-PPh$_2$)W(CO)$_4$(CN*i*Pr) (5): A yellow solution of Na[CpW(CO)$_3$]·2DME[11] (0.350 g, 0.65 mmol) in THF (100 mL) was cooled to 0 °C. A solution of PPh$_2$Cl (0.132 mL, 0.71 mmol) in THF (50 mL) was then slowly added to the above solution. After 1 h, the color of the solution turned to orange red. A solution of W(CO)$_4$(CN*i*Pr)(NCEt)[12] (0.250 g, 0.60 mmol) in THF (40 mL) was then added slowly to the above solution. After stirring overnight at room temperature, the solvent was removed and the residue was chromatographed on silica gel. Elution with CH$_2$Cl$_2$/hexanes (1:4) gave the yellow product. Yield: 0.10 g (18%). C$_{28}$H$_{22}$NO$_7$PW$_2$ (883): calcd. C 38.08, H 2.51; found C 38.05, H 2.23. MS (FAB): m/z = 884 [M + 1]$^+$. Spectroscopic data are given in Table 1 of the Supporting Information.

Structure Determinations of CpW(CO)$_2$(CNPr)(μ-PPh$_2$)W(CO)$_5$ (3a and 3a′), CpW(CO)$_2$(μ-PPh$_2$)W(CO)$_4$(CNPr*)(W−W)* (4a-*cis*) and CpW(CO)$_3$(μ-PPh$_2$)W(CO)$_4$(CN*i*Pr) (5): Crystals of complexes **3a**, **3a′**, **4a-*cis*** and **5** were grown by slow diffusion of hexanes into a saturated CH$_2$Cl$_2$ solution of the relevant complex at 0 °C in air. Diffraction measurements were made with an Enraf−Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation. Structures were solved by direct methods and refined by full-matrix least square using SHELXL-93 or NRCVAX programs. 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 1. Selected interatomic distances and bond angles are given in Table 2 of the Supporting Information (see also footnote on the first page of this article). CCDC-154007 (**3a**), -154008 (**3a′**), -173249 (**4a-cis**), and -172971 (**5**) contain the supplementary crystallographic data for this paper (excluding structure factors). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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