

- (23) M. Elgen and K. Kustin, *J. Am. Chem. Soc.*, **84**, 1355 (1962).
 (24) See, e.g., C. W. Pyun, *J. Chem. Educ.*, **48**, 194 (1971).
 (25) This treatment is valid providing that the equilibrium distribution of oxidant chlorine species is maintained over the course of the redox reaction. Proton transfers involving the HOCl-OCI⁻ equilibrium are "instantaneous";²⁶ from our analysis of reaction 1, it was also apparent that the exact kinetic solution²⁴ corresponds closely to the results obtained assuming rapid pre-equilibrium between HOCl and Cl₂, i.e., under the experimental conditions $k_7 > k_1(\text{H}_2\text{O}_2)$. Thus, the approximations of the present kinetic analysis are well met.
 (26) M. Elgen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).
 (27) G. P. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).
 (28) G. Zimmerman and F. C. Strong, *J. Am. Chem. Soc.*, **79**, 2063 (1957); J. C. Evans and G. Y-S. Lo, *J. Chem. Phys.*, **44**, 3638 (1966); H. W. Dodgen, A. D. Jordan, and R. B. Jordan, *J. Phys. Chem.*, **77**, 2149 (1973).
 (29) A. E. Cahill and H. Taube, *J. Am. Chem. Soc.*, **74**, 2312 (1952).
 (30) See, e.g., W. P. Jencks, "Catalysis in Chemistry and Enzymology", McGraw-Hill, New York, N.Y., 1969, p 193 ff.
 (31) J. Jander, *Z. Anorg. Allg. Chem.*, **280**, 276 (1955).
 (32) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", Elsevier, Amsterdam, 1966, p 80 ff.
 (33) D. G. Lister and D. J. Millen, *Trans. Faraday Soc.*, **67**, 601 (1971).
 (34) Electrophilic substitution on organic molecules, however, proceeds more rapidly with Cl₂ than HOCl;³² inasmuch as OH⁻ is a poorer leaving group than Cl⁻, reactivities of HOCl and Cl₂ with H₂O₂ will likely depend on the relative extent of bond formation and breaking in the transition state.^{32,35}
 (35) Cf. (a) J. Hine "Physical Organic Chemistry", McGraw-Hill, New York, N.Y., 1962, p 223; (b) E. S. Gould, "Mechanisms and Structure in Organic Chemistry", Holt, Reinhart and Winston, New York, N.Y., 1959, pp. 261, 443.
 (36) B. Makower and W. C. Bray, *J. Am. Chem. Soc.*, **55**, 4765 (1933); B. Makower, *ibid.*, **56**, 1315 (1934).
 (37) W. H. Woodruff and D. W. Margerum, *Inorg. Chem.*, **12**, 961 (1973).
 (38) *Natl. Bur. Stand. (U.S.), Tech. Note, No. 270-3* (1968).
 (39) W. M. Latimer, "Oxidation Potentials", 2nd ed, Prentice-Hall, Englewood Cliffs, N.J., 1952.
 (40) G. G. Jayson, B. J. Parsons, and A. J. Swallow, *J. Chem. Soc., Faraday Trans.*, **69**, 1597 (1973).
 (41) B. H. J. Bielski and J. M. Gebicki, *Adv. Radiat. Chem.*, **2**, 177 (1970).
 (42) P. B. Merkel and D. R. Kearns, *J. Am. Chem. Soc.*, **94**, 7244 (1972).
 (43) R. J. Browne and E. A. Ogryzlo, *Can. J. Chem.*, **43**, 2915 (1965).
 (44) A. U. Khan and M. Kasha, *J. Am. Chem. Soc.*, **92**, 3293 (1970).
 (45) See, e.g., E. Berliner, *J. Chem. Educ.*, **43**, 124 (1966).
 (46) N. G. Lordi and J. Epstein, *J. Am. Chem. Soc.*, **80**, 509 (1958).
 (47) M. Anbar and H. Taube, *J. Am. Chem. Soc.*, **80**, 1073 (1958).
 (48) One point of concern is the relative magnitudes of rate constants for H₂OCl₂ decomposition required for self-consistency. Assignment of $k_{43} \approx 2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ (eq 10b) requires that the relationship $k_{31} \approx k_{34}$ hold. The redox rate laws require that $k_{34} \leq 10^{-1} k_4[\text{H}_2\text{O}_2]$ (eq 3); furthermore, for DMFu to be an effective scavenger of H₂OCl₂ in the presence of H₂O₂, $k_5[\text{DMFu}] \geq 10k_4[\text{H}_2\text{O}_2]$. Since $k_6 \leq 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and the experimental conditions are $[\text{H}_2\text{O}_2] \approx 10^{-2} \text{ M}$, $[\text{H}_2\text{O}_2]/[\text{DMFu}] \approx 10^2$, the magnitudes of k_{31} and k_{34} can only be $\leq 10^4 \text{ s}^{-1}$. Accepting these values, it follows that $[\text{H}_2\text{OCl}_2]/[\text{HOCl}] \geq 10^{-7}$, $[\text{H}_2\text{OCl}_2]/[\text{H}_3\text{O}^+] \geq 10^{-7}$ for the reaction conditions, consistent with the notion that H₂OCl₂ is an unstable intermediate more strongly acidic than H₃O⁺ ion.
 (49) Cf. R. P. Bell and E. Gelles, *J. Chem. Soc.*, 2734 (1951); J. Arotzky and M. C. R. Symons, *Q. Rev., Chem. Soc.*, **16**, 282 (1962).
 (50) Reference 35a, pp 362-363.
 (51) M. Anbar, S. Guttman, and R. Rein, *J. Am. Chem. Soc.*, **81**, 1816 (1959).
 (52) G. A. Hamilton in "Molecular Mechanisms of Oxygen Activation", O. Hayaishi, Ed., Academic Press, New York, N.Y., 1974, Chapter 10.
 (53) See, e.g., J. March, "Advanced Organic Chemistry", McGraw-Hill, New York, N.Y., 1968, p 643 ff.

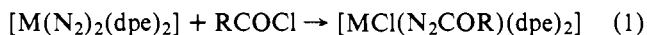
Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 8.¹ Diazoalkane Complexes of Molybdenum and Tungsten

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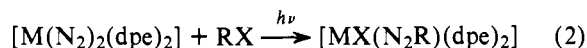
Contribution from the Department of Industrial Chemistry, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan. Received January 25, 1978

Abstract: The hydrazido(2-) complexes $[\text{M}(\text{NNH}_2)(\text{dpe})_2][\text{BF}_4]$ (M = Mo or W, dpe = Ph₂PCH₂CH₂PPh₂) obtained from *trans*- $[\text{M}(\text{N}_2)_2(\text{dpe})_2]$ and HBF₄ in THF readily condense with a variety of aldehydes and ketones to produce a new series of diazoalkane or hydrazone-type complexes $[\text{M}(\text{N}=\text{N}=\text{CRR}')(\text{dpe})_2][\text{BF}_4]$ in good yields. This reaction is remarkably accelerated in the presence of a trace of an acid. The structure of the diazoalkane complex $[\text{W}\{\text{N}=\text{C}(\text{CH}_3)\text{CH}_2\text{COCH}_3\}(\text{dpe})_2][\text{BF}_4] \cdot \text{THF}$ has been determined from three-dimensional x-ray counter data. The complex crystallized in space group *P*1 with $a = 13.577$ (15), $b = 21.440$ (25), $c = 11.204$ (13) Å; $\alpha = 102.36$ (3), $\beta = 100.00$ (3), $\gamma = 70.27$ (5)°; $V = 2980.5$ (58) Å³; and $Z = 2$. The coordination geometry about the tungsten atom is octahedral with the diazoalkane ligand and fluoride anion in a *trans* position. The W-N-N linkage is essentially linear and the angle N-N-C is 125.2 (19)°. The W-N, N-N, and N-C distances are 1.770 (17), 1.317 (25), and 1.300 (30) Å, respectively. The methyl group attached to the C=N bond is held in a distorted sandwich position relative to two phenyl groups, which accounts for the unusually higher shift of the methyl resonance in the ¹H NMR spectrum.

The formation of carbon-nitrogen bonds from coordinated dinitrogen is an important elementary step for the direct conversion of dinitrogen into organonitrogen compounds. The first examples of formation of organonitrogen ligands from coordinated dinitrogen were found in the reaction of organic acid halides with $[\text{M}(\text{N}_2)_2(\text{dpe})_2]$ (**1**) (M = Mo or W, dpe = Ph₂PCH₂CH₂PPh₂) and $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_3\text{L}]$, which yielded acyl- and aroyldiazenido complexes as shown in the equation²



Following this discovery, two groups independently found the alkylation reactions of coordinated dinitrogen in molybdenum and tungsten dinitrogen complexes **1** with alkyl halides to form alkyldiazenido complexes.^{2b,3,4}



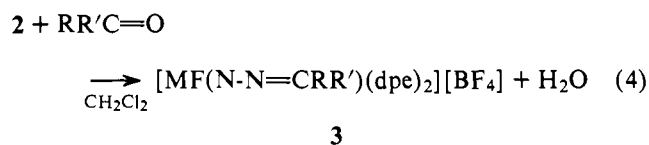
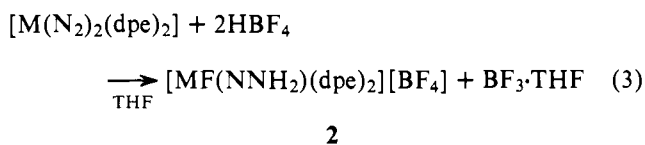
X-Ray structural analyses of $[\text{MoCl}(\text{N}_2\text{COPh})(\text{dpe})_2]$ ⁵ and $[\text{MoI}(\text{N}_2\text{C}_6\text{H}_{11})(\text{dpe})_2]$ ³ clearly showed that these complexes contained a carbon-nitrogen bond with an essentially linear Mo-N-N group. However, analogous acyl-, aroyl-, or alkyl-diazenido complexes have not yet been obtained from dinitrogen complexes with monophosphines $[\text{M}(\text{N}_2)_2\text{L}_4]$ (M = Mo or W, L = monotertiary phosphine). The reaction of $[\text{M}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]$ with methyl bromide yields, for instance, $[\text{MBr}_4(\text{PMe}_2\text{Ph})_2] + 2\text{N}_2$, and there is no sign of alkylated nitrogen-containing products.⁶

Recently we briefly described a new potential method for making carbon-nitrogen bonds from coordinated dinitrogen which consists of two steps, i.e., the formation of a diaz-

ido(2-) complex on treating the dinitrogen complex **1** ($M = Mo$) with an acid and the condensation reaction of the hydrazido(2-) complex with aldehydes and ketones to afford diazoalkane or hydrazone-type complexes.⁷ This method is very useful for preparing diazoalkane complexes, although Chatt and his co-workers^{8,18} recently obtained the analogous diazoalkane complexes $[WBr(N-N=CRR')(dpe)_2]Br$ ($R, R' = H$ or CH_3) by the action of *gem*-dibromide $RR'CB\gamma_2$ on the dinitrogen complex **1** ($M = W$). Here we describe in detail the preparation and physical properties of diazoalkane complexes of molybdenum and tungsten and the result of x-ray structural analysis of a diazoalkane complex $[WF(N-N=C(CH_3)CH_2COCH_3)(dpe)_2][BF_4] \cdot THF$.

Results and Discussion

Preparation of Diazoalkane Complexes of Molybdenum and Tungsten. Dinitrogen complexes of molybdenum and tungsten **1** easily react with an aqueous fluoroboric acid in THF to form the hydrazido(2-) complexes $[MF(NNH_2)(dpe)_2][BF_4]$ (**2**) ($M = Mo$ or W) in good yields:^{9,10}



The x-ray structural analysis of the complex **2** ($M = Mo$) showed that the $Mo-N-N$ linkage is essentially linear and two hydrogen atoms are attached to the terminal nitrogen.⁹ These hydrazido(2-) complexes **2** readily condense with a variety of aldehydes and ketones in dichloromethane to afford a new series of diazoalkane or hydrazone-type complexes $[MF(N-N=CRR')(dpe)_2][BF_4]$ (**3**) in good yields as shown in eq 4. All of the complexes **3** are isolated as brown to green crystals and are fairly stable in air. In the condensation reaction of the hydrazido(2-) complex **2** ($M = Mo$) with propionaldehyde, the quantitative formation of water according to eq 4 was observed by gas chromatographic analysis of the reaction mixture.

When aldehydes are used in this condensation reaction, the reaction proceeds easily at room temperature. Especially the reaction of formaldehyde, acetaldehyde, or propionaldehyde with the hydrazido(2-) complex **2** ($M = Mo$) finishes within 0.5 h. In contrast to aldehydes, ketones are comparatively inactive. Thus, the condensation reaction with acetone hardly proceeds after the 26 h stirring at room temperature. The diazoalkane complex **3** ($M = Mo$) derived from acetone is only obtained in a moderate yield at a refluxing temperature. This reaction is, however, remarkably accelerated in the presence of a trace of an acid as is usually found in the condensation reaction of carbonyl compounds with hydrazines. Thus, in the presence of a catalytic amount of fluoroboric acid, acetone condenses at room temperature with the hydrazido(2-) complex **2** ($M = Mo$) to afford the diazoalkane complex in a good yield. Ketones with bulky groups such as acetophenone and benzophenone do not, however, condense with the hydrazido(2-) complex **2** even in the presence of an acid. This indicates that the nucleophilic attack of the hydrazido(2-) ligand on the positive carbonyl carbon is greatly affected by the bulkiness of the carbonyl compound.

In the ¹H NMR spectra, two hydrogen atoms attached to the terminal nitrogen in the hydrazido(2-) complex of molybdenum **2** ($M = Mo$) shows a resonance at 5.2 ppm,⁹ while

those in the tungsten complex **2** ($M = W$) give rise to a band at 4.5 ppm. This suggests that the terminal nitrogen in the complex **2** ($M = W$) is more electron rich (vide post) and attacks, therefore, more easily the positive carbonyl carbons of aldehydes and ketones. However, the condensation reaction with the tungsten complex **2** ($M = W$) is slower than that with the molybdenum complex **2** ($M = Mo$), and speculation on the mechanism must await further investigations.

It is interesting to note that this condensation reaction is extremely slow in THF. For instance, the reaction of **2** ($M = Mo$) with propionaldehyde almost finishes within 20 min in dichloromethane, but in THF the condensation does not proceed at all after 20 h stirring under the same conditions.

Preparation of diazoalkane complexes **3** does not necessarily require the isolation of the hydrazido(2-) complex **2**. The diazoalkane complexes **3** ($M = W$, $R = CH_3$, $R' = CH_2CO-CH_3$; $M = Mo$ or W , $R = Ph$, $R' = H$) are obtained directly from the dinitrogen complex **1**; the dinitrogen complex **1** is, first, treated with an aqueous fluoroboric acid in THF to form the hydrazido(2-) complex **2** and after concentration of the solution to about one-third, a solution of a carbonyl compound in dichloromethane is added to give a diazoalkane complex **3**.

It is well known that with hydrazine many α,β -unsaturated aldehydes and ketones react by successive 1,2 and 1,4 addition to give cyclic products called pyrazolines,¹¹ and 1,3-diketones such as acetylacetone react to form pyrazoles.¹² Expecting the analogous reactions, we treated several α,β -unsaturated aldehydes and acetylacetone with the hydrazido(2-) complex **2**; however, formation of heterocyclic compounds was not observed. Crotonaldehyde and cinnamaldehyde yield only usual hydrazone-type complexes retaining a double bond. In the case of acetylacetone, one carbonyl group condenses with the hydrazido(2-) complex **2** and the other remains free.

Spectroscopic Properties of Diazoalkane Complexes. All of the diazoalkane complexes **3** except for $[MoF(N-N=CH_2)(dpe)_2][BF_4]$ give rise to strong $\nu(C=N)$ bands in the 1510–1595-cm⁻¹ region of the infrared spectrum as shown in Table I. The $\nu(C=N)$ band at 1565 cm⁻¹ of $[MoF(N-N=CHCH_2CH_3)(dpe)_2][BF_4]$ shifts to 1550 cm⁻¹ upon ¹⁵N substitution. In the case of $[MoF(N-N=CH_2)(dpe)_2][BF_4]$, a band assigned to $\nu(C=N)$ was not observed. Chatt et al.⁸ also could not find any band due to $\nu(C=N)$ in an analogous complex $[WBr(N-N=CH_2)(dpe)_2]Br$ obtained from the dinitrogen complex **1** ($M = W$) and dibromomethane.

The exact location of the $\nu(C=N)$ band depends on the structure of groups attached to the $C=N$ bond. The $\nu(C=N)$ bands of diazoalkane complexes **3** ($M = Mo$) derived from benzaldehyde or cinnamaldehyde appear comparatively at lower frequencies (1525 and 1510 cm⁻¹, respectively) by the effect of conjugation between $C=N$ and $C=C$ bonds. However, the diazoalkane complex **3** ($M = Mo$) obtained from crotonaldehyde gives rise to the $\nu(C=N)$ band at 1565 cm⁻¹, which may indicate that the $C=N$ bond and the $C=C$ bond does not lie on the same plane and there is only little resonance between the two double bonds. The complex **3** derived from acetylacetone shows a strong band assigned to $\nu(C=O)$ ($M = Mo$, 1710 cm⁻¹; $M = W$, 1725 cm⁻¹) as well as an intense band assigned to $\nu(C=N)$ ($M = Mo$, 1570 cm⁻¹; $M = W$, 1595 cm⁻¹). This means that only one carbonyl group of acetylacetone condenses with the hydrazido(2-) complex **2** and the remaining carbonyl group exists as the keto form.

The $\nu(C=N)$'s of diazoalkane complexes **3** are found to be lower than those of hydrazones ($\nu(C=N)$ 1612, 1604 cm⁻¹ in $CH_3CH=N-NHCH_3$) or azines ($\nu(C=N)$ 1627 cm⁻¹ in $PhCH=N-N=CHPh$), which is compatible with longer carbon-nitrogen bond lengths of the complexes **3** compared with those of azines, as described later. In other words, the complexes **3** are described by two resonance structures, i and

Table I. Analytical Data and Characteristic IR Bands of Diazoalkane Complexes

complex	yield, ^a %	anal., ^c %					IR, ^d cm ⁻¹	
		C	H	N	F	P	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{O})$
[MoF(N-N=CH ₂)(dpe) ₂][BF ₄]	37	60.86 (61.16)	4.89 (4.85)	3.70 (2.69)				
[MoF(N-N=CHCH ₃)(dpe) ₂][BF ₄] ·CH ₂ Cl ₂	78	55.78 (57.96)	4.57 (4.79)	2.16 (2.46)			1575	
[MoF(N-N=CHCH ₂ CH ₃)(dpe) ₂][BF ₄]	87	61.52 (61.81)	5.07 (5.10)	2.50 (2.62)			1565	
[MoF(¹⁵ N- ¹⁵ N=CHCH ₂ CH ₃)(dpe) ₂]- [BF ₄]	64						1550	
[MoF(N-N=CHPh)(dpe) ₂][BF ₄]	63	63.29 (63.45)	4.87 (4.88)	2.56 (2.51)	8.46 (8.51)	11.13 (11.09)	1525	
[MoF(N-N=CHCH ₂ Ph)(dpe) ₂][BF ₄] ·THF	40	63.87 (63.90)	5.05 (5.37)	2.07 (2.33)			1560	
[MoF(N-N=CHCH=CHCH ₃)(dpe) ₂]- [BF ₄]	37	62.09 (62.23)	5.08 (5.05)	2.63 (2.59)			1565	
[MoF(N-N=CHCH=CHPh)(dpe) ₂]- [PF ₆] ·THF	63	61.03 (61.32)	5.19 (5.08)	2.15 (2.20)	10.18 (10.45)		1510	
[MoF{N-N=C(CH ₃)CH ₂ COCH ₃ }(dpe) ₂]- [BF ₄] ·THF	70	61.95 (61.93)	5.45 (5.46)	2.56 (2.37)			1570	1710
[MoF{N-N=C(CH ₃) ₂ }(dpe) ₂][BF ₄] ·(CH ₃) ₂ CO	45	62.29 (61.82)	5.42 (5.38)	2.34 (2.49)			1585	1705
[MoF(N-N=C ₆ H ₁₀)(dpe) ₂][BF ₄] ·CH ₂ Cl ₂	74	58.14 (59.36)	4.92 (5.08)	1.79 (2.35)			1575	
[WF(N-N=CHCH ₂ CH ₃)(dpe) ₂][BF ₄]	89	56.93 (57.11)	4.72 (4.72)	2.40 (2.42)			1580	
[WF(N-N=CHPh)(dpe) ₂][BF ₄]	76 ^b	58.88 (58.82)	4.54 (4.53)	2.29 (2.33)			1540	
[WF{N-N=C(CH ₃)CH ₂ COCH ₃ }(dpe) ₂]- [BF ₄] ·THF	74 ^b	57.18 (57.64)	5.15 (5.09)	2.18 (2.20)	7.79 (7.48)		1595	1725

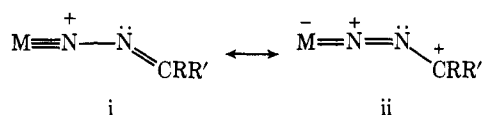
^a Based on the complex **2** (M = Mo, W). ^b Based on the complex **1** (M = W). ^c Calculated values are in parentheses. ^d KBr disks.

Table II. NMR Data of Diazoalkane Complexes^a

complex	resonance, ppm ^d (coupling, ^e integrated value), assignment
	¹ H NMR
[MoF(N-N=CH ₂)(dpe) ₂][BF ₄]	4.9 (d, 1 H), NNCH ₂ ; 6.2 (d, 1 H), NNCH ₂
[MoF(N-N=CHCH ₃)(dpe) ₂][BF ₄] ·CH ₂ Cl ₂	1.0 (d, 3 H), NNCHCH ₃ ; 5.7 (q, 1 H), NNCHCH ₃
[MoF(N-N=CHCH ₂ CH ₃)(dpe) ₂][BF ₄]	0.6 (t, 3 H), CHCH ₂ CH ₃ ; 1.4 (m, 2 H), CHCH ₂ CH ₃ ; 5.4 (t, 1 H), NNCHCH ₂
[MoF(N-N=CHPh)(dpe) ₂][BF ₄]	5.6 (s, 1 H), NNCHPh
[MoF(N-N=CHCH ₂ Ph)(dpe) ₂][BF ₄] ·THF	2.7 (d, 2 H), NNCHCH ₂ Ph; 5.4 (t, 1 H), NNCHCH ₂ Ph
[MoF(N-N=CHCH=CHCH ₃)(dpe) ₂][BF ₄] ^f	1.0 (d, 3 H), CH=CHCH ₃ ; 5.6 (br, 1 H), NNCHCH=CH
[MoF(N-N=CHCH=CHPh)(dpe) ₂][PF ₆] ·THF	5.5 (d, 1 H), NNCHCH=CH; 6.2 (m, 2 H), olefinic protons
[MoF{N-N=C(CH ₃)CH ₂ COCH ₃ }(dpe) ₂][BF ₄] ·THF	-0.3 (s, 3 H), NC(CH ₃); 2.2 (s, 3 H), CH ₂ COCH ₃ ; 3.0 (s, 2 H), CH ₂ COCH ₃
[MoF{N-N=C(CH ₃) ₂ }(dpe) ₂][BF ₄] ·(CH ₃) ₂ CO ^b	-0.4 (s, 3 H), NNC(CH ₃) ₂ ; 1.4 (s, 3 H), NNC(CH ₃) ₂
[MoF(N-N=C ₆ H ₁₀)(dpe) ₂][BF ₄] ·CH ₂ Cl ₂ ^b	0.1, 0.8, 1.2, 1.5 (m, 10 H), NNC ₆ H ₁₀
[WF(N-N=CHCH ₂ CH ₃)(dpe) ₂][BF ₄]	0.7 (t, 3 H), CHCH ₂ CH ₃ ; 1.3 (m, 2 H), CHCH ₂ CH ₃ ; 5.5 (t, 1 H), NNCHCH ₂
[WF(N-N=CHPh)(dpe) ₂][BF ₄] ^c	5.8 (s, 1 H), NNCHPh
[WF{N-N=C(CH ₃)CH ₂ COCH ₃ }(dpe) ₂][BF ₄] ·THF	-0.6 (s, 3 H), NC(CH ₃); 2.1 (s, 3 H), CH ₂ COCH ₃ ; 2.7 (s, 2 H), CH ₂ COCH ₃
	¹⁹ F NMR ^g
[MoF(N-N=CHCH ₂ CH ₃)(dpe) ₂][BF ₄]	50.3 (qi, 1 F), Mo-F; 83.0 (s, 4 F), BF ₄

^a CD₂Cl₂ solution. ^b CD₂Cl₂ or (CD₃)₂CO solution. ^c CDCl₃ solution. ^d HMDS or Me₄Si standard. ^e s = singlet, d = doublet, t = triplet, q = quartet, qi = quintet, and m = multiplet. ^f Resonances due to olefinic protons may be overlapped with those of phenyl groups. ^g Higher field than benzotrifluoride.

ii. There is a clear trend that diazoalkane complexes of tungsten **3** (M = W) show higher $\nu(\text{C}=\text{N})$'s than corresponding

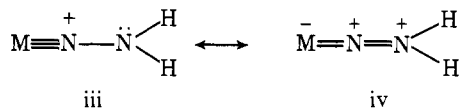


molybdenum complexes **3** (M = Mo). This indicates that tungsten has stronger back-donating capacity than molybdenum and contribution of the canonical structure i is larger in the case of tungsten. This difference of back-donating capacities between tungsten and molybdenum is also reflected in the N-H resonances in the ¹H NMR spectra of the hydrazido(2-) complexes **2** (M = Mo or W) (vide supra), since the electronic

Table III. Selected Bond Distances (Å) and Angles (deg) of [WF{N=N=C(CH₃)CH₂COCH₃}(dpe)₂][BF₄]·THF

atoms	distances	atoms	angles
W-N(1)	1.770 (17)	W-N(1)-N(2)	173.8 (15)
W-F(1)	2.019 (14)	N(1)-N(2)-CN(1)	125.2 (19)
W-P(1)	2.536 (7)	N(2)-CN(1)-CN(2)	121.5 (23)
W-P(2)	2.501 (6)	N(2)-CN(1)-CN(4)	125.4 (22)
W-P(3)	2.531 (6)	CN(2)-CN(1)-CN(4)	112.9 (23)
W-P(4)	2.520 (8)	CN(1)-CN(2)-CN(3)	113.9 (29)
N(1)-N(2)	1.317 (25)	CN(2)-CN(3)-O	116.8 (38)
N(2)-CN(1)	1.300 (30)	CN(2)-CN(3)-CN(5)	111.3 (39)
CN(1)-CN(2)	1.525 (43)	O-CN(3)-CN(5)	131.8 (46)
CN(1)-CN(4)	1.515 (38)	N(1)-W-F(1)	179.3 (7)
CN(2)-CN(3)	1.490 (53)	N(1)-W-P(1)	98.0 (6)
CN(3)-O	1.198 (58)	N(1)-W-P(2)	99.4 (6)
CN(3)-CN(5)	1.470 (79)	N(1)-W-P(3)	86.5 (6)
C(1)-C(2)	1.476 (51)	N(1)-W-P(4)	88.2 (6)
C(3)-C(4)	1.356 (66)	F(1)-W-P(1)	82.7 (4)
B(1)-FB(1)	1.458 (89)	F(1)-W-P(2)	81.0 (4)
B(1)-FB(2)	1.254 (78)	F(1)-W-P(3)	92.9 (4)
B(1)-FB(3)	1.370 (76)	F(1)-W-P(4)	91.5 (4)
B(1)-FB(4)	1.183 (93)	P(1)-W-P(2)	79.5 (2)
C-C (Ph)	1.379 (av)	P(3)-W-P(4)	77.6 (2)
C-H	1.089 (av)	P(1)-W-P(3)	175.5 (2)
		P(2)-W-P(4)	172.1 (2)
		P(1)-W-P(4)	102.1 (2)
		P(2)-W-P(3)	100.1 (2)
		FB-B(1)-FB	108.1 (av)

structure of these diazoalkane complexes may be represented as a combination of the analogous canonical forms iii and iv.^{9,13}



In these diazoalkane complexes **3**, the diazoalkane ligand and fluoride anion are trans to each other. Thus, the ¹⁹F NMR spectrum of [MoF{N=N=C(CH₃)CH₂COCH₃}(dpe)₂][BF₄] shows a band at 83.0 ppm above benzotrifluoride assigned to fluoroborate anion and a quintet band at 50.3 ppm (*J*_{F-P} = 30 Hz) in a ratio of ca. 4:1.

Table IV. Comparison of Bond Lengths (Å)

	M-N	N-N	N=C
[WF{N=N=C(CH ₃)CH ₂ COCH ₃ }(dpe) ₂][BF ₄]·THF ^a	1.770 (17)	1.317 (25)	1.300 (30)
[WBr{N=N=C(CH ₃) ₂ }(dpe) ₂]Br ^b	1.74 (1)	1.34 (2)	1.28 (2)
[WBr{N=N=CH(CH ₂) ₃ OH}(dpe) ₂][PF ₆] ^c	1.78	1.31	1.29
<i>trans</i> -[PtH{PhHN=N=C(CH ₃) ₂ }(PPh ₃) ₂][BF ₄]-C ₆ H ₆ ^d	2.166 (6)	1.407 (8)	1.273 (9)
<i>p</i> -CH ₃ OC ₆ H ₄ CH=N=N=CHC ₆ H ₄ OCH ₃ - <i>p</i> ^e		1.410	1.283
<i>o</i> -HOC ₆ H ₄ CH=N=N=CHC ₆ H ₄ OH- <i>o</i> ^f		1.407 (4)	1.274 (4)

^a This work. ^b Reference 18. ^c P. C. Bevan, J. Chatt, R. A. Head, P. B. Hitchcock, and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, 509 (1976). ^d Reference 17. ^e Reference 15. ^f Reference 16.

Table V. Crystallographic Data and Intensity Collections of [WF{N=N=C(CH₃)CH₂COCH₃}(dpe)₂][BF₄]·THF

<i>a</i> , Å	13.577 (15)	systematic absences	none
<i>b</i> , Å	21.440 (25)	space group	<i>P</i> $\bar{1}$
<i>c</i> , Å	11.204 (13)	<i>F</i> (000)	1288
α , deg	102.36 (3)	crystal dimensions, mm	0.33 × 0.36 × 2.6
β , deg	100.00 (3)	μ , cm ⁻¹	22.1
γ , deg	70.27 (5)	2 θ limits, deg	55.0
<i>V</i> , Å ³	2980.5 (58)	scan speed (2 θ)	2.0°/min
<i>Z</i>	2	scan range (2 θ)	$\Delta(2\theta) = 2.0^\circ + 0.9 \tan \theta$
density, g/cm ³ (calcd)	1.42		

¹H NMR data of diazoalkane complexes **3** are shown in Table II. The complexes **3**, which are obtained from the condensation of diazido(2-) complexes **2** with carbonyl compounds, may be regarded as hydrazone-type complexes and the groups on the nitrogen-bearing carbon are inequivalent. Thus, diazomethane hydrogens in [MoF{N=N=CH₂}(dpe)₂][BF₄] show a pair of doublets at 4.9 and 6.2 ppm. The 2-diazopropane complex **3** (M = Mo) gives rise to two singlets separated by 1.8 ppm and one singlet appears at higher field than hexamethyldisiloxane. An analogous higher shift of a resonance due to a methyl group attached to the C=N bond is also observed in ¹H NMR spectra of diazoalkane complexes **3** (M = Mo or W) derived from acetylacetone.

Since the groups on the nitrogen-bearing carbon in diazoalkane complexes **3** are inequivalent, two geometric isomers, *syn* and *anti* forms, are possible about the C=N bond if the groups are different from each other. However, ¹H NMR spectra of diazoalkane complexes clearly show that the complexes **3** consist of one isomer; for instance, the 1-diazopropane complex **3** (M = Mo) gives rise to a triplet at 5.4 ppm assigned to the methine proton, a multiplet at 1.4 ppm assigned to methylene protons, and a triplet at 0.6 ppm assigned to methyl protons in a ratio of 1:2:3 and no bands assigned to another isomer are observed.

The ¹H NMR spectra of diazoalkane complexes **3** (M = Mo or W) obtained from acetylacetone show that the diazoalkane ligand exists exclusively as 2-azo-4-oxopentane (keto form) even in a dichloromethane solution.

As an aid to understanding the spectroscopic properties of diazoalkane complexes, especially the higher shifts of a resonance due to a methyl group attached to the C=N bond in the ¹H NMR spectra of the 2-diazopropane and 2-diazo-4-oxopentane complexes **3**, and because of current interest in the bonding of diazoalkane to transition metals, the crystal structure of [WF{N=N=C(CH₃)CH₂COCH₃}(dpe)₂][BF₄]-THF was determined and the results are reported in the next section.

Structure of [WF{N=N=C(CH₃)CH₂COCH₃}(dpe)₂][BF₄]-THF (4). The structure of the diazoalkane complex **4** was found to consist of discrete cation, anion, and solvent THF species occupying general positions in space group *P* $\bar{1}$. The perspective views of the complex are shown in Figures 1 and 2.

This complex has octahedral geometry with the diazoalkane ligand and fluoride anion in a *trans* position. Selected bond

Table VI. Positional and Thermal Parameters of Nonhydrogen Atoms of $[\text{WF}\{\text{N}=\text{C}(\text{CH}_3)\text{CH}_2\text{COCH}_3\}(\text{dpe})_2][\text{BF}_4]\cdot\text{THF}$

Atom	x^a	y	z	U_{11} or B^b	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	3909 (1)	2523 (0)	1821 (1)	43 (0)	51 (0)	61 (0)	-19 (0)	-1 (0)	23 (0)
P(1)	2426 (5)	2089 (3)	671 (6)	75 (3)	84 (4)	89 (4)	-49 (3)	-7 (3)	20 (3)
P(2)	3799 (4)	2827 (3)	-243 (5)	67 (3)	63 (3)	64 (3)	-21 (2)	14 (2)	7 (2)
P(3)	5489 (4)	2868 (3)	2902 (6)	68 (3)	79 (4)	82 (4)	-35 (3)	-4 (3)	22 (3)
P(4)	4241 (3)	2082 (4)	3815 (6)	80 (4)	107 (5)	95 (4)	-43 (4)	-16 (3)	51 (4)
F(1)	4813 (8)	1636 (5)	975 (12)	60 (6)	53 (6)	115 (10)	5 (5)	-1 (6)	8 (6)
N(1)	3130 (12)	3301 (8)	2575 (13)	79 (10)	74 (10)	46 (8)	-28 (8)	23 (8)	16 (8)
N(2)	2620 (14)	3865 (8)	3246 (15)	85 (11)	77 (11)	66 (10)	-22 (9)	9 (9)	33 (9)
CN(1)	1707 (17)	4270 (10)	2903 (21)	82 (14)	67 (13)	86 (15)	-13 (11)	16 (12)	25 (11)
CN(2)	1190 (26)	4924 (15)	3730 (29)	136 (26)	107 (22)	114 (22)	31 (19)	28 (19)	21 (18)
CN(3)	1659 (29)	4958 (18)	5039 (33)	158 (31)	135 (26)	124 (27)	-4 (23)	27 (23)	50 (22)
CN(4)	1101 (18)	4193 (13)	1640 (27)	66 (14)	100 (18)	133 (23)	-23 (13)	7 (14)	26 (16)
CN(5)	2412 (40)	5341 (31)	5306 (47)	195 (47)	316 (68)	186 (45)	-104 (46)	-44 (35)	-16 (44)
O	1422 (28)	4647 (20)	5650 (30)	227 (33)	287 (38)	168 (26)	-8 (29)	64 (25)	95 (26)
C(1)	2275 (30)	2151 (20)	-1018 (24)	197 (34)	218 (36)	69 (17)	-153 (31)	-39 (19)	37 (20)
C(2)	3152 (20)	2305 (14)	-1377 (24)	103 (17)	122 (20)	104 (18)	-84 (16)	23 (14)	6 (15)
C(3)	5380 (28)	2998 (17)	4571 (24)	181 (31)	166 (29)	77 (17)	-110 (26)	35 (18)	1 (18)
C(4)	5012 (32)	2563 (25)	4938 (28)	214 (37)	352 (56)	94 (21)	-221 (41)	-53 (22)	101 (29)
C(111)	1104 (15)	2531 (11)	1098 (26)	50 (11)	80 (14)	159 (23)	-30 (10)	-22 (13)	56 (15)
C(112)	201 (21)	2633 (14)	198 (27)	93 (17)	111 (19)	124 (22)	-49 (15)	-42 (16)	37 (17)
C(113)	-792 (22)	2979 (18)	610 (31)	84 (17)	162 (28)	144 (26)	-37 (18)	-51 (18)	75 (23)
C(114)	-938 (19)	3206 (16)	1793 (35)	55 (14)	132 (24)	209 (34)	-14 (14)	-8 (17)	84 (24)
C(115)	-86 (18)	3085 (17)	2725 (30)	53 (13)	165 (28)	159 (27)	-21 (15)	24 (15)	72 (23)
C(116)	937 (16)	2773 (13)	2345 (22)	60 (12)	130 (20)	91 (16)	-34 (13)	7 (11)	52 (15)
C(121)	2587 (16)	1223 (9)	669 (20)	79 (13)	52 (11)	90 (15)	-28 (10)	38 (12)	-4 (10)
C(122)	1978 (23)	1012 (12)	1287 (34)	117 (21)	64 (14)	212 (34)	-27 (14)	35 (22)	55 (18)
C(123)	2129 (19)	326 (15)	1322 (43)	140 (28)	83 (19)	265 (46)	-35 (19)	20 (29)	69 (24)
C(124)	2851 (30)	-139 (14)	751 (45)	154 (31)	63 (17)	296 (52)	-43 (19)	34 (32)	36 (24)
C(125)	3441 (33)	37 (16)	9 (48)	180 (37)	82 (21)	276 (53)	-39 (23)	67 (36)	-16 (27)
C(126)	3299 (31)	723 (17)	130 (44)	176 (34)	105 (23)	297 (52)	-92 (24)	123 (36)	-34 (28)
C(211)	4985 (17)	2673 (10)	-976 (18)	90 (15)	66 (12)	63 (12)	-7 (11)	36 (11)	17 (10)
C(212)	5213 (20)	3177 (12)	-1384 (23)	102 (17)	82 (15)	95 (17)	-44 (13)	27 (14)	12 (13)
C(213)	6155 (21)	3067 (15)	-1839 (23)	110 (19)	129 (22)	78 (16)	-63 (17)	28 (14)	8 (15)
C(214)	6870 (22)	2439 (15)	-1951 (31)	97 (19)	117 (22)	157 (27)	-25 (16)	78 (20)	7 (20)
C(215)	6661 (38)	1964 (19)	-1590 (62)	219 (46)	104 (26)	477 (91)	3 (27)	246 (57)	64 (39)
C(216)	5763 (28)	2070 (17)	-1053 (50)	129 (25)	100 (23)	372 (64)	16 (19)	138 (35)	83 (31)
C(221)	3033 (16)	3730 (10)	-380 (18)	77 (13)	78 (13)	58 (12)	-12 (11)	1 (10)	36 (10)
C(222)	2280 (27)	3843 (16)	-1371 (25)	165 (29)	119 (23)	75 (18)	28 (21)	-6 (18)	21 (17)
C(223)	1766 (30)	4539 (21)	-1427 (31)	161 (30)	191 (35)	103 (24)	27 (26)	-15 (21)	84 (25)
C(224)	1912 (25)	5040 (16)	-534 (30)	120 (23)	134 (24)	145 (26)	7 (19)	61 (21)	75 (21)
C(225)	2655 (21)	4882 (11)	441 (27)	106 (18)	67 (14)	143 (23)	-3 (13)	20 (16)	59 (15)
C(226)	3226 (17)	4208 (10)	517 (21)	82 (14)	62 (12)	94 (15)	-29 (11)	18 (12)	22 (11)
C(311)	5538 (16)	3665 (11)	2669 (22)	60 (11)	80 (14)	100 (16)	-31 (10)	17 (11)	14 (12)
C(312)	6066 (15)	3665 (12)	1678 (24)	48 (11)	101 (17)	127 (20)	-29 (11)	-7 (12)	42 (15)
C(313)	6043 (24)	4279 (17)	1403 (33)	106 (21)	149 (28)	172 (30)	-67 (21)	-21 (20)	84 (24)
C(314)	5477 (26)	4880 (18)	2041 (40)	122 (24)	136 (27)	237 (42)	-79 (22)	-38 (26)	82 (28)
C(315)	4934 (25)	4911 (4)	2986 (36)	119 (23)	75 (18)	200 (36)	-38 (16)	0 (23)	-10 (20)
C(316)	4948 (22)	4295 (13)	3298 (30)	99 (19)	83 (17)	155 (27)	-34 (14)	23 (18)	0 (17)
C(321)	6798 (17)	2294 (12)	2748 (25)	61 (13)	87 (16)	128 (21)	-25 (11)	-34 (13)	30 (15)
C(322)	7642 (21)	2441 (14)	3522 (38)	77 (17)	93 (20)	232 (40)	-19 (15)	-4 (21)	47 (23)
C(323)	8704 (23)	2005 (21)	3408 (38)	75 (18)	199 (38)	199 (37)	-61 (22)	-56 (21)	53 (30)
C(324)	8905 (27)	1442 (23)	2531 (46)	80 (22)	209 (42)	248 (49)	-39 (25)	6 (26)	-36 (37)
C(325)	8046 (29)	1272 (30)	2046 (67)	72 (22)	269 (60)	474 (94)	11 (29)	-38 (36)	-166 (59)
C(326)	7027 (24)	1712 (19)	2067 (43)	71 (19)	155 (32)	278 (49)	14 (19)	-40 (24)	-109 (33)
C(411)	3081 (16)	2177 (11)	4619 (21)	72 (13)	95 (15)	95 (16)	-43 (12)	-19 (11)	61 (13)
C(412)	2747 (18)	1616 (14)	4482 (28)	66 (13)	116 (20)	153 (24)	-36 (13)	10 (15)	68 (18)
C(413)	1827 (25)	1710 (16)	5007 (35)	120 (23)	116 (23)	191 (33)	-41 (19)	23 (23)	67 (23)
C(414)	1286 (22)	2316 (18)	5550 (27)	91 (18)	167 (30)	105 (20)	21 (19)	25 (16)	51 (20)
C(415)	1554 (24)	2877 (16)	5651 (24)	129 (23)	139 (24)	71 (16)	-27 (19)	11 (15)	31 (16)
C(416)	2455 (21)	2811 (14)	5150 (23)	104 (18)	108 (19)	84 (17)	-25 (15)	-4 (14)	37 (15)
C(421)	5078 (23)	1229 (19)	3895 (39)	92 (19)	174 (32)	238 (40)	11 (20)	30 (22)	153 (31)
C(422)	5564 (33)	993 (26)	4959 (46)	168 (35)	252 (51)	233 (48)	13 (34)	0 (33)	209 (45)
C(423)	6232 (44)	316 (30)	4994 (56)	220 (54)	256 (58)	269 (56)	-8 (45)	-13 (45)	166 (49)
C(424)	6166 (50)	-67 (28)	4000 (56)	304 (69)	228 (51)	266 (59)	69 (48)	56 (52)	147 (46)
C(425)	5725 (86)	82 (36)	2780 (52)	949 (169)	259 (70)	123 (43)	131 (89)	113 (72)	-8 (45)
C(246)	5124 (70)	796 (26)	2965 (69)	503 (131)	145 (41)	362 (89)	104 (60)	170 (91)	146 (50)
B(1)	8530 (43)	3312 (26)	-3132 (61)	173 (45)	139 (39)	273 (68)	-38 (34)	112 (47)	26 (42)
FB(1)	9207 (42)	3673 (20)	-2348 (36)	534 (71)	257 (38)	241 (36)	-187 (44)	-16 (40)	41 (30)
FB(2)	8926 (27)	2725 (11)	-2904 (33)	333 (41)	115 (17)	362 (43)	-26 (21)	177 (35)	61 (21)
FB(3)	8888 (24)	3414 (12)	-4122 (29)	253 (30)	157 (20)	271 (32)	-26 (20)	111 (26)	63 (20)
FB(4)	7656 (28)	3652 (15)	-2983 (57)	255 (36)	165 (25)	899 (113)	-49 (24)	343 (57)	29 (42)

Table VI (Continued)

Atom	x^a	y	z	U_{11} or B^b
OT ^c	94	-54	253	15.0
CT(1) ^c	95	-64	352	15.0
CT(2) ^c	32	-103	382	15.0
CT(3) ^c	-27	-112	253	15.0
CT(4) ^c	3	-66	163	15.0

^a The quantities given in the table are the positional coefficients $\times 10^4$. ^b The quantities given in the table are the anisotropic thermal coefficients $\times 10^3$ and the isotropic thermal coefficients $\times 1$. The form of the anisotropic thermal ellipsoid as $\exp[-2\pi(\hbar^2 a^* U_{11} + k^2 b^* U_{22} + l^2 c^* U_{33} + 2hka^* b^* U_{12} + 2hla^* c^* U_{13} + 2klb^* c^* U_{23})]$. ^c The quantities of this atom are the positional coefficients $\times 10^3$.

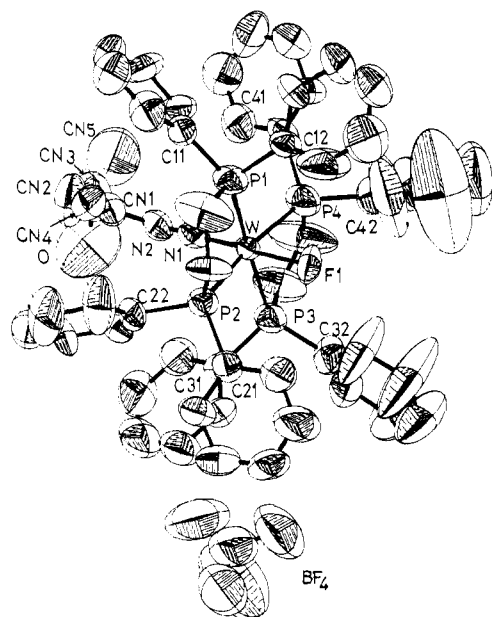


Figure 1. Perspective view of $[\text{WF}(\text{N}=\text{N}=\text{C}(\text{CH}_3)\text{CH}_2\text{COCH}_3)(\text{dpe})_2][\text{BF}_4]\cdot\text{THF}$. The shapes of the atoms in this drawing represent 50% probability of thermal motions.

distances and angles are shown in Table III.

The W-N-N linkage is essentially linear and the angle N-N-C is $125.2(19)^\circ$. The C=N distance of $1.300(30)$ Å found in this complex is longer than an ordinary C=N bond distance of 1.27 Å, which is compatible with the low $\nu(\text{C}=\text{N})$ observed at 1595 cm^{-1} . Accompanying the elongation of the C=N bond, the N-N bond possesses some double bond character. The bond orders of the C=N and N-N bonds in this complex are calculated to be about 1.7 and 1.4, respectively, by Allman's method.¹⁴ Furthermore, the six atoms, W, N(1), N(2), CN(2), CN(1), and CN(4), nearly lie on the same plane. These facts indicate that the electronic structure of the complex **4** may be described as a combination of the two resonance structures i and ii. On the other hand, in azines such as anisaldehyde azine and salicylaldehyde azine, the central N-N bond of the $-\text{CH}=\text{N}-\text{N}=\text{CH}-$ moiety is rather long (1.41 Å) and C=N bonds are accordingly short (1.28 Å),^{15,16} indicating that there is only little resonance (Table IV). In an acetone phenylhydrazone complex of platinum, $\text{trans}-[\text{PtH}\{\text{PhHNN}=\text{C}(\text{CH}_3)_2\}(\text{PPh}_2)_2][\text{BF}_4]\cdot\text{C}_6\text{H}_6$,¹⁷ in which the hydrazone is attached via an sp^2 nitrogen atom, there is also little overlap between the metal orbitals and the π orbitals of the hydrazone ligand.

In the complex **4**, the methyl group attached to the C=N bond is held in a distorted sandwich position relative to two phenyl groups. The distances from one phenyl group (3.48 , 3.88 , 4.11 , 4.06 , 3.77 , and 3.39 Å) show a relatively close approach to one edge, while the distances from the other phenyl group (3.51 , 3.81 , 3.97 , 3.82 , 3.52 , and 3.35 Å) indicate a relatively close approach to two edges of the phenyl ring. This peculiar position of the methyl group is reflected in the higher shift of the CH_3 resonance in the ^1H NMR spectrum as de-

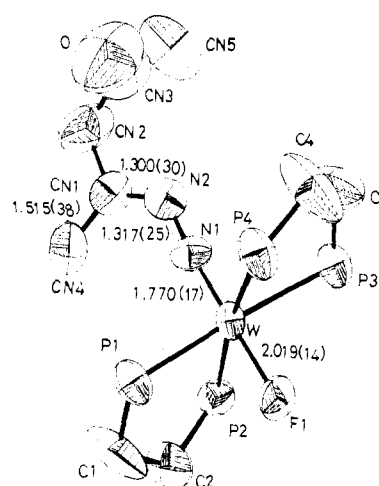


Figure 2. Perspective view of $[\text{WF}(\text{N}=\text{N}=\text{C}(\text{CH}_3)\text{CH}_2\text{COCH}_3)(\text{dpe})_2][\text{BF}_4]\cdot\text{THF}$. The shapes of the atoms in this drawing represent 50% probability of thermal motions.

scribed above. The angles P1-W-N1 and P2-W-N1 are $98.0(6)$ and $99.4(6)^\circ$, respectively, and rather larger than 90° . On the other hand, the angles of P3-W-N1 and P4-W-N1 are $86.5(6)$ and $88.2(6)^\circ$, respectively. This reflects a considerable steric repulsion of the methyl group bonded to the C=N bond toward one of dpe ligands. Recently Chatt et al.¹⁸ have carried out the x-ray structure analysis of $[\text{WBr}\{\text{N}=\text{N}=\text{C}(\text{CH}_3)_2\}(\text{dpe})_2]\text{Br}$ obtained from the dinitrogen complex **1** ($M = \text{W}$) and 2,2-dibromopropane and accounted for the higher shift of a band assigned to one of two methyl groups in a similar way.

As described above, diazoalkane complexes **3** consist of one isomer, although two geometric isomers are possible about the C=N bond. This may be ascribed to the predominant situation of a smaller group (H or CH_3) bonded to the C=N bond in a constricted position between the phenyl groups, where the smaller group is located in an anti position toward the lone pair of the terminal nitrogen.

Experimental Section

General. All reactions were carried out under an atmosphere of pure nitrogen or argon gas except for those with extremely air-stable compounds. Solvents were purified by the usual methods, rigorously dried, and distilled under nitrogen atmosphere. Carbonyl compounds and potassium hexafluorophosphate were commercially obtained and used without further purification. The complexes $\text{trans}-[\text{Mo}(\text{N}_2)_2(\text{dpe})_2]$,¹⁹ $\text{trans}-[\text{Mo}(\text{N}_2)_2(\text{dpe})_2]$,¹⁹ $\text{trans}-[\text{W}(\text{N}_2)_2(\text{dpe})_2]$,²⁰ and $\text{trans}-[\text{MoF}(\text{NNH}_2)(\text{dpe})_2][\text{BF}_4]$ ⁹ were prepared by published methods. Elemental analyses were by Dr. G. Reuter (West Germany). Infrared spectra were determined with a Nihon-bunko double-beam spectrometer or a Hitachi 215 spectrometer. NMR spectra were recorded on a JEOL PS-100 spectrometer (^1H 100 MHz, ^{19}F 94 MHz) or a Hitachi R-40 spectrometer (^1H 90 MHz). GLC analyses were performed using a Hitachi 023 gas chromatograph. Analytical and other data are given in Tables I and II.

Preparation of $\text{trans}-[\text{WF}(\text{NNH}_2)(\text{dpe})_2][\text{BF}_4]\cdot\text{CH}_2\text{Cl}_2$. To a vermilion suspension of the complex **1** ($M = \text{W}$) (400 mg, 0.386 mmol) in THF (9 mL) was added an excess of a 42% aqueous HBF_4 solution

Table VII. Positional Parameters for the Hydrogen Atoms of $[\text{WF}\{\text{N}-\text{N}=\text{C}(\text{CH}_3)\text{CH}_2\text{COCH}_3\}(\text{dpe})_2][\text{BF}_4]\cdot\text{THF}$.

atom	x^a	y	z
HC(21)	40 (19)	497 (12)	370 (22)
HC(22)	118 (19)	537 (12)	339 (22)
H(11)	210 (19)	178 (12)	-156 (23)
H(12)	150 (19)	255 (12)	-120 (22)
H(21)	293 (19)	248 (12)	-220 (23)
H(22)	376 (19)	181 (12)	-160 (23)
H(31)	610 (19)	303 (12)	502 (23)
H(32)	478 (19)	352 (12)	487 (22)
H(41)	454 (19)	283 (12)	561 (23)
H(42)	568 (19)	218 (12)	540 (22)
H(112)	34 (19)	245 (12)	-71 (23)
H(113)	-144 (19)	307 (12)	-1 (22)
H(114)	-174 (19)	352 (12)	198 (22)
H(115)	-26 (19)	323 (12)	372 (22)
H(116)	165 (20)	265 (12)	311 (23)
H(122)	136 (19)	138 (12)	163 (22)
H(123)	165 (19)	22 (12)	187 (23)
H(124)	302 (19)	-62 (12)	80 (23)
H(125)	394 (19)	-31 (12)	-72 (22)
H(126)	383 (19)	84 (12)	-26 (22)
H(212)	466 (19)	367 (12)	-139 (22)
H(213)	625 (19)	349 (12)	-221 (23)
H(214)	772 (19)	228 (12)	-230 (22)
H(215)	715 (19)	147 (12)	-179 (22)
H(216)	572 (19)	170 (12)	-62 (23)
H(222)	203 (19)	352 (12)	-205 (22)
H(223)	129 (19)	467 (12)	-223 (23)
H(224)	144 (20)	553 (12)	-72 (22)
H(225)	286 (19)	528 (12)	115 (23)
H(226)	383 (19)	408 (12)	124 (22)
H(312)	648 (19)	320 (12)	118 (23)
H(313)	651 (19)	431 (12)	67 (23)
H(314)	551 (19)	541 (12)	188 (23)
H(315)	444 (19)	541 (12)	349 (23)
H(316)	450 (19)	429 (12)	402 (22)
H(322)	740 (19)	290 (12)	420 (23)
H(323)	932 (19)	224 (12)	414 (23)
H(324)	972 (19)	115 (12)	233 (23)
H(325)	813 (20)	79 (12)	163 (23)
H(326)	643 (19)	157 (12)	172 (23)
H(412)	313 (19)	116 (12)	404 (23)
H(413)	159 (19)	127 (12)	500 (23)
H(414)	57 (19)	237 (12)	599 (23)
H(415)	119 (19)	332 (12)	611 (23)
H(416)	267 (20)	327 (12)	506 (23)
H(422)	544 (19)	145 (12)	580 (22)
H(423)	680 (19)	20 (12)	584 (22)
H(424)	667 (19)	-58 (12)	400 (23)
H(425)	529 (19)	-29 (12)	203 (23)
H(426)	486 (19)	101 (12)	211 (22)

^a The quantities given in the table are the positional coefficients $\times 10^3$.

(0.15 mL) at -20°C and this mixture was gradually warmed to room temperature. The mixture changed to a yellow-orange solution. The solvent was then slowly evaporated to dryness at room temperature. The resulting sticky solid was crystallized from dichloromethane/hexane, yielding the pure complex as a dichloromethane solvate (342 mg, yield 74%): $\nu(\text{NH})$ 3330, 3250 cm^{-1} ; $\delta(\text{NNH}_2)$ 4.5 ppm (CDCl_3 solution). Anal. Calcd for $\text{C}_{53}\text{H}_{52}\text{N}_2\text{F}_5\text{Cl}_2\text{P}_4\text{BW}$: C, 52.96; H, 4.37; N, 2.33; Cl, 5.90. Found: C, 53.26; H, 4.29; N, 2.26; Cl, 6.09.

Preparation of $[\text{MoF}(\text{N}-\text{N}=\text{CH}_2)(\text{dpe})_2][\text{BF}_4]$. (1) The mixture of the complex **2** ($\text{M} = \text{Mo}$) (169 mg, 0.164 mmol) and dichloromethane (2.5 mL) was cooled to -196°C , on which excess of formaldehyde was condensed from its aqueous solution (17%) under vacuum. This mixture was warmed to room temperature and stirred overnight. From the afforded green-brown solution, solvent was evaporated to dryness at room temperature. The resulting solid was crystallized from THF/ether, yielding green-brown crystals, which were filtered off, washed with ether and hexane, and then dried in vacuo (63 mg, yield 37%).

(2) To the complex **2** ($\text{M} = \text{Mo}$) (82 mg, 0.080 mmol) were added dichloromethane (2 mL) and a 17% aqueous formaldehyde solution (52 mg, 0.64 mmol). After the solution was stirred for 20 min at room temperature, the brown-green solution was dried up and crystallized from THF/ether, yielding a yellow solid. The solid was filtered off, washed with hexane and ether, and dried (28 mg, yield 34%).

Preparation of $[\text{MoF}(\text{N}-\text{N}=\text{CHCH}_3)(\text{dpe})_2][\text{BF}_4]\cdot\text{CH}_2\text{Cl}_2$. To the stirred solution of the complex **2** ($\text{M} = \text{Mo}$) (112 mg, 0.109 mmol) in dichloromethane (2 mL) was added an 80% aqueous acetaldehyde solution (0.06 mL) at room temperature. After 5 min, the resulting green-brown solution was filtered and hexane (4 mL) was added to the filtrate to give brown crystals, which were filtered off, washed with ether and hexane, and then dried in vacuo (90 mg, yield 78%).

Preparation of $[\text{MoF}(\text{N}-\text{N}=\text{CHCH}_2\text{CH}_3)(\text{dpe})_2][\text{BF}_4]$. (1) To the stirred solution of the complex **2** ($\text{M} = \text{Mo}$) (133 mg, 0.129 mmol) in dichloromethane (2 mL) was added propionaldehyde (76 μL , 1.1 mmol) at room temperature. After 0.5 h, the resulting brown-green solution was filtered and hexane (4 mL) was added to the filtrate to give brown-green crystals, which were filtered off, washed with ether and hexane, and then dried in vacuo (115 mg, yield 87%).

(2) Propionaldehyde (75 μL) was added to a solution of the complex **2** ($\text{M} = \text{Mo}$) (105 mg, 0.102 mmol) in acetone (1.5 mL). After the solution was stirred for 45 h at room temperature, GLC analysis (Porapak Q, 2-m stainless column, 150°C) disclosed the formation of water (0.85 mol/Mo). The complex $[\text{MoF}(\text{N}-\text{N}=\text{CHCH}_2\text{CH}_3)(\text{dpe})_2][\text{BF}_4]$ was obtained from this solution by adding hexane (3 mL) to it (104 mg, yield 93%).

Preparation of $[\text{MoF}(\text{N}-\text{N}=\text{CHPh})(\text{dpe})_2][\text{BF}_4]$. (1) To the complex **2** ($\text{M} = \text{Mo}$) (284 mg, 0.276 mmol) were added dichloromethane (3 mL) and then benzaldehyde (221 μL , 2.21 mmol) at room temperature. After stirring for 20 h, the resulting brown-green solution was filtered and ether was added to the filtrate to give a mixture of green and red crystals. After they were separated manually, both complexes were recrystallized from dichloromethane/ether and then dichloromethane/hexane. Green crystals of $[\text{MoF}(\text{N}-\text{N}=\text{CHPh})(\text{dpe})_2][\text{BF}_4]$ were filtered off, washed with ether and hexane, and dried in vacuo (75 mg, yield 24%). Red crystals of by-product did not contain nitrogen (25 mg). Anal. C, 61.10; H, 4.99; N, 0.00.

(2) The complex **2** ($\text{M} = \text{Mo}$) (391 mg, 0.380 mmol) was dissolved in dichloromethane (6 mL) and then benzaldehyde (293 μL , 2.93 mmol) and a 42% aqueous HBF_4 solution (20 μL) were added. After stirring for 9 h, this solution was filtered and hexane (10 mL) was added to give a green solid, which was recrystallized from dichloromethane/hexane. Pale green crystals obtained were filtered off, washed with ether and hexane, and dried in vacuo (266 mg, yield 63%).

Preparation of $[\text{MoF}(\text{N}-\text{N}=\text{CHCH}_2\text{Ph})(\text{dpe})_2][\text{BF}_4]\cdot\text{THF}$. The complex **2** ($\text{M} = \text{Mo}$) (161 mg, 0.156 mmol) was dissolved in dichloromethane (3 mL) and then phenylacetaldehyde (40–50% in diethyl phthalate) (334 μL , 1.14–1.41 mmol) was added at room temperature. After stirring for 1 h, the solvent was evaporated to dryness. The resulting solid was recrystallized from THF/ether, yielding dark green crystals, which were filtered off, washed with ether and hexane, and then dried in vacuo (75 mg, yield 40%).

Preparation of $[\text{MoF}(\text{N}-\text{N}=\text{CHCH}=\text{CHCH}_3)(\text{dpe})_2][\text{BF}_4]$. To the stirred solution of the complex **2** ($\text{M} = \text{Mo}$) (194 mg, 0.189 mmol) in dichloromethane (4 mL) was added crotonaldehyde (124 μL , 1.51 mmol) at room temperature. After 24 h, the resulting dark green solution was filtered and hexane (8 mL) was added to the filtrate to give a pale green, crystalline solid. The solid was recrystallized from dichloromethane/hexane, yielding pale green crystals, which were filtered off, washed with ether and hexane, and then dried in vacuo (76 mg, yield 37%).

Preparation of $[\text{MoF}(\text{N}-\text{N}=\text{CHCH}=\text{CHPh})(\text{dpe})_2][\text{PF}_6]\cdot\text{THF}$. To the stirred solution of the complex **2** ($\text{M} = \text{Mo}$) (134 mg, 0.130 mmol) in dichloromethane (3 mL) was added cinnamaldehyde (131 μL , 1.04 mmol) at room temperature. After 22 h, potassium hexafluorophosphate (119 mg, 0.647 mmol) was added and stirred for another 2 h. From the resulting dark green suspension, solvent was evaporated to dryness and the resulting oil was crystallized from THF/hexane, yielding a yellow, crystalline solid, which was filtered off, washed with ether and hexane, and dried in vacuo (105 mg, yield 63%).

Preparation of $[\text{MoF}(\text{N}-\text{N}=\text{C}(\text{CH}_3)\text{CH}_2\text{COCH}_3)(\text{dpe})_2][\text{BF}_4]\cdot\text{THF}$. To the stirred solution of **2** ($\text{M} = \text{Mo}$) (149 mg, 0.145 mmol) in dichloromethane (3 mL) were added acetylacetone (120 μL , 1.17 mmol) and then a 42% aqueous HBF_4 solution (60 μL). After stirring

for 10 h at refluxing temperature, the resulting brown solution was filtered and then solvent was dried up in vacuo. The brown oil obtained was crystallized from THF/ether, yielding brown crystals, which were filtered off, washed with ether and hexane, and dried in vacuo (120 mg, yield 70%).

Preparation of [MoF(N-N=C(CH₃)₂)(dpe)₂][BF₄](CH₃)₂CO. The complex **2** (M = Mo) (119 mg, 0.176 mmol) was dissolved in acetone (4 mL) and this solution was stirred for 23 h at refluxing temperature. The resulting green-brown solution was filtered and hexane (8 mL) was added to the filtrate to give green-brown crystals of [MoF(N-N=C(CH₃)₂)(dpe)₂][BF₄] as acetone solvate, which were filtered off, washed with ether and hexane, and then dried in vacuo (50 mg, 38%). When a 42% aqueous solution (20 μ L) was added to the stirred solution of the complex **2** (M = Mo) in acetone, condensation reaction finished only in 1 h at refluxing temperature and in 3.5 h even at room temperature (yield 40–45%). In the absence of HBF₄, the complex **2** (M = Mo) was recovered after 26 h stirring at room temperature. Solvating acetone was easily removed by recrystallization from dichloromethane/hexane.

Preparation of [MoF(N-N=C₆H₁₀)(dpe)₂][BF₄]\cdot CH₂Cl₂. To the stirred solution of the complex **2** (M = Mo) (120 mg, 0.117 mmol) in dichloromethane (2 mL) were added cyclohexanone (96 μ L, 0.92 mmol) and then a 42% aqueous HBF₄ solution (25 μ L). After stirring for 6 h at room temperature, the resulting solution was filtered and hexane (4 mL) was added to the filtrate to give brown-green crystals, which were filtered off, washed with ether and hexane, and then dried in vacuo (103 mg, yield 74%). In the absence of HBF₄, the change of the color of the reaction mixture was not observed after 43 h stirring at room temperature.

Preparation of [WF(N-N=CHCH₂CH₃)(dpe)₂][BF₄]. To the stirred solution of the complex **2** (M = W) (158 mg, 0.131 mmol) in dichloromethane (4 mL) was added propionaldehyde (75 μ L, 1.05 mmol) at room temperature. After 3 h, the resulting brown-green solution was filtered and hexane (8 mL) was added to the filtrate to give dark green crystals, which were filtered off, washed with ether and hexane, and then dried in vacuo (135 mg, yield 89%).

Preparation of [WF(N-N=CHPh)(dpe)₂][BF₄]. To the stirred suspension of the complex **1** (M = W) (798 mg, 0.770 mmol) in THF (20 mL) was added a 42% aqueous HBF₄ solution (0.25 mL) at -20 °C, and this mixture was gradually warmed to room temperature. After stirring for 1 h at room temperature, the resulting orange solution was filtered and solvent was evaporated in vacuo to reduce the initial volume to ca. 7 mL. Dichloromethane (13 mL) and excess of benzaldehyde (0.4 mL) were then added, and the solution was stirred for 2 days at room temperature. The afforded green solution was filtered and hexane (40 mL) was added to the filtrate to give green crystals, which were filtered off, washed with ether and hexane, and then dried in vacuo (567 mg, yield 76%).

Preparation of [WF(N-N=C(CH₃)CH₂COCH₃)(dpe)₂][BF₄]\cdot THF. To the stirred suspension of the complex **1** (M = W) (258 mg, 0.249 mmol) in THF (6 mL) was added a 42% aqueous HBF₄ solution (137 μ L) at -20 °C, and this mixture was gradually warmed to room temperature. After stirring for 1 h at room temperature, the resulting orange solution was filtered and solvent was evaporated in vacuo to reduce the initial volume to ca. 2 mL. Dichloromethane (4 mL) and acetylacetone (204 μ L, 1.98 mmol) were then added, and this solution was stirred for 1 week. After solvent was evaporated to dryness, the resulting oil was crystallized from THF/ether, yielding brown crystals, which were filtered off, washed with ether and hexane, and then dried in vacuo (233 mg, yield 74%).

Crystallographic Data of the Complex [WF(N-N=C(CH₃)CH₂COCH₃)(dpe)₂][BF₄]\cdot THF. A suitable crystal of the title complex was sealed in a glass capillary under nitrogen. Preliminary film data showed that the crystals belong to the triclinic system characteristic of the centrosymmetric space group $P\bar{1}$ or noncentric space group $P1$. The centrosymmetric space group was shown to be the correct one on the basis of the following results: (a) the acceptable positional parameters, thermal parameters, and agreement indexes in successful refinements; (b) the clear and distinct location of 50 unique hydrogen atoms except for one methyl and solvent's hydrogens in a difference Fourier synthesis. Using least-squares procedure based on the angular positions of 12 hand-centered reflections in diverse regions of reciprocal space, accurate unit cell dimensions were determined. See Table V for pertinent crystal information and details of data collection. The density of the crystal could not be measured because of its instability toward water.

Data collection was carried out using a Rigaku four-circle dif-

fractometer. Background counts were measured in both ends of the scan range with both the counter and crystal stationary. The intensities of four standard reflections were measured every 50 reflections, and two of the four were found to decrease uniformly and linearly about 15% during the course of data collection. The observed intensities were modified to correct for this apparent isotropic crystal decomposition.

The intensities of 11 555 unique reflections were measured ($I \geq 0$) out to 2θ ($\text{Mo K}\alpha$) = 55.0°. Only reflections with $F_o^2 \geq 3\sigma(F_o)^2$ were used in subsequent calculations. Lorentz and polarization corrections were applied. An absorption correction was made regarding the shape of the crystal as a cylinder. A total of 4931 reflections were considered unobserved ($F_o^2 < 3\sigma(F_o)^2$).

Structure Refinement.²¹ The structure was solved using a Patterson synthesis to locate the tungsten atom. Subsequent refinements and difference Fourier syntheses were used to locate the remaining atoms, including 50 hydrogen atoms. The structure was refined using block-diagonal least-squares techniques. The isotropic model converged to R indexes of $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.156$ and $R_w = [w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2} = 0.184$. During the refinements, the quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure amplitudes and the weights, w , are taken as $w = 1$ for $|F_o| \leq 39$, and as $w = (39/|F_o|)^2$ for $|F_o| > 39$. Atomic scattering factors were taken from Cromer and Waber's tabulation.^{22a} The anomalous dispersion terms for W and P were included in F_c .^{22b}

Indeed a reasonable position for the THF molecule could be obtained from the difference Fourier map. However, neither this model for THF nor elaborate ones subsequently devised refined properly; excessively high thermal parameters in the solvent molecule may result from partial occupancy as well as from possible disorder. From this point onward we elected to position the THF molecule in a manner that best fit the electron density map but not to vary its position. At this stage, the structure was refined by block-diagonal least squares using anisotropic thermal factors for nonhydrogen atoms except the solvent's atoms. A difference Fourier synthesis was computed to reveal clear peaks of hydrogen atoms. Then the final cycle was carried out including the positional parameters of the above hydrogen atoms, the isotropic temperature parameters of which were fixed at 7.0 Å².

The final refinement resulted in final values of 0.106 and 0.129 for R and R_w , respectively. The standard deviation of an observation of unit weight $[\Sigma_w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, was 4.2, where the number of reflections (m) was 6624 and the number of refined parameters (n) was 841. In the final cycle no parameters shifted by more than 0.5 of their estimated standard deviations. An analysis of $w(|F_o| - |F_c|)^2$ as a function of setting angles, $|F_o|$, and Miller indexes revealed that agreement was worse at low angles. This is to be expected in view of our inadequate treatment for the scattering of the rather ill-defined solvent molecule. Although some improvement in R indexes might have been achieved through the assignment of anisotropic thermal parameters to the hydrzone groups, it was felt that the structural parameters of interest would not have been better defined. In this regard the geometry of the inner coordination sphere proved to be insensitive to the model used for the solvent scattering. The maximum density in a final difference Fourier synthesis was 1.3 e/Å³, about 25% of that of a carbon atom in previous Fourier syntheses.

The positional and thermal parameters obtained from the last cycle of refinement are listed in Table VI with the associated standard deviations estimated from the inverse matrix. Table VII lists the positional parameters of hydrogen atoms, while their thermal parameters were fixed at 7.0 Å².

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Supplementary Material Available: A listing of structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) Part 7: M. Sato, T. Tatsumi, M. Hidai, and Y. Uchida, *J. Organomet. Chem.*, **152**, 239 (1978).
- (2) (a) J. Chatt, G. A. Heath, and G. J. Leigh, *J. Chem. Soc., Chem. Commun.*, **444** (1972); (b) J. Chatt, A. A. Diamantis, G. A. Heath, N. E. Hooper, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, **688** (1977).
- (3) V. W. Day, T. A. George, and S. D. A. Iske, *J. Am. Chem. Soc.*, **97**, 4127 (1975).

- (4) A. A. Diamantis, J. Chatt, G. J. Leigh, and G. A. Heath, *J. Organomet. Chem.*, **84**, C11 (1975); D. C. Bubby and T. A. George, *ibid.*, **118**, C16 (1976).
 (5) T. Tatsumi, M. Hida, and Y. Uchida, *Inorg. Chem.*, **14**, 2530 (1975).
 (6) P. C. Bevan, J. Chatt, G. J. Leigh, and E. G. Leelamani, *J. Organomet. Chem.*, **139**, C59 (1977).
 (7) M. Hida, Y. Mizobe, and Y. Uchida, *J. Am. Chem. Soc.*, **98**, 7824 (1976).
 (8) R. Ben-Shoshan, J. Chatt, W. Hussain, and G. J. Leigh, *J. Organomet. Chem.*, **112**, C9 (1976); P. C. Bevan, J. Chatt, A. A. Diamantis, R. A. Head, G. A. Heath, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1711 (1977).
 (9) M. Hida, T. Kodama, M. Sato, M. Harakawa, and Y. Uchida, *Inorg. Chem.*, **15**, 2694 (1976).
 (10) J. Chatt, A. J. Pearman, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1520 (1976); 1852 (1977).
 (11) For example, J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry", W. A. Benjamin, New York, N.Y., 1964, p 491.
 (12) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 441.
 (13) G. A. Heath, R. Mason, and K. M. Thomas, *J. Am. Chem. Soc.*, **96**, 259 (1974).
 (14) S. Patai, Ed., "The Chemistry of the Hydrazo, Azo, and Azoxy Groups", Part 1, Wiley, New York, N.Y., 1975, p 23, and references cited therein.
 (15) J. L. Galgr'e and J. Falgouirets, *Acta Crystallogr., Sect. B*, **24**, 1523 (1968).
 (16) G. Arcorito, M. Bonamico, A. Domenicano, and A. Vacilago, *J. Chem. Soc. B*, 733 (1969).
 (17) S. Krogsrud, L. Toniolo, U. Croatto, and J. A. Ibers, *J. Am. Chem. Soc.*, **99**, 5277 (1977).
 (18) J. Chatt, R. A. Head, P. B. Hitchcock, W. Hussain, and G. J. Leigh, *J. Organomet. Chem.*, **133**, C1 (1977).
 (19) M. Hida, K. Tominari, and Y. Uchida, *Chem. Commun.*, 1392 (1969); *J. Am. Chem. Soc.*, **94**, 110 (1972).
 (20) J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 2074 (1974).
 (21) The UNICS program system for the HITAC 8700/8800 computers was employed at Tokyo University Computer Center: Sakurai's RSLC-3 lattice constants program, Ueda's PAMI Patterson and minimum function program, Iwasaki's ANSFR-2 Fourier synthesis program, Ashida's HBLS-4 block-diagonal least-squares and Fourier program, Ashida's DAPH distance, angle, best plane, etc., program, and modified Johnson's ORTEP thermal ellipsoid plot program.
 (22) (a) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2a; (b) D. T. Cromer and D. Liberman, *ibid.*, Table 2.3.1.

Synthetic, Physicochemical, and Structural Study of Phosphacymantrenes

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Abstract: The reaction of 1-phenyl-3,4-dimethylphosphole with $Mn_2(CO)_{10}$ at 150 °C in boiling xylene yields 3,4-dimethylphosphacymantrene as the main product together with a heavier complex tentatively identified as (3,4-dimethylphospholyl)-trimanganese dodecacarbonyl. Phosphacymantrene itself and its 3-methyl derivative are analogously prepared starting from 1-phenylphosphole and 1-phenyl-3-methylphosphole, respectively. 3,4-Dimethylphosphacymantrene is acylated on the α carbon by $CH_3COCl-AlCl_3$ in boiling dichloromethane and by $C_6H_5COCl-AlCl_3$ in boiling tetrachlorethane. The phosphorus atom does not react with quaternizing agent nor with mild oxidant such as iodine. On the contrary its reactivity toward nucleophiles is high. In that case the phosphacymantrene moiety is destroyed. For example, *n*-butyllithium with 3,4-dimethylphosphacymantrene yields 1-butyl-3,4-dimethylphosphole. On the basis of the ¹³C NMR and IR data of the CO groups it appears that the phospholyl nucleus is a weaker electron donor toward the $Mn(CO)_3$ moiety than the cyclopentadienyl nucleus. Phosphacymantrenes are also characterized by a high ¹J(P-C) coupling constant (ca. 65 Hz) and a very shielded phosphorus atom. The crystal structure of $[\eta^5-PC_4H(CH_3)_2(COC_6H_5)]Mn(CO)_3$ was determined from three-dimensional x-ray diffraction counter data. The molecule crystallizes with four formula units in the monoclinic space group $P2_1/n$, with $a = 20.995$ (5), $b = 10.869$ (3), $c = 6.784$ (2) Å, and $\beta = 90.17$ (3)°. The final indexes, based on the least-squares refinement of 235 variables for 1047 observations ($I > 3\sigma(I)$), are $R(F_o) = 0.046$, $R_w = 0.056$. The π -bonded phospholyl ring is aromatic but is slightly puckered. The four carbon atoms of the ring are coplanar and the phosphorus atom lies out of this plane by 0.048 Å on the opposite side to manganese. The three bonds C-C (phospholyl ring) are equivalent. Their average length, 1.420 (8) Å, is the same as in several π -bonded cyclopentadienyl rings. The bond P-C (benzoyl) is longer by 0.065 (12) Å than the bond P-C (hydrogen); their average length (1.765 (7) Å) is intermediate between a single and a double bond (P-C). The other parts of the molecule are not altered when compared to other manganese cyclopentadienyl complexes.

In both nitrogen and sulfur organic chemistries, a great emphasis is put on aromatic heterocycles, e.g., pyrrole, pyridine, and thiophene. This is, for a notable part, due to the extreme ease of their functionalization which allows the synthesis of a tremendous array of derivatives. One of the most powerful tools for grafting a functional group onto these rings is the C-electrophilic substitution (e.g., Friedel-Crafts). On the contrary, a rather frustrating situation is encountered when studying the phosphorus analogues of these compounds, namely, phospholes and λ^3 phosphorins; indeed, the synthesis of their functional derivatives is always rather difficult because direct C-functionalization of these rings is impossible (both electrophilic and nucleophilic attacks occur at the phosphorus atom^{2,3}). Thus, rather complex procedures were devised to obtain some simple derivatives of these heterocycles. See, for example, ref 4 and 5.

When starting our work on phosphacymantrenes (phos-

pholymanganese tricarbonyls), we had two ideas in mind: first, to synthesize the first phosphorus heterocycles with a true aromatic chemistry; second, to use an undoubtedly aromatic tricoordinated phosphorus heterocycle as a reference to discriminate between the various "proofs" for and against aromaticity in the phosphole nucleus. Indeed, this last point is still a very controversial matter.³ For that purpose, we focused our attention on the phospholyl derivatives since the phospholyl anions are isoelectronic with thiophenes and, thus, potentially strongly aromatic.⁶ Nevertheless electrophilic attacks always occur at phosphorus in the free anions⁷ because of the strong negative charge which is borne by the heteroatom. Thus, we chose more precisely to study the phospholyl π -aromatic complexes. We selected the manganese tricarbonyl derivatives because they were isoelectronic with the long-known thiophenechromium tricarbonyls⁸ and because, recently, an arsenic analogue was briefly described.⁹ The results of the first ex-