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Conversion of a stannyl–phosphenium complex into a stannylene–phosphine complex of Mo and W: double bond migration from M=P to M=Sn

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Abstract

Four-legged piano-stool complexes, $Cp(CO)_2(SnR_3)M\{\overline{PN(Me)CH_2CH_2N}Me(OMe)\}$, containing a stannyl group ($SnPh_3$, $SnMe_3$, Sn^nBu_3) and diamino-substituted phosphite ($\overline{PN(Me)CH_2CH_2N}Me(OMe)$ which is abbreviated as PNN(OMe)) were prepared for Mo and W, and the reactions of these complexes with a Lewis acid ($BF_3{\cdot}OEt_2$ and TMSOTf) were examined. For the $SnPh_3$ and $SnMe_3$ complexes, stannylene complexes $[Cp(CO)_2(SnR_2)M\{PNN(R)\}]X$ ($X = OTf^-$ or BF_4^-) were formed with migration of an R group from Sn to P. X-ray analyses of $[Cp(CO)_2(SnPh_2)W\{PNN(Ph)\}]OTf$ and $[Cp(CO)_2(SnMe_2)W\{PNN(Me)\}]OTf$ reveal that these complexes are regarded as stannylene tungsten complexes stabilized by an oxygen of OTf^-. In the reaction of the Sn^nBu_3 complex with TMSOTf, the corresponding stannylene complex and an unexpected neutral phosphenium complex, $Cp(CO)_2M\{PNN\}$, were formed. However, when $BF_3{\cdot}OEt_2$ was used in place of TMSOTf, cationic phosphenium complexes in addition to a neutral phosphenium complex were observed. In any case, an OMe anion abstraction by a Lewis acid takes place at the first stage to give a cationic phosphenium complex, and then aryl or alkyl migration takes place to give a stannylene complex. A relatively strong $Sn–^nBu$ bond retards the alkyl migration, resulting in the observation of the cationic phosphenium complexes.

Keywords: Phosphenium complex; Stannylene complex; Migration; Double bond

1. Introduction

The wide-ranging applications of metal carbenes (M=C) in organometallic chemistry have aroused interest in transition metal complexes containing metal–heteroatom multiple bonds [1]. A cationic phosphenium ($^+PR_2$) has attracted significant attention as a ligand for transition metals because it is isolobal with a singlet carbene and its heavier congeners (silylene, germylene, stannylene, and plumbylene). Since the first report of a cationic phosphenium complex of iron by Parry in 1978 [2], research efforts have been directed toward the development of general and effective methods for the preparation of cationic phosphenium complexes. Several methods have been developed to prepare many phosphenium complexes, and a few review articles appeared recently [3–7].

In contrast to the synthetic approach, information on the reactivity of the phosphenium complexes is sparse. During the course of our investigation on cationic phosphenium complexes of transition metals [8], it was found that a Group 8 transition metal complex formulated as $Cp(CO)(ER_3)M\{PNN(OMe)\}$ (**a**) (M = Fe, Ru; E = C, Si, Ge, Sn. PNN(OMe) stands for $\overline{PN(Me)CH_2CH_2N}Me(OMe)$ here) reacts with a Lewis acid to give a cationic phosphenium complex $[Cp(CO)(ER_3)M\{PNN\}]^+$ (**b**). However, the successive reaction hinges on the type of E (Scheme 1) [9]. When E is a tin atom, one of the R groups on the Sn migrates to the phosphenium P to give a stannylene complex (**d**). This reaction is of interest because it corresponds to a double-bond migration from M=P to M=Sn. Some other

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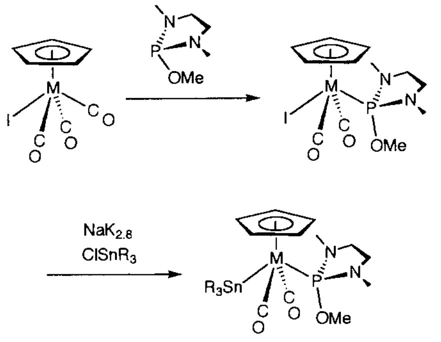
reactions related to the migration involving a cationic phosphenium ligand have been reported [10].

To check the scope and the limitation of this type of a double-bond migration in a coordination sphere, we examined the reaction of stannyl complexes of Group 6 transition metals with a Lewis acid. The results of the reaction of $Cp(CO)_2(SnR_3)M\{PNN(OMe)\}$ (M = Mo, W) are reported in this paper.

2. Results and discussion

2.1. Preparation of $Cp(CO)_2(SnR_3)M\{PNN(OMe)\}$ ($M = Mo$, W; $R = Ph$, Me, ^nBu)

To obtain $Cp(CO)_2(SnR_3)M\{PNN(OMe)\}$, $Cp(CO)_2IM\{PNN(OMe)\}$ was first prepared in the reaction of $Cp(CO)_3IM$ with PNN(OMe). The isolated $Cp(CO)_2IM\{PNN(OMe)\}$ is a mixture of the *cis* and *trans* isomers. They could be separated by column chromatography for the W complex, but they gradually isomerize in solution and reach equilibrium. It was found that the *cis* isomer is a kinetic product. In the case of the Mo complex, since the isomerization rate is fast, it is difficult to separate the mixture into the two geometrical isomers. A mixture of *cis* and *trans* isomers of $Cp(CO)_2IM\{PNN(OMe)\}$ was treated with $NaK_{2.8}$ and then SnR_3Cl to give $Cp(CO)_2(SnR_3)M\{PNN(OMe)\}$ (Eq. (1)). The stannyl complexes thus obtained were characterized by IR, ^1H-, ^{13}C-, ^{31}P-, and ^{119}Sn-NMR spectra and elemental analyses.

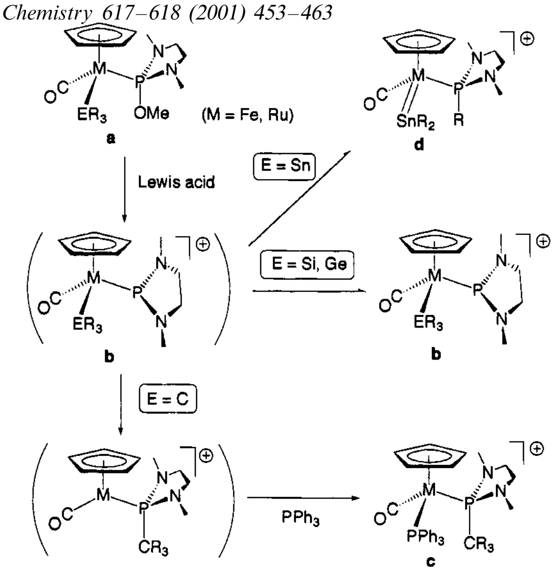


Mo-1a	:	M = Mo,	R = Ph
Mo-2a	:	Mo	Me
Mo-3a	:	Mo	^{n}Bu
W-1a	:	W	Ph
W-2a	:	W	Me
W-3a	:	W	^{n}Bu

(1)

(1)

For all stannyl complexes prepared in this paper, a resonance assigned to CO in the ^{13}C-NMR spectra showed one doublet, arising from the coupling with ^{31}P, flanked by satellite lines due to coupling with ^{119}Sn and ^{117}Sn, and with ^{183}W in the case of tungsten complexes. In both ^1H- and ^{13}C-NMR spectra, NCH_3 gave rise to one doublet due to the coupling with ^{31}P. These results show that all the stannyl complexes have *trans* geometry. It has been reported that the corresponding methyl complexes, $Cp(CO)_2(Me)M\{PNN(OMe)\}$ (M = Mo, W), exist in solution as a mixture of the *cis* and *trans* isomers in equilibrium [10b]. The reason for the preferred *trans* geometry of these stannyl complexes may arise from the steric hindrance between the PNN(OMe) ligand and the relatively bulky stannyl ligand ($SnPh_3$, $SnMe_3$, and Sn^nBu_3) compared with Me.



Scheme 1.

On going from $SnPh_3$ to $SnMe_3$ and to Sn^nBu_3 for *trans*-$Cp(CO)_2(SnR_3)M\{PNN(OMe)\}$ (that is, **Mo-1a** → **Mo-2a** → **Mo-3a** and **W-1a** → **W-2a** → **W-3a**), coupling constants show the following trends: J_{P-Sn} observed in the ^{31}P-NMR spectra decreases (148.8 → 132.1 → 113.5 Hz for the Mo complexes, and 137.7 → 124.7 → 109.8 Hz for the W complexes), J_{C-Sn} (carbonyl C) decreases (150.8 → 136.6 → 132.4 Hz for the Mo complexes, and 138.0 → 124.4 → 119.6 Hz for the W complexes), J_{Sn-W} greatly decreases (404.6 → 262.3 → 234.4 Hz), J_{P-W} slightly increases (422.4 → 441.0 → 444.8 Hz), J_{C-P} (carbonyl C) shows almost the same value (30.5 → 28.8 → 30.1 Hz for the Mo complexes, and 25.6 → 23.3 → 23.2 Hz for the W complexes), and J_{C-W} (carbonyl C) slightly increases (155.0 → 159.3 → 159.9 Hz). These trends indicate that the M–Sn bond becomes weaker on going from $SnPh_3$ to $SnMe_3$ and to Sn^nBu_3, whereas the M–P bond is not strongly affected.

2.2. Reaction of $Cp(CO)_2(SnPh_3)M\{PNN(OMe)\}$ ($M = Mo$, W) with a Lewis acid

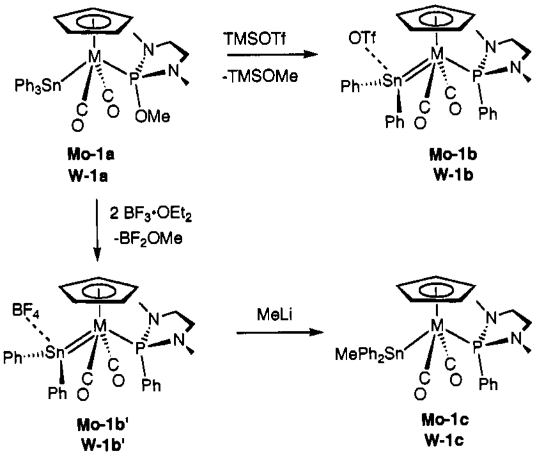
The results in the reaction of the triphenylstannyl complexes (**Mo-1a**, **W-1a**) with a Lewis acid, trimethylsilyl triflate (TMSOTf) and $BF_3 \cdot OEt_2$, are summarized in Scheme 2.

CH_2Cl_2 solutions of **Mo-1a** and **W-1a** were treated with TMSOTf at room temperature (r.t.). From the reaction mixtures, pale yellow powders were isolated. Although the isolated complexes are so air- and moisture-sensitive that the correct elemental analysis data could not be obtained, the satisfactory spectroscopic data were obtained, which established the formation of a stannylene complex formulated as $[Cp(CO)_2(SnPh_2)M\{PNN(Ph)\}]OTf$ (**Mo-1b** and **W-1b**). The ^{31}P-NMR spectra show a singlet at 157.05 ppm with Sn satellites ($J_{P-Sn} = 190.2$ Hz) for **Mo-1b** and a singlet at 123.38 ppm with Sn and W satellites ($J_{P-Sn} = 183.8$ Hz, $J_{P-W} = 323.6$ Hz) for **W-1b**. The ^{119}Sn-NMR spectra show a doublet due to a coupling with P at 459.14 for **Mo-1b** and 335.32 ppm for **W-1b**, which are at considerably lower fields than those of the starting complexes, **Mo-1a** (74.97) and **W-1a** (-1.98 ppm). These very low field chemical shifts strongly suggest the formation of an M = Sn fragment [9b–d,11,12]. The coupling constant between P and Sn is about 50 larger for **Mo-1b** and 45 Hz larger for **W-1b** than those of **Mo-1a** and **W-1a**, respectively. For **W-1b**, the Sn–W coupling constant is more than 200 Hz greater than that of **W-1a**. These data together with those of ^1H- and ^{13}C-NMR spectra support the formation of a stannylene complex.

In the case of **W-1b**, the X-ray structure analysis could be performed. The structure is shown in Fig. 1. The complex can be described as a base-stabilized stannylene complex. The OMe group on the phosphorus in **W-1a** disappears, and is replaced by a phenyl group. This means that a phenyl group migration takes place from an Sn to a P in the W coordination sphere. The structural details will be discussed later. The spectroscopic data of **W-1b** show that there may be an equilibrium between base-stabilized and base-free stannylene forms in solution.

The reaction of **M-1a** (M = Mo and W) with $BF_3 \cdot OEt_2$ in place of TMSOTf was next examined. The ^{31}P- and ^{119}Sn-NMR spectra of the reaction mixture suggest the formation of the corresponding stannylene complex (**M-1b′**) (see Scheme 2). The ^{31}P-NMR chemical shifts of **Mo-1b′** (155.63 ppm) and **W-1b′** (119.27 ppm) are very close, respectively, to those of **Mo-1b** and **W-1b** prepared from **M-1a** and TMSOTf. The ^{119}Sn-NMR chemical shifts of **Mo-1b′** (416.40 ppm) and **W-1b′** (293.17 ppm) are at about 42 ppm higher field than those of **Mo-1b** and **W-1b**, respectively. The higher field shift may arise from the stabilization effect of the base on the stannylene ligand.

Several efforts to isolate **Mo-1b′** and **W-1b′** came into failure for their instability. Confirming the stannylene formation, they were converted into an isolable complex. The stannylene complex **M-1b′** was treated with MeLi. After work up, $Cp(CO)_2(SnPh_2Me)M\{PNN(Ph)\}$ (**Mo-1c**, 73% yield and **W-1c**, 77% yield) was isolated and characterized by ^1H-, ^{13}C-, ^{31}P-, ^{119}Sn-NMR and IR spectroscopies as well as by elemental analyses.



Scheme 2.

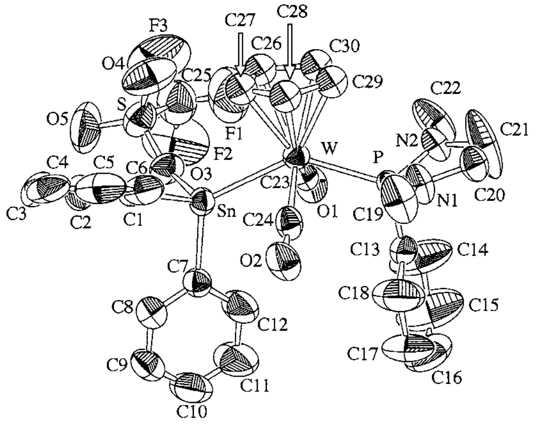
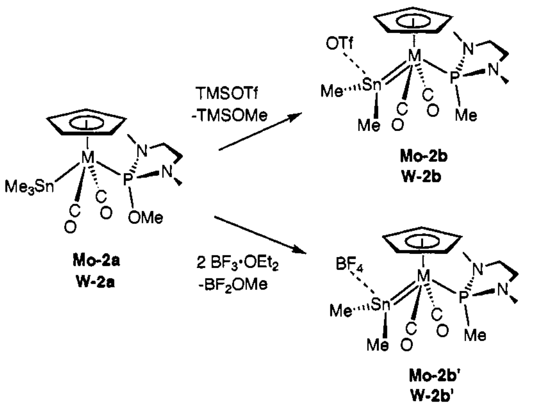


Fig. 1. Crystal structure of **W-1b** with the numbering scheme. Thermal ellipsoids are drawn at 50% probability.



Scheme 3.

2.3. Reaction of $Cp(CO)_2(SnMe_3)M\{PNN(OMe)\}$ ($M = Mo$, W) with a Lewis acid

Monitoring the reaction of a trimethylstannyl complex (**2a**) with TMSOTf and that with $BF_3 \cdot OEt_2$ by ^{31}P-NMR measurements revealed that these reactions were not clean, that is, several kinds of complexes were formed. However, the ^{31}P- and ^{119}Sn-NMR spectra evidenced the formation of the corresponding stannylene complex (**Mo-2b**, **W-2b**, **Mo-2b′**, and **W-2b′**) (Scheme 3). In the reaction of **W-2a** with TMSOTf, a single crystal of **W-2b** was obtained. The X-ray structure analysis was undertaken and revealed that **W-2b** is a base-stabilized stannylene complex like **W-1b** (Fig. 2). The structural details will be discussed later.

2.4. Reaction of $Cp(CO)_2(Sn^nBu_3)M\{PNN(OMe)\}$ ($M = Mo$, W) with a Lewis acid

A tri-*n*-buthylstannyl complex (**M-3a**) showed somewhat complicated but interesting results in the reaction with a Lewis acid (see Scheme 4). The ^{31}P-NMR spectrum of the reaction mixture of **Mo-3a** with TMSOTf exhibited a singlet at 164.11 ppm with Sn satellites ($J_{P\text{-}Sn} = 166.5$ Hz), a singlet at 272.46 ppm and some unidentified resonances. The former singlet is attributed to a stannylene complex, **Mo-3b**. A singlet at 272.46 ppm could be assigned to a neutral phosphenium, **Mo-d** [13] (the complex may also be referred to as a 3e-donor terminal phosphide complex). The detailed discussion of the formation of **Mo-d** in this reaction will be presented elsewhere.

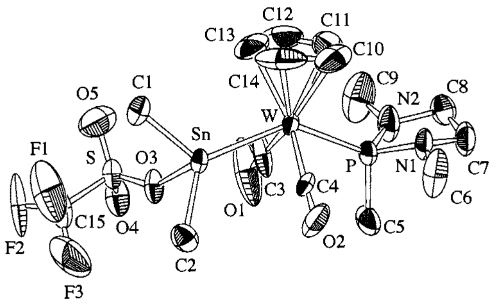
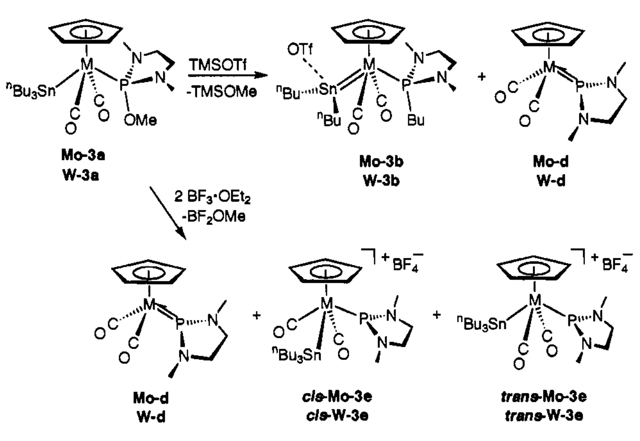


Fig. 2. Crystal structure of **W-2b** with the numbering scheme. Thermal ellipsoids are drawn at 50% probability.



Scheme 4.

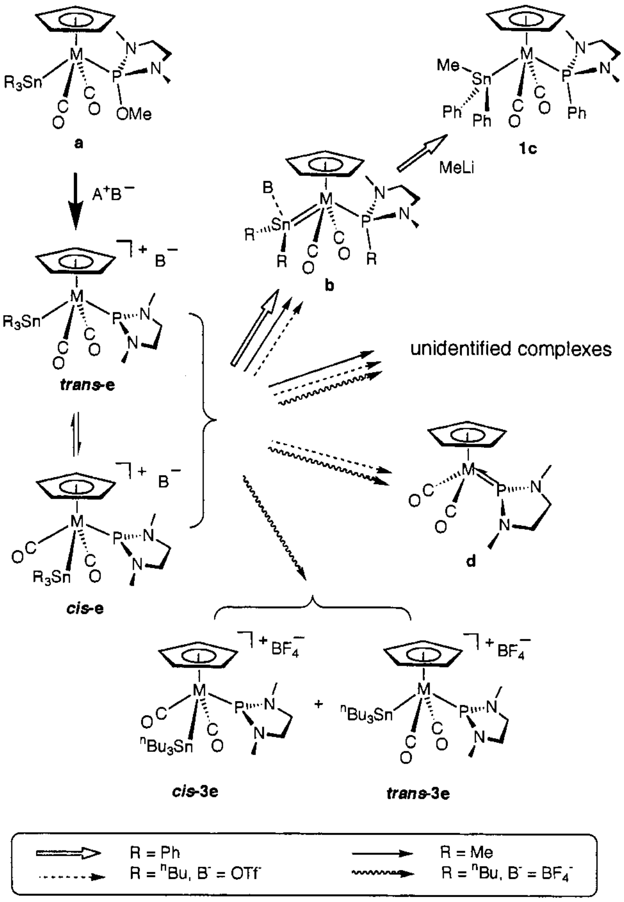
The reaction of **Mo-3a** with $BF_3 \cdot OEt_2$ was monitored by the ^{31}P-NMR spectroscopy. A singlet at 272.46 ppm due to **Mo-d**, two broad singlets at 334.71 and 310.08 ppm attributed to phosphenium complexes and some unidentified resonances were observed. However, a resonance due to a corresponding stannylene complex was not detected. In the reaction of **W-3a** with $BF_3 \cdot OEt_2$, relatively sharp resonances were observed in the ^{31}P-NMR spectrum at −20°C. In addition to a singlet at 244.61 ppm with W satellites ($J_{P\text{-}W} = 218.1$ Hz) due to **W-d** and several unidentified resonances, a singlet at 298.07 ppm with Sn and W satellites ($J_{P\text{-}Sn} = 42.5$, $J_{P\text{-}W} = 516.4$ Hz) and a singlet at 282.76 ppm with Sn and W satellites ($J_{P\text{-}Sn} = 291.6$ and $J_{P\text{-}W} = 543.1$ Hz) were observed. These relatively low field chemical shifts and the large P-W coupling constants (greater than 500 Hz) compared with that of **W-3a** ($J_{P\text{-}W} = 444.8$ Hz) and that of $Cp(CO)_2IW\{PNN(OMe)\}$ ($J_{P\text{-}W} = 387.0$ for the *cis* isomer and $J_{P\text{-}W} = 368.4$ Hz for the *trans* isomer) are characteristic of a phosphenium complex, **W-3e**. The large difference in $J_{P\text{-}Sn}$ (42.5 vs. 291.6 Hz) between the two singlets strongly suggest that the former is assigned to a *cis* isomer (*cis*-**W-3e**) and the latter to a *trans* isomer (*trans*-**W-3e**).

2.5. A view of the reaction of $Cp(CO)_2(SnR_3)M\{PNN(OMe)\}$ with a Lewis acid

The products in the reaction of a stannyl complex $Cp(CO)_2(SnR_3)M\{PNN(OMe)\}$ with a Lewis acid were found to hinge on the kinds of R in the stannyl group in any case, and on those of a Lewis acid used in a particular case ($R = {}^nBu$), but to be independent of whether a central transition metal is Mo or W. The reaction scheme is summarized in Scheme 5. In any case, an OMe anion abstraction by a Lewis acid uniformly takes place at the first stage of the reaction to give a cationic phosphenium complex **e**.

In the case of the triphenylstannyl complex, although the cationic phosphenium complex is not detected presumably due to its high reactivity, the reaction proceeds cleanly to give a stannylene complex **1b** with a phenyl migration from a tin to a phosphenium phosphorus. When TMSOTf is used as a Lewis acid, stannylene complexes are isolated in fairly good yields (77% for **Mo-1b**, 76% for **W-1b**). When $BF_3 \cdot OEt_2$ is used, the resulting stannylene complexes are not able to be isolated as a solid, but they can be converted into isolable complexes in good yield by the reaction with MeLi (73% for **Mo-1c**, 77% for **W-1c**). In contrast, the reactions of the trimethylstannyl complex yield several kinds of products involving the corresponding stannylene complexes irrespective of the kinds of Lewis acid. In the case of the tri-*n*-buthylstannyl complex, the corresponding stannylene complexes (**Mo-3b** and **W-3b**) and unexpected neutral phosphenium complexes (**Mo-d** and **W-d**) are formed when TMSOTf is used. However, when $BF_3{\cdot}OEt_2$ is used, cationic phosphenium complexes (**Mo-3e** and **W-3e**) in addition to neutral phosphenium complexes are detected, but the stannylene complexes are not detected.

We have already reported for the corresponding stannyl–phosphenium iron complexes that an OTf^- anion promotes an alkyl migration from Sn to P in a phosphenium complex [9c]. A nucleophilic attack of the oxygen in OTf^- to the Sn would induce the alkyl migration. It has been reported that the reactivity sequence for tin–carbon bonds in electrophilic cleavage reactions is generally phenyl > methyl > butyl [14]. Therefore, the difference in reactivity of the cationic phosphenium complexes **e** may be understood as follows. Since the Sn–Ph bond in $[Cp(CO)_2(SnPh_3)M\{PNN\}]^+$ is susceptible to electrophilic cleavage, the complex readily and so cleanly undergoes phenyl migration to give the corresponding stannylene complex **M-1b**. Since the Sn–Me bond in $[Cp(CO)_2(SnMe_3)M\{PNN\}]^+$ is resistant to Sn–C bond cleavage compared with the corresponding Sn–Ph bond, $[Cp(CO)_2(SnMe_3)M\{PNN\}]^+$ may have a longer life time, though it is not enough to be detected spectroscopically. Therefore, the phosphenium complex may undergo some intermolecular reactions in addition to the alkyl migration being presumably an intramolecular reaction. In the reaction of $Cp(CO)_2(Sn^nBu_3)M\{PNN(OMe)\}$ with $BF_3{\cdot}OEt_2$, the resulting cationic phosphenium complex $[Cp(CO)_2(Sn^nBu_3)M\{PNN\}]^+$ has a relatively strong Sn–C bond and there is no OTf^- which tends to promote the alkyl migration. Therefore, the cationic phosphenium complexes (**M-3e** and **W-3e**) are observed and the alkylmigration products are not.



Scheme 5.

Table 1
Summary of crystal data for **W-1b** and **W-2b**

	W-1b	W-2b
Formula	$C_{30}H_{30}F_3N_2O_5PS$-SnW	$C_{15}H_{24}F_3N_2O_5PS$-SnW
Formula weight	921.15	734.93
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/c$
Cell constants		
a (Å)	17.513(2)	7.346(2)
b (Å)	10.7492(6)	13.319(2)
c (Å)	18.740(4)	23.603(5)
β (°)	110.39(l)	93.15(2)
V (Å^3)	3306.6(7)	2305.9(8)
Z	4	4
D_{calc} (g cm^{-3})	1.85	2.12
μ (cm^{-1})	44.04	62.85
Crystal size (mm)	0.50 × 0.50 × 0.25	0.25 × 0.38 × 0.25
Radiation (Å)	Mo–K$_\alpha$ ($\lambda = 0.71069$)	Mo–K$_\alpha$ ($\lambda = 0.71069$)
Scan technique	ω–2θ	ω–2θ
Scan range (°)	$3 < 2\theta < 55$	$3 < 2\theta < 55$
Number of unique data	8705	5663
Number of unique data $F_o > 3\sigma(F_o)$	5263	3513
R	0.032	0.039
R_w	0.032	0.038

2.6. X-ray structures of W-1b and W-2b

X-ray structure analyses of **W-1b** and **W-2b** were undertaken. The ORTEP drawings of **W-1b** and **W-2b** are displayed in Figs. 1 and 2, respectively. The cell constants and the data collection parameters are summarized in Table 1. The selected bond distances and angles are listed in Tables 2 and 3.

Both complexes have typical four-legged piano-stool structures, and two carbonyl ligands are situated in mutually *trans* positions. The W–P bond distances

Table 2
Selected bond distances (Å) and angles (°) for **W-1b**

Bond distances			
W–Sn	2.709(1)	P–N2	1.662(6)
W–P	2.428(1)	P–C13	1.828(7)
W–C23	1.964(6)	F1–C25	1.35(1)
W–C24	1.967(7)	F2–C25	1.28(1)
Sn–O3	2.160(4)	F3–C25	1.28(1)
Sn–C1	2.147(6)	O1–C23	1.162(7)
Sn–C7	2.149(7)	O2–C24	1.156(9)
S–O3	1.467(5)	N1–C19	1.402(9)
S–O4	1.399(7)	N1–C20	1.445(9)
S–O5	1.444(7)	N2–C21	1.419(10)
S–C25	1.79(1)	N2–C22	1.439(9)
P–N1	1.669(5)	C20–C21	1.44(1)
Bond angles			
Sn–W–P	135.76(4)	N1–P–N2	92.2(3)
Sn–W–C23	74.9(2)	N1–P–C13	105.9(3)
Sn–W–C24	71.8(2)	N2–P–C13	105.5(3)
P–W–C23	81.1(2)	Sn–O3–S	136.9(3)
P–W–C24	80.0(2)	P–N1–C19	128.6(5)
C23–W–C24	105.7(3)	P–N1–C20	112.8(4)
W–Sn–O3	113.6(1)	C19–N1–C20	118.5(6)
W–Sn–C1	118.6(2)	P–N2–C21	111.8(5)
W–Sn–C7	122.5(1)	P–N2–C22	126.0(5)
O3–Sn–C1	98.6(2)	C21–N2–C22	120.9(6)
O3–Sn–C7	92.5(2)	N1–C20–C21	108.4(6)
C1–Sn–C7	105.6(2)	N2–C21–C20	110.7(7)
O3–S–O4	113.2(3)	W–C23–O1	174.2(6)
O3–S–O5	112.4(4)	W–C24–O2	176.1(5)
O3–S–C25	100.9(4)	S–C25–F1	107.7(7)
O4–S–O5	120.2(4)	S–C25–F2	111.9(9)
O4–S–C25	105.6(5)	S–C25–F3	111.2(7)
O5–S–C25	101.4(5)	F1–C25–F2	107.2(8)
W–P–N1	117.3(2)	F1–C25–F3	108(1)
W–P–N2	118.1(2)	F2–C25–F3	110.5(9)
W–P–C13	114.9(2)		

(2.428 for **W-1b** and 2.425 Å for **W-2b**) are slightly shorter than those reported as a normal W–P dative bond (2.47–2.69 Å) [15].

With **W-1b**, the W–Sn bond distance is 2.709 Å. This bond is significantly shorter than a normal W–Sn single bond; 2.837 for Cp(CO)$_2$W(=C(H)C$_6$H$_4$Me-4)(SnPh$_3$) [16], 2.813 for (CO)$_3$(MeCN)$_2$W(SnPh$_3$) [17], and 2.768 Å for Cp$_2$W(HgI)(SnPh$_3$) [18]. This is also slightly shorter than the W–Sn distances for stannylene tungsten complexes reported; 2.722 for (CO)$_5$W(=SnCl$_2$·THF), 2.737 for (CO)$_5$W(=SnCl$_2$·2THF), and 2.751 Å for (CO)$_5$W(=Sn(C$_3$H$_2^t$Bu-2,4,6)(CH$_2$CMe$_2$C$_6$H$_3^t$Bu-3,5) [19]. The WSnC1C7 unit is distorted from a trigonal plane (the sum of angles around Sn amounts 346.7°). The Sn–O3 bond distance (2.160 Å) is significantly shorter than that for oxygen-stabilized stannylene complexes; 2.276 and 2.344 [20], 2.29 [21], 2.223, 2.356 and 2.350 [19], 2.343 [9c], 2.346 Å (vide infra). Therefore, **W-1b** may be classified into base stabilized stannylene complexes, but bear character, to some extent, of a stannyl complex with two phenyl and OTf substituents on the tin.

With **W-2b**, the W–Sn bond distance is 2.745 Å, which is longer than that for **W-1b**. However, the WSnC1C2 unit forms a fairly good trigonal plane (the sum of angles around Sn amounts 358.5°). The Sn–O3 bond distance (2.346 Å) falls in the range of an Sn–O dative bond listed above. Therefore, **W-2b** can be regarded as a cationic stannylene complex weakly stabilized by TfO$^-$. Electron donating ability of a methyl group may make a stannylene fragment stable, which leads to a weak Sn–OTf bond.

3. Experimental

3.1. General remarks

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. All solvents were purified by distillation: THF was distilled from sodium–benzophenone, hexane and pentane were distilled from sodium metal, and CH$_2$Cl$_2$ was distilled from P$_2$O$_5$. All solvents were stored under a nitrogen

Table 3
Selected bond distances (Å) and angles (°) for **W-2b**

Bond distances			
W–Sn	2.745(1)	P–N2	1.665(8)
W–P	2.425(2)	P–C5	1.80(1)
W–C3	1.93(1)	F1–C15	1.31(1)
W–C4	1.94(1)	F2–C15	1.30(1)
Sn–O3	2.346(6)	F3–C15	1.30(1)
Sn–C1	2.131(9)	O1–C3	1.17(1)
Sn–C2	2.14(1)	O2–C4	1.16(1)
S–O3	1.434(6)	N1–C6	1.43(1)
S–O4	1.436(7)	N1–C7	1.45(1)
S–O5	1.410(8)	N2–C8	1.48(1)
S–C15	1.78(1)	N2–C9	1.40(2)
P–N1	1.679(8)	C7–C8	1.51(2)
Bond angles			
Sn–W–P	140.03(6)	N1–P–N2	92.8(4)
Sn–W–C3	77.5(3)	N1–P–C5	104.7(5)
Sn–W–C4	72.6(3)	N2–P–C5	104.7(5)
P–W–C3	79.6(3)	Sn–O3–S	145.2(4)
P–W–C4	79.9(3)	P–N1–C6	120.2(8)
C3–W–C4	100.2(5)	P–N1–C7	110.7(7)
W–S–O3	105.6(2)	C6–N1–C7	115.1(8)
W–Sn–C1	121.1(3)	P–N2–C8	113.2(8)
W–Sn–C2	126.5(3)	P–N2–C9	127.3(8)
O3–Sn–C1	91.3(3)	C8–N2–C9	116(1)
O3–Sn–C2	84.0(3)	W–C3–O1	175(1)
C1–Sn–C2	110.9(4)	W–C4–O2	178.1(9)
O3–S–O4	113.3(4)	N1–C7–C8	105.5(8)
O3–S–O5	113.7(5)	N2–C8–C7	106.0(8)
O3–S–C15	102.8(5)	S–C15–F1	112(1)
O4–S–O5	117.0(5)	S–C15–F2	112.8(9)
O4–S–C15	102.6(5)	S–C15–F3	111.9(9)
O5–S–C15	105.2(6)	F1–C15–F2	107(1)
W–P–N1	117.7(3)	F1–C15–F3	107(1)
W–P–N2	119.7(3)	F2–C15–F3	105(1)
W–P–C5	114.2(3)		

atmosphere. TMSOTf and $BF_3{\cdot}OEt_2$ were distilled prior to use. Other reagents employed in this study were used as received. Column chromatography was carried out quickly in air on Merck aluminium oxide 90.

IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer. A JEOL LA-300 multinuclear spectrometer was used to obtain ^{1}H-, ^{13}C-, ^{31}P-, ^{119}Sn-NMR spectra. The reference was as follows: for ^{1}H- and ^{13}C-NMR data, $Si(CH_3)_4$ as an internal standard; for ^{31}P-NMR data, 85% H_3PO_4 as an external standard; for ^{119}Sn-NMR data, $Sn(CH_3)_4$ as an external standard. Elemental analyses were performed on a Perkin–Elmer 2400CHN elemental analyzer.

3.2. Preparation of [Cp(CO)$_2$IM{PNN(OMe)}] (M = Mo, W)

A solution of $Cp(CO)_3IMo$ (1728 mg, 4.65 mmol) in CH_2Cl_2 (40 ml) was treated with PNN(OMe) (0.80 ml, 5.40 mmol) at room temperature (r.t.) with stirring for 10 h. The solvent was removed under reduced pressure and the residue was dissolved in a small amount of THF. The solution was loaded on an alumina column, and eluted with THF. The red band eluted was collected, and the solvent was removed in vacuo to give $Cp(CO)_2IMo$\{PNN(OMe)\} as a red powder (2016 mg, 4.10 mmol, 88%). Anal. Calc. for $C_{12}H_{18}IMoN_2O_3P$: C, 29.29; H, 3.69; N, 5.69. Found: C, 29.18; H, 3.63; N, 5.57%. For the *cis* isomer: IR (νCO, in CH_2Cl_2): 1964, 1888. ^{1}H-NMR (δ, in $CDCl_3$): 2.65 (d, $J_{H-P} = 11.5$ Hz, 3H, NCH_3), 2.72 (d, $J_{H-P} = 11.0$ Hz, 3H, NCH_3), 3.06–3.10 (m, 2H, NCH_2), 3.26–3.31 (m, 2H, NCH_2), 3.35 (d, $J_{H-P} = 11.2$ Hz, 3H, OCH_3), 5.42 (s, 5H, C_5H_5). ^{13}C-NMR (δ, in $CDCl_3$): 33.39 (d, $J_{C-P} = 6.1$ Hz, NCH_3), 33.93 (d, $J_{C-P} = 13.4$ Hz, NCH_3), 52.58 (d, $J_{C-P} = 2.4$ Hz, NCH_2), 52.86 (d, $J_{C-P} = 12.2$ Hz, OCH_3), 53.01 (d, $J_{C-P} = 2.4$ Hz, NCH_2), 92.59 (s, C_5H_5), 237.89 (d, $J_{C-P} = 3.3$ Hz, CO), 250.41 (d, $J_{C-P} = 40.3$ Hz, CO). ^{31}P-NMR (δ, in CH_2Cl_2): 150.55 (s). For the *trans* isomer: IR (νCO, in CH_2Cl_2): 1964, 1888. ^{1}H-NMR (δ, in $CDCl_3$): 2.84 (d, $J_{H-P} = 10.7$ Hz, 6H, NCH_3), 3.14–3.19 (m, 2H, NCH_2), 3.41 (d, $J_{H-P} = 12.2$ Hz, 3H, OCH_3), 3.44–3.48 (m, 2H, NCH_2), 5.16 (d, $J_{H-P} = 2.2$ Hz, 5H, C_5H_5). ^{13}C-NMR (δ, in $CDCl_3$): 33.30 (d, $J_{C-P} = 11.0$ Hz, NCH_3), 51.33 (d, $J_{C-P} = 11.0$ Hz, OCH_3), 51.82 (d, $J_{C-P} = 2.4$ Hz, NCH_2), 92.10 (s, C_5H_5), 230.46 (d, $J_{C-P} = 36.6$ Hz, CO). ^{31}P-NMR (δ, in CH_2Cl_2): 162.51 (s).

[$Cp(CO)_2IW$\{PNN(OMe)\}] was prepared by refluxing a benzene solution (110 ml) for 4.5 h containing $Cp(CO)_3IW$ (2479 mg, 5.61 mmol) and PNN(OMe) (0.80 ml, 5.40 mmol). The purification was carried out in a manner similar to that for the corresponding Mo complex to give a red powder of [$Cp(CO)_2IW$\{PNN(OMe)\}] (2916 mg, 5.03 mmol, 93%). Anal. Calc. for $C_{12}H_{18}IN_2O_3PW$: C, 24.85; H, 3.13; N, 4.83. Found: C, 24.78; H, 3.11; N, 4.69%. The isolated complex is a mixture of the *cis* and *trans* isomers. They could be separated by means of column chromatography on alumina with hexane–CH_2Cl_2 (1/2). The *cis* isomer is eluted first. For the *cis* isomer: IR (νCO, in CH_2Cl_2): 1953, 1868. ^{1}H-NMR (δ, in $CDCl_3$): 2.63 (d, $J_{H-P} = 11.2$ Hz, 3H, NCH_3), 2.71 (d, $J_{H-P} = 10.9$ Hz, 3H, NCH_3), 3.12–3.18 (m, 2H, NCH_2), 3.36 (d, $J_{H-P} = 11.2$ Hz, 3H, OCH_3), 3.38–3.44 (m, 2H, NCH_2), 5.54 (s, 5H, C_5H_5). ^{13}C-NMR (δ, in $CDCl_3$): 33.57 (d, $J_{C-P} = 9.1$ Hz, NCH_3), 34.60 (d, $J_{C-P} = 12.8$ Hz, NCH_3), 53.18 (s, NCH_2), 53.23 (s, NCH_2), 53.35 (s, OCH_3), 90.82 (s, C_5H_5), 228.06 (d, $J_{C-P} = 7.5$ Hz, CO), 241.30 (d, $J_{C-P} = 32.4$ Hz, CO). ^{31}P-NMR (δ, in CH_2Cl_2): 115.85 (s with W satellites, $J_{P-^{183}W} = 387.0$ Hz). For the *trans* isomer: IR (νCO, in CH_2Cl_2): 1959, 1871. ^{1}H-NMR (δ, in $CDCl_3$): 2.81 (d, $J_{H-P} = 10.6$ Hz, 6H, NCH_3), 3.13–3.17 (m, 2H, NCH_2), 3.43 (d, $J_{H-P} = 12.2$ Hz, 3H, OCH_3), 3.43–3.48 (m, 2H, NCH_2), 5.24 (d, $J_{H-P} = 2.0$ Hz, 5H, C_5H_5). ^{13}C-NMR (δ, in $CDCl_3$): 33.31 (d, $J_{C-P} = 13.6$ Hz, NCH_3), 51.66 (s, OCH_3), 52.65 (s, NCH_2), 90.43 (s, C_5H_5), 221.76 (d with W satellites, $J_{C-P} = 27.2$, $J_{C-^{183}W} = 162.2$ Hz CO). ^{31}P-NMR (δ, in CH_2Cl_2): 123.36 (s with W satellites, $J_{P-^{183}W} = 368.4$ Hz).

*3.3. Preparation of [Cp(CO)$_2$(SnPh$_3$)Mo{PNN(OMe)}] (**Mo-1a**)*

A solution of [$Cp(CO)_2IMo$\{PNN(OMe)\}] (1069 mg, 2.17 mmol) in THF (20 ml) was treated with $NaK_{2.8}$ (1.0 ml, 6.49 mmol) at r.t. with stirring for 1 h. The color of the solution changed from red to pale yellow. After an excess of $NaK_{2.8}$ was filtered off, the filtrate was added to the THF solution of $SnPh_3Cl$ (1000 mg, 2.59 mmol) at r.t. The reaction mixture was stirred for 2 h. The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2. The extract was loaded on an alumina column, and eluted with a mixture of 1:1 hexane–CH_2Cl_2. The pale yellow band eluted first was collected, and the solvents were removed in vacuo to give **Mo-1a** as a white powder (1286 mg, 1.80 mmol, 83%). Anal. Calc. for $C_{30}H_{33}MoN_2O_3PSn$: C, 50.38; H, 4.65; N, 3.92. Found: C, 50.07; H, 4.53; N, 3.94%. IR (νCO, in CH_2Cl_2): 1909, 1837. ^{1}H-NMR (δ, in $CDCl_3$): 2.84 (d, $J_{H-P} = 10.9$ Hz, 6H, NCH_3), 3.15–3.26 (m, 2H, NCH_2), 3.37 (d, $J_{H-P} = 12.2$ Hz, 3H, OCH_3), 3.40–3.50 (m, 2H, NCH_2), 4.97 (d, $J_{H-P} = 1.0$ Hz, 5H, C_5H_5), 7.25–7.33 (m, 9H, Ph), 7.61–7.65 (m, 6H, Ph). ^{13}C-NMR (δ, in $CDCl_3$): 33.54 (d, $J_{C-P} = 11.0$ Hz, NCH_3), 51.91 (d, $J_{C-P} = 2.4$ Hz, NCH_2), 52.35 (d, $J_{C-P} = 11.0$ Hz, OCH_3), 88.44 (s, C_5H_5), 127.62 (s, Ph), 127.78 (s with Sn satellites, $J_{C-^{119}Sn} = 42.7$ Hz, Ph), 137.07 (s with Sn satellites, $J_{C-^{119}Sn} = 35.4$ Hz, Ph), 145.12 (s with Sn satellites, $J_{C-^{119}Sn} = 358.8$ Hz, Ph), 231.88 (d with Sn satellites, $J_{C\text{–}P} = 30.5$ Hz, $J_{C\text{–}^{119}Sn} = 150.8$ Hz, CO). ^{31}P-NMR (δ, in CH_2Cl_2): 171.00 (s with Sn satellites, $J_{P\text{–}^{119}Sn} = 148.8$ Hz). ^{119}Sn-NMR (δ, in $CDCl_3$): 74.97 (d, $J_{^{119}Sn\text{–}P} = 146.1$ Hz).

*3.4. Preparation of [Cp(CO)$_2$(SnMe$_3$)Mo{PNN(OMe)}](**Mo-2a**)*

A treatment of [Cp(CO)$_2$IMo{PNN(OMe)}] (2920 mg, 5.93 mmol) with $NaK_{2.8}$ (1.5 ml, 9.09 mmol) followed by $SnMe_3Cl$ (1340 mg, 6.73 mmol) in a manner similar to that for **Mo-1a** gave a white powder of **Mo-2a** (2534 mg, 4.79 mmol, 81%). Anal. Calc. for $C_{15}H_{27}MoN_2O_3PSn$: C, 34.06; H, 5.14; N, 5.30. Found: C, 34.11; H, 4.85; N, 5.28%. IR (νCO, in CH_2Cl_2): 1897, 1823. ^{1}H-NMR (δ, in $CDCl_3$): 0.33 (s with Sn satellites, $J_{H\text{–}^{119}Sn} = 45.5$ Hz, 9H, $SnCH_3$), 2.80 (d, $J_{H\text{–}P} = 11.6$ Hz, 6H, NCH_3), 3.11–3.22 (m, 2H, NCH_2), 3.31 (d, $J_{H\text{–}P} = 12.1$ Hz, 3H, OCH_3), 3.36–3.44 (m, 2H, NCH_2), 4.94 (s, 5H, C_5H_5). ^{13}C-NMR (δ, in $CDCl_3$): -5.55 (s with Sn satellites, $J_{C\text{–}^{119}Sn} = 252.9$ Hz, $SnCH_3$), 33.65 (d, $J_{C\text{–}P} = 10.7$ Hz, NCH_3), 51.70 (d, $J_{C\text{–}P} = 3.2$ Hz, NCH_2), 52.16 (d, $J_{C\text{–}P} = 9.6$ Hz, OCH_3), 87.92 (s, C_5H_5), 231.82 (d with Sn satellites, $J_{C\text{–}P} = 28.8$ Hz, $J_{C\text{–}^{119}Sn} = 136.6$ Hz, CO). ^{31}P-NMR (δ, in CH_2Cl_2): 177.70 (s with Sn satellites, $J_{P\text{–}^{119}Sn} = 132.1$ Hz). ^{119}Sn-NMR (δ, in CH_2Cl_2): 128.87 (d, $J_{^{119}Sn\text{–}P} = 133.3$ Hz).

*3.5. Preparation of [Cp(CO)$_2$(Sn^{n}Bu$_3$)Mo{PNN(OMe)}] (**Mo-3a**)*

A treatment of [Cp(CO)$_2$IMo{PNN(OMe)}] (3060 mg, 6.22 mmol) with $NaK_{2.8}$ (1.5 ml, 9.09 mmol) followed by Sn^nBu_3Cl (1.70 ml, 6.27 mmol) in a manner similar to that for **Mo-1a** gave a white powder of **Mo-3a** (3237 mg, 4.94 mmol, 79%). Anal. Calc. for $C_{24}H_{45}MoN_2O_3PSn$: C, 43.99; H, 6.92; N, 4.28. Found: C, 44.14; H, 6.68; N, 4.30%. IR (νCO, in CH_2Cl_2): 1894, 1821. ^{1}H-NMR (δ, in $CDCl_3$): 0.90 (t, $J_{H\text{–}H} = 7.3$ Hz, 9H, Bu), 1.05–1.13 (m, 6H, Bu), 1.35 (d, $J_{H\text{–}H} = 7.6$ Hz, 6H, Bu), 1.49–1.61 (m, 6H, Bu), 2.81 (d, $J_{H\text{–}P} = 11.2$ Hz, 6H, NCH_3), 3.14–3.21 (m, 2H, NCH_2), 3.32 (d, $J_{H\text{–}P} = 11.9$ Hz, 3H, OCH_3), 3.37–3.42 (m, 2H, NCH_2), 4.97 (d, $J_{H\text{–}P} = 1.0$ Hz, 5H, C_5H_5). ^{13}C-NMR (δ, in $CDCl_3$): 13.70 (s with Sn satellites, $J_{C\text{–}^{119}Sn} = 248.5$ Hz, Bu), 13.80 (s, Bu), 27.66 (s with Sn satellites, $J_{C\text{–}^{119}Sn} = 59.0$ Hz, Bu), 30.21 (s with Sn satellites, $J_{C\text{–}^{119}Sn} = 19.7$ Hz, Bu), 33.72 (d, $J_{C\text{–}P} = 11.6$ Hz, NCH_3), 51.84 (d, $J_{C\text{–}P} = 3.5$ Hz, NCH_2), 52.16 (d, $J_{C\text{–}P} = 10.4$ Hz, OCH_3), 87.53 (s, C_5H_5), 232.20 (d with Sn satellites, $J_{C\text{–}P} = 30.1$ Hz, $J_{C\text{–}^{119}Sn} = 132.4$ Hz, CO). ^{31}P-NMR (δ, in CH_2Cl_2): 177.38 (s with Sn satellites, $J_{C\text{–}^{119}Sn} = 113.5$ Hz). ^{119}Sn-NMR (δ, in CH_2Cl_2): 117.00 (d, $J_{^{119}Sn\text{–}P} = 116.1$ Hz).

*3.6. Preparation of [Cp(CO)$_2$(SnPh$_3$)W{PNN(OMe)}] (**W-1a**)*

A treatment of [Cp(CO)$_2$IW{PNN(OMe)}] (2533 mg, 4.37 mmol) with $NaK_{2.8}$ (1.0 ml, 6.49 mmol) followed by $SnPh_3Cl$ (1710 mg, 4.44 mmol) in a manner similar to that for **Mo-1a** gave a white powder of **W-1a** (2952 mg, 3.68 mmol, 84%). Anal. Calc. for $C_{30}H_{33}N_2O_3PSnW$: C, 44.87; H, 4.14; N, 3.49. Found: C, 44.77; H, 4.06; N, 3.51%. IR (νCO, in CH_2Cl_2): 1903, 1828. ^{1}H-NMR (δ, in $CDCl_3$): 2.78 (d, $J_{H\text{–}P} = 11.2$ Hz, 6H, NCH_3), 3.11–3.18 (m, 2H, NCH_2), 3.34 (d, $J_{H\text{–}P} = 12.2$ Hz, 3H, OCH_3), 3.37–3.40 (m, 2H, NCH_2), 5.02 (d, $J_{H\text{–}P} = 0.7$ Hz, 5H, C_5H_5), 7.25–7.32 (m, 9H, Ph), 7.59–7.69 (m, 6H, Ph). ^{13}C-NMR (δ, in $CDCl_3$): 33.78 (d, $J_{C\text{–}P} = 9.8$ Hz, NCH_3), 51.73 (s, NCH_2), 52.87 (d, $J_{C\text{–}P} = 11.0$ Hz, OCH_3), 86.99 (s, C_5H_5), 127.64 (s, Ph), 127.76 (s with Sn satellites, $J_{C\text{–}^{119}Sn} = 42.8$ Hz, Ph), 137.19 (s with Sn satellites, $J_{C\text{–}^{119}Sn} = 35.4$ Hz, Ph), 144.54 (s with Sn satellites, $J_{C\text{–}^{119}Sn} = 368.7$ Hz, Ph), 222.43 (d with Sn and W satellites, $J_{C\text{–}P} = 25.6$ Hz, $J_{C\text{–}^{119}Sn} = 138.0$ Hz, $J_{C\text{–}^{183}W} = 155.0$ Hz, CO). ^{31}P-NMR (δ, in CH_2Cl_2): 134.50 (s with Sn and W satellites, $J_{P\text{–}^{119}Sn} = 137.7$ Hz, $J_{P\text{–}^{183}W} = 422.4$ Hz). ^{119}Sn-NMR (δ, in CH_2Cl_2): -1.98 (d with W satellites, $J_{^{119}Sn\text{–}P} = 140.6$ Hz, $J_{^{119}Sn\text{–}^{183}W} = 404.6$ Hz).

*3.7. Preparation of [Cp(CO)$_2$(SnMe$_3$)W{PNN(OMe)}] (**W-2a**)*

A treatment of [Cp(CO)$_2$IW{PNN(OMe)}] (2356 mg, 4.06 mmol) with $NaK_{2.8}$ (1.5 ml, 9.09 mmol) followed by $SnMe_3Cl$ (880 mg, 4.42 mmol) in a manner similar to that for **Mo-1a** gave a white powder of **W-2a** (1885 mg, 3.06 mmol, 75%). Anal. Calc. for $C_{15}H_{27}N_2O_3PSnW$: C, 29.20; H, 4.41; N, 4.54. Found: C, 29.25; H, 4.20; N, 4.50%. IR (νCO, in CH_2Cl_2): 1890, 1815. ^{1}H-NMR (δ, in $CDCl_3$): 0.34 (s with Sn satellites, $J_{H\text{–}^{119}Sn} = 45.4$ Hz, 9H, $SnCH_3$), 2.76 (d, $J_{H\text{–}P} = 11.5$ Hz, 6H, NCH_3), 3.12–3.17 (m, 2H, NCH_2), 3.32 (d, $J_{H\text{–}P} = 12.2$ Hz, 3H, OCH_3), 3.38–3.41 (m, 2H, NCH_2), 5.01 (s, 5H, C_5H_5). ^{13}C-NMR (δ, in $CDCl_3$): -6.69 (s with Sn satellites, $J_{C\text{–}^{119}Sn} = 258.8$ Hz, $SnCH_3$), 33.91 (d, $J_{C\text{–}P} = 9.7$ Hz, NCH_3), 51.50 (d, $J_{C\text{–}P} = 2.5$ Hz, NCH_2), 52.86 (d, $J_{C\text{–}P} = 8.6$ Hz, OCH_3), 86.50 (s, C_5H_5), 222.66 (d with Sn and W satellites, $J_{C\text{–}P} = 23.3$ Hz, $J_{C\text{–}^{119}Sn} = 124.4$ Hz, $J_{C\text{–}^{183}W} = 159.3$ Hz, CO). ^{31}P-NMR (δ, in CH_2Cl_2): 141.70 (s with Sn and W satellites, $J_{P\text{–}^{119}Sn} = 124.7$ Hz, $J_{P\text{–}^{183}W} = 441.0$ Hz). ^{119}Sn-NMR (δ, in CH_2Cl_2): 45.04 (d with W satellites, $J_{^{119}Sn\text{–}P} = 128.9$ Hz, $J_{^{119}Sn\text{–}^{183}W} = 262.3$ Hz).

*3.8. Preparation of [Cp(CO)$_2$(Sn^{n}Bu$_3$)W{PNN(OMe)}] (**W-3a**)*

A treatment of [Cp(CO)$_2$IW{PNN(OMe)}] (2600 mg, 4.48 mmol) with $NaK_{2.8}$ (1.5 ml, 9.09 mmol) followed by Sn^nBu_3Cl (1.20 ml, 4.42 mmol) in a manner similar to that for **Mo-1a** gave a white powder of **W-3a** (2718 mg, 3.66 mmol, 82%). Anal. Calc. for $C_{24}H_{45}N_2O_3PSnW$: C, 38.79; H, 6.10; N, 3.77. Found: C, 38.70; H, 5.92; N, 3.82%. IR (νCO, in CH_2Cl_2): 1888, 1812. ^{1}H-NMR (δ, in $CDCl_3$): 0.90 (t, $J_{H-H} = 7.3$ Hz, 9H, Bu), 1.05–1.11 (m, 6H, Bu), 1.34 (d, $J_{H-H} = 7.3$ Hz, 6H, Bu), 1.48–1.59 (m, 6H, Bu), 2.77 (d, $J_{H-P} = 11.6$ Hz, 6H, NCH_3), 3.12–3.19 (m, 2H, NCH_2), 3.33 (d, $J_{H-P} = 12.2$ Hz, 3H, OCH_3), 3.38–3.41 (m, 2H, NCH_2), 5.03 (d, $J_{H-P} = 1.0$ Hz, 5H, C_5H_5). ^{13}C-NMR (δ, in $CDCl_3$): 12.60 (s with Sn satellites, $J_{C-^{119}Sn} = 253.9$ Hz, Bu), 13.82 (s, Bu), 27.64 (s with Sn satellites, $J_{C-^{119}Sn} = 57.3$ Hz, Bu), 30.33 (s with Sn satellites, $J_{C-^{119}Sn} = 18.3$ Hz, Bu), 33.96 (d, $J_{C-P} = 9.8$ Hz, NCH_3), 51.63 (d, $J_{C-P} = 2.4$ Hz, NCH_2), 52.81 (d, $J_{C-P} = 9.7$ Hz, OCH_3), 86.07 (s, C_5H_5), 222.95 (d with Sn and W satellites, $J_{C-P} = 23.2$ Hz, $J_{C-^{119}Sn} = 119.6$ Hz, $J_{C-^{183}W} = 159.9$ Hz, CO). ^{31}P-NMR (δ, in CH_2Cl_2): 141.07 (s with Sn and W satellites, $J_{P-^{119}Sn} = 109.8$ Hz, $J_{P-^{183}W} = 444.8$ Hz). ^{119}Sn-NMR (δ, in CH_2Cl_2): 37.72 (d with W satellites, $J_{^{119}Sn-P} = 113.2$ Hz, $J_{^{119}Sn-^{183}W} = 234.4$ Hz).

3.9. Reaction of *M-1a* (*M* = *Mo*, *W*) with *TMSOTf*

A solution of **Mo-1a** (403 mg, 0.56 mmol) in CH_2Cl_2 (7 ml) was treated with TMSOTf (0.10 ml, 0.55 mmol) at r.t. with stirring for 5 h. The color of the solution changed from pale yellow to yellow. The solvent was removed under reduced pressure and the residue was washed with hexane. Hexane was diffused slowly to a CH_2Cl_2 solution of the residue to result in a pale yellow supernatant and a black oil. The supernatant was transferred to another Schlenk tube by cannula under nitrogen atmosphere, and the solvents were removed in vacuo to give a pale yellow powder of **Mo-1b** (354 mg, 0.43 mmol, 77%). IR (νCO, in CH_2Cl_2): 1920, 1847. ^{1}H-NMR (δ, in $CDCl_3$): 2.82 (d, $J_{H-P} = 11.9$ Hz, 6H, NCH_3), 3.27 (m, 4H, NCH_2), 5.37 (s, 5H, C_5H_5), 7.31–7.67 (m, 15H, Ph). ^{13}C-NMR (δ, in $CDCl_3$): 34.40 (d, $J_{C-P} = 8.6$ Hz, NCH_3), 51.81 (s, NCH_2), 90.53 (s, C_5H_5), 119.29 (q, $J_{C-F} = 318.6$ Hz, CF_3) 128.21 (d, $J_{C-P} = 9.8$ Hz, PPh), 128.68 (s, SnPh), 129.56 (s, SnPh), 129.87 (d, $J_{C-P} = 11.0$ Hz, PPh), 130.64 (s, PPh), 134.95 (s with Sn satellites, $J_{C-^{119}Sn} = 47.7$ Hz, SnPh), 139.85 (d, $J_{C-P} = 33.0$ Hz, PPh), 148.18 (s with Sn satellites, $J_{C-^{119}Sn} = 317.1$ Hz, SnPh), 230.81 (d, $J_{C-P} = 28.1$ Hz, CO). ^{31}P-NMR (δ, in CH_2Cl_2): 157.05 (s with Sn satellites, $J_{P-^{119}Sn} = 190.2$ Hz). ^{119}Sn-NMR (δ, in situ): 459.14 (d, $J_{^{119}Sn-P} = 192.1$ Hz).

A treatment of **W-1a** (463 mg, 0.58 mmol) with TMSOTf (0.10 ml, 0.55 mmol) in a manner similar to that for **Mo-1b** gave a pale yellow powder of **W-1b** (404 mg, 0.44 mmol, 76%). IR (νCO, in CH_2Cl_2): 1926, 1847. ^{1}H-NMR (δ, in $CDCl_3$): 2.79 (d, $J_{H-P} = 11.2$ Hz, 6H, NCH_3), 3.25 (m, 4H, NCH_2), 5.47 (s, 5H, C_5H_5), 7.39–7.73 (m, 15H, Ph). ^{13}C-NMR (δ, in $CDCl_3$): 34.39 (d, $J_{C-P} = 7.3$ Hz, NCH_3), 51.49 (s, NCH_2), 89.13 (s, C_5H_5), 119.22 (q, $J_{C-F} = 318.6$ Hz, CF_3), 128.10 (d, $J_{C-P} = 8.5$ Hz, PPh), 128.60 (s with Sn satellites, $J_{C-^{119}Sn} = 48.8$ Hz, SnPh), 129.56 (s, SnPh), 130.27 (d, $J_{C-P} = 11.0$ Hz, PPh), 130.67 (s, PPh), 135.10 (s with Sn satellites, $J_{C-^{119}Sn} = 46.4$ Hz, SnPh), 140.02 (d, $J_{C-P} = 41.5$ Hz, PPh), 147.42 (s with Sn satellites, $J_{C-^{119}Sn} = 343.0$ Hz, SnPh), 222.01 (d with W satellites, $J_{C-P} = 20.8$ Hz, $J_{C-^{183}W} = 151.4$ Hz, CO). ^{31}P-NMR (δ, in CH_2Cl_2): 123.38 (s with Sn and W satellites, $J_{P-^{119}Sn} = 183.8$ Hz, $J_{P-^{183}W} = 323.6$ Hz). ^{119}Sn-NMR (δ, in CH_2Cl_2): 335.32 (d with W satellites, $J_{^{119}Sn-P} = 188.1$ Hz, $J_{^{119}Sn-^{183}W} = 610.1$ Hz).

3.10. Reaction of *M-1a* (*M* = *Mo*, *W*) with $BF_3{\cdot}OEt_2$

A solution of **Mo-1a** (400 mg, 0.56 mmol) in CH_2Cl_2 (7 ml) was treated with $BF_3{\cdot}OEt_2$ (0.14 ml, 1.12 mmol) at r.t. with stirring for 5 h. The color of the solution changed from pale yellow to yellow. An effort to isolate **Mo-1b′** came into failure for instability of the product. Confirming the formation of **Mo-1b′**, the reaction mixture was cooled to −78°C and treated with a diethylether solution of MeLi (0.7 ml, 0.7 mmol). The solution was warmed to r.t. with stirring for 22 h. The solvents were removed under reduced pressure and the residue was loaded on an alumina column, and eluted with a CH_2Cl_2–hexane (1/1). The pale yellow band eluted first was collected, and the solvents were removed in vacuo to give **Mo-1c** as a white powder (283 mg, 0.41 mmol, 73%). Anal. Calc. for $C_{30}H_{33}MoN_2O_2PSn$: C, 51.53; H, 4.76; N, 4.01. Found: C, 51.78; H, 4.77; N, 4.04%. IR (νCO, in CH_2Cl_2): 1900, 1828. ^{1}H-NMR (δ, in $CDCl_3$): 0.73 (s with Sn satellites, $J_{H-Sn} = 44.9$ Hz, 3H, $SnCH_3$), 2.69 (d, $J_{H-P} = 11.6$ Hz, 6H, NCH_3), 3.12 (d, $J_{H-P} = 2.0$ Hz, 2H, NCH_2), 3.14 (s, 2H, NCH_2), 4.95 (d, $J_{H-P} = 1.0$ Hz, 5H, C_5H_5), 7.17–7.66 (m, 15H, Ph). ^{13}C-NMR (δ, in $CDCl_3$): −6.11 (s with Sn satellites, $J_{C-^{119}Sn} = 266.1$ Hz, $SnCH_3$), 34.23 (d, $J_{C-P} = 9.7$ Hz, NCH_3), 51.63 (d, $J_{C-P} = 2.5$ Hz, NCH_2), 89.15 (s, C_5H_5), 127.51 (s, SnPh), 127.64 (s with Sn satellites, $J_{C-^{119}Sn} = 42.7$ Hz, SnPh), 127.64 (d, $J_{C-P} = 9.8$ Hz, PPh), 129.65 (s, PPh), 130.17 (d, $J_{C-P} = 12.2$ Hz, PPh), 136.41 (s with Sn satellites, $J_{C-^{119}Sn} = 34.2$ Hz, SnPh), 140.88 (d with Sn satellites, $J_{C-P} = 29.3$ Hz, $J_{C-^{119}Sn} = 9.5$ Hz, PPh), 145.70 (s with Sn satellites, $J_{C-^{119}Sn} = 352.8$ Hz, SnPh), 233.23 (d with Sn satellites, $J_{C-P} = 25.6$ Hz, $J_{C-^{119}Sn} = 146.4$ Hz, CO). ^{31}P-NMR (δ, in CH_2Cl_2): 166.24 (s with Sn satellites, $J_{P-^{119}Sn} = 143.7$ Hz). ^{119}Sn-NMR (δ, in CH_2Cl_2): 81.46 (d, $J_{^{119}Sn-P} = 146.1$ Hz).

When **W-1a** (398 mg, 0.50 mmol) was treated with $BF_3{\cdot}OEt_2$ (0.12 ml, 0.96 mmol), the spectroscopic measurements of the reaction mixture suggested a formation of **W-1b′**: ^{31}P-NMR (δ, in situ): 119.27 (br.).

^{119}Sn-NMR (δ, in situ): 293.17 (d, $J_{^{119}Sn-P} = 152.6$ Hz). Subsequently, a diethylether solution of MeLi (0.6 ml, 0.6 mmol) was added to the reaction mixture in a manner similar to that for **Mo-1c** to give a pale yellow powder of **W-1c** (300 mg, 0.38 mmol, 77%). Anal. Calc. for $C_{30}H_{33}N_2O_2PSnW$: C, 45.78; H, 4.23; N, 3.56. Found: C, 45.63; H, 4.17; N, 3.57%. IR (νCO, in CH_2Cl_2): 1893, 1818. ^{1}H-NMR (δ, in $CDCl_3$): 0.72 (s with Sn satellites, $J_{H-^{119}Sn} = 44.9$ Hz, 3H, $SnCH_3$), 2.71 (d, $J_{H-P} = 11.6$ Hz, 6H, NCH_3), 3.18 (d, $J_{H-P} = 3.6$ Hz, 2H, NCH_2), 3.21 (s, 2H, NCH_2), 5.06 (d, $J_{H-P} = 1.0$ Hz, 5H, C_5H_5), 7.24–7.58 (m, 15H, Ph). ^{13}C-NMR (δ, in $CDCl_3$): -7.10 (s with Sn satellites, $J_{C-^{119}Sn} = 275.9$ Hz, $SnCH_3$), 34.41 (d, $J_{C-P} = 9.7$ Hz, NCH_3), 51.50 (s, NCH_2), 87.82 (s, C_5H_5), 127.59 (d, $J_{C-P} = 3.6$ Hz, PPh), 127.65 (s with Sn satellites, $J_{C-^{119}Sn} = 41.5$ Hz, SnPh), 127.76 (s, SnPh), 129.81 (d, $J_{C-P} = 2.5$ Hz, PPh), 130.72 (d, $J_{C-P} = 11.0$ Hz, PPh), 136.60 (s with Sn satellites, $J_{C-^{119}Sn} = 34.2$ Hz, SnPh), 141.23 (d with Sn satellites, $J_{C-P} = 37.8$ Hz, $J_{C-^{119}Sn} = 12.2$ Hz, PPh), 145.05 (s with Sn satellites, $J_{C-^{119}Sn} = 360.1$ Hz, SnPh), 224.42 (d with Sn and W satellites, $J_{C-P} = 19.5$ Hz, $J_{C-^{119}Sn} = 133.0$ Hz, $J_{C-^{183}W} = 158.1$ Hz, CO). ^{31}P-NMR (δ, in CH_2Cl_2): 130.52 (s with Sn and W satellites, $J_{P-^{119}Sn} = 145.2$ Hz, $J_{P-^{183}W} = 362.9$ Hz). ^{119}Sn-NMR (δ, in CH_2Cl_2): -1.02 (d with W satellites, $J_{^{119}Sn-P} = 146.1$ Hz, $J_{^{119}Sn-^{183}W} = 313.8$ Hz).

*3.11. Reaction of **M-2a** (M = Mo, W) with TMSOTf*

A treatment of **Mo-2a** with TMSOTf in a manner similar to that for **Mo-1b** resulted in a complicated reaction. The spectroscopic measurements in situ, however, suggested a formation of **Mo-2b**: ^{31}P-NMR (δ, in situ): 162.56 (s with Sn satellites, $J_{P-^{119}Sn} = 201.7$ Hz). ^{119}Sn-NMR (δ, in situ): 655.79 (d, $J_{^{119}Sn-P} = 194.8$ Hz).

A treatment of **W-2a** with TMSOTf in a manner similar to that for **Mo-1b** resulted in a complicated reaction. The spectroscopic measurements in situ, however, suggested a formation of **W-2b**. The solvent of the reaction mixture was removed under reduced pressure and the residue was recrystallized from CH_2Cl_2–hexane system at -10°C to give several yellow crystals of **W-2b**: ^{13}C-NMR (δ, in CH_2Cl_2): 5.61 (s with Sn satellites, $J_{C-^{119}Sn} = 201.4$ Hz, $SnCH_3$), 21.82 (d, $J_{C-P} = 29.3$ Hz, PCH_3), 33.88 (d, $J_{C-P} = 7.3$ Hz, NCH_3), 51.41 (s, NCH_2), 88.83 (s, C_5H_5), 119.33 (q, $J_{C-F} = 317.4$ Hz, CF_3), 220.83 (d with Sn and W satellites, $J_{C-P} = 19.5$ Hz, $J_{C-^{119}Sn} = 152.0$ Hz, $J_{C-^{183}W} = 152.0$ Hz, CO). ^{31}P-NMR (δ, in CH_2Cl_2): 125.14 (s with Sn and W satellites, $J_{P-^{119}Sn} = 194.3$ Hz, $J_{P-^{183}W} = 315.7$ Hz). ^{119}Sn-NMR (δ, in CH_2Cl_2): 526.53 (d, $J_{^{119}Sn-P} = 203.2$ Hz).

*3.12. Reaction of **M-2a** (M = Mo, W) with $BF_3 \cdot OEt_2$*

A treatment of **M-2a** with $BF_3 \cdot OEt_2$ in a manner similar to that for **Mo-1b′** resulted in a complicated reaction. The spectroscopic measurements in situ, however, suggested a formation of **M-2b′**. **Mo-2b′**: ^{31}P-NMR (δ, in situ): 163.14 (br.). ^{119}Sn-NMR (δ, in situ): 575.80 (br.). **W-2b′**: ^{31}P-NMR (δ, in situ): 124.40 (br.). ^{119}Sn-NMR (δ, in situ): 445.93 (br.).

*3.13. Reaction of **M-3a** (M = Mo, W) with TMSOTf*

A treatment of **Mo-3a** (380 mg, 0.58 mmol) with TMSOTf (0.10 ml, 0.55 mmol) in a manner similar to that for **Mo-1b** resulted in a complicated reaction. The spectroscopic measurements in situ, however, suggested a formation of **Mo-3b** and **Mo-d**. The reaction mixture was condensed and was kept standing at -10°C to give yellow crystals of **Mo-d** (42 mg, 0.13 mmol, 22%). **Mo-3b**: ^{31}P-NMR (δ, in situ): 164.11 (s with Sn satellites, $J_{P-^{119}Sn} = 166.5$ Hz). ^{119}Sn-NMR (δ, in situ): 667.08 (d, $J_{^{119}Sn-P} = 167.9$ Hz). **Mo-d**: ^{31}P-NMR (δ, in THF): 272.46 (s).

A treatment of **W-3a** (474 mg, 0.64 mmol) with TMSOTf (0.11 ml, 0.61 mmol) in a manner similar to that for **Mo-1b** resulted in a complicated reaction. The spectroscopic measurements in situ, however, suggested a formation of **W-3b** and **W-d**. The reaction mixture was condensed and was kept standing at -10°C to give yellow crystals of **W-d** (70 mg, 0.17 mmol, 26%). **W-3b**: ^{31}P-NMR (δ, in situ): 126.91 (s with Sn and W satellites, $J_{P-^{119}Sn} = 155.5$ Hz, $J_{P-^{183}W} = 396.1$ Hz). ^{119}Sn-NMR (δ, in situ): 539.44 (d, $J_{^{119}Sn-P} = 158.4$ Hz). **W-d**: Anal. Calc. for $C_{11}H_{15}N_2O_2PW$: C, 31.30; H, 3.58; N, 6.64. Found: C, 31.32; H, 3.48; N, 6.60%. IR (νCO, in benzene): 1910, 1838. ^{1}H-NMR (δ, in C_6D_6): 2.42 (d, $J_{H-P} = 5.7$ Hz, 6H, NCH_3), 2.58–2.66 (m, 4H, NCH_2), 5.15 (s, 5H, C_5H_5). ^{13}C-NMR (δ, in C_6D_6): 34.23 (d, $J_{C-P} = 15.1$ Hz, NCH_3), 51.28 (d, $J_{C-P} = 2.3$ Hz, NCH_2), 86.53 (s, C_5H_5), 222.83 (d, $J_{C-P} = 9.1$ Hz, CO). ^{31}P-NMR (δ, in benzene): 244.61 (s with W satellites, $J_{P-^{183}W} = 718.1$ Hz).

*3.14. Reaction of **M-3a** (M = Mo, W) with $BF_3 \cdot OEt_2$*

A treatment of **M-3a** with $BF_3 \cdot OEt_2$ in a manner similar to that for **Mo-1b′** resulted in a complicated reaction. The spectroscopic measurements in situ, however, suggested a formation of **M-d**, and *cis* and *trans*-**M-3e**. *cis*-**Mo-3e**: ^{31}P-NMR (δ, in situ): 334.71 (br.). *trans*-**Mo-3e**: ^{31}P-NMR (δ, in situ): 310.08 (br.). *cis*-**W-3e**: ^{31}P-NMR (δ, in situ/-20°C): 298.07 (s with Sn and W satellites, $J_{P-^{119}Sn} = 42.5$ Hz, $J_{P-^{183}W} = 516.4$ Hz). *trans*-**W-3e**: ^{31}P-NMR (δ, in situ/-20°C): 282.76 (s with Sn and W satellites, $J_{P-^{119}Sn} = 291.6$ Hz, $J_{P-^{183}W} = 543.1$ Hz).

*3.15. X-ray structure determination for **W-1b** and **W-2b***

Crystallographic and experimental details of X-ray crystal structure analyses are given in Table 1. Suitable crystals of **W-1b** and **W-2b** were mounted independently on an Enraf–Nonius CAD-4 automatic diffractometer. Data were collected at room temperature. Intensities were collected for Lorents and polarization effects in the usual manner. The structures were solved by a combination of direct methods [22] and Fourier synthesis [23] and refined by full matrix least-squares calculations. During the course of the refinement, it was found that the Cp ring carbon atoms of **W-2b** were disordered. Therefore, they were refined by using two rigid models with an occupancy factor = 0.5 and isotropic thermal parameters for each carbon atom. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated isotropically. An empirical absorption correction using the program DIFABS [24] was applied. Final values of $R = 0.032$ and $R_w = 0.039$ for compound **W-1b** and $R = 0.032$ and $R_w = 0.038$ for compound **W-2b**, were obtained ($R_w = [\Sigma_w||F_o| - |F_c||^2/\Sigma_w|F_o|^2]^{1/2}$ and $w = 4F_o^2/\sigma^2(F_o)$). All calculations were performed using TEXSAN [25] with neutral atom scattering factors from Cromer and Waber [26], $\Delta f'$ and $\Delta f''$ values [27], and mass attenuation coefficients [28].

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