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Condensation of triketones with tungsten hydrazido(2-) complexes derived from a dinitrogen complex: formation of mononuclear or dinuclear diazoalkane complexes[☆,1]

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Abstract

The tungsten hydrazido(2-) complex *cis,mer*-$[WCl_2(NNH_2)(PMe_2Ph)_3]$, readily derived from a dinitrogen complex *cis*-$[W(N_2)_2(PMe_2Ph)_4]$, reacted with 1,3,5-triketones $RCOCH_2COCH_2COPh$ (R = Me, Ph) to give the diazoalkane complexes *cis,mer*-$[WCl_2(NN{=}CRCH_2COCH_2COPh)(PMe_2Ph)_3]$ (R = Me (**3**), Ph) via the condensation between the hydrazido(2-) ligand and one terminal carbonyl group in the triketone. By contrast, the reaction of the hydrazido(2-) complex *cis,trans*-$[WCl_2(NNH_2)(CO)(PMe_2Ph)_2]$ with $PhCOCH_2COCH_2COPh$ resulted in the formation of a dinuclear μ-bis(diazoalkane) complex $[WCl_2(CO)(PMe_2Ph)_2(NN{=}CPhCH_2COCH_2CPh{=}NN)WCl_2(CO)(PMe_2Ph)_2]$ (**5**). The structures of **3** and **5** in the solid state have been determined unequivocally by X-ray analysis. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Diazoalkane complex; Tungsten complex; Nitrogen fixation; X-ray structure

1. Introduction

Direct conversion of molecular nitrogen into organonitrogen compounds under mild conditions has been recognized as one of the most challenging topics in organic synthesis. The reactivity of the N_2 molecule coordinated to transition metals has been studied extensively in this context [1,2]. However, well characterized N_2 complexes which undergo the C–N bond forming reactions are still rare. In this regard, Mo and W complexes of the type $[M(N_2)_2(L)_4]$ (L = *t*-phosphine) are noteworthy, since the N_2 ligand in these complexes, e.g. *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (**1a**; M = Mo, W) and *trans*-$[M(N_2)_2(dppe)_2]$ (**1b**; M = Mo, W; dppe = $Ph_2PCH_2CH_2PPh_2$), exhibits exceptionally high reactivities and various intriguing reactions have been demonstrated to give organo-nitrogen ligands and compounds [3]. One of the most versatile reactions leading to the C–N bond generation appears to be the formation of the diazoalkane complexes *cis,mer*-$[MX_2(N\text{-}N{=}CRR')(PMe_2Ph)_3]$ (Scheme 1) and *trans*-$[MF(NN{=}CRR')(dppe)_2][BF_4]$ (X = Cl, Br, I) [4] by the condensation of a series of aldehydes and ketones $RR'C{=}O$ with the hydrazido(2-) complexes *cis,mer*-$[MX_2(NNH_2)(PMe_2Ph)_3]$ and *trans*-$[MF(NNH_2)(dppe)_2][BF_4]$, which are readily available by protonation of the N_2 complexes **1** with inorganic acids.

The reactions of these hydrazido(2-) complexes with acetylacetone give rise to the formation of the diazoalkane complexes *cis,mer*-$[MX_2(NN{=}CMeCH_2COMe)(PMe_2Ph)_3]$ (M = Mo, X = Cl [4b]; M = W, X = Br [4a]; M = W, X = Cl [5]) and *trans*-

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[☆] Dedicated to the memory of the late Professor Rakuro Okawara.

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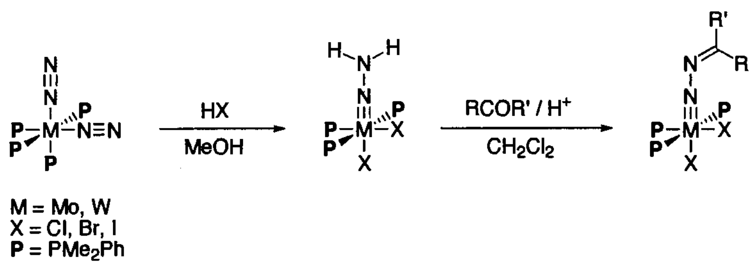
[1] Preparation and properties of molybdenum and tungsten dinitrogen complexes. Part 57. For Part 56: see Ref. [1].

PII: S0022-328X(98)00976-0



Scheme 1.

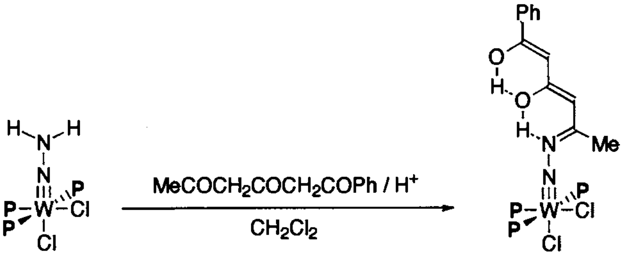
$[\mathrm{MF(NN{=}CMeCH_2COMe)(dppe)_2}][\mathrm{BF_4}]$ (M = Mo, W) [4c] by the condensation between the hydrazido(2-) ligand and only one carbonyl group of acetylacetone. X-ray diffraction studies as well as the spectroscopic data have disclosed that the latter dppe complexes exist as the keto form both in a solid state and in solution, whereas the presence of an equilibrium between the keto- and enol-diazoalkane forms has been inferred for the former $\mathrm{PMe_2Ph}$ complexes in solution from their ^{1}H-NMR spectra [4a,b][2]. A detailed study on the diazoalkane complexes derived from a range of 1,3-diketones is now in progress and the results will be reported elsewhere in due course [6].

This condensation method has now been extended to the reactions of the hydrazido(2-) complexes $[\mathrm{WCl_2(NNH_2)(L)(PMe_2Ph)_2}]$ (L = $\mathrm{PMe_2Ph}$ (**2a**), CO (**2b**)) with 1,3,5-triketones. We have found that the condensation takes place at one or two terminal carbonyl groups of the triketones to give mononuclear or dinuclear diazoalkane complexes, where the structure of the products depends upon the nature of the triketone substituent and the ligand L in **2**.

2. Results and discussion

2.1. Condensation of **2a** with $\mathrm{MeCOCH_2COCH_2COPh}$

The hydrazido(2-) complex **2a** reacted with three equivalents of the triketone $\mathrm{MeCOCH_2COCH_2COPh}$ in $\mathrm{CH_2Cl_2}$ at room temperature (r.t.) in the presence of a catalytic amount of aqueous HCl to give the diazoalkane complex *cis,mer*-$[\mathrm{WCl_2(NN{=}CMeCH_2COCH_2COPh)(PMe_2Ph)_3}]$ (**3**) in moderate yield (Reaction (1)). The condensation occurred only at the terminal acetyl group of the triketone. This regioselectivity presumably arises from the steric effect exerted by both the $\mathrm{PMe_2Ph}$ ligands and the chloride cis to the hydrazido(2-) ligand. Similar steric effects were previously observed in the case of monoketones. Thus, **2a** reacts with MeCOPh to give *cis,mer*-$[\mathrm{WCl_2(NN{=}CMePh)(PMe_2Ph)_3}]$ but not with more sterically encumbered PhCOPh under the same conditions [4a], whereas even the latter ketone readily reacts with the less hindered hydrazido(2-) ligand in **2b** [7].



2a **3**

(1)

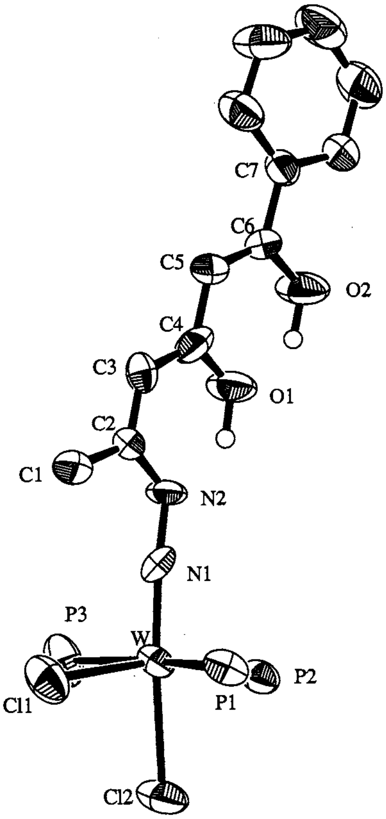


Fig. 1. Molecular structure of **3**. Carbon atoms in the $\mathrm{PMe_2Ph}$ ligands and all hydrogen atoms except for those interacting with the oxygen atoms are omitted for clarity.

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[2] In the text of this paper, the formula of triketones and the diazoalkane ligands are uniformly described in the keto form as a matter of convenience.

Table 1
Selected bond lengths (Å) and bond angles (°) for **3**

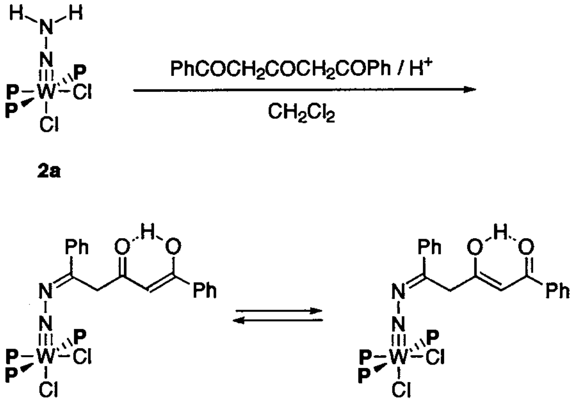
Bond lengths (Å)			
W–Cl(1)	2.478(4)	O(2)–C(6)	1.31(2)
W–Cl(2)	2.499(4)	N(1)–N(2)	1.33(1)
W–P(1)	2.517(4)	N(2)–C(2)	1.32(2)
W–P(2)	2.464(4)	C(2)–C(3)	1.34(2)
W–P(3)	2.508(4)	C(3)–C(4)	1.42(2)
W–N(1)	1.79(1)	C(4)–C(5)	1.44(2)
O(1)–C(4)	1.28(2)	C(5)–C(6)	1.39(2)
Bond angles (°)			
Cl(1)–W–Cl(2)	86.6(1)	P(2)–W–N(1)	94.1(4)
Cl(1)–W–P(1)	84.6(1)	P(3)–W–N(1)	89.5(3)
Cl(1)–W–P(2)	165.5(1)	W–N(1)–N(2)	172.8(9)
Cl(1)–W–P(3)	82.4(1)	N(1)–N(2)–C(2)	122(1)
Cl(1)–W–N(1)	100.3(4)	N(2)–C(2)–C(1)	119(1)
Cl(2)–W–P(1)	89.2(1)	N(2)–C(2)–C(3)	120(1)
Cl(2)–W–P(2)	79.0(1)	C(1)–C(2)–C(3)	121(1)
Cl(2)–W–P(3)	89.5(1)	C(2)–C(3)–C(4)	125(1)
Cl(2)–W–N(1)	172.8(3)	O(1)–C(4)–C(3)	121(1)
P(1)–W–P(2)	95.8(1)	O(1)–C(4)–C(5)	115(1)
P(1)–W–P(3)	167.0(1)	C(3)–C(4)–C(5)	124(1)
P(1)–W–N(1)	93.4(3)	C(4)–C(5)–C(6)	122(1)
P(2)–W–P(3)	96.7(1)	O(2)–C(6)–C(5)	123(1)
O(2)–C(6)–C(7)	113(1)	C(5)–C(6)–C(7)	124(1)

The detailed structure of **3** has been clarified by the X-ray analysis. The ORTEP drawing is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. The diazoalkane ligand occupies the site *trans* to one Cl ligand in the slightly distorted octahedron with the essentially linear W–N–N linkage (172.8(9)°) and the bent N–N–C array (122(1)°). These bond angles as well as the W–N and N–N bond distances (1.79(1) and 1.33(1) Å) are comparable to those in the other related diazoalkane complexes [7,8]. All the non-hydrogen atoms in this ligand and the W atom lie nearly on the same plane. Thus, the W, two O, two N, and C(1)–C(6) atoms are almost coplanar within 0.13(1) Å and the dihedral angle between this plane and the phenyl ring attached to the C(6) atom is only 7.1°. The bond order is estimated to be between one and two for all of the four C–C bonds in the C(2)–C(6) chain and also for one N–C and two C–O bonds, while the C–C–C angles around the C(3) and C(5) atoms are 125(1) and 122(1)°, respectively. These bonding parameters observed for the diazoalkane ligand in **3** may be interpreted as a mixture of the three tautomers shown in Scheme 2, viz. the diazoalkane form **3-i** in which an enol proton is hydrogen-bonded to the terminal N atom and the two alkenylhydrazido(2-) forms, **3-ii** and **3-iii**. Appearance of the broad and intense IR band centered at 1584 cm^{-1} (KBr method) is diagnostic of the highly conjugated nature of the diazoalkane ligand.

The ^{1}H-NMR spectrum of **3** has shown that two kinds of species exist in solution in a 2:1 ratio. The signals of the major component are consistent with a mixture of the three structures manifested by the X-ray analysis where the rapid interchange between the three tautomers **3-i–iii** is presumably occurring. With respect to the two low-field signals at δ 16.45 and 11.98, the former more deshielded resonance has been assigned to the proton interacting with the two O atoms and the latter to that bridging the O and N atoms. On the other hand, the remaining signals arising from the minor component is diagnostic of the structure containing only one hydrogen bonding owing to the appearance of the characteristic methylene resonance at δ 2.53 (Fig. 2). The structure of this minor species may be described by a mixture of two diazoalkane forms **3-iv** and **3-v** in Scheme 3. The presence of a weak band at 1624 cm^{-1} in addition to a strong band at 1584 cm^{-1} in the IR spectrum (KBr method) probably implicates the presence of this minor species in a small amount even in the solid state. Instead, it might be possible to assign this component to the species represented by the structures **3-vi** and **3-vii**. However, this seems unlikely because the chemical shift of 16.52 ppm observed for this hydrogen-bonded proton is rather comparable to that of the proton interacting with two O atoms and much lower than that of the proton attached to one O and one N atoms. As for the compounds obtained from the 1:1 condensation of a 1,3-diketone with a monoamine, the ^{1}H-NMR study showed the preferential existence of the keto-amine form over the other two tautomeric forms (Scheme 4) [9].

2.2. Condensation of **2a** with $PhCOCH_2COCH_2COPh$

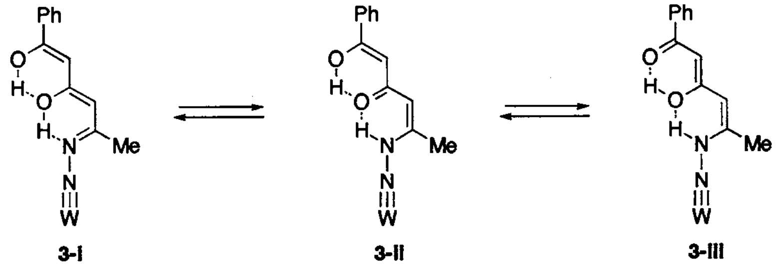
The reaction of **2a** with the triketone $PhCOCH_2COCH_2COPh$ also afforded the diazoalkane complex *cis,mer*-[$WCl_2(NN{=}CPhCH_2COCH_2COPh)(PMe_2Ph)_3$] (**4**) (Reaction (2)). However, because of a steric effect (vide supra), the present reaction proceeded more slowly than that with $MeCOCH_2COCH_2COPh$ and a longer reaction time was required to obtain **4**.



2a

4 (2)

Due to the poor quality of the diffraction data, refinements of the X-ray structure of **4** to the satisfac-

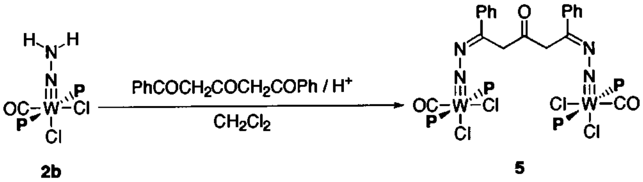


Scheme 2.

tory level were not successful. Nevertheless, the preliminary result has unambiguously shown the atom connecting scheme for **4** illustrated in Reaction (2), indicating that **2a** condensed with only one terminal carbonyl group of the triketone. The spectral data of **4** are consistent with this structure. Thus, the ^{1}H-NMR spectrum exhibits the resonances due to only one species, which shows the signals assignable to the methylene, methine, and hydrogen-bonded OH protons at δ 3.88, 6.82, and 16.24, respectively. The strong IR bands at 1597 and 1568 cm^{-1} are diagnostic of the hydrogen-bonded $PhCOCH_2CO$ moiety and the C–N double bond, respectively, in the diazoalkane ligand. The absence of the alkenylhydrazido(2-) form, which is favored in the case of **3**, may be explained by the difference in the orientation of the $PhCOCH_2COCH_2$ group between **3** and **4**. Thus, because of the steric effect, the Ph group attached to the C atom in the C=N bond in **4** is presumably capable of occupying only the *exo* position, i.e. the *syn* site with respect to the lone pair of the terminal N atom, and this prohibits the occurrence of the hydrogen-bonding interaction between the N atom and the $PhCOCH_2COCH_2$ moiety.

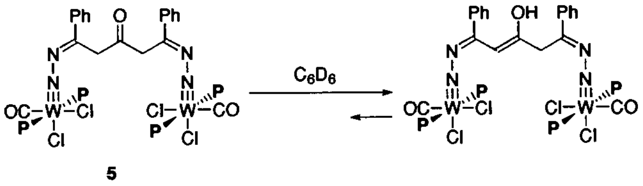
2.3. Condensation of **2b** with $PhCOCH_2COCH_2COPh$

In contrast to the above reactions forming **3** and **4**, treatment of the hydrazido(2-) complex *cis,trans*-$[WCl_2(NNH_2)(CO)(PMe_2Ph)_2]$ (**2b**) with $PhCOCH_2COCH_2COPh$ in the presence of a catalytic amount of aqueous HCl resulted in the condensation of both of the two terminal carbonyl groups in the triketone to give a dinuclear μ-bis(diazoalkane) complex $[WCl_2(CO)(PMe_2Ph)_2(NN{=}CPhCH_2COCH_2CPh{=}NN)WCl_2(CO)(PMe_2Ph)_2]$ (**5**) (Reaction (3)).



(3)

The X-ray analysis has been undertaken to clarify the detailed structure of **5**. The ORTEP drawing is depicted in Fig. 3 and the pertinent bonding parameters are summarized in Table 2. As shown in Fig. 3, **5** has a dinuclear structure in which two *cis,trans*-$WCl_2(CO)(PMe_2Ph)_2$ units are connected by the μ-$NN{=}CPhCH_2COCH_2CPh{=}CNN$ ligand[3]. The molecule in the crystal has a C_2 symmetry around the rotation axis which coincides with the C(3)–O(1) bond. In the bridging bis(diazoalkane) ligand, the phenyl group binds to the C=N bond at the *syn* position with respect to the lone pair of the N(2) atom as observed in **4**. The C(1)–C(2) and C(2)–C(3) bond lengths of 1.500(8) and 1.521(8) Å, respectively, are not exceptional as the C–C single bond distance, while the N(2)–C(1) and C(3)–O(1) lengths of 1.305(7) and 1.17(1) Å both fall in the range of the double bond distances. These bond lengths, as well as the bond angles relating to this moiety, are consistent with the keto-diazoalkane structure and, as expected, the IR spectrum recorded by the KBr method shows the characteristic ν(C=O) and ν(C=N) bands at 1684 and 1568 cm^{-1}, respectively. Interestingly, the ^{1}H-NMR spectrum indicates that **5** takes the enol form exclusively in a benzene solution (Reaction (4)).



(4)

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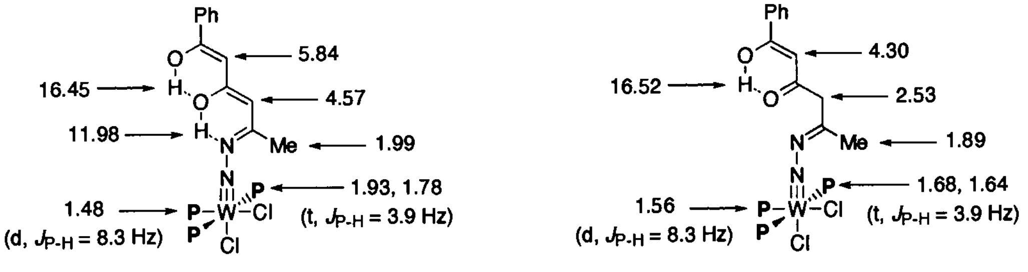
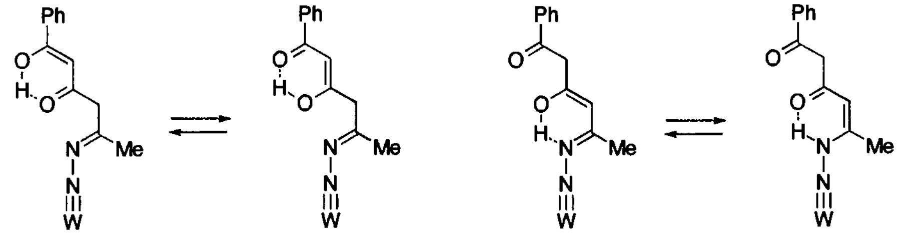
[3] The X-ray structure of the related ditungsten μ-bis(diazoalkane) complex $[(dppe)_2WF(NN{=}CHCHMeCHMeCH{=}NN)WF(dppe)_2]$ has appeared recently: Y. Ishii, H. Miyagi, S. Jitsukuni, H. Seino, B.S. Harkness, M. Hidai, J. Am. Chem. Soc. 114 (1992) 9890.



3-i – 3-iii **3-iv, 3-v**

Fig. 2. Assignment of the ^{1}H-NMR signals for **3**. Only one structure is shown for each component.

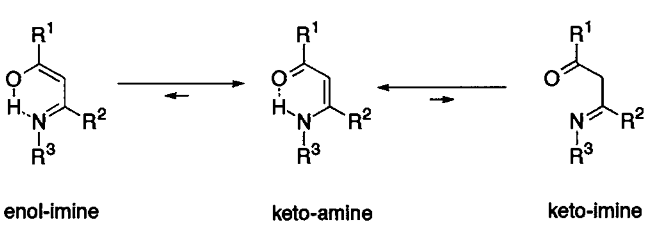


3-iv **3-v** **3-vi** **3-vii**

Scheme 3.

3. Experimental

All manipulations were performed under an atmosphere of N_2 using standard Schlenk techniques. Solvents were dried and distilled by common procedures, and degassed before use. The hydrazido(2-) complexes **2a** [10] and **2b** [7] were prepared by the modified literature methods, while the triketones RCOCH$_2$COCH$_2$COPh (R = Me, Ph) were synthesized according to the published procedures [11]. IR spectra were recorded on a Shimadzu FTIR-8100M spectrometer, and NMR spectra were obtained by a JEOL JNM-EX-270 spectrometer. For the ^{1}H-NMR data shown below, the resonances due to the aromatic protons are omitted. Elemental analysis was carried out using a Perkin-Elmer 2400 series II CHN analyzer. Amounts of the solvated molecules in the crystals were determined by the ^{1}H-NMR spectroscopy and confirmed by elemental analysis.



Scheme 4.

3.1. Preparation of *cis,mer*-[WCl$_2$(NN=CMeCH$_2$COCH$_2$COPh)(PMe$_2$Ph)$_3$] (3)

To a suspension of **2a** (142 mg, 0.200 mmol) in CH$_2$Cl$_2$ (7 cm^3) was added three equivalents of MeCOCH$_2$COCH$_2$COPh (123 mg, 0.600 mmol) and the mixture was stirred at r.t. in the presence of a catalytic amount of aqueous HCl. The initial orange color rapidly changed to yellow in ca. 10 min. The resultant solution was dried up and the residue was washed with ether and hexane successively to remove excess triketone. A yellow solid remained was redissolved in CH$_2$Cl$_2$ and hexane was layered on it. Brown crystals of **2** deposited, which were filtered off, washed with hexane, and then dried in vacuo (123 mg, 70%). Found: C, 48.49; H, 5.09; N, 2.90%. Calc. for $C_{36}H_{45}O_2N_2P_3Cl_2W$: C, 48.83; H, 5.12; N, 3.16%. IR (KBr): ν(C=O), 1624, 1584 cm^{-1}; ν(C=N), 1561 cm^{-1}. For ^{1}H-NMR data, see Fig. 2.

3.2. Preparation of *cis,mer*-[WCl$_2$(NN=CPhCH$_2$COCH$_2$COPh)(PMe$_2$Ph)$_3$] (4)

Complex **4** was obtained from **2a** and PhCOCH$_2$COCH$_2$COPh in the similar way to that for preparing **3** except that the reaction was carried out in the presence of one equivalent of aqueous HCl for 5 h. Color: brown. Yield: 70%. Found: C, 52.08; H, 5.08; N, 2.85%. Calc. for $C_{41}H_{47}O_2N_2P_3Cl_2W$: C, 51.97; H, 5.00; N, 2.96%. IR (KBr): ν(C=O), 1597 cm^{-1}; ν(C=N), 1568

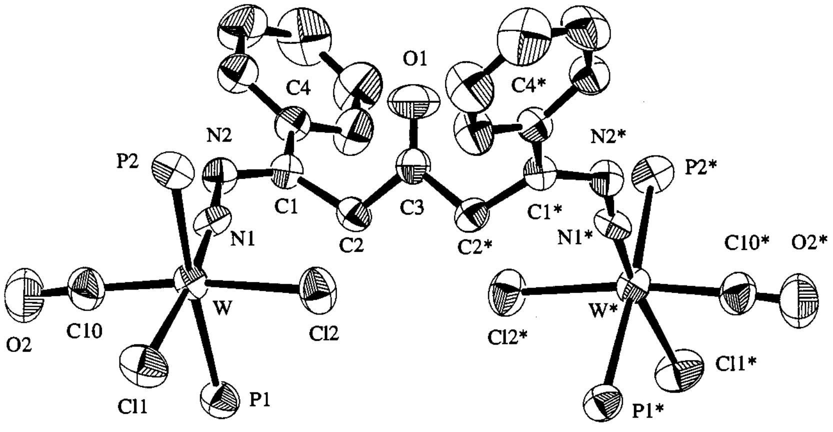


Fig. 3. Molecular structure of **5**. Carbon atoms in the PMe_2Ph Ligands and all hydrogen atoms are omitted for clarity.

cm^{-1}. ^1H-NMR (C_6D_6): δ 16.24 (br, 1H, OH), 6.82 (s, 1H, C=CH), 3.88 (s, 2H, CH_2CO), 1.89 and 1.64 (t, 6H each, $J_{P-H} = 3.9$ Hz, PMe), 1.56 (d, 6H, $J_{P-H} = 8.8$ Hz, PMe).

3.3. Preparation of [$WCl_2(CO)(PMe_2Ph)_2(NN{=}CPh\text{-}CH_2COCH_2CPh{=}NN)WCl_2(CO)(PMe_2Ph)_2$] (5)

To a green solution of **2b** (213 mg, 0.362 mmol) in CH_2Cl_2 (6 cm^3) was added $PhCOCH_2COCH_2COPh$ (106 mg, 0.398 mmol) and the mixture was stirred at r.t. for 5 h in the presence of a catalytic amount of aqueous HCl. The resultant yellow solution was dried up and the residue was washed with hexane. Recrystallization of the remaining solid from CH_2Cl_2–hexane gave **5** as brown crystals, which were filtered off, washed with hexane, and then dried in vacuo (235 mg, 93%). Found: C, 40.41; H, 4.01; N, 3.29%. Calc. for $C_{51}H_{58}O_3N_4P_4Cl_4W_2\cdot 2CH_2Cl_2$: C, 40.33; H, 3.96; N, 3.55%. IR (KBr): ν(CO), 1946 cm^{-1}; ν(C=O), 1684 cm^{-1}; ν(C=N), 1568 cm^{-1}. ^1H-NMR (C_6D_6): δ 16.20 (br, 1H, OH), 6.72 (s, 1H, C=CH), 3.29 (s, 2H, CH_2CO), 1.89, 1.86, 1.84, and 1.80 (t, 6H each, $J_{P-H} =$ 3.9 Hz, PMe).

Table 2
Selected bond lengths (Å) and bond angles (°) for **5**

Bond lengths (Å)			
W–Cl(1)	2.437(2)	O(1)–C(3)	1.17(1)
W–Cl(2)	2.491(2)	O(2)–C(10)	1.172(7)
W–P(1)	2.527(2)	N(1)–N(2)	1.331(6)
W–P(2)	2.529(2)	N(2)–C(1)	1.305(7)
W–N(1)	1.763(5)	C(1)–C(2)	1.500(8)
W–C(10)	1.943(7)	C(2)–C(3)	1.521(8)
Bond angles (°)			
Cl(1)–W–Cl(2)	88.09(7)	P(2)–W–N(1)	91.0(2)
Cl(1)–W–P(1)	85.02(7)	P(2)–W–C(10)	96.2(2)
Cl(1)–W–P(2)	90.33(6)	N(1)–W–C(10)	91.1(3)
Cl(1)–W–N(1)	172.0(2)	W–N(1)–N(2)	173.0(5)
Cl(1)–W–C(10)	80.9(2)	N(1)–N(2)–C(1)	117.8(5)
Cl(2)–W–P(1)	88.89(7)	N(2)–C(1)–C(2)	123.4(6)
Cl(2)–W–P(2)	84.34(7)	N(2)–C(1)–C(4)	116.7(6)
Cl(2)–W–N(1)	99.9(2)	C(2)–C(1)–C(4)	119.9(6)
Cl(2)–W–C(10)	168.9(2)	C(1)–C(2)–C(3)	114.7(6)
P(1)–W–P(2)	171.91(6)	O(1)–C(3)–C(2)	124.4(4)
P(1)–W–N(1)	94.5(2)	C(2)–C(3)–C(2)*	111.2(9)
P(1)–W–C(10)	89.6(2)	W–C(10)–O(2)	174.4(7)

Table 3
X-ray crystallographic data for **3** and **5**

	3	**5**
Empirical formula	$C_{36}H_{45}N_2O_2Cl_2P_3W$	$C_{51}H_{58}N_4O_3Cl_4P_2W_2$
Formula weight	885.44	1408.45
Crystal color	Brown	Yellow
Crystal dimensions (mm)	0.3 × 0.3 × 1.0	0.7 × 0.6 × 0.4
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c* (no. 15)	*C2/c* (no. 15)
a (Å)	35.611(3)	24.631(2)
b (Å)	11.544(2)	9.355(2)
c (Å)	20.576(3)	24.631(2)
β (°)	109.269(9)	93.785(5)
V (Å^3)	7984(1)	5662(1)
Z	8	4
$D_{calc.}$ (g cm^{-3})	1.473	1.652
μ(Mo–K_α) (cm^{-1})	31.83	44.09
F(000)	3552	2768
Radiation (Å)	Mo–K_α (λ = 0.7107)	Mo–K_α (λ = 0.7107)
Monochromator	Graphite	Graphite
Temperature	Room temperature	Room temperature
Scan method	$\omega/2\theta$	$\omega/2\theta$
Scan rate (° min^{-1})	16	16
$2\theta_{max}$ (°)	55	55
No. of unique reflections	9626	6903
Transmission factors	0.8241–0.9997	0.8178–0.9975
No. of data used ($I > 3\sigma(I)$)	4701	4739
No. of variables	394	308
R, R_w	0.063, 0.053	0.038, 0.030
Max residual (e Å^{-3})	1.91	1.48

Table 4
Atomic coordinates and equivalent temperature factors for non-hydrogen atoms in **3**

Atom	x	y	z	B_{eq}
W	0.17001(2)	0.15973(5)	−0.20716(3)	3.53(1)
Cl(1)	0.2277(1)	0.2670(3)	−0.2191(2)	5.9(1)
Cl(2)	0.1711(1)	0.3021(3)	−0.1150(2)	6.0(1)
P(1)	0.2219(1)	0.0418(3)	−0.1192(2)	4.4(1)
P(2)	0.1134(1)	0.0915(3)	−0.1738(2)	4.0(1)
P(3)	0.1317(1)	0.3025(3)	−0.2963(3)	5.8(1)
O(1)	0.1078(3)	−0.1964(7)	−0.3844(5)	6.3(3)
O(2)	0.0666(3)	−0.3675(8)	−0.4358(5)	6.9(3)
N(1)	0.1631(3)	0.0533(9)	−0.2732(5)	3.4(3)
N(2)	0.1538(3)	−0.0298(8)	−0.3208(5)	3.8(3)
C(1)	0.2116(4)	0.014(1)	−0.3498(6)	4.5(4)
C(2)	0.1767(4)	−0.055(1)	−0.3577(6)	3.2(3)
C(3)	0.1671(4)	−0.143(1)	−0.4027(6)	3.8(3)
C(4)	0.1329(4)	−0.215(1)	−0.4153(6)	4.5(4)
C(5)	0.1247(4)	−0.313(1)	−0.4605(6)	3.8(4)
C(6)	0.0918(4)	−0.385(1)	−0.4689(6)	4.1(4)
C(7)	0.0826(4)	−0.488(1)	−0.5132(7)	3.9(4)
C(8)	0.1045(4)	−0.514(1)	−0.5577(8)	5.5(5)
C(9)	0.0960(5)	−0.612(1)	−0.5959(8)	7.0(5)
C(10)	0.0646(5)	−0.681(1)	−0.5942(9)	7.2(5)
C(11)	0.0420(4)	−0.650(1)	−0.5510(8)	6.4(5)
C(12)	0.0503(4)	−0.556(1)	−0.5117(7)	4.9(4)
C(13)	0.2356(5)	0.089(1)	−0.0313(7)	7.4(5)
C(14)	0.2703(4)	0.038(1)	−0.1286(8)	6.8(5)
C(15)	0.2120(4)	−0.112(1)	−0.1144(7)	4.3(4)
C(16)	0.2054(4)	−0.165(2)	−0.0588(8)	5.8(4)
C(17)	0.1976(5)	−0.285(2)	−0.060(1)	6.9(5)
C(18)	0.1964(5)	−0.348(2)	−0.116(1)	7.7(6)
C(19)	0.2043(5)	−0.296(1)	−0.170(1)	7.1(5)
C(20)	0.2114(4)	−0.181(1)	−0.1716(8)	4.9(4)
C(21)	0.1228(4)	0.038(1)	−0.0894(7)	5.8(4)
C(22)	0.0736(4)	0.193(1)	−0.1782(8)	7.0(5)
C(23)	0.0864(4)	−0.030(1)	−0.2231(7)	3.8(4)
C(24)	0.0480(5)	−0.019(1)	−0.267(1)	7.6(6)
C(25)	0.0270(5)	−0.116(2)	−0.303(1)	9.9(6)
C(26)	0.0474(6)	−0.223(1)	−0.2947(9)	6.7(6)
C(27)	0.0844(5)	−0.231(1)	−0.2520(8)	5.7(5)
C(28)	0.1041(4)	−0.138(1)	−0.2165(7)	4.6(4)
C(29)	0.144(1)	0.285(3)	−0.380(2)	3(1)
C(30)	0.150(1)	0.461(3)	−0.272(3)	5(1)
C(37)	0.154(1)	0.307(6)	−0.377(5)	5(2)
C(38)	0.125(2)	0.442(5)	−0.272(5)	12(2)
C(31)	0.0821(7)	0.341(4)	−0.313(2)	16.1
C(32)	0.067(1)	0.435(3)	−0.287(1)	16.1
C(33)	0.026(2)	0.454(2)	−0.308(2)	16.1
C(34)	0.0003(7)	0.379(4)	−0.355(2)	16.1
C(35)	0.015(1)	0.285(3)	−0.381(2)	16.1
C(36)	0.056(2)	0.266(3)	−0.360(2)	16.1
C(39)	0.0765(6)	0.264(3)	−0.352(1)	6.0
C(40)	0.045(1)	0.336(2)	−0.352(2)	6.0
C(41)	0.0061(8)	0.306(3)	−0.391(2)	6.0
C(42)	−0.0014(6)	0.204(3)	−0.429(1)	6.0
C(43)	0.030(1)	0.132(2)	−0.429(1)	6.0
C(44)	0.0690(8)	0.162(2)	−0.390(1)	6.0

3.4. *X-ray crystallographic studies of **3** and **5***

The X-ray diffraction studies were carried out at r.t. by using the single crystals of **3** and **5** obtained by recrystallization from THF/hexane, which were sealed in glass capillaries under N_2 and transferred to a Rigaku AFC 7R diffractometer. The orientation matrices and unit cell parameters were derived from the least-squares fit of 25 machine-centered reflections with $35 < 2\theta < 40°$. No significant decay in the intensities of three standard reflections was observed during data collections. Intensity data were corrected for the Lorentz and polarization effects and for absorption. Crystallographic data are summarized in Table 3.

Structure solution and refinements were performed using the teXsan crystallographic software package [12]. The heavy atom positions were determined by the use of the Patterson methods program DIRDIF92 PATTY [13]. Remaining non-hydrogen atoms were located by the subsequent Fourier syntheses. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques except for the disordered carbon atoms of the methyl and phenyl groups attached to P(3) in **3**. Hydrogen atoms were placed at the calculated

Table 5
Atomic coordinates and equivalent temperature factors for non-hydrogen atoms in **5**

Atom	x	y	z	B_{eq}
W	0.13738(1)	0.07496(3)	0.15024(1)	3.013(6)
Cl(1)	0.21498(7)	0.2370(2)	0.15738(9)	4.90(5)
Cl(2)	0.13430(7)	0.0907(2)	0.25094(7)	4.53(5)
P(1)	0.08081(7)	0.3001(2)	0.14170(8)	3.79(5)
P(2)	0.19980(7)	−0.1354(2)	0.17115(8)	3.66(5)
O(1)	0	−0.2728(8)	0.2500	6.2(2)
O(2)	0.1552(2)	0.1024(7)	0.0268(2)	6.6(2)
N(1)	0.0819(2)	−0.0407(5)	0.1352(2)	3.1(1)
N(2)	0.0414(2)	−0.1263(6)	0.1174(2)	3.1(1)
C(1)	−0.0007(2)	−0.1360(7)	0.1468(3)	2.9(2)
C(2)	−0.0054(2)	−0.0556(7)	0.1990(2)	3.0(2)
C(3)	0	−0.147(1)	0.2500	3.3(2)
C(4)	−0.0460(3)	−0.2283(8)	0.1253(3)	3.2(2)
C(5)	−0.0973(3)	−0.2147(9)	0.1448(3)	4.9(2)
C(6)	−0.1392(3)	−0.300(1)	0.1242(4)	6.1(3)
C(7)	−0.1304(3)	−0.398(1)	0.0853(4)	6.8(3)
C(8)	−0.0794(3)	−0.415(1)	0.0651(3)	5.8(2)
C(9)	−0.0377(3)	−0.3265(8)	0.0857(3)	4.1(2)
C(10)	0.1512(3)	0.089(1)	0.0737(3)	4.4(2)
C(11)	0.1069(3)	0.437(1)	0.0997(3)	5.7(2)
C(12)	0.0696(3)	0.395(1)	0.2036(3)	6.1(3)
C(13)	0.0131(3)	0.2588(8)	0.1091(3)	3.6(2)
C(14)	−0.0334(3)	0.268(1)	0.1387(3)	5.3(2)
C(15)	−0.0829(3)	0.221(1)	0.1134(4)	6.0(3)
C(16)	−0.0848(4)	0.167(1)	0.0622(4)	6.7(3)
C(17)	−0.0397(4)	0.161(1)	0.0328(3)	6.1(3)
C(18)	0.0092(3)	0.205(1)	0.0584(3)	5.2(2)
C(19)	0.1709(3)	−0.2574(9)	0.2179(3)	5.9(2)
C(20)	0.2646(3)	−0.089(1)	0.2067(3)	5.9(2)
C(21)	0.2165(3)	−0.2535(7)	0.1162(3)	3.5(2)
C(22)	0.1849(3)	−0.2554(8)	0.0677(3)	4.2(2)
C(23)	0.1956(3)	−0.351(1)	0.0275(3)	5.6(2)
C(24)	0.2372(4)	−0.450(1)	0.0352(4)	5.9(3)
C(25)	0.2681(3)	−0.448(1)	0.0832(4)	6.0(3)
C(26)	0.2580(3)	−0.3532(9)	0.1240(3)	4.9(2)

positions and included with fixed parameters at the final stages of the refinement. Final coordinates of non-hydrogen atoms in **3** and **5** are collected in Tables 4 and 5, respectively.

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References

[1] Y. Nishibayashi, S. Iwai, M. Hidai, J. Am. Chem. Soc., in press.

[2] (a) M. Hidai, Y. Mizobe, Chem. Rev. 95 (1995) 1115. (b) S. Gambarotta, J. Organomet. Chem. 500 (1995) 117. (c) T.A. Bazhenova, A.E. Shilov, Coord. Chem. Rev. 144 (1995) 69. (d) R.L. Richards, Coord. Chem. Rev. 154 (1996) 83.

[3] (a) M. Hidai, Y. Ishii, Bull. Chem. Soc. Jpn. 69 (1996) 819. (b) M. Hidai, Y. Mizobe, in: Molybdenum Enzymes, Cofactors, and Model Systems, American Chemical Society, Washington, DC, 1993, p. 346.

[4] (a) P.C. Bevan, J. Chatt, M. Hidai, G.J. Leigh, J. Organomet. Chem. 160 (1978) 165. (b) Y. Mizobe, Y. Uchida, M. Hidai, Bull. Chem. Soc. Jpn. 53 (1980) 1781. (c) M. Hidai, Y. Mizobe, M. Sato, T. Kodama, Y. Uchida, J. Am. Chem. Soc. 100 (1978) 5740.

[5] M. Hidai, S. Aramaki, K. Yoshida, T. Kodama, T. Takahashi, Y. Uchida, Y. Mizobe, J. Am. Chem. Soc. 108 (1986) 1562.

[6] Y. Harada, Y. Mizobe, Y. Ishii, M. Hidai, Bull. Chem. Soc. Jpn., in press.

[7] T. Aoshima, T. Tamura, Y. Mizobe, M. Hidai, J. Organomet. Chem. 435 (1992) 85.

[8] (a) H. Oshita, Y. Mizobe, M. Hidai, J. Organomet. Chem. 461 (1993) 43. (b) Y. Harada, Y. Mizobe, T. Aoshima, H. Oshita, M. Hidai, Bull. Chem. Soc. Jpn. 71 (1998) 183.

[9] G.O. Dudek, R.H. Holm, J. Am. Chem. Soc. 84 (1962) 2691.

[10] J. Chatt, A.J. Pearman, R.L. Richards, J. Chem. Soc. Dalton Trans. (1978) 1766.

[11] M.L. Miles, T.M. Harris, C.R. Hauser, J. Org. Chem. 30 (1965) 1007.

[12] teXsan: Crystal Structure Analysis Package, Molecular Structure Cooporation, 1985 and 1992.

[13] P.T. Beurskens et al., The DIRDIF Program System: Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.