Syntheses of Tungsten Diazoalkane Complexes from a Dinitrogen Complex and Diketones. Conversion of Molecular Nitrogen into Pyrazoles via the Diazoalkane Complexes as Intermediates[1)]

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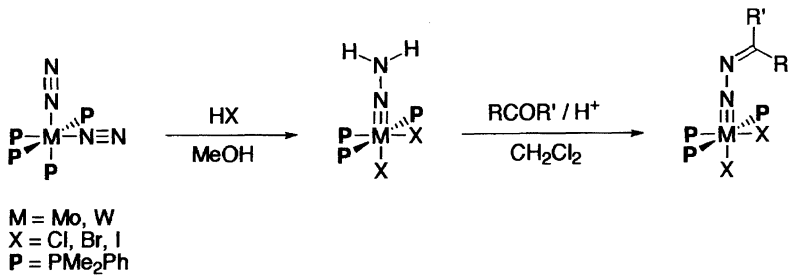
The hydrazido(2-) complexes $[WCl_2(NNH_2)(L)(PMe_2Ph)_2]$ (L = PMe_2Ph, CO), derived from the dinitrogen complex *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**1**), reacted with β-diketones $R^1COCHR^2COR^3$ (R^1 = Me, Bu^t, Ph; R^2 = H, Me; R^3 = Me, Et, Bu^t, Ph) to afford a series of diazoalkane complexes $[WCl_2(NN{=}CR^1CHR^2COR^3)(L)(PMe_2Ph)_2]$. The detailed structure of *cis,mer*-$[WCl_2(NN{=}CMeCH_2COPh)(PMe_2Ph)_3]$ has been determined by X-ray analyses. These diazoalkane complexes were treated with a KOH/EtOH mixture to produce pyrazoles in moderate yields, whereas the reaction of **1** with a $MeCOCH_2COPh$/KOH/EtOH mixture resulted in the direct formation of 5-methyl-3-phenylpyrazole.

Reactivities of coordinated dinitrogen in transition metal complexes have been investigated extensively to achieve syntheses of nitrogenous compounds from molecular nitrogen under mild conditions.[2)] Of particular importance is direct conversion of dinitrogen into organo-nitrogen compounds by the aid of transition metal catalysis. In this context, the C–N bond-forming reactions at the coordinated N_2 are attracting much attention.[3)] Condensation of the hydrazido(2-) complexes derived from the N_2 complexes of the type $[M(N_2)_2(L)_4]$ (M = Mo, W; L = tertiary phosphine) with aldehydes and ketones to give diazoalkane complexes appears to be the most versatile method to obtain organo-nitrogen ligands from N_2. Thus, the hydrazido(2-) complexes *cis,mer*-$[MX_2(NNH_2)(PMe_2Ph)_3]$ and *trans*-$[MF(NNH_2)(dppe)_2][BF_4]$ (M = Mo, W; X = Cl, Br, I; dppe = $Ph_2PCH_2CH_2PPh_2$) readily react with numerous RR′C=O molecules, affording the diazoalkane complexes *cis,mer*-$[MX_2(NN{=}CRR')(PMe_2Ph)_3]$[4)] (Scheme 1) and *trans*-$[MF(NN{=}CRR')(dppe)_2][BF_4]$,[5)] respectively. Importantly, treatment of *cis,mer*-$[WBr_2(NN{=}CMe_2)(PMe_2Ph)_3]$ with $LiAlH_4$ gives a mixture of Me_2CHNH_2 and NH_3, while that with HBr gas results in the formation of a mixture of $Me_2C{=}N{-}N{=}CMe_2$ and N_2H_4.[4a)] As an extension of the latter reaction, one-pot synthesis of a series of ketazines from *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**1**) and the alcohol/ketone mixture has been exploited more recently. This synthesis is believed to involve a diazoalkane species as the key intermediate.[6)]

The condensation method has also been extended to the reactions with phthalaldehyde,[7)] 2,5-dimethoxytetrahydrofuran,[8)] and diketone. Thus, the hydrazido(2-) complexes *cis,mer*-$[WX_2(NNH_2)(PMe_2Ph)_3]$ (X = Cl (**2a**), Br) react with acetylacetone to give *cis,mer*-$[WX_2(NN{=}CMeCH_2COMe)(PMe_2Ph)_3]$ (X = Cl (**3**),[9)] Br[4a)]). Quite recently, we have found that **3** affords 3,5-dimethylpyrazole in high yield when treated with a KOH/EtOH mixture. Since pyrazoles are important nitrogen-containing heterocyclic compounds,[10)] which are generally available from the condensation reactions of β-diketones with hydrazine,[11)] we have embarked on direct syntheses of pyrazoles from dinitrogen. Here we wish to describe syntheses of new diazoalkane

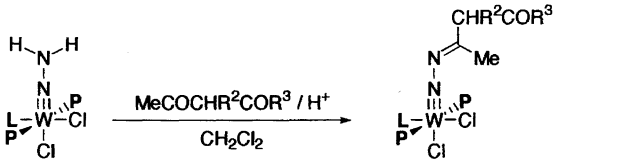


Scheme 1.

complexes from the reactions of the hydrazido(2-) complexes $[WCl_2(NNH_2)(L)(PMe_2Ph)_2]$ (L = PMe_2Ph (**2a**), CO (**2b**)) with various β-diketones and the formation of pyrazoles therefrom. As a related work, reactions of **2** with 1,3,5-triketones have also been investigated recently, which will be reported separately elsewhere.[12]

Results and Discussion

Condensation of 2 with Diketones. Reactions of the hydrazido(2-) complexes **2** with 4 molar amounts of β-diketones $MeCOCHR^2COR^3$ (R^2 = H, Me; R^3 = Me, Et, Ph)[13] at room temperature in the presence of a catalytic amount of aqueous HCl resulted in the formation of a series of the diazoalkane complexes $[WCl_2(NN{=}CMeCHR^2COR^3)(L)(PMe_2Ph)_2]$ (**3**—**9**) (Eq. 1).



2a: L = PMe_2Ph
2b: L = CO

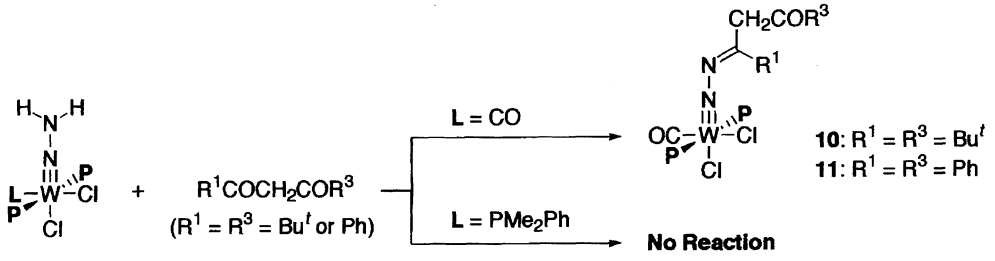
3: R^2 = H, R^3 = Me, L = PMe_2Ph
4: R^2 = H, R^3 = Me, L = CO
5: R^2 = Me, R^3 = Me, L = PMe_2Ph
6: R^2 = Me, R^3 = Me, L = CO
7: R^2 = H, R^3 = Et, L = PMe_2Ph
8: R^2 = H, R^3 = Ph, L = PMe_2Ph
9: R^2 = H, R^3 = Ph, L = CO

(1)

In the reactions of the non-symmetrical diketones (R^2 = H; R^3 = Et, Ph), the condensation proceeded selectively at the MeCO group, viz. the less hindered carbonyl group. This may be caused by the steric effect of the ligands in **2**. Accordingly, diketones such as $PhCOCH_2COPh$ and $Bu^tCOCH_2COBu^t$ did not react with **2a**, whereas the less encumbered hydrazido(2-) ligand in **2b**, generated from **2a** by replacement of one PMe_2Ph ligand with CO, did react with these diketones smoothly and the corresponding diazoalkane complexes *cis,trans*-$[WCl_2(NN{=}CR^1CH_2COR^3)(CO)(PMe_2Ph)_2]$ (R^1 = R^3 = Bu^t (**10**), Ph (**11**)) were produced (Scheme 2). This result correlates well to our previous finding on the difference between **2a** and **2b** in the reactivities toward PhCOPh; i.e., the former does not react with this ketone, but the latter gives *cis,trans*-$[WCl_2(NN{=}CPh_2)(CO)(PMe_2Ph)_2]$.[14]

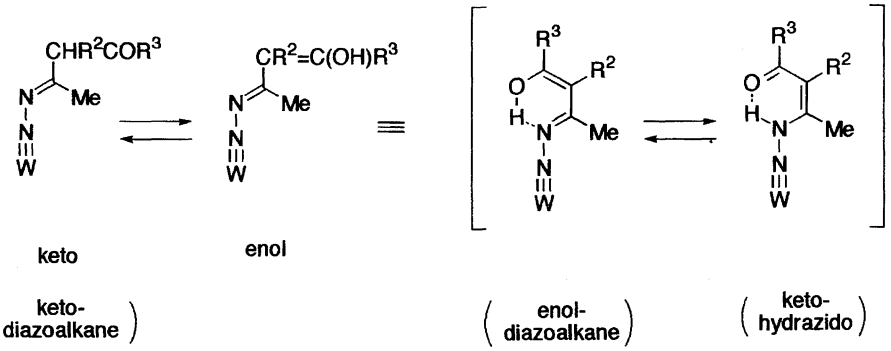
The reactions of **2a** with diketones of the other type such as acetonylacetone and 1,2-diacetylbenzene occurred analogously and the corresponding diazoalkane complexes *cis,mer*-$[WCl_2(NN{=}CMeR)(PMe_2Ph)_3]$ (R = CH_2CH_2COMe, C_6H_4COMe-*o*) were isolated.

As for the structure of the diazoalkane complexes derived from acetylacetone, we have already shown by the single-crystal X-ray diffraction study that the diphosphine complex *trans*-$[WF(NN{=}CMeCH_2COMe)(dppe)_2][BF_4]$ (**12**) is present in a keto-diazoalkane form.[5] This feature was also observed in its IR spectrum recorded by the KBr method, showing the strong bands at 1725 and 1595 cm^{-1} characteristic of ν(C=O) and ν (C=N), respectively. Furthermore, the ^1H NMR data indicated that the keto-diazoalkane structure is preserved exclusively even in the solution state.[5] In contrast, for the monophosphine complex *cis,mer*-$[WBr_2(NN{=}CMeCH_2COMe)(PMe_2Ph)_3]$, it has been concluded from the ^1H NMR criteria that the complex exists as the mixture of the keto and enol forms in an approximately 1 : 1 ratio in solution, although the IR spectrum was indicative of the keto form being predominant in a solid state (Scheme 3); however, the detailed structure of the enol form was not



10: R^1 = R^3 = Bu^t
11: R^1 = R^3 = Ph

Scheme 2.



Scheme 3.

Table 1. Selected ^{1}H NMR Data for $[WCl_2(NN{=}CR^1CHR^2COR^3)(L)(PMe_2Ph)_2]$[a]

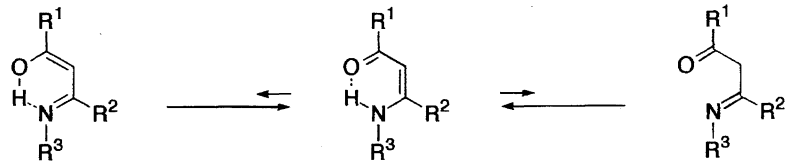
					Keto[b]	Enol[b]		
	L	R^1	R^2	R^3	$\delta(CCH_2)$	$\delta(OH)$	$\delta(C{=}CH)$	Keto : Enol[b]
3	PMe_2Ph	Me	H	Me	2.35	13.24	4.56	40 : 60
4	CO	Me	H	Me	2.67	16.21	4.98	50 : 50
5	PMe_2Ph	Me	Me	Me	2.06			100 : 0
6	CO	Me	Me	Me	2.48			100 : 0
7	PMe_2Ph	Me	H	Et	3.26			100 : 0
8	PMe_2Ph	Me	H	Ph	2.94	14.05	5.43	15 : 85
9	CO	Me	H	Ph		13.28	5.04	0 : 100
10	CO	Bu^t	H	Bu^t	2.93			100 : 0
11	CO	Ph	H	Ph	4.02	17.8	4.30	90 : 10

a) In C_6D_6. b) The keto form denotes the keto-diazoalkane form, while the enol form is interpreted as the mixture of two tautomers, enol-diazoalkane and keto-hydrazido forms. See Ref. 16.

Table 2. IR Data for $[WCl_2(NN{=}CR^1CHR^2COR^3)(L)(PMe_2Ph)_2]$[a]

					Keto[b]		Enol[b]	
	L	R^1	R^2	R^3	ν(C=O)	ν(C=N)	ν(C=N/C=C)	ν(C=O)
3	PMe_2Ph	Me	H	Me	1717	1572	1624	
4	CO	Me	H	Me	1716	1578	1620	1937
5	PMe_2Ph	Me	Me	Me	1717	1576		
6	CO	Me	Me	Me	1723	1570		1953
7	PMe_2Ph	Me	H	Et	1713	1574		
8	PMe_2Ph	Me	H	Ph			1576	
9	CO	Me	H	Ph	1716	1570	1609	1946
10	CO	Bu^t	H	Bu^t	1701	1534		1948
11	CO	Ph	H	Ph	1688	1518	1597	1948

a) cm^{-1}; KBr disk. b) See footnote b in Table 1.



Scheme 4.

clarified.[4a,15]

Now a significant number of the diazoalkane complexes with PMe_2Ph ligands are obtained by using various β-diketones. The pertinent ^{1}H NMR and IR data of these complexes as well as **3** are summarized in Tables 1 and 2. Interestingly, the keto/enol ratios of the complexes depend significantly upon the nature of the substituents in the diazoalkane ligands. Thus, **3** and **4** have both the keto and enol forms in an almost 1 : 1 ratio in solution, as reported previously for the Br analogue of **3** (vide supra). On the other hand, complexes **5**—**7**, **10**, and **11** are present in the keto form solely or much predominantly, whereas **8** and **9** somehow favor the enol form. It is to be noted that Schiff bases obtained from the reaction of β-diketones with equimolar amines or anilines generally prefer the keto-enamine form to the keto-imine structure in solution (Scheme 4).[16]

The IR spectra recorded by the KBr methods are almost congruent with the ^{1}H NMR data (Table 2). Thus, **3** and **4** exhibit not only a pair of strong bands characteristic of ν(C=O) and ν(C=N) ascribable to the keto form but also a broad band at ca. 1620 cm^{-1} tentatively assigned to ν(C=C/C=N) of the enol form (vide infra), suggesting that considerable amounts of the enol forms are also present even in the solid state. Also for **11**, the presence of the enol form is presumed to some extent. On the other hand, the spectra of **5**—**7** and **10** show only absorptions diagnostic of the keto form and this feature is in good agreement with the ^{1}H NMR data. By contrast, in the spectra of **8** and **9** the intense ν(C=C/C=N) bands due to the enol form appeared, while the absorptions characteristic of the keto form are relatively weak or essentially unobservable. These features of **8** and **9** in the solid state correspond well to their solution structures which favor the enol form. To confirm unequivocally the solid state structure of the enol form, the X-ray crystallography has been undertaken, since the isolation of high-quality single crystals was successful for **8**.

An ORTEP drawing of **8** is depicted in Fig. 1, while the important bonding parameters in **8** are listed in Table 3. As

shown in Fig. 1, **8** has a slightly distorted octahedral structure, in which two Cl and three PMe_2Ph ligands occupy mutually cis and meridional positions, respectively. In the diazoalkane ligand trans to one Cl ligand, the W, N(1), N(2), C(1)—C(4), and O atoms are almost coplanar within 0.23(1) Å and the dihedral angle between this least-square plane and the benzene ring attached to C(4) is 34.1°. It is noteworthy that the C(4)–O bond distance at 1.30(1) Å is much longer than that of the typical C–O double bond length (1.22 Å). These structural features are indicative that this ligand exists as the enol form **8-i** in Scheme 5, where the orientation of the C(4)–O bond suggests the presence of the hydrogen-bonding interaction of the enol proton with N(2). This was also expected from its IR spectrum, which showed neither ν(C=O) nor ν(C=N) band typical of the keto form **8-iii**. Furthermore, the X-ray analysis has disclosed that the lengths of not only the C(4)–O bond but also the C(4)–C(3), C(3)–C(2), and C(2)–N(2) bonds at 1.38(2), 1.40(2), and 1.36(1) Å, respectively, are all diagnostic of a bond order of between one and two. This may be interpreted in terms of the contribution of the alkenylhydrazido(2-) structure **8-ii** toward **8-i**.[16] The intense IR band at 1576 cm^{-1} may arise from the highly conjugated linkage in **8** extending from the oxygen to the N(2) atom, and presumably further to the W atom.

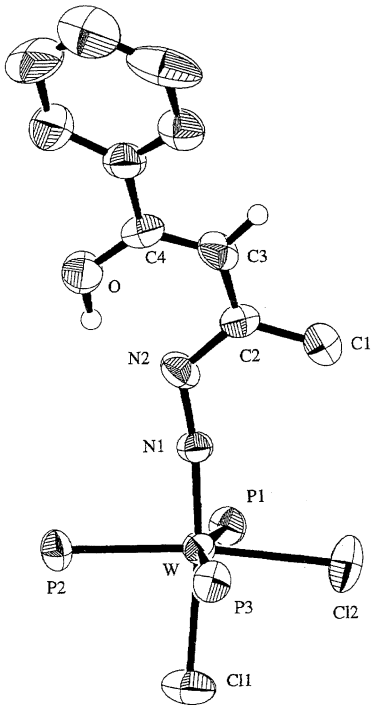
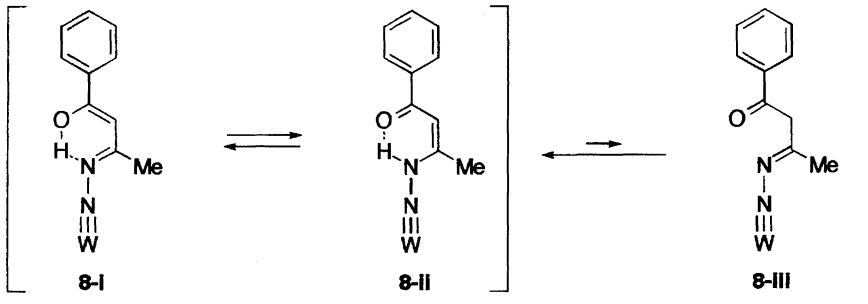


Fig. 1. ORTEP drawing of **8**. The hydrogen atoms on the C(3) and O atoms are placed by supposing only the enol-diazoalkane structure. Substituents around the P atoms are omitted for clarity.

Table 3. Selected Bond Lengths and Angles in **8**

(a) Bond length (Å)			
W–Cl(1)	2.384(3)	O–C(4)	1.30(1)
W–Cl(2)	2.514(3)	N(1)–N(2)	1.38(1)
W–P(1)	2.490(3)	N(2)–C(2)	1.36(1)
W–P(2)	2.415(3)	C(2)–C(3)	1.40(2)
W–P(3)	2.553(3)	C(3)–C(4)	1.38(2)
W–N(1)	1.785(8)		
(b) Bond angle (°)			
Cl(1)–W–Cl(2)	88.4(1)	P(2)–W–P(3)	93.6(1)
Cl(1)–W–P(1)	86.4(1)	P(2)–W–N(1)	88.1(3)
Cl(1)–W–P(2)	85.8(1)	P(3)–W–N(1)	88.4(3)
Cl(1)–W–P(3)	90.8(1)	W–N(1)–N(2)	171.5(7)
Cl(1)–W–N(1)	173.7(3)	N(1)–N(2)–C(2)	121.4(9)
Cl(2)–W–P(1)	81.4(1)	N(2)–C(2)–C(1)	120(1)
Cl(2)–W–P(2)	172.7(1)	N(2)–C(2)–C(3)	117(1)
Cl(2)–W–P(3)	82.1(1)	C(1)–C(2)–C(3)	124(1)
Cl(2)–W–N(1)	97.6(3)	C(2)–C(3)–C(4)	126(1)
P(1)–W–P(2)	102.6(1)	O–C(4)–C(3)	121(1)
P(1)–W–P(3)	163.33(9)	O–C(4)–C(5)	116(1)
P(1)–W–N(1)	96.2(3)	C(3)–C(4)–C(5)	123(1)

It is interesting to compare the bond distances in the diazoalkane ligand in **8** with those in the keto-diazoalkane complex **12**[4c] and the cationic alkenylhydrazido(2-) (or keto-enamine type) complex *mer*-[W(acac)(NNHCMeCHCOMe)-$(PMe_2Ph)_3$]Br (**13**; acac = acetylacetonate)[9] (Table 4). The bonding schemes for the organo-dinitrogen ligands clarified by the X-ray analyses for **12** and **13** are illustrated in Fig. 2. In spite of the significantly large deviations with respect to the bond lengths in **12** and **13**, the data listed in Table 3 clearly show the elongation of the C(4)–O bond and shortening of the C(4)–C(3) bond in **8** compared with those in **12** and **13**, while the C(3)–C(2) and C(2)–N(2) distances in **8** lie between the values found for the corresponding C–C and



Scheme 5.

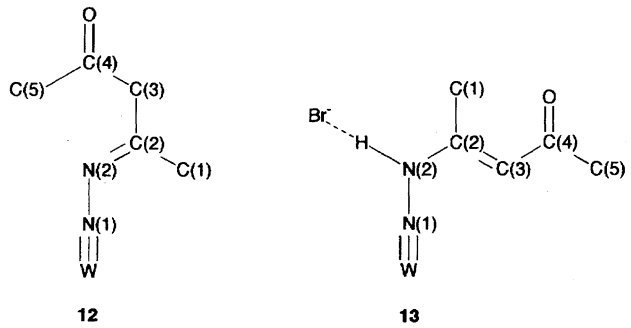


Fig. 2. Atom connecting schemes of the diazoalkane ligands in **12** and **13**.

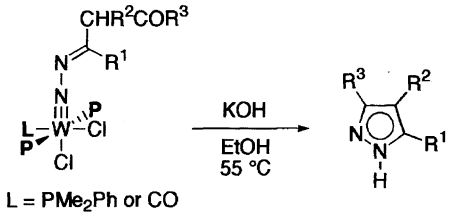
Table 4. Comparison of Important Bond Distances in the Diazoalkane Ligands

Bond	Distances (Å)		
	8	**12**	**13**
O–C(4)	1.30(1)	1.20(6)	1.20(4)
C(4)–C(3)	1.38(2)	1.49(5)	1.43(4)
C(3)–C(2)	1.40(2)	1.53(4)	1.33(4)
C(2)–N(2)	1.36(1)	1.30(3)	1.40(4)
N(2)–N(1)	1.38(1)	1.32(3)	1.38(3)
N(1)–W	1.785(8)	1.77(2)	1.79(1)

C–N bonds in **12** and **13**. These data support the conclusion that the structure of **8** can be represented by a combination of two tautomeric forms, **8-i** and **8-ii**.

Reactions of Diazoalkane Complexes with a KOH/EtOH Mixture Yielding Pyrazoles. We have previously reported the reaction of the dinitrogen complex **1** with various ketones RR′C=O in R″OH to give ketazines RR′C=N–N=CRR′ (Scheme 6).[6] Addition of KOH to this reaction system significantly improves the yields of ketazines. Although the reactions carried out in EtOH in place of MeOH are much slower, comparable yields of ketazines are attainable by the addition of KOH even for the reactions in EtOH. Precise mechanisms operating in these reaction systems are still uncertain. However, as illustrated in Scheme 6, a diazoalkane spieces seems to be present as the key intermediate stage. This might be converted to a hydrazone by protonolysis and then to the final product of a ketazine through condensation with a ketone. Indeed, it has been confirmed that treatment of the isolable diazoalkane complex *cis,mer*-[$WCl_2(NN{=}CMe_2)(PMe_2Ph)_3$] with KOH in MeOH gives $Me_2C{=}N{-}NH_2$ in significant yields together with some $Me_2C{=}N{-}N{=}CMe_2$.[6]

Now, we have examined the reactions of the diazoalkane complexes reported here with a KOH/EtOH mixture. If the diazoalkane complexes derived from β-diketones react similarly, the hydrazones may be produced in situ first, and then converted to pyrazoles through the intramolecular condensation (Eq. 2).



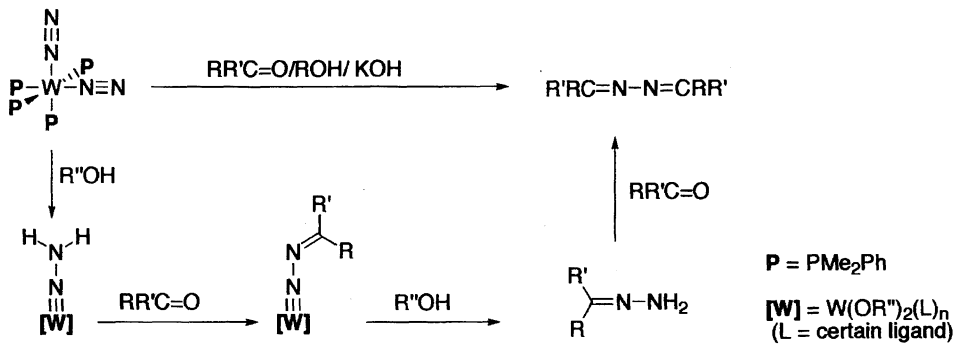
(2)

As summarized in Table 5, it has been found that the reactions readily proceed at 55 °C in an expected manner and the pyrazoles are obtained in moderate yields from **3**—**5** and **8**—**11**.[18] As for the conversion of coordinated dinitrogen into a pyrazole, formation of 5-amino-4-cyanopyrazole was observed previously by the electro-reduction of the dicyanovinylhydrazido(2-) complex *trans*-[$WF\{NNHCH{=}C(CN)_2\}(dppe)_2$]-[$BF_4$] derived from *trans*-[$W(N_2)_2(dppe)_2$]. The supposed mechanism involves the release of $H_2N{-}NHCH{=}C(CN)_2$, which cyclizes to the pyrazole.[19]

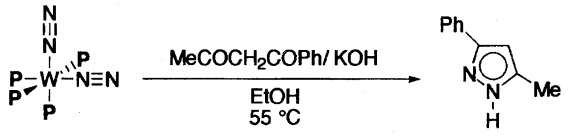
Finally, one-pot synthesis of pyrazoles from the parent dinitrogen complex **1** has also been attempted. Thus, treatment of **1** with a benzoylacetone/EtOH/KOH mixture resulted in the formation of the expected 5-methyl-3-phenylpyrazole (Eq. 3).

Table 5. Reactions of Diazoalkane Complexes with a EtOH/KOH Mixture Yielding Pyrazoles

Complex	L	R^1	R^2	R^3	Yield/%
3	PMe_2Ph	Me	H	Me	85
4	CO	Me	H	Me	39
5	PMe_2Ph	Me	Me	Me	52
8	PMe_2Ph	Me	H	Ph	58
9	CO	Me	H	Ph	75
10	CO	Bu^t	H	Bu^t	47
11	CO	Ph	H	Ph	77



Scheme 6.



(3)

However, the yield of the pyrazole (37%) did not exceed that from the corresponding diazoalkane complex **8** (58%).

Experimental

General. All manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried and distilled by common procedures and degassed before use. The dinitrogen complex **1**[20] as well as hydrazido(2-) complexes **2a**[21] and **2b**[14] were prepared by the modified literature methods. Diketones were obtained commercially and used without further purification. 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 aromatic protons are omitted. Elemental analyses were done by a Perkin–Elmer 2400 series II CHN analyzer. Amounts of the solvated molecules in the crystals were determined by both ^{1}H NMR spectroscopy and elemental analyses. GLC analyses were performed on a Shimadzu GC-14A instrument using a 25 m×0.25 mm CBP1 or CBP10 fused silica capillary column. GC-MS analyses (70 eV) were carried out on a Shimadzu GC-MS QP-2000 spectrometer.

Preparation of *cis,mer*-[WCl_2(NN=CMeCH$_2$COMe)(PMe_2Ph)$_3$] (3). Since the previous report included only the in-situ generation and tentative assignment of **3**, details are shown below.

To a suspension of **2a** (734 mg, 1.05 mmol) in CH_2Cl_2 (20 ml) was added 4 molar amounts of acetylacetone (0.45 ml, 4.29 mmol). The mixture was stirred at room temperature for 5 h in the presence of a catalytic amount of aqueous HCl. The initial orange suspension gradually turned to a dark brown solution. The resultant solution was dried up and the residue was washed with hexane. Recrystallization of the remaining solid from CH_2Cl_2–hexane yielded **3** as brown crystals; these were filtered off, washed with hexane, and then dried in vacuo (557 mg, 68%). Found: C, 44.60; H, 5.37; N, 3.71%. Calcd for $C_{29}H_{41}Cl_2N_2OP_3W$: C, 44.58; H, 5.29; N. 3.59%. ^{1}H NMR (C_6D_6) δ = 13.24 (br, 0.6H, OH), 4.56 (s, 0.6H, C=CH), 2.35 (s, 0.8H, CH_2CO); resonances due to the methyl groups in three PMe_2Ph ligands and the diazoalkane ligand are overlapping in the region of 2.1—1.4 ppm.

In the similar ways were prepared [WCl_2(NN=CR^{1}CHR^{2}COR^3)(L)($PMe_2Ph)_2$] (**4**: R^1 = Me, R^2 = H, R^3 = Me, L = CO; **5**: R^1 = R^2 = R^3 = Me, L = PMe_2Ph; **6**: R^1 = R^2 = R^3 = Me, L = CO; **7**: R^1 = Me, R^2 = H, R^3 = Et, L = PMe_2Ph; **8**: R^1 = Me, R^2 = H, R^3 = Ph, L = PMe_2Ph; **9**: R^1 = Me, R^2 = H, R^3 = Ph, L = CO; **10**: R^1 = Bu^t, R^2 = H, R^3 = Bu^t, L = CO; **11**: R^1 = Ph, R^2 = H, R^3 = Ph, L = CO), *cis,mer*-[WCl_2(NN=CMeCH$_2$CH$_2$COMe)($PMe_2Ph)_3$] (**14**), and *cis,mer*-[WCl_2(NN=CMeC$_6$H$_4$COMe-*o*)($PMe_2Ph)_3$] (**15**) from either **2a** or **2b** with diketone R^{1}COCHR^{2}COR^3. Complexes **6** and **7** were characterized only spectroscopically.

4. Color: brown. Yield: 49%. Found: C, 37.42; H, 4.39; N, 3.98%. Calcd for $C_{22}H_{30}Cl_2N_2O_2P_2W\cdot 0.5CH_2Cl_2$: C, 37.87; H, 4.38; N, 3.93%. ^{1}H NMR (C_6D_6) δ = 16.2 (br, 0.5H, OH), 4.98 (s, 0.5H, C=CH), 2.67 (s, 1H, CH_2CO), 1.62 (s, 1.5H, COMe), 1.52 (s, 1.5H, C*Me*OH), 1.21 and 1.13 (s, 1.5H each, NNCMe); resonances assignable to the PMe_2Ph methyl protons are overlapping in the region of 1.91—1.82 ppm.

5. Color: brown. Yield: 62%. Found: C, 44.81; H, 5.49; N, 3.35%. Calcd for $C_{30}H_{43}Cl_2N_2OP_3W$: C, 45.30; H, 5.45; N, 3.52%. ^{1}H NMR (C_6D_6) δ = 2.06 (q, 1H, J = 5.3 Hz, C*H*MeCO), 1.99 and 1.67 (t, 6H, each, J_{P-H} = 4.0 Hz, P*Me*$_2$Ph), 1.71 (s, 3H, COMe), 1.60 (d, 3H, J = 5.3 Hz, CH*Me*CO), 1.55 (d, 6H, J_{P-H} = 8.6 Hz, P*Me*$_2$Ph), 1.52 (s, 3H, NN=CMe); other resonances derived from the diazoalkane ligand in the enol form are overlapping in the region of 1.71—1.52 ppm.

6. Color: brown. Yield: 65%. ^{1}H NMR (C_6D_6) δ = 2.48 (q, 1H, J = 6.8 Hz, C*H*MeCO), 1.89 and 1.87 (t, 6H each, J_{P-H} = 3.9 Hz, P*Me*$_2$Ph), 1.48 (s, 3H, COMe), 1.10 (s, 3H, NN=CMe), 0.76 (d, 3H, J = 6.8 Hz, CH*Me*CO).

7. Color: brown. Yield: 75%. ^{1}H NMR (C_6D_6) δ = 3.26 (s, 2H, CH_2CO), 2.46 (q, 2H, J = 7.3 Hz, COC*H*$_2$Me), 1.91 and 1.69 (t, 6H each, J_{P-H} = 3.9 Hz, P*Me*$_2$Ph), 1.57 (d, 6H, J_{P-H} = 8.8 Hz, P*Me*$_2$Ph), 1.42 (s, 3H, NN=CMe), 1.06 (t, 3H, J = 7.3 Hz, CH_2*Me*).

8. Color: brown. Yield: 65%. Found: C, 45.56; H, 5.01; N, 3.28%. Calcd for $C_{34}H_{43}Cl_2N_2OP_3W\cdot CH_2Cl_2$: C, 45.28; H, 4.89; N, 3.02%. ^{1}H NMR (C_6D_6) δ = 14.05 (br, 0.85H, OH), 5.43 (s, 0.85H, C=CH), 2.94 (s, 0.3H, CH_2CO), 1.98 and 1.87 (t, 0.9H each, J_{P-H} = 4.0 Hz, P*Me*$_2$Ph), 1.95 and 1.68 (t, 5.1H each, J_{P-H} = 4.0 Hz, P*Me*$_2$Ph), 1.90 (s, 2.55H, NNCMe), 1.59 (s, 0.45H, NNCMe), 1.54 (d, 5.1H, J_{P-H} = 8.3 Hz, P*Me*$_2$Ph), 1.48 (d, 0.9H, J_{P-H} = 8.3 Hz, P*Me*$_2$Ph).

9. Color: brown. Yield: 69%. Found: C, 44.09; H, 4.24; N, 3.62%. Calcd for $C_{27}H_{32}O_2N_2P_2Cl_2W$: C, 44.23; H, 4.40; N, 3.82%. ^{1}H NMR (C_6D_6) δ = 13.28 (br, 1H, OH), 5.04 (s, 1H,

Table 6. X-Ray Crystallographic Data for **8**

(a) Crystal data	
Empirical formula	$C_{34}H_{43}Cl_2N_2OP_3W$
Formula weight	843.40
Crystal color	Brown
Crystal dimension/mm	0.5×0.2×0.3
Crystal system	Monoclinic
Space group	$P2_1$ (No. 4)
a/Å	9.252(2)
b/Å	18.698(3)
c/Å	10.612(1)
β/deg	94.97(1)
V/Å^3	1828.9(5)
Z	2
d(calcd)/g cm^{-3}	1.531
μ (Mo $K\alpha$)/cm^{-1}	34.67
F(000)	844
(b) Data collection	
Radiation	Mo $K\alpha$ (λ =0.7107 Å)
Monochromator	Graphite
Temperature	Room temperature
Scan method	$\omega/2\theta$
Scan rate/deg min^{-1}	16
$2\theta_{max}$/deg	55
No. of unique reflections	4323
Transmittion factor	0.8138—1.000
(c) Structure solution and refinements	
No. of data used	3746 ($I>3\sigma(I)$)
No. of variables	387
R, R_w	0.039, 0.030
Max residual/electron Å^3	0.97

C=CH), 1.90 and 1.87 (t, 6H each, J_{P-H} = 4.0 Hz, PMe_2Ph), 1.23 (s, 3H, NN=CMe).

10. Color: brown. Yield: 80%. Found: C, 44.28; H, 5.77; N, 3.87%. Calcd for $C_{28}H_{42}Cl_2N_2O_2P_2W$: C, 44.52; H, 5.60; N, 3.71%. ^{1}H NMR (C_6D_6) δ = 2.93 (s, 2H, CH_2CO), 1.93 and 1.86 (t, 6H each, J_{P-H} = 4.0 Hz, PMe_2Ph), 1.17 (s, 9H, COBu^t), 0.85 (s, 9H, NN=CBu^t).

11. Color: green. Yield: 86%. Found: C, 47.89; H, 4.55; N, 3.82%. Calcd for $C_{32}H_{34}Cl_2N_2O_2P_2W$: C, 48.33; H, 4.31; N, 3.52%. ^{1}H NMR (C_6D_6) δ = 17.8 (br, 0.1H, OH), 4.30 (s, 0.1H, C=CH), 4.02 (s, 1.8H, CH_2CO), 1.85 and 1.83 (t, 6H each, J_{P-H} = 3.9 Hz, PMe_2Ph).

14. Color: brown. Yield: 61%. Found: C, 44.79; H, 5.40; N, 3.35%. Calcd for $C_{30}H_{43}Cl_2N_2OP_3W$: C, 45.30; H, 5.45; N, 3.52%. IR (KBr) ν(C=O), 1713 cm^{-1}; ν(C=N), 1589 and 1572 cm^{-1}. ^{1}H NMR (C_6D_6) δ = 2.07 (t, 2H, J = 5.6 Hz, CH_2COMe), 1.97 and 1.67 (t, 6H each, J_{P-H} = 4.0 Hz, PMe_2Ph), 1.71 (s, 3H, COMe), 1.62 (t, 2H, J = 5.6 Hz, CH_2CH_2COMe), 1.55 (d, 6H, J_{P-H} = 8.2 Hz, PMe_2Ph), 1.52 (s, 3H, NN=CMe).

Table 7. Atomic Coordinates and Equivalent Temperature Factors for Non-Hydrogen Atoms in **8**

Atom	x	y	z	B_{eq}
W	0.02514(4)	0.0166	0.05546(4)	2.608(7)
Cl(1)	0.1910(3)	−0.0798(2)	0.0385(3)	4.84(8)
Cl(2)	0.1362(4)	0.0768(2)	−0.1248(3)	4.96(8)
P(1)	−0.1245(3)	−0.0406(2)	−0.1232(3)	3.26(7)
P(2)	−0.0507(3)	−0.0463(2)	0.2373(3)	3.27(7)
P(3)	0.2188(3)	0.0887(2)	0.1861(3)	3.56(7)
O	−0.3466(9)	0.1760(4)	0.3053(8)	5.1(2)
N(1)	−0.1025(8)	0.0849(4)	0.0847(7)	2.8(2)
N(2)	−0.202(1)	0.1330(5)	0.125(1)	3.6(2)
C(1)	0.153(1)	0.2146(6)	−0.049(1)	4.7(3)
C(2)	−0.221(1)	0.1985(6)	0.071(1)	3.2(3)
C(3)	−0.300(2)	0.2486(6)	0.135(2)	3.9(4)
C(4)	−0.351(1)	0.2387(7)	0.252(1)	3.6(3)
C(5)	−0.420(1)	0.2962(7)	0.321(1)	4.1(3)
C(6)	−0.514(1)	0.2802(7)	0.410(1)	5.8(4)
C(7)	−0.576(2)	0.336(1)	0.478(1)	7.8(5)
C(8)	−0.538(2)	0.406(1)	0.461(1)	7.1(5)
C(9)	−0.441(2)	0.4214(8)	0.370(2)	7.3(5)
C(10)	−0.385(1)	0.3682(7)	0.302(1)	4.4(3)
C(11)	−0.243(1)	−0.1188(7)	−0.104(1)	5.7(4)
C(12)	−0.019(1)	−0.0694(7)	−0.253(1)	5.1(4)
C(13)	−0.250(1)	0.027(1)	−0.1986(8)	2.5(2)
C(14)	−0.224(1)	0.0610(6)	−0.311(1)	4.7(3)
C(15)	−0.316(2)	0.1112(8)	−0.366(1)	6.2(4)
C(16)	−0.447(2)	0.1241(7)	−0.315(1)	6.2(4)
C(17)	−0.472(1)	0.0912(8)	−0.207(1)	6.0(4)
C(18)	−0.375(1)	0.0401(6)	−0.146(1)	4.8(3)
C(19)	0.091(2)	−0.092(1)	0.335(1)	6.0(5)
C(20)	−0.129(1)	0.013(1)	0.355(1)	6.1(3)
C(21)	−0.189(1)	−0.1130(6)	0.2110(9)	2.6(2)
C(22)	−0.336(1)	0.0920(6)	0.190(1)	4.6(3)
C(23)	−0.444(1)	−0.1409(8)	0.169(1)	5.1(4)
C(24)	−0.411(2)	−0.2106(8)	0.161(1)	5.9(4)
C(25)	−0.266(2)	−0.2343(9)	0.174(2)	5.5(5)
C(26)	−0.156(1)	−0.1852(6)	0.203(1)	4.0(3)
C(27)	0.387(1)	0.0410(7)	0.235(1)	6.9(4)
C(28)	0.290(1)	0.1692(7)	0.114(1)	5.8(4)
C(29)	0.165(1)	0.1299(7)	0.330(1)	4.0(3)
C(30)	0.210(1)	0.1006(8)	0.449(1)	6.1(4)
C(31)	0.155(2)	0.131(1)	0.557(1)	10.1(6)
C(32)	0.055(2)	0.184(1)	0.547(2)	11.4(8)
C(33)	0.014(2)	0.213(1)	0.432(2)	8.6(5)
C(34)	0.071(2)	0.1849(8)	0.325(1)	6.2(4)

Reactions of a Series of Diazoalkane Complexes with a EtOH/KOH Mixture. On treatment of **3** (100 mg, 0.13 mmol) in EtOH (4 ml) with ca. 10 molar amounts of KOH at 55 °C for 5 h, a dark brown suspension turned to a pale brown suspension. The product mixture was neutralized with a KH_2PO_4/NaOH buffer solution (pH = ca. 7) and then extracted with ether. Formation of 3,5-dimethylpyrazole was confirmed by comparing its ^{1}H NMR, IR, and GC-MS spectra with those of the authenticated compound and the yield was determined by the GLC analysis. Reactions of the other diazoalkane complexes (**4**, **5** and **8**—**11**) with a KOH/EtOH mixture along with the reaction of **1** with a benzoylacetone/KOH/EtOH mixture were carried out similarly and the pyrazoles produced were analyzed analogously.[22]

X-Ray Crystallographic Studies of 8. The X-ray diffraction study was carried out at room temperature using a single crystal of **8** obtained by recrystallization from THF–hexane, which was sealed in a glass capillary 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 the data collection. Intensity data were corrected for the Lorentz and polarization effects and for absorption. Crystallographic data are summarized in Table 6.

Structure solution and refinements were performed using the teXsan crystallographic software package.[23] The heavy atom positions were determined by the use of the Patterson methods program DIRDIF92 PATTY.[24] Remaining non-hydrogen atoms were located by the subsequent Fourier syntheses. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares technique, while hydrogen atoms were placed at the calculated positions and included with fixed parameters at the final stages of refinements. Final coordinates of non-hydrogen atoms in **8** are collected in Table 7.[25]

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17) The structure **8-ii** is also a tautomeric form possible for **8** along with **8-i** and **8-iii**, corresponding to the keto-enamine structure of Schiff bases in Scheme 4. However, it is practically impossible to distinguish the two tautomers, **8-i** and **8-ii**, by the use of common spectroscopic methods, since the interconversion between these two forms are extremely rapid due to only the small displacement in the position of the acidic proton.

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25) The figure of the whole view of **8** with atom-numbering scheme, the tables listing hydrogen atom coordinates, anisotropic thermal parameters of non-hydrogen atoms, extensive bond distances and angles, and complete $F_o - F_c$ data for **8** are deposited as Document No. 71058 at the Office of the Editor of Bull. Chem. Soc. Jpn.