

*Journal of Organometallic Chemistry*, 423 (1992) 39–50  
 Elsevier Sequoia S.A., Lausanne  
 JOM 22174

## Preparation and properties of molybdenum and tungsten dinitrogen complexes

### XXXIV \*. Nucleophilic addition reactions of hydrazido(2 – ) complexes with diphenylketene: characterization of new acylhydrazido(2 – ) complexes of molybdenum and tungsten

Takayuki Aoshima, Yasushi Mizobe, Masanobu Hidai \*,

*Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113 (Japan)*

and Junichi Tsuchiya

*Engineering Research Institute, Faculty of Engineering, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo, 113 (Japan)*

(Received June 8th, 1991)

#### Abstract

Nucleophilic attack of the terminal nitrogen in the hydrazido(2 – ) complexes  $[\text{MCl}_2(\text{NNH}_2(\text{PMe}_2\text{Ph})_3)]$  (**1**; M = Mo, W) on the electron deficient carbon in diphenylketene resulted in the formation of the new acylhydrazido(2 – ) complexes *cis,mer*- $[\text{MCl}_2(\text{NNHCOCHPh}_2)(\text{PMe}_2\text{Ph})_3]$  (**2**). Complexes **2** are diamagnetic in solid form and the structure of **2** (M = W) has been determined by X-ray analysis. Crystal data: space group  $C2/c$ ,  $a = 26.137(7)$ ,  $b = 13.154(6)$ ,  $c = 25.983(10)$  Å,  $\beta = 113.57(2)^\circ$ ,  $Z = 8$ ,  $R = 0.093$  for 2134 reflections. On the other hand, the NMR and EPR study has revealed that **2** in solution is to be considered as a mixture of the diamagnetic and paramagnetic species. Complexes **2** further reacted with excess pyridine (Py) to give the cationic acylhydrazido(2 – ) complexes *mer*- $[\text{MCl}(\text{Py})(\text{NNHCOCHPh}_2)(\text{PMe}_2\text{Ph})_3]\text{Cl}$  (**3**) in high yields, which are diamagnetic both in a solid form and in solution. The structure of **3** (M = W) has also been characterized by X-ray crystallography. Crystal data: space group  $P2_1/a$ ,  $a = 21.954(10)$ ,  $b = 13.784(7)$ ,  $c = 14.835(7)$  Å,  $\beta = 92.74(5)^\circ$ ,  $Z = 4$ ,  $R = 0.043$  for 4903 reflections.

#### Introduction

The transformation of molecular nitrogen into organo-nitrogen compounds under mild conditions has great potential value and several carbon–nitrogen bond

\* For Part XXXIII, see ref. 1.

forming reactions of coordinated dinitrogen in transition metal complexes have been explored for this purpose [2]. The Mo and W dinitrogen complexes with bidentate tertiary phosphine ligands  $[M(N_2)_2(dppe)_2]$  ( $dppe = Ph_2PCH_2CH_2PPh_2$ ) react with various organic halides to give a series of complexes with organo-nitrogen ligands such as diazenido (MNNR), hydrazido(2-) ( $MNNR_2$ ), and diazoalkane ( $MNNCR_2$ ) complexes [3]. However, similar reactions with dinitrogen complexes with monodentate tertiary phosphine ligands lead only to mixed halophosphine-metal complexes and total loss of dinitrogen [4]. A more versatile route to C-N bond formation has been developed by our group using hydrazido(2-) ( $MNNH_2$ ) complexes, which are readily obtained by protonation of Mo and W dinitrogen complexes containing not only bidentate tertiary phosphine ligands but also monodentate tertiary phosphine ligands. Thus, the hydrazido(2-) complexes react with aldehydes and ketones to form a variety of diazoalkane complexes [5].

Previously we reported that treatment of  $[MBr(NNH_2)(dppe)_2]Br$  ( $M = Mo, W$ ) with PhNCO results in the formation of phenylsemicarbazido(2-) complexes  $[MBr(NNHCONHPh)(dppe)_2]Br$  by the nucleophilic addition of  $NNH_2$  ligands to PhNCO (eq. 1) [6]. However, full details of these products were not available because of their poor solubility.

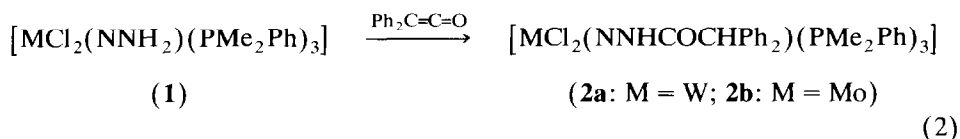


During our further study on the reactivity of the hydrazido(2-) complexes, we found that hydrazido(2-) complexes  $[MCl_2(NNH_2)(PMe_2Ph)_3]$  (**1a**:  $M = W$ ; **1b**:  $M = Mo$ ) react with diphenylketene to give new acylhydrazido(2-) complexes  $[MCl_2(NNHCOCHPh_2)(PMe_2Ph)_3]$  (**2a**:  $M = W$ ; **2b**:  $M = Mo$ ) by the analogous nucleophilic addition of the  $NNH_2$  group to the ketene. Here we wish to report the details of the properties of complexes **2** as well as those of the cationic acylhydrazido(2-) complexes  $[MCl(Py)(NNHCOCHPh_2)(PMe_2Ph)_3]Cl$  (**3a**:  $M = W$ ; **3b**:  $M = Mo$ ;  $Py =$  pyridine) derived from **2** by successive treatment with excess pyridine. Anomalous magnetic behaviour observed for **2** in solution is also described.

## Results and discussion

### *Preparation and the structure of $[MCl_2(NNHCOCHPh_2)(PMe_2Ph)_3]$ (**2**)*

Treatment of the hydrazido(2-) complexes **1** with diphenylketene in  $CH_2Cl_2$  at room temperature, enabled the new acylhydrazido(2-) complexes  $[MCl_2(NNHCOCHPh_2)(PMe_2Ph)_3]$  (**2**) to be isolated in moderate yields (eq. 2). These complexes show a characteristic strong band assignable to  $\nu(C=O)$  in their IR spectra at  $1680\text{ cm}^{-1}$  for **2a** and  $1690\text{ cm}^{-1}$  for **2b**, respectively. These values are compatible with those in the common amido compounds. A similar band has been found in the IR spectra of the acyl- and aroylhydrazido(2-) complexes  $[MCl(NNHCOR)(dppe)_2]Cl$  [7].



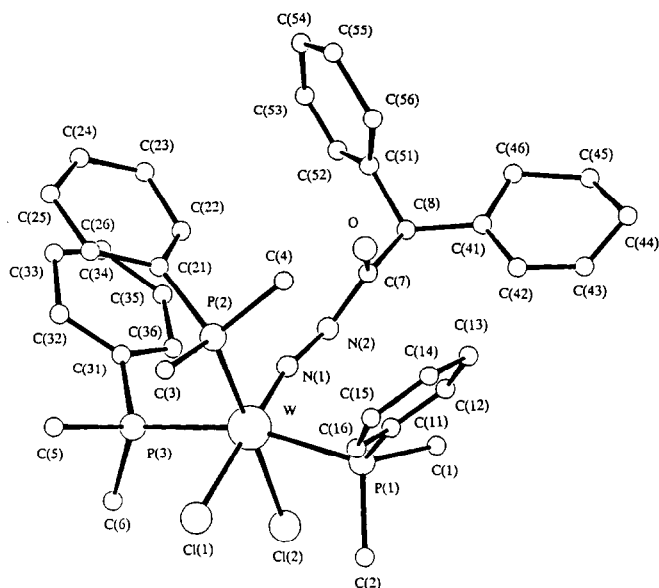


Fig. 1. Perspective view and atom numbering scheme of complex **2a**.

The X-ray analysis, performed to determine the structure of  $[\text{WCl}_2(\text{NNHCO-CHPh}_2)(\text{PMe}_2\text{Ph})_3]$  (**2a**), unambiguously disclosed the coordination geometry around the W atom as well as the bonding scheme in the acylhydrazido(2-) ligand. However, since good crystals could not be obtained, the final  $R$  and  $R_w$  values were 0.093 and 0.114, respectively, and further trials to decrease these indices were not successful.

Complex **2a** has a distorted octahedral structure with the acylhydrazido(2-) ligand *trans* to one Cl ligand (Fig. 1). Three phosphine and two chloride ligands occupy the mutually *meridional* and *cis* positions, respectively, in octahedron. The almost linear W–N(1)–N(2) linkage ( $167(3)^\circ$ ) and the N(1)–N(2)–C(7) bond angle of  $122(4)^\circ$  are diagnostic of the N-substituted hydrazido(2-) ligand [8]. Selected bond distances and angles are shown in Table 1.

### Solution studies

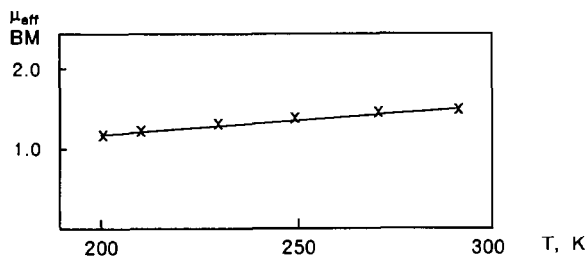
Measurement of the magnetic susceptibility of **2a** by the Faraday method has shown that **2a** is diamagnetic in the solid state ( $\mu_{\text{eff}} = 0.0 \mu_{\text{B}}$ ). However, its  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra in  $\text{CD}_2\text{Cl}_2$  at room temperature revealed only the significantly broadened resonances to be expected of a paramagnetic species. The magnetic susceptibility determined by Evans' method [9] at 293 K is  $1.5 \mu_{\text{B}}$ , which confirms the presence of the paramagnetic isomer(s) of **2a** in solution. As shown in Fig. 2, the susceptibility measurement at various temperatures has demonstrated that the  $\mu_{\text{eff}}$  value decreases as the temperature decreases. This indicates some favouring of the diamagnetic form at low temperatures, although significant broadening of the resonances in NMR spectra even at 203 K ( $\mu_{\text{eff}} = 1.2 \mu_{\text{B}}$ ) precludes detailed characterization of the diamagnetic species present in solution. As expected, a solution of **2a** is EPR active and its EPR spectrum in toluene at room temperature shows a strong resonance at  $g = 1.99$  due to the major paramagnetic species

Table 1

Selected bond lengths (Å) and angles (deg) for complex **2a**

<i>(a) In the coordination sphere of tungsten</i>			
W-Cl(1)	2.44(1)	W-Cl(2)	2.55(2)
W-P(1)	2.48(1)	W-P(2)	2.46(2)
W-P(3)	2.50(1)	W-N(1)	1.70(3)
Cl(1)-W-Cl(2)	86.0(4)	Cl(1)-W-P(1)	86.2(4)
Cl(1)-W-P(2)	90.3(4)	Cl(1)-W-P(3)	83.3(4)
Cl(1)-W-N(1)	177.5(12)	Cl(2)-W-P(1)	80.7(5)
Cl(2)-W-P(2)	176.2(4)	Cl(2)-W-P(3)	87.8(5)
Cl(2)-W-N(1)	91.6(12)	P(1)-W-N(1)	93.8(12)
P(1)-W-P(2)	98.4(5)	P(1)-W-P(3)	164.9(4)
P(2)-W-P(3)	92.5(5)	P(2)-W-N(1)	92.2(12)
P(3)-W-N(1)	96.3(12)		
<i>(b) In the acylhydrazido(2-) ligand</i>			
N(1)-N(2)	1.37(5)	N(2)-C(7)	1.37(6)
C(7)-O	1.25(8)	C(7)-C(8)	1.54(7)
C(8)-C(41)	1.48(8)	C(8)-C(51)	1.49(6)
W-N(1)-N(2)	167(3)	N(1)-N(2)-C(7)	122(4)
N(2)-C(7)-C(8)	118(5)	O-C(7)-C(8)	118(4)
N(2)-C(7)-O	122(4)	C(7)-C(8)-C(51)	114(5)
C(7)-C(8)-C(41)	112(4)	C(41)-C(8)-C(51)	118(4)

present in this solution, together with a weak resonance at  $g = 1.89$  (Fig. 3(a)). Appearance of the former resonance as a quartet can be interpreted by the substantial delocalization of the unpaired electrons from the W centre towards the three P atoms in  $\text{PMe}_2\text{Ph}$  ligands ( $A_p = 34 \pm 1$  G). This strongly suggests the paramagnetism observed here results mainly from the high spin state of the W centre, which has three W-P bonds intact. Analogous phosphorous hyperfine coupling has also been observed for the EPR resonance of the related molybdenum complexes with phosphine ligands such as  $[\text{Mo}(\text{N}(\text{Ph})\text{N}=\text{NNPh})(\text{CO})_2(\text{PEt}_3)_2]^-$  ( $A_p = 55.6$  G) [10] and  $\text{trans-}[\text{MoCl}(\text{NMe})(\text{dppe})_2]^{2+}$  ( $A_p = 20.0$  G) [11]. The intensity of this signal observed for **2a** decreases with temperature (Fig. 3), as previously reported for the spin-crossover complex  $[\text{Fe}(\text{AMP})_3]^{2+}$  (AMP: 2-(aminomethyl) pyridine) in solution [12]. This feature is consistent with the temperature dependence of the  $\mu_{\text{eff}}$  values described above.

Fig. 2.  $\mu_{\text{eff}}$  ( $\mu_B$ ) vs. temperature (K) curve for complex **2a** in  $\text{CD}_2\text{Cl}_2$  solution.

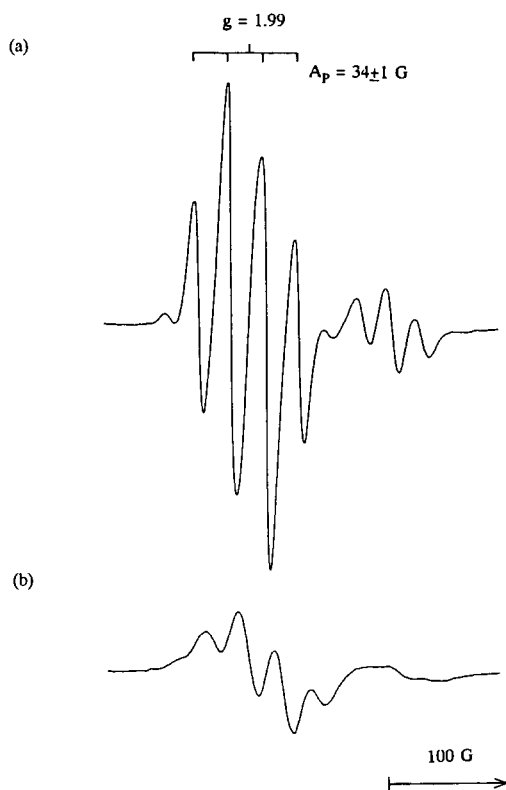
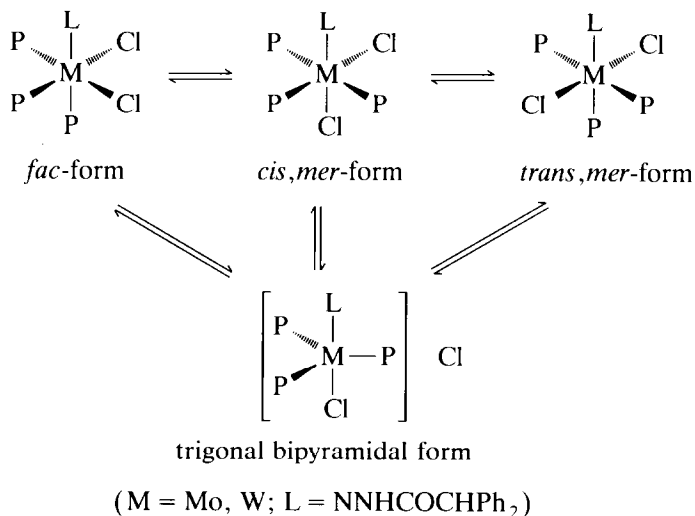


Fig. 3. EPR spectra of complex **2a** in toluene (a) at 299 K, and (b) at 213 K.

Katz and Strous [13] have shown that  $[\text{Fe}(\text{AMP})_3]\text{I}_2$  in the solid state contains two crystallographically independent isomers within the same lattice at room temperature, where one is the high-spin *mer*-isomer and the other is the *fac*-isomer existing as an interconverting mixture of high-spin and low-spin species. They suggested that the spin state is strongly influenced by the complex geometry. Presumably the paramagnetic nature of **2a** in solution state can be explained by the presence of analogous geometric and spin isomerism.

In the case of the Mo complex **2b**, its EPR spectrum in toluene solution also shows the presence of the paramagnetic species. However, as estimated by Evans's method [9] its amount is essentially negligible. Thus the  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of **2b** exhibit sharp resonances. The  $^{31}\text{P}$  NMR spectrum recorded at room temperature consisted of three pairs of one triplet and one doublet in a 1:2 intensity ratio together with a broad singlet (see Experimental), indicating the presence of four isomers. The ratio of these four species are estimated to be 3:1:1:0.3. The  $^1\text{H}$  NMR spectrum recorded at room temperature shows a much more complicated feature in the P-Me region and the assignment of the resonances to these isomers is not successful. On the other hand, the temperature-variable  $^1\text{H}$  NMR study has demonstrated that only one isomer is predominant at low temperatures. Taking the result of the X-ray analysis of **2a** into account, this isomer may be assigned as *cis,mer*- $[\text{MoCl}_2(\text{NNHCOCHPh}_2)(\text{PMe}_2\text{Ph})_3]$  and accordingly *trans*-, *mer*- and

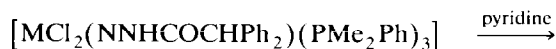
*fac*-isomers as well as the cationic species  $[\text{MoCl}(\text{NNHCOCHPh}_2)(\text{PMe}_2\text{Ph})_3]\text{Cl}$  generated by the dissociation of one Cl ligand presumably correspond to the latter three species observed at higher temperatures. The geometric isomerism observed in the NMR spectra for **2b** also strongly suggests such an isomerism for **2a** in solution, although in the latter case some isomers are present in a high-spin state.



The temperature-dependent spin-state equilibria have attracted much attention in recent years [14] and in particular the study of spin-state equilibrium system in solution [15] is of fundamental importance for the understanding of the role of spin-multiplicity changes in thermal and photochemical electron transfer processes. In this context, the reactivities of **2** are under continuing investigation.

#### *Preparation and characterization of $[\text{MCl}(\text{Py})(\text{NNHCOCHPh}_2)(\text{PMe}_2\text{Ph})_3]\text{Cl}$ (**3**)*

Pyridine reacts readily with complexes **2** at room temperature to afford the cationic acylhydrazido(2-) complexes  $[\text{MCl}(\text{Py})(\text{NNHCOCHPh}_2)(\text{PMe}_2\text{Ph})_3]\text{Cl}$  (**3**), after the displacement of one chloride ligand by pyridine (eq. 3).



(2)



(3)

The perspective view of the cation in **3a** (M = W) determined by the X-ray analysis is shown in Fig. 4. Selected bond distances and angles are given in Table 2. Complexes **3a** also has an octahedral geometry with the acylhydrazido(2-) and chloride ligands in mutually *trans* positions. For **3a**, the hydrogen attached to the terminal nitrogen was unequivocally observed in the final difference Fourier map. The W–N(1)–N(2) linkage is almost linear, while the N(1)–N(2)–H(N2) and N(1)–N(2)–C(7) angles are 124(6) and 121.1(8)°, respectively. The W, N(1), N(2), C(7), O, C(8), and H(N2) atoms lie nearly on the same plane and the observed N(1)–N(2) distance (1.344(11) Å) indicates a bond order larger than unity. These

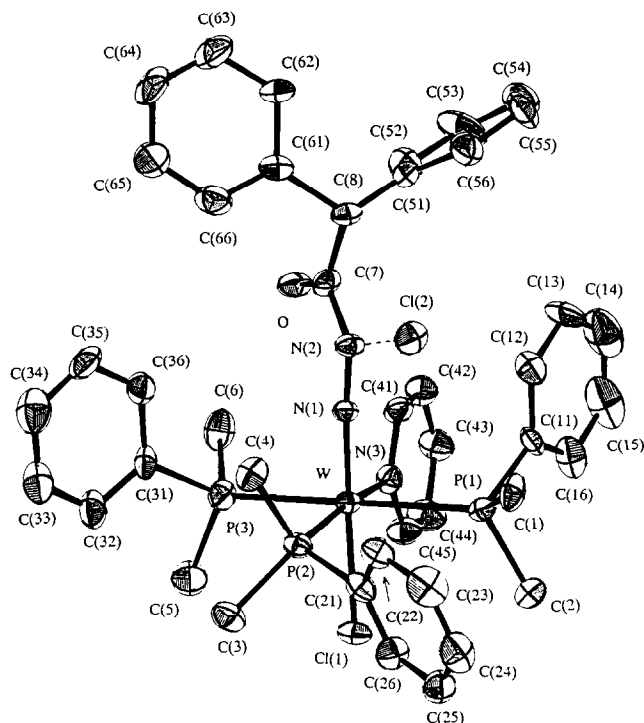
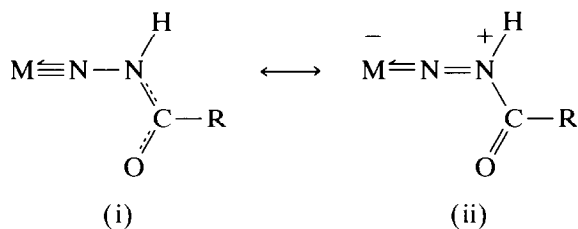


Fig. 4. Perspective view and atom numbering scheme of complex **3a**.

features can be explained by some contribution of the canonical structure (ii) consisting of the  $sp^2$  hybridized N(2) atom towards the structure (i) in the acylhydrazido(2-) ligand [6].



Complexes **3** show a strong band in their IR spectra at  $2500 \text{ cm}^{-1}$  for **3a** ( $\text{M} = \text{W}$ ) and  $2380 \text{ cm}^{-1}$  for **3b** ( $\text{M} = \text{Mo}$ ), respectively, assignable to  $\nu(\text{NH})$ . These unusually low values for  $\nu(\text{NH})$  can be explained by the presence of strong hydrogen bonding between NH proton and the Cl anion, which is confirmed by the X-ray analysis of **3a** ( $\text{H}(\text{N}2) - \text{Cl}(2)$  distance:  $2.00(11) \text{ \AA}$ ). The characteristic strong  $\nu(\text{C}=\text{O})$  band in the acylhydrazido(2-) ligand appears at  $1680 \text{ cm}^{-1}$  for **3a** and  $1685 \text{ cm}^{-1}$  for **3b**, respectively. These values are compatible with those in complex **2** described above and the observed C–O distance ( $1.214(13) \text{ \AA}$ ) in **3a** corresponds well to that of the C–O double bonds ( $1.22 \text{ \AA}$ ).

In contrast to **2**, both complexes **3** are diamagnetic even in solution and their  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra showed that **3** are present in the meridional structure

Table 2

Selected bond lengths (Å) and angles (deg) for complex **3a**

<i>(a) In the coordination sphere of tungsten</i>			
W–N(1)	1.753(8)	W–N(3)	2.237(9)
W–P(1)	2.518(3)	W–P(2)	2.475(3)
W–P(3)	2.522(3)	W–Cl(1)	2.461(3)
P(1)–W–P(2)	97.8(1)	P(1)–W–P(3)	168.4(1)
P(1)–W–Cl(1)	87.4(1)	P(1)–W–N(1)	90.0(3)
P(1)–W–N(3)	84.4(2)	P(2)–W–P(3)	93.2(1)
P(2)–W–Cl(1)	83.2(1)	P(2)–W–N(1)	91.7(3)
P(2)–W–N(3)	171.6(2)	P(3)–W–Cl(1)	90.3(1)
P(3)–W–N(1)	93.4(3)	P(3)–W–N(3)	84.3(2)
Cl(1)–W–N(1)	173.9(3)	Cl(1)–W–N(3)	88.8(2)
N(1)–W–N(3)	96.5(3)		
<i>(b) In the acylhydrazido(2-) ligand and its hydrogen bonds</i>			
N(1)–N(2)	1.344(11)	N(2)–C(7)	1.380(13)
N(2)–H(N2)	1.05(11)	C(7)–O	1.214(13)
C(7)–C(8)	1.512(15)	C(8)–C(51)	1.513(17)
C(8)–C(61)	1.548(15)	H(N2)–Cl(2)	2.00(11)
N(2)–Cl(2)	2.973(9)		
W–N(1)–N(2)	170.5(7)	N(1)–N(2)–H(N2)	124(6)
N(1)–N(2)–C(7)	121.1(8)	N(2)–C(7)–O	122.0(10)
N(2)–C(7)–C(8)	112.3(9)	O–C(7)–C(8)	125.6(9)
C(7)–C(8)–C(51)	110.1(9)	C(7)–C(8)–C(61)	110.5(9)
C(51)–C(8)–C(61)	114.2(9)	Cl(2)–H(N2)–N(2)	152(9)

exclusively, which is disclosed for **3a** in a crystalline form. The large chemical shifts of the NH protons to the low field (14.7 and 15.6 ppm observed for **3a** and **3b**, respectively) are consistent with the presence of the hydrogen bonding described above.

Formation of **3** from **2** is essentially quantitative and addition of excess Py to the  $\text{CD}_2\text{Cl}_2$  solution of **2a** resulted in the rapid change of the broad signals due to **2a** into the sharp resonances attributable to only the diamagnetic **3a** in the  $^1\text{H}$  NMR spectrum. In the case of the Mo complex **2b**, the analogous  $^1\text{H}$  and  $^{31}\text{P}$  NMR study also showed that four geometric isomers observed for **2b** were quantitatively converted into **3b** only.

## Experimental

Unless otherwise noted, all reactions were carried out in freshly distilled dry solvents under a nitrogen atmosphere using standard Schlenk techniques. Complexes **1** [16] and diphenylketene [17] were prepared by literature methods.

### $[\text{WCl}_2(\text{NNHCOCHPh}_2)(\text{PMe}_2\text{Ph})_3] \cdot 0.5\text{CH}_2\text{Cl}_2$ (**2a**)

To a suspension of  $[\text{WCl}_2(\text{NNH}_2)(\text{PMe}_2\text{Ph})_3]$  (500 mg, 0.72 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 ml) was added diphenylketene (155 mg, 0.80 mmol) and the mixture was stirred for 4 h at room temperature, during which time the red-brown suspension changed to a homogeneous purple solution. After addition of hexanes (15 ml), the solution



was filtered, concentrated to ca. 20 ml and then cooled to  $-10^{\circ}\text{C}$ . Purple crystals of the title compound deposited as  $0.5\text{CH}_2\text{Cl}_2$  solvate (447 mg, 67%). Anal. Found: C, 48.68; H, 4.89; N, 2.34; Cl, 11.16.  $\text{C}_{38.5}\text{H}_{46}\text{N}_2\text{OP}_3\text{Cl}_3\text{W}$  calc.: C, 49.40; H, 4.96; N, 2.99; Cl, 11.36%. IR (KBr):  $\nu(\text{C}=\text{O})$   $1680\text{ cm}^{-1}$ .

$[\text{MoCl}_2(\text{NNHCOCHPh}_2)(\text{PMe}_2\text{Ph})_3] \cdot 0.5\text{CH}_2\text{Cl}_2$  (**2b**)

Complex **2b** was prepared from  $[\text{MoCl}_2(\text{NNH}_2)(\text{PMe}_2\text{Ph})_3]$  and diphenylketene in 47% yield as green crystals, following an analogous procedure to that for **2a**. Anal. Found: C, 54.77; H, 5.46; N, 3.25; Cl, 12.16.  $\text{C}_{38.5}\text{H}_{46}\text{N}_2\text{OP}_3\text{Cl}_3\text{Mo}$  calc.: C, 54.52; H, 5.48; N, 3.30; Cl, 12.54%.  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ,  $21^{\circ}\text{C}$ , 400 MHz): *cis,mer*-form;  $\delta$  4.11 (s,  $\text{NNHCOCHPh}_2$ ) 1.74, 1.61 (pt: pseudo triplet,  $\text{PMe}_2\text{Ph}$ ), 1.28 (d,  $J(\text{PH}) = 8.6\text{ Hz}$ ,  $\text{PMe}_2\text{Ph}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $21^{\circ}\text{C}$ , 162 MHz): *cis,mer*-form; 15.35 (tu: triplet for  $\text{P}_{\text{unique}}$ , relative intensity: 3,  $J(\text{PP}') = 17\text{ Hz}$ ), 3.00 (dtr: doublet for  $\text{P}_{\text{trans}}$ , 6). Others: 18.16 (tu, 1,  $J(\text{PP}') = 17\text{ Hz}$ ), 1.56 (dtr, 2); 13.10 (br, tu, 1,  $J(\text{PP}') = 17\text{ Hz}$ ), 2.47 (br, dtr, 2);  $-3.32$  (br, s, 1). IR (KBr):  $\nu(\text{C}=\text{O})$   $1690\text{ cm}^{-1}$ .

$[\text{WCl}(\text{Py})(\text{NNHCOCHPh}_2)(\text{PMe}_2\text{Ph})_3]\text{Cl}$  (**3a**)

Complex **2a** (290 mg, 0.31 mmol) was dissolved in pyridine (15 ml) and the solution stirred for 1 h at room temperature. The resultant red solution was evaporated to dryness in vacuo and the residue was crystallized from  $\text{CH}_2\text{Cl}_2$ /hexanes, yielding the title compound as red crystals (240 mg, 76%). Anal. Found: C, 52.44; H, 5.20; N, 3.97; Cl, 7.41.  $\text{C}_{43}\text{H}_{50}\text{N}_3\text{OP}_3\text{Cl}_2\text{W}$  calc.: C, 53.10; H, 5.19; N, 4.32; Cl, 7.29%.  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.41, 1.44 (t, 6H each,  $J(\text{PH}) = 3.7\text{ Hz}$ ,  $\text{PMe}_2\text{Ph}$ ), 1.80 (d, 6H,  $J(\text{PH}) = 8.6\text{ Hz}$ ,  $\text{PMe}_2\text{Ph}$ ), 5.84 (s, 1H,  $\text{NNHCOCHPh}_2$ ), 14.66 (s, 1H,  $\text{NNHCOCHPh}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$   $-14.60$  (str: singlet for  $\text{P}_{\text{trans}}$ ,  $J(\text{WP}) = 290\text{ Hz}$ ),  $-16.51$  (su: singlet for  $\text{P}_{\text{unique}}$ ,  $J(\text{WP}) = 340\text{ Hz}$ ). IR (KBr):  $\nu(\text{NH})$  2500 (s),  $\nu(\text{C}=\text{O})$  1680 (s)  $\text{cm}^{-1}$ .

$[\text{MoCl}(\text{Py})(\text{NNHCOCHPh}_2)(\text{PMe}_2\text{Ph})_3]\text{Cl}$  (**3b**)

Complex **3b** was prepared from complex **2b** and pyridine in 70% yield as red crystals, following an analogous procedure to that for **3a**. Anal. Found: C, 57.91; H, 5.74; N, 4.52.  $\text{C}_{43}\text{H}_{50}\text{N}_3\text{OP}_3\text{Cl}_2\text{Mo}$  calc.: C, 58.37; H, 5.71; N, 4.75%.  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.29, 1.28 (t, 6H each,  $J(\text{PH}) = 3.8\text{ Hz}$ ,  $\text{PMe}_2\text{Ph}$ ), 1.60 (d, 6H,  $J(\text{PH}) = 8.3\text{ Hz}$ ,  $\text{PMe}_2\text{Ph}$ ), 5.83 (s, 1H,  $\text{NNHCOCHPh}_2$ ), 15.64 (s, 1H,  $\text{NNHCOCHPh}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  2.23 (dtr,  $J(\text{PP}') = 15\text{ Hz}$ ), 11.76 (tu). IR (KBr):  $\nu(\text{NH})$  2380 (s),  $\nu(\text{C}=\text{O})$  1685 (s)  $\text{cm}^{-1}$ .

*Physical measurements*

NMR spectra were measured on a JEOL GX-400 spectrometer and chemical shifts are reported in parts per million referred to  $\text{Me}_4\text{Si}$  for  $^1\text{H}$ , and to external  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$ . IR spectra were recorded on a Shimadzu IR-408 spectrometer by KBr method. EPR spectra were obtained at X-band frequencies on a JEOL JEX-FEIX spectrometer. Magnetic susceptibility of complex **3a** in a solid state was measured by Faraday method using a Shimadzu MB-100 susceptometer, where Pascal constants used for ligand diamagnetism correction were taken from ref. 18. Measurements of magnetism in  $\text{CD}_2\text{Cl}_2$  solution were carried out according to Evans's method [9], using hexamethyldisiloxane as a reference compound. Correc-

tion for the density change of solvent with temperature was included in the calculation [9b].

#### *Collection of the X-ray diffraction data*

$[WCl_2(NNHCOCHPh_2)(PMe_2Ph)_3] \cdot 0.5CH_2Cl_2$  (**2a**). A violet cubic crystal with dimensions  $0.16 \times 0.13 \times 0.10$  mm was sealed in a Pyrex glass capillary and used for data collection. Accurate cell dimensions were determined by least-squares refinement of 14 machine-centred reflections. Intensities were measured with a Rigaku AFC-5 diffractometer using graphite monochromatized Mo- $K_\alpha$  radiation ( $\lambda = 0.71069$ ). Analysis of the systematic absences observed for  $hkl$ , ( $h + k \neq 2n$ ) and  $h0l$ , ( $l \neq 2n$ ), indicated space group to be  $Cc$  or  $C2/c$ . The intensity statistics strongly indicated  $C2/c$ , a choice substantiated by the subsequent solution and refinement of the structure. Three standard reflections were measured every 100 reflections to monitor experimental consistency. For these reflections, there was no observable decay. Lorentz and polarization corrections were applied. An empirical absorption correction was made based on  $\psi$  scans. The details of data collection are given in Table 3.

$[WCl(Py)(NNHCOCHPh_2)(PMe_2Ph)_3]Cl$  (**3a**). A deep red cubic crystal with dimensions  $0.28 \times 0.16 \times 0.16$  mm was sealed in a Pyrex glass capillary and used for data collection. Accurate cell dimensions were determined by least-squares refinement of 20 machine-centred reflections. Intensities were measured with a Rigaku AFC-6A diffractometer using graphite monochromatized Mo- $K_\alpha$  radiation ( $\lambda = 0.71069$ ). Analysis of the systematic absences observed for  $0k0$ , ( $k \neq 2n$ ), and  $h0l$ , ( $h \neq 2n$ ), indicated the space group  $P2_1/a$ . Monitoring three intensity standards after every 100 reflections of exposure showed no decay. Lorentz and polarization corrections and an empirical absorption correction from the crystal shape and size was applied. The details of data collection are given in Table 3.

#### *Structure solution and refinement [19]*

$[WCl_2(NNHCOCHPh_2)(PMe_2Ph)_3] \cdot 0.5CH_2Cl_2$  (**2a**). The position of the tungsten atom was determined by using the direct methods program MULTAN78. Subsequent cycles of difference Fourier synthesis and block-diagonal least squares refinement revealed the positions of all other non-hydrogen atoms. At the final stage, all non hydrogen atoms were refined by using anisotropic thermal parameters, where the hydrogen atoms were not included in the structure refinement. The positions of the solvating  $CH_2Cl_2$  could not be determined in the final Fourier map.

$[WCl(Py)(NNHCOCHPh_2)(PMe_2Ph)_3]Cl$  (**3a**). The structure was solved and refined by the same method as above. Some hydrogen atoms were observed in the final difference Fourier map and the remaining hydrogen atoms were placed at the calculated positions. These hydrogen atoms were refined isotropically.

#### **Acknowledgements**

We thank Mr. Y. Abe (Kanagawa University) for his assistance in X-ray diffraction measurement and Professor Y. Fukuda (Ochanomizu Women's University) for his assistance in magnetic susceptibility measurement. Financial support by the Ministry of Education, Science and Culture, Japan is appreciated.

Table 3

Details of X-ray crystallography for  $[\text{WCl}_2(\text{NNHCOCHPh}_2)_2(\text{PMe}_2\text{Ph})_3] \cdot 0.5\text{CH}_2\text{Cl}_2$  (**2a**) and  $[\text{WCl}(\text{Py})(\text{NNHCOCHPh}_2)_2(\text{PMe}_2\text{Ph})_3]\text{Cl}$  (**3a**)

	<b>2a</b>	<b>3a</b>
<i>(a) Crystal data</i>		
empirical formula	$\text{WCl}_3\text{P}_3\text{ON}_2\text{C}_{38.5}\text{H}_{46}$	$\text{WCl}_2\text{P}_3\text{ON}_3\text{C}_{43}\text{H}_{50}$
formula weight	935.98	972.62
colour	purple	red
crystal system	Monoclinic	Monoclinic
space group	$C2/c$	$P2_1/a$
$a/\text{\AA}$	26.137(7)	21.954(10)
$b/\text{\AA}$	13.154(6)	13.784(7)
$c/\text{\AA}$	25.983(10)	14.835(7)
$\beta/\text{deg}$	113.57(2)	92.74(5)
$V/\text{\AA}^3$	8187.8	4484.3
$Z$	8	4
$d_{\text{calcd}}/\text{g cm}^{-3}$	1.518	1.441
$F(000)$	3752	1960
crystal size mm	$0.16 \times 0.13 \times 0.10$	$0.28 \times 0.16 \times 0.16$
$\mu/\text{cm}^{-1}$	32.26	28.90
<i>(b) Data collection</i>		
diffractometer	Rigaku AFC-5	Rigaku AFC-6A
monochromator	graphite	graphite
scan range/deg	$5.0 < 2\theta < 55.0$	$3.0 < 2\theta < 50.0$
scan method	$\omega$ ( $5.0 < 2\theta < 55.0$ )	$\omega$ ( $3.0 < 2\theta < 30.0$ ), $\omega - 2\theta$ ( $30.0 < 2\theta < 50.0$ )
scan speed/deg min <sup>-1</sup>	8	4
No. of unique data collected	9774	7322
No. of data used ( $F_0 > 5\sigma(F_0)$ )	2134	4903
<i>(c) Solution and refinement</i>		
No. of parameters refined	410	679
$R; R_w^a$	0.093, 0.114	0.043, 0.051
Max residual peak/e $\text{\AA}^{-3}$	1.97 (around W)	0.96 (around W)

<sup>a</sup>  $R = \sum (|F_o| - |F_c|) / \sum |F_o|$ ;  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ , where  $w = 1/\sigma^2(F_o)$ .

## References

- 1 H. Miyagi, Y. Ishii, T. Aoshima, Y. Mizobe and M. Hidai, *Chem. Lett.*, (1991) 611.
- 2 Recent reviews: (a) M. Hidai, in T.G. Spiro (Ed.), *Molybdenum Enzyme*, John Wiley and Sons, New York, (1985) p 285. (b) M. Hidai and Y. Mizobe, in P.S. Braterman (Ed.), *Reactions of Coordinated Ligands*, Plenum Press, New York, Vol. 2 (1989) p 53. (c) R. Henderson, G.J. Leigh and C.J. Pickett, *Adv. Inorg. Chem. Radiochem.*, 27 (1983) 197. (d) J.R. Dilworth and R.L. Richards, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Pergamon, Oxford, Vol. 8 (1982) p 1073. (e) H.M. Colquhoun, *Acc. Chem. Res.*, 17 (1984) 23.
- 3 (a) J. Chatt, R.A. Head, G.J. Leigh and C.J. Pickett, *J. Chem. Soc., Dalton Trans.*, (1978) 1638. (b) J. Chatt, A.A. Diamantis, G.A. Heath, N.E. Hooper and J. Leigh, *ibid.*, (1977) 688. (c) R. Ben-Shoshan, J. Chatt, G.J. Leigh and W. Hussain, *ibid.*, (1980) 771.
- 4 T.A. George and R.A. Kovar, *Inorg. Chem.*, 20 (1981) 285.
- 5 (a) M. Hidai, Y. Mizobe, M. Sato, T. Kodama and Y. Uchida, *J. Am. Chem. Soc.*, 100 (1978) 5740. (b) Y. Mizobe, Y. Uchida and M. Hidai, *Bull. Chem. Soc. Jpn.*, 53 (1980) 1781. (c) P.C. Bevan, J. Chatt, M. Hidai and G.J. Leigh, *J. Organomet. Chem.*, 160 (1978) 165.

- 6 K. Iwanami, Y. Mizobe, T. Takahashi, T. Kodama, Y. Uchida and M. Hidai, *Bull. Chem. Soc. Jpn.*, 54 (1981) 1773.
- 7 (a) T. Tatsumi, M. Hidai and Y. Uchida, *Inorg. Chem.*, 14 (1975) 2530. (b) M. Sato, T. Kodama, M. Hidai and Y. Uchida, *J. Organomet. Chem.*, 152 (1978) 239. (c) J. Chatt, A.A. Diamantis, G.A. Heath, N.E. Hooper and G.J. Leigh, *J. Chem. Soc., Dalton Trans.*, (1977) 688. (d) H.M. Colquhoun, *Transition Met. Chem.*, 6 (1981) 57.
- 8 (a) F.C. March, R. Mason and M. Thomas, *J. Organomet. Chem.*, 96 (1975) C43. (b) V.W. Day, T.A. George, S.D. Allen Iske and S.D. Wagner, *J. Organomet. Chem.*, 112 (1976) C55.
- 9 (a) D.F. Evans, *J. Chem. Soc.*, (1959) 2003. (b) D. Ostfield and I.A. Cohen, *J. Chem. Educ.*, 49 (1972) 829.
- 10 S.W. Lee and W.C. Trogler, *Organometallics*, 9 (1990) 1470.
- 11 D.L. Hughes, D.J. Lowe, M.Y. Mohammed, C.J. Pickett and N.M. Pinhal, *J. Chem. Soc., Dalton Trans.*, (1990) 2021.
- 12 H.L. Chum, J.A. Vanin and M.I.D. Holanda, *Inorg. Chem.*, 21 (1982) 1146.
- 13 B.A. Katz and C.E. Strouse, *Inorg. Chem.*, 19 (1980) 658.
- 14 Recent reviews: (a) P. Gutlich, *Struct. Bond.*, 44 (1981) 83. (b) E. König, G. Ritter and S.K. Kulshrestha, *Chem. Rev.*, 85 (1985) 219. (c) J.K. Beattie, *Adv. Inorg. Chem.*, 32 (1988) 2.
- 15 For example: (a) L.L. Martin, K.S. Hagen and A.M. Sargeson, *J. Chem. Soc., Chem. Commun.*, 19 (1988) 1313. (b) M.A. Hoselton, L.J. Wilson and R.S. Drago, *J. Am. Chem. Soc.*, 97 (1975) 1722. (c) H.L. Chum, J.A. Vanin and M.I.D. Holanda, *Inorg. Chem.*, 21 (1982) 1146. (d) J.P. Jesson, S. Trofimenko and D.R. Eaton, *J. Am. Chem. Soc.*, 89 (1967) 3158. (e) L.J. Wilson, D. Georges and M.A. Hoselton, *Inorg. Chem.*, 14 (1975) 2968. (f) K.A. Reeder, E.V. Dose and L.J. Wilson, *Inorg. Chem.*, 17 (1978) 1071.
- 16 J. Chatt, A.J. Pearman and R.L. Richards, *J. Chem. Soc., Dalton Trans.*, (1978) 1766.
- 17 L.L. Smith and H.H. Hehn, *Org. Synth. Coll. Vol. III*, (1955) 356.
- 18 B. Figgis and J. Lewis, in J. Lewis and R.G. Wilkins (Eds.), *Modern Coordination Chemistry*, Interscience, New York, (1960) p 403.
- 19 T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res.*, 55 (1979) 69.