= −0.12 e). The C_4H_4 moiety is more negatively charged in II (−1.78 e) than in I (−1.45 e), as expected for the presence of the second Fe′ atom. Furthermore, it is very interesting to compare the OP's of the metallacycles: in II we note an OP(C_4–C_4') value larger than OP(C_3–C_4) in contrast with the same quantities in I. Bearing in mind the bonding scheme between Fe′ and the organic moiety (see Figure 1), this is indicative that the π_3^* orbital is highly populated due to the back-bonding interactions with the two Fe′ atoms. Finally, we want to point out the very high value for the OP(Fe–C_3) both in I and in II even larger than the Fe–CO OP's. An accurate analysis of the eigenvectors shows that the π contributions to the Fe–C_3 interaction are negligible and that both n^+ and n^- combinations of the two radical lobes contribute to the bonding.

Concluding Remarks

The present paper points out the capability of the pseudopotential method to calculate, with relatively low computational efforts, the valence electronic structure at ab initio levels for molecules containing two or more transition metals. The theoretical results furnished a detailed picture of the bonding scheme in both I and II type molecules, clarifying the role played by the semibridging or asymmetrically bridging carbonyl groups.[30] In the dinuclear derivative the semibridging carbonyl contributes to the charge transferring from the iron atom in the ring, in accordance with Cotton's proposal.[5] In the trinuclear derivative direct metal–metal interactions are forbidden by the conversion of the semibridging into asymmetrically bridging carbonyl. The theoretical data also predict a high stability for the ferracyclopentadienyl ring due to a very strong Fe–C interaction only σ in nature. This is confirmed by the well-known chemical behavior of II, which decomposes at 150 °C to give I, where the ferracyclopentadienyl ring is preserved.

Acknowledgment. Thanks are due to the Ministero della Pubblica Istruzione (Grant MPI 12/2/15) and to the CNR of Rome for generous financial support of this study. We thank also Dr. J. P. Daudey for a copy of the PSHONDO program.

Registry No. I, 59447-66-4; I′, 95120-71-1; II, 95120-69-7; III, 95120-70-0.

---

(30) Very similar conclusions on the nature of the bonding of semibridging carbonyl groups have been reached recently by: Bénard, M.; Dedieu, A.; Nakamura, S. *Nouv. J. Chim.* **1984**, *8*, 149.

Contribution from the Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Tokyo 113, Japan

Reactions of $[W(N_2)_2(dpe)_2]$ with $HFeCo_3(CO)_{12}$ in Aqueous and Halogenated Solvents To Form Hydrazido(2−) Hydroxo Complexes of Tungsten(IV) and Dihalo Complexes of Tungsten(III). Crystal Structure of $[WCl_2(dpe)_2]BF_4 \cdot {}^1/_3CH_2Cl_2$

MINORU IMAEDA, HIROSHI NISHIHARA, KOJI NAKANO, HIKARU ICHIDA, AKIKO KOBAYASHI,
TARO SAITO,*[1] and YUKIYOSHI SASAKI

Received July 3, 1984

Reactions of $[W(N_2)_2(dpe)_2]$ (dpe = 1,2-bis(diphenylphosphino)ethane) with $HFeCo_3(CO)_{12}$ in water–tetrahydrofuran formed $[W(OH)(NNH_2)(dpe)_2][FeCo_3(CO)_{12}]$. Treatment of an anion-exchanged derivative $[W(OH)(NNH_2)(dpe)_2]PF_6$ with acetone in the presence of $HFeCo_3(CO)_{12}$ afforded $[W(OH)(NNCMe_2)(dpe)_2]PF_6$. No hydrazido(2−) complex formed in dichloromethane, and $[WCl_2(dpe)_2][FeCo_3(CO)_{12}]$ was obtained. This complex and its anion-exchanged derivatives showed the NMR spectra characteristic of paramagnetic ($\mu_{eff} \simeq 1.5\ \mu_B$) complexes. The X-ray crystal structure of $[WCl_2(dpe)_2]BF_4 \cdot {}^1/_3CH_2Cl_2$ (**10**) was determined. Complex **10** crystallized in the trigonal $P\bar{3}$ space group, with a = 21.027 (3) Å, c = 11.091 (2) Å, V = 4246.8 (15) Å^3, and Z = 3. With 3208 unique reflections, R converged to 0.079 (R_w = 0.091). The Mo–Cl distance was 2.312 (5) Å.

Introduction

There have been significant advances in the chemistry of dinitrogen complexes of molybdenum and tungsten[2] since the first report on the protonation of coordinated dinitrogen in $[W(N_2)_2(dpe)_2]$,[3] notably in mechanistic elucidation of the protonation reactions.[4]

We reported in a previous paper that coordinated dinitrogen could be protonated by acidic hydridometal carbonyls such as $HFeCo_3(CO)_{12}$, $HCo(CO)_4$, or $H_2Fe(CO)_4$.[5] These hydride complexes have counteranions that do not coordinate to the metal center, in contrast to X^- in simple acids HX,[2] and we isolated hydrazido(2−) complexes $[W(OR)(NNH_2)(dpe)_2]A$ (A = $FeCo_3(CO)_{12}$, $Co(CO)_4$, $Co_3(CO)_{10}$,[5] $HFe_3(CO)_{11}$, $HFe_4(CO)_{13}$.[6] They contained an alkoxide ligand from solvent alcohols, and participation of alcohols in the protonation reaction was suggested.[5] In this paper, we describe the results of similar reactions in water–tetrahydrofuran, benzene, toluene, dichloromethane, dibromomethane, or dichloroethane. The purpose of the present work was to study the role of solvents in protonating the coordinated dinitrogen. We have found the formation of a new hydrazido(2−) complex coordinated with a hydroxide anion in water–tetrahydrofuran and new tungsten(III) halide complexes in halogenated solvents.

Experimental Section

The preparation and workup were carried out in nitrogen atmosphere. Tetrahydofuran (THF) and diethyl ether were distilled from $LiAlH_4$,

---

(1) Present address: Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan.

(2) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.

(3) Chatt, J.; Heath, G. A.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1972**, 1010.

(4) (a) Chatt, J.; Richards, R. L. *J. Organomet. Chem.* **1982**, *239*, 65. (b) Anderson, S. N.; Fakley, M. E.; Richards, R. L.; Chatt, J. *J. Chem. Soc., Dalton Trans.* **1981**, 1973. (c) Baumann, J. A.; George, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 6154. (d) Bassard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. K. *Inorg. Chem.* **1983**, *22*, 1968. (e) George, T. A.; Koczon, L. M. *J. Am. Chem. Soc.* **1983**, *105*, 6334. (f) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461. (g) Henderson, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 917.

(5) Nishihara, H.; Mori, T.; Tsurita, Y.; Nakano, K.; Saito, T.; Sasaki, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4367.

(6) Saito, T. 2nd China-Japan-USA Symposium on Organometallic and Inorganic Chemistry, Shanghai, 1982; Abstract B31J.

0020-1669/85/1324-1246$01.50/0 © 1985 American Chemical Society

after drying with Na. Hexane, benzene, and toluene were distilled from Na. Halogenated solvents were distilled from CaH_2. Acetone was dried over $CaSO_4$ and distilled. Infrared spectra were recorded with a Hitachi 260-30 spectrometer, and NMR spectra were recorded with a JEOL FX 90Q spectrometer. Elemental analyses were undertaken in the Department of Chemistry, The University of Tokyo. Magnetic susceptibilities were measured with a Faraday balance in the Department of Chemistry, Ochanomizu University.

Synthesis. Starting compounds $[W(N_2)_2(dpe)_2]$[7] and $HFeCo_3(CO)_{12}$[8] were prepared according to literature methods.

Preparations. $[W(OH)(NNH_2)(dpe)_2][FeCo_3(CO)_{12}]$ (1). A solution of $[W(N_2)_2(dpe)_2]$ (0.63 g, 0.61 mmol) and $HFeCo_3(CO)_{12}$ (0.37 g, 0.65 mmol) in THF (60 mL) and H_2O (8 mL) mixed solvent was stirred at 0 °C for 18 h. The solvents were distilled off in vacuo. The product was dissolved in CH_2Cl_2 (15 mL) and filtered, and diethyl ether (40 mL) was added to precipitate black crystals at 0 °C. The crystals were recrystallized from CH_2Cl_2–diethyl ether; yield 0.28 g (29%). Anal. Calcd for $C_{64}H_{51}Co_3FeN_2O_{13}P_4W$: C, 48.15; H, 3.22; N, 1.75. Found: C, 48.06; H, 3.15; N, 1.79.

$[W(OH)(NNH_2)(dpe)_2]BPh_4{\cdot}2H_2O$ (2). Diethyl ether (70 mL) was added to a filtered solution of **1** (0.22 g, 0.14 mmol) and $NaBPh_4$ (0.5 g, 1.5 mmol) in THF (20 mL), and it was left overnight at 0 °C. Yellow crystals were filtered, washed with diethyl ether (30 mL), and recrystallized from CH_2Cl_2–diethyl eteher; yield 0.08 g (42%). Anal. Calcd for $C_{76}H_{75}BN_2O_3P_4W$: C, 66.00; H, 5.47; N, 2.02. Found: C, 65.97; H, 5.43; N, 2.04.

$[W(OH)(NNH_2)(dpe)_2]PF_6$ (3). Hexane (80 mL) was added to a filtered solution of **1** (4.9 g, 3.1 mmol) and n-Bu_4NPF_6 (1.23 g, 3.3 mmol) in THF (80 mL). Yellow precipitates were dissolved in CH_2Cl_2 (30 mL), undissolved fine particles were removed by centrifugation, and hexane (30 mL) was added to form yellow crystals, yield 1.59 g (44%). Anal. Calcd for $C_{52}H_{51}F_6N_2OP_5W$: C, 53.26; H, 4.38; N, 2.39. Found: C, 53.23; H, 4.65; N, 2.11.

$[W(OH)(NNH_2)(dpe)_2]BF_4$ (4). Hexane (70 mL) was added to a filtered solution of **1** (4.56 g, 2.86 mmol) and n-Bu_4NBF_4 (0.93 g, 2.82 mmol) in THF (100 mL). Yellow precipitates were washed with a 1:1 mixed solvent (30 mL) of THF and hexane three times and dissolved in CH_2Cl_2 (50 mL). After centrifugation, hexane (70 mL) was added to precipitate a yellow product that was washed with diethyl ether and dried: yield 1.70 g (54%). Anal. Calcd for $C_{52}H_{51}BF_4N_2OP_4W$: C, 56.04; H, 4.61; N, 2.51. Found: C, 56.07; H, 5.10; N, 2.35.

$[W(OH)(NNCMe_2)(dpe)_2]PF_6{\cdot}(CH_3)_2CO$ (5). A solution of **3** (0.67 g, 0.57 mmol) and $HFeCo_3(CO)_{12}$ (0.067 g, 0.11 mmol) in acetone (40 mL) was stirred at room temperature for 2 days. Hexane (15 mL) was added to the concentrated (25 mL) solution to precipitate brown crystals, which were washed with a 1:1 mixed solvent of THF and hexane and recrystallized from acetone–hexane; yield 0.23 g (32%). Anal. Calcd for $C_{58}H_{61}F_6N_2O_2P_5W$: C, 54.81; H, 4.84; N, 2.20. Found: C, 54.16; H, 4.49; N, 1.98.

$[WCl_2(dpe)_2][FeCo_3(CO)_{12}]$ (6). A solution of $[W(N_2)_2(dpe)_2]$ (2.34 g, 2.26 mmol) and $HFeCo_3(CO)_{12}$ (1.31 g, 2.30 mmol) in CH_2Cl_2 (40 mL) was stirred at room temperature for 2 days. Diethyl ether (100 mL) was added to the filtered solution to precipitate black crystals that were recrystallized from CH_2Cl_2–diethyl ether; yield 2.10 g (57%). Anal. Calcd for $C_{64}H_{48}Cl_2Co_3FeO_{12}P_4W$: C, 47.44; H, 2.99; Cl, 4.38. Found: C, 47.11; H, 3.04; Cl, 4.74.

Use of dichloroethane instead of dichloromethane gave the same product with 60% yield. Anal. Found: C, 47.13; H, 3.00; Cl, 4.15.

$[WBr_2(dpe)_2][FeCo_3(CO)_{12}]$ (7). Use of CH_2Br_2 instead of CH_2Cl_2 in the preparation of **6**, gave **7** in 43% yield. Anal. Calcd for $C_{64}H_{48}Br_2Co_3FeO_{12}P_4W$: C, 44.97; H, 2.83; Br, 9.35. Found: C, 45.08; H, 2.80; Br, 9.37.

$[WCl_2(dpe)_2]BPh_4{\cdot}CH_2Cl_2$ (8). A solution of $[W(N_2)_2(dpe)_2]$ (1.00 g, 0.96 mmol) and $HFeCo_3(CO)_{12}$ (0.58 g, 1.01 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 3 days. The solvent was removed, and the product was treated with $NaBPh_4$ (0.25 g, 0.72 mmol) in a 1:1 mixed solvent (30 mL) of THF and hexane. The precipitates were filtered and washed with a 1:1 mixed solvent (30 mL) of THF and hexane. Yellow precipitates were dissolved in CH_2Cl_2 (25 mL), and hexane (20 mL) was added to precipitate the product that was recrystallized from CH_2Cl_2–diethyl ether. Anal. Calcd for $C_{77}H_{70}BCl_4P_4W$: C, 63.53; H, 4.85; Cl, 9.74. Found: C, 63.56; H, 5.08; Cl, 9.32.

$[WCl_2(dpe)_2]PF_6{\cdot}(CH_3)_2CO$ (9). A solution of **6** (0.57 g, 0.35 mmol) and n-Bu_4NPF_6 (0.20 g, 0.54 mmol) in THF (30 mL) was stirred at room temperature and concentrated to 20 mL. Diethyl ether (10 mL) was added to the solution, which was left at 0 °C. Precipitates were filtered and washed with a 1:1 mixed solvent (5 mL) of THF and diethyl ether and recrystallized from acetone–hexane. Anal. Calcd for $C_{55}H_{54}Cl_2F_6OP_5W$: C, 52.65; H, 4.33; Cl, 5.65. Found: C, 52.28; H, 4.21; Cl, 5.56.

Table I. Crystallographic Data for $[WCl_2(dpe)_2]BF_4{\cdot}{}^1/_3CH_2Cl_2$ (10)

cryst size/mm	0.25 × 0.25 × 0.60
cryst syst	trigonal
space gp	$P\bar{3}$
a/Å	21.027 (3)
c/Å	11.091 (2)
V/Å^3	4246.8 (15)
Z	3
D_{measd}/g cm^{-3}	1.40
D_{calcd}/g cm^{-3}	1.37
μ/cm^{-1}	23.3
radiation (λ/Å) (graphite monochromatized)	Mo Kα (0.710 69)
scan mode	ω–2θ
scan range/deg	4–60
octants	$+h, +k, \pm l$
scan rate/deg min^{-1}	2.0
std reflcns (no decay obsd)	3 every 100
no. of unique data collcd	5716
no. of unique data used with $I > 3\sigma(I)$	3208

$[WCl_2(dpe)_2]BF_4{\cdot}{}^1/_3CH_2Cl_2$ (10). Hexane (30 mL) was added to a filtered solution of **6** (1.06 g, 0.65 mmol) and n-Bu_4NBF_4 (0.27 g, 0.80 mmol) in THF (40 mL) to precipitate a yellow product that was washed twice with a 1:1 mixed solvent of THF and hexane. The precipitates were dissolved in CH_2Cl_2 (20 mL), and diethyl ether (30 mL) was added to the filtered solution to give precipitates that were recrystallized from CH_2Cl_2–hexane; yield 0.47 g (62%). Anal. Calcd for $C_{52.33}H_{48.67}BCl_{2.67}F_4P_4W$: C, 54.00; H, 4.22; Cl, 8.13. Found: C, 52.77; H, 4.15; Cl, 8.23.

$[H[W(N_2)_2(dpe)_2]][FeCo_3(CO)_{12}]$ (11). $[W(N_2)_2(dpe)_2]$ (0.40 g, 0.38 mmol) was treated with $HFeCo_3(CO)_{12}$ (0.25 g, 0.44 mmol) in CH_2Cl_2 (15 mL) at 3 °C for 24 h. Hexane was added to precipitate a violet product, yield 0.30 g (48%). Anal. Calcd for $C_{64}H_{49}Co_3FeN_4O_{12}P_4W$: C, 47.85; H, 3.07; N, 3.49. Found: C, 47.15; H, 3.11; N, 3.11.

$[H[W(N_2)(dpe)_2]][FeCo_3(CO)_{12}]{\cdot}{}^1/_2CH_2Cl_2$ (12). $[W(N_2)_2(dpe)_2]$ (0.40 g, 0.38 mmol) was treated with $HFeCo_3(CO)_{12}$ (0.25 g, 0.44 mmol) in CH_2Cl_2 (20 mL) at 25 °C for 2 h. Hexane (35 mL) was added to precipitate a violet product, yield 0.4 g (63%). Anal. Calcd for $C_{64.5}H_{50}ClCo_3FeN_2O_{12}P_4W$: C, 47.79; H, 3.11; N, 1.73. Found: C, 46.72; H, 3.10; N, 1.91.

Reaction of $[W(N_2)_2(dpe)_2]$ with $HFeCo_3(CO)_{12}$ in Benzene. $[W(N_2)_2(dpe)_2]$ (0.30 g, 0.29 mmol) was treated with $HFeCo_3(CO)_{12}$ (0.20 g, 0.35 mmol) in benzene (20 mL) at room temperature for 16 h. After filtration, the dark brown residue was washed with benzene (10 mL) and crystallized from CH_2Cl_2–toluene to give a black product. Anal. Calcd for $C_{64.5}H_{50}ClCo_3FeN_2O_{12}P_4W$ ($[H[W(N_2)(dpe)_2]][FeCo_3(CO)_{12}]{\cdot}{}^1/_2CH_2Cl_2$): C, 47.79; H, 3.11; N, 1.73. Found: C, 47.99; H, 2.88; N, 1.69. The attempts to recrystallize it resulted in the loss of nitrogen content. Similar reaction in toluene for several days afforded a complex that was washed with toluene and dried. Anal. Found: C, 47.20; H, 2.92; N, 2.25. The attempts to obtain a pure complex by recrystallization failed.

X-ray Data Collection and Structure Determination. Yellow single crystals of **10** were grown from dichloromethane–hexane. The Weissenberg photographs of the crystals showed Laue symmetry $\bar{3}$ with no systematic absence, which was pertinent only to the space group $P3$ or $P\bar{3}$. A hexagonal-prismatic crystal of 0.60-mm length and 0.25-mm width was used for the X-ray intensty measurements. The unit cell dimensions were determined by least-squares refinement using 41 reflections (28° < 2θ < 36°). Intensity data were collected on a Rigaku automated diffractometer Model AFC5, at 20 °C and were corrected for Lorentz and polarization factors and absorption, where the transmission factors were calculated from the shape of the crystal using DABEX program[9] to range from 0.536 to 0.609. The crystallographic data are given in Table I.

The structure of **10** was solved by the heavy-atom method assuming the space group of $P3$ at the beginning. As successive refinements showed the structure had a center of symmetry, we concluded that the space group of the crystal was $P\bar{3}$. The position of W was determined from a Patterson map, and subsequent Fourier synthesis revealed P, Cl, C, B, and F atoms. Positional and thermal parameters were refined by the block-diagonal least-squares method, minimizing the function ($|F_o|$

---

(7) Dilworth, J. R.; Richards, R. L. *Inorg. Synth.* **1980**, *20*, 119.

(8) Chini, P.; Colli, L.; Peraldo, M. *Gazz. Chim. Ital.* **1960**, *90*, 1005.

(9) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180.

Table II. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\times 10^3$) for 10 with Esd's in Parentheses

	x	y	z	B, Å^2
W	5000 (0)	5000 (0)	5000 (0)	23 (0)
P1	6090 (2)	4818 (3)	5261 (4)	29 (2)
P2	4504 (3)	3970 (3)	6575 (4)	31 (2)
Cl1	4622 (3)	4103 (2)	3530 (3)	36 (2)
CB1	5716 (10)	3849 (10)	5699 (18)	44 (8)
CB2	5173 (11)	3633 (12)	6729 (18)	47 (9)
C11	6669 (10)	4897 (11)	3968 (14)	37 (8)
C12	6392 (11)	4304 (11)	3107 (14)	43 (9)
C13	6799 (12)	4385 (12)	2078 (18)	50 (9)
C14	7474 (11)	5007 (12)	1875 (16)	47 (9)
C15	7761 (12)	5584 (13)	2715 (18)	55 (10)
C16	7337 (10)	5513 (11)	3754 (16)	42 (7)
C21	6738 (9)	5389 (12)	6420 (14)	44 (8)
C22	7073 (10)	6168 (12)	6335 (15)	45 (8)
C23	7575 (12)	6624 (14)	7189 (21)	61 (10)
C24	7765 (13)	6324 (15)	8149 (21)	68 (12)
C25	7450 (12)	5568 (15)	8230 (17)	61 (12)
C26	6939 (11)	5074 (13)	7364 (15)	48 (9)
C31	3629 (10)	3138 (9)	6219 (13)	32 (6)
C32	3618 (12)	2655 (11)	5310 (18)	49 (8)
C33	2953 (14)	2054 (13)	5012 (24)	67 (10)
C34	2315 (15)	1903 (14)	5537 (25)	76 (12)
C35	2328 (12)	2382 (13)	6436 (21)	61 (10)
C36	2986 (12)	3023 (12)	6770 (21)	55 (9)
C41	4353 (9)	4128 (10)	8121 (12)	32 (6)
C42	4157 (11)	4631 (11)	8432 (16)	42 (8)
C43	4001 (11)	4720 (12)	9644 (15)	46 (9)
C44	4008 (13)	4251 (12)	10540 (17)	53 (10)
C45	4183 (16)	3737 (13)	10210 (16)	67 (13)
C46	4368 (14)	3649 (13)	9012 (16)	57 (11)
B1	6667 (0)	3333 (0)	8968 (36)	43 (8)
F1	6667 (0)	3333 (0)	7666 (17)	49 (4)
F2	6094 (8)	3408 (8)	9329 (13)	77 (3)

$- |F_c|)^2$. Anisotropic temperature factors were used for W, P, Cl, and C atoms. Isotropic temperature factors were used for B and F. As one of the three BF_4^- anions existed on the $\bar{3}$ axis and one CH_2Cl_2 molecule in that neighborhood, their atomic parameters were disordered and their positions were not refined. The real and imaginary corrections for anomalous dispersion were included for the W, P, Cl, C, B, and F atoms. The final $R = \sum||F_o| - |F_c||/\sum|F_o|$ was 0.079. ($R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ 0.091.) The neutral atomic scattering factors were used.[10] Calculations were performed with UNICS programs[11] on a HITAC M-280H computer at the Computer Centre of The University of Tokyo. Final atomic coordinates for 10 are listed in Table II.

Magnetic Susceptibility Measurements. The magnetic susceptibilities of the halide complexes were measured by using a Faraday balance at room temperature. The correction of diamagnetic contributions was done by subtraction of diamagnetic susceptibilities of reactants and products in a postulated equation of formation of the complex in question. For example

$$\underset{A}{[W(N_2)_2(dpe)_2]} + Cl_2 + \underset{B}{HFeCo_3(CO)_{12}} = \underset{C}{[WCl_2(dpe)_2][FeCo_3(CO)_{12}]} + 2N_2 + {}^1/_2H_2$$

$$\chi_c(\text{para}) = \chi_c(\text{measd}) - [\chi_A + \chi_B + \chi_{Cl_2} - 2\chi_{N_2} - {}^1\!/_2\chi_{H_2}]$$

The diamagnetic susceptibilities of A and B were measured, and other data were taken from the literature.[12]

Results and Discussion

The reaction in H_2O–THF afforded the hydrazido(2–) hydroxo complex $[W(OH)(NNH_2)(dpe)_2][FeCo_3(CO)_{12}]$ (**1**). The counteranion $FeCo_3(CO)_{12}^-$ could be readily exchanged by reaction with salts such as $NaBPh_4$, n-Bu_4NPF_6, or n-Bu_4NBF_4 and BPh_4^- (**2**), PF_6^- (**3**), and BF_4^- (**4**) derivatives formed. The infrared and ^1H NMR spectral data are shown in Table III. The stretching frequencies and chemical shifts of the OH group are close to the values of other hydroxo complexes of transition metals,[13] and the NNH_2 group exhibits stretching frequencies and chemical shifts near those of the alkoxo hydrazido(2–) complexes.[5] The hydrogens of OH and NNH_2 groups were labile, and on treatment of complex **1** with D_2O, ν(OH) at 3636 cm^{-1} shifted to ν(OD) at 2685 cm^{-1} and $\nu(NNH_2)$ at 3358 and 3266 cm^{-1} to $\nu(NND_2)$ at 2500 and 2440 cm^{-1}.

Table III. IR and ^1H NMR Data of Hydroxo Complexes

	IR data[a]/cm^{-1}			^1H NMR data[b]		
compd	ν(OH)	ν(NH)	other	δ(OH)	$\delta(NNH_2)$	other
1	3630	3350 3260		−0.3 (s)[e]	3.6 (br)[f]	
2	3620	3340 3260		−0.2 (s)	3.7 (br)	
3	3620	3350 3270		−0.2 (br)	4.0 (br)	
4	3610	3350 3280		−0.4 (br)	4.1 (br)	
5	3650		2920[c] 1590[d]	0.5 (br)		1.3 (s)[g] −0.4 (s)[g]

[a] KBr pellet. [b] CD_2Cl_2 solution (Me_4Si). [c] ν(CH) of CH_3. [d] ν(N=C). [e] Singlet. [f] Broad singlet. [g] $\delta(CH_3)$.

Table IV. Selected Interatomic Distances and Angles of 10 with Estimated Standard Deviations in Parentheses

	(a) Bond Distances/Å		
W-P1	2.522 (5)	W-P2	2.563 (5)
W-Cl1	2.312 (5)	P1-CB1	1.85 (2)
CB1-CB2	1.52 (3)	CB2-P2	1.87 (3)
P1-C11	1.83 (2)	P1-C21	1.82 (3)
P2-C31	1.84 (2)	P2-C41	1.80 (2)
B1-F1	1.44 (4)	B1-F2	1.35 (4)
	(b) Bond Angles/deg		
P1-W-P2	79.1 (2)	P1-W-Cl1	85.7 (2)
P2-W-Cl1	87.9 (1)	F1-B1-F2	107 (3)

Formation of the hydrazido(2–) hydroxo complex can be interpreted formally in terms of the oxidative addition of H_2O either to W–N_2 or to W–NNH moiety.[14]

On treatment of **3** dissolved in THF with aqueous hydrobromic acid, $[WBr(NNH_2)(dpe)_2]Br$ formed.[15] Treatment of **3** with $HFeCo_3(CO)_{12}$ in THF gave $[WF(NNH_2)(dpe)_2]PF_6$.[16]

No condensation reaction of the NNH_2 group in **3** with acetone occurred by refluxing in acetone for 3 days.[17] However, the condensation reaction in the presence of a catalytic amount of $HFeCo_3(CO)_{12}$ proceeded readily at room temperature to form $[W(OH)(NNCMe_2)(dpe)_2]PF_6\cdot(CH_3)_2CO$ (**5**). Use of HBr as an acid catalyst converted the hydroxo ligand into bromide. The cluster acid is thus useful for the reaction in which the coordination of the conjugate base to the metal center is undesirable. The ^1H NMR chemical shifts of the methyl protons in **5** are at δ 1.2 and −0.4, indicating inequivalence of the CH_3 environment,[18] which

---

(10) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974, Vol. IV.

(11) Sakurai, T. "The Universal Crystallographic Computation Program System", Crystallographic Society of Japan, 1967.

(12) Weast, R. C., Ed. "CRC Handbook of Chemistry and Physics", 64th ed.; CRC Press: Cleveland, OH, 1983.

(13) (a) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993. (b) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546.

(14) Oxidative addition to water to transition-metal complexes has been studied for activation of water, e.g.: (a) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027. (b) Yoshida, T.; Okano, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 3411.

(15) Anal. Calcd for $C_{52}H_{50}Br_2N_2P_4W$: C, 53.35; H, 4.31; N, 2.39; Br, 13.65. Found: C, 52.25; H, 4.09; N, 2.32; Br, 13.90. Cf. ref 20.

(16) Anal. Calcd for $C_{52}H_{50}F_7N_2P_5W$: C, 53.17; H, 4.29; N, 2.38. Found: C, 52.88; H, 4.39; N, 2.37.

(17) Hidai, M.; Mizobe, Y.; Sato, M.; Kodama, T. Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5740.

(18) Chatt, J.; Head, R. A.; Hitchcock, P. B.; Hussain, W.; Leigh, G. J. *J. Organomet. Chem.* **1977**, *133*, Cl.

was also shown by the X-ray structure determination of the compound.[19]

Treatment of $[W(N_2)_2(dpe)_2]$ with $HFeCo_3(CO)_{12}$ in dichloromethane at 3 °C gave a violet complex **11**. The elemental analysis agreed with the formula $[H[W(N_2)_2(dpe)_2]][FeCo_3(CO)_{12}]$, and the anionic nature of $[FeCo_3(CO)_{12}]1^-$ was evident from the ν(CO) (1806 cm^{-1} of the bridging carbonyl group, which shifted from the corresponding ν(CO) of $HFeCo_3(CO)_{12}$ (1888 cm^{-1}),[5] thus excluding the possibility that complex **11** was a mere mixture of the two reactants. No band of ν(N–H) was present in the infrared spectra, and ν(W–H) was obscured by the strong ν(CO) bands. The NMR spectra did not show any band for the hydride. The data imply that the complex was a 1:1 adduct of the dinitrogen complex and the cluster acid, which may be like the one that Henderson[49] proposed from his kinetic study of the reaction of $[W(N_2)_2(dpe)_2]$ with HX. We cannot, however, completely rule out the possibility that **11** was a hydride similar to $[WH(N_2)_2(dpe)_2][HCl_2]$ isolated by Chatt et al. from the reaction of $[W(N_2)_2(dpe)_2]$ with just 2 mol of HCl.[20]

Complex **11** was labile in solution, and attempts to recrystallize it from dichloromethane–hexane resulted in the loss of dinitrogen content to form complex **12**. This complex was also obtained in the reaction of $[W(N_2)_2(dpe)_2]$ with $HFeCo_3(CO)_{12}$ in dichloromethane for 2 h at room temperature. The elemental analysis was consistent with $[H[W(N_2)(dpe)_2]][FeCo_3(CO)_{12}]\cdot{}^1/_2CH_2Cl_2$, and neither ν(N–H) nor ν(W–H) was detected in the infrared spectra. When **12** was stirred in dichloromethane for 3 days at room temperature, the dichloro complex **6** formed. It seems likely that the coordinatively unsaturated tungsten center in **12** had some interaction with the Cl atom of CH_2Cl_2[21] and chlorine atoms were abstracted from dichloromethane to form **6**. Neither **11** nor **12** formed $[W(OCH_3)(NNH_2)(dpe)_2][FeCo_3(CO)_{12}]$[5] by the treatment with methanol. This apparently means that complexes **11** and **12** were not the intermediates for the formation of the hydrazido(2–) methoxo complex. When $[W(N_2)_2(dpe)_2]$ was treated with $HFeCo_3(CO)_{12}$ in benzene or toluene at room temperature, adducts of the two reactants with varying contents of dinitrogen formed and recrystallization from CH_2Cl_2–ether gave a complex with similar elemental analysis to that of **12**.

The reactions in dichloroethane or dibromomethane also gave halide complexes $[WX_2(dpe)_2][FeCo_3(CO)_{12}]$ (X = Cl (**6**), Br (**7**)). The anion exchange gave complexes **8–10**. They were paramagnetic, and magnetic susceptibilities μ_{eff} of **6**, **7**, and **10** were 1.50, 1.65, and 1.46 μ_B, respectively, at room temperature. As the values were near 1.48 μ_B for a similar tungsten(III) complex, $[WCl_2(dpe)_2]Cl$,[22] we concluded that our complexes were also tungsten(III) ones. ^{1}H NMR spectra of these halide complexes were very different from those of the diamagnetic hydrazido(2–) alkoxide[5] or hydroxide, **1–5**, complexes. The signals of the methylene protons of dpe ligands were not observable, and those of the phenyl protons showed three temperature-dependent chemical shifts; e.g, **6** had rather broad singlets at δ 10.5, 8.1, and 7.2 at 30 °C that shifted to lower field on cooling the sample. These spectral features are characteristic of some paramagnetic complexes and resemble those of $[WCl_4(PMe_2Ph)_2]$.[23]

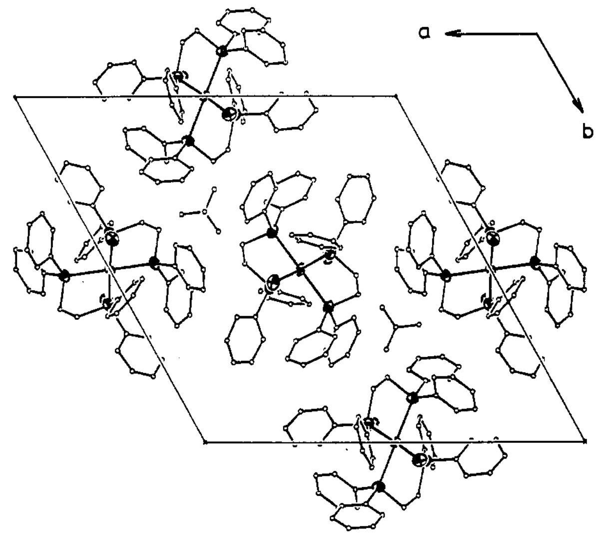

Figure 1. Projection of a unit cell of $[WCl_2(dpe)_2]BF_4\cdot{}^1/_3CH_2Cl_2$ along the *c* axis.

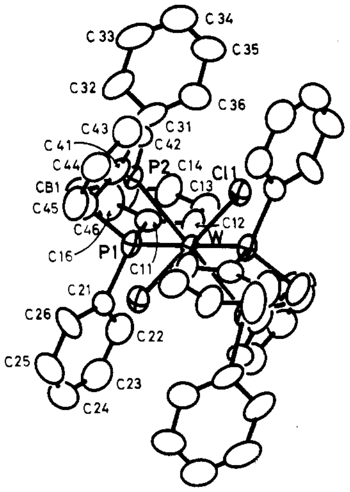

Figure 2. ORTEP drawing of $[WCl_2(dpe)_2]BF_4\cdot{}^1/_3CH_2Cl_2$ and numbering scheme of atoms. The thermal ellipsoids are drawn at the 50% probability level.

The molecular structure of **10** was determined by X-ray crystallography. The crystal belongs to the space group $P\bar{3}$, and tungsten atoms are located at the centers of the unit cell and on the *ac* and *bc* planes. Two BF_4^- anions exist on the 3 axis and are surrounded by three $[WCl_2(dpe)_2]^+$ ions. The other BF_4^- is on the $\bar{3}$ axis running through the origin, and CH_2Cl_2 exists near the axis, making them disordered as described in Experimental Section. The BF_4^- ion on the 3 axis is shown in the *c*-axis projection (Figure 1). The *X* and *Y* coordinates of P2 are nearly the same as those of Cl1, and they are overlapped in the figure. This is also seen from the angle (about 45°) that the plane of W, the four P atoms, and the *c* axis makes.

The cation $[WCl_2(dpe)_2]^+$ consists of an octahedral coordination sphere with four phosphorus atoms of dpe ligands and two chlorine atoms in trans positions (Figure 2). The W–P distances are 2.522 (5) and 2.563 (5) Å, which are a little longer than those in other $[W(dpe)_2]$ type complexes.[17,24,25] The W–Cl distance is 2.312 (5) Å and is shorter than that in $[WCl(NNH_2)(dpe)_2]BPh_4$ (2.421 Å)[24] and in $[WCl_3(NNH_2)(PMe_2Ph)_2]$ (2.446, 2.508 Å).[26] And,

---

(19) Single crystals of **5** grown from acetone–hexane belonged to the space group $P\bar{1}$, with a = 13.813 (3) Å, b = 12.205 (2) Å, c = 11.134 (2) Å, α = 111.05 (2)°, β = 118.13 (2)°, γ = 59.85 (2)°, V = 1413.1 (6) Å^3, and Z = 1. The structure was solved by the heavy-atom method with the similar procedure described for complex **10**. With 4440 unique reflections, R converged to 0.064. As there was disorder of OH and $NNCMe_2$ groups above and below the plane consisting of W and four P atoms, refinements of the positions of the O and N atoms bonded to W were impossible. One of the two methyl groups of the diazoalkane ligand is between two phenyl groups whereas the other is projected outward. The other part of the structure around the tungsten resembles those of similar diazoalkane complexes.[17,18,27]

(20) Chatt, J.; Heath, G. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2074.

(21) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 3475.

(22) Boorman, P. M.; Greenwood, N. N.; Hilden, M. A. *J. Chem. Soc. A* **1968**, 2466.

(23) Moss, J. R.; Shaw, B. L. *J. Chem. Soc. A* **1970**, 595.

(24) Heath, G. A.; Mason, R.; Thomas, K. M. *J. Am. Chem. Soc.* **1974**, 96, 259.

(25) March, F. C.; Mason, R.; Thomas, K. M. *J. Organomet. Chem.* **1975**, *96*, C43.

(26) Chatt, J.; Fakley, M. E.; Hitchcock, P. B.; Richards, R. L.; Luong-Thi, N. T. *J. Chem. Soc., Dalton Trans.* **1982**, 345.

in fact, the distance is shorter than most of the W–Cl distances recently reported.[28-32] The smaller trans influence of Cl may be responsible for the shortness of the bond distance.[24] As crystallographic analysis of monomeric W(III) complexes is rare,[33] comparison of the W–Cl bond distance in W(III) complexes is difficult. The P–W–P angles are almost the same as those in other $W(dpe)_2$ type complexes. The W–Cl vector slightly bends toward P1 and P2, making P1–W–Cl, and P2–W–Cl angles smaller than 90°.

The structure determination of **10** suggests that the reaction product of $[W(N_2)_2(dpe)_2]$ and $HFeCo_3(CO)_{12}$, (**6**), in dichloromethane is also a dichloro complex and not an alternative such as $[WH(dpe)_2][FeCo_3(CO)_{12}]\cdot CH_2Cl_2$, which we had suspected before the X-ray structure determination.

Formation of no hydrazido(2–) complexes in the aprotic solvents in the present study makes a marked contrast with the very facile formation of alkoxide hydrazido(2–) complexes in alcohols[5] or a hydrazido(2–) hydroxo complex in an aqueous solvent. Although the exact sequence of the reaction is still not clear, the coordination of an oxygen ligand ROH or H_2O to the tungsten center probably makes the metal electron rich and this electron flow is transmitted to the reaction center of dinitrogen that is to be protonated. Thus, the influence of electron-donating ligands upon the protonation[4b,34] seems crucial. In the case of simpler acids HX, coordinated X plays the role of electron donor to the metal but an oxygen ligand from alcohols or water is necessary for the present reaction using the cluster acid incapable of coordinating to the tungsten.

Acknowledgment. We thank Dr. Y. Fukuda for the measurements of magnetic susceptibilities.

Supplementary Material Available: Listings of structure factors, anisotropic thermal factors (Table V), and nonessential bond distances and angles (Table VI) (25 pages). Ordering information is given on any current masthead page.

---

(27) Bevan, P. C.; Chatt, J.; Head, R. A.; Hitchcock, P. B.; Leigh, G. J. *J. Chem. Soc., Chem. Commun.* **1976**, 509.

(28) Cotton, F. A.; Felthouse, T. R.; Lay, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 1431.

(29) Jackson, R. B.; Streib, W. E. *Inorg. Chem.* **1971**, *10*, 1760.

(30) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1977**, *16*, 2407.

(31) Bradley, D. C.; Hursthouse, M. B.; Malik, K. M.; Nielson, A. J.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1983**, 2651.

(32) Bell, J. M.; Boorman, P. M.; Moinihan, K. M.; Datel, V. D.; Richardson, J. F.; Collison, D.; Mabbs, F. E. *J. Chem. Soc., Dalton Trans.* **1983**, 2479.

(33) Dori, Z. *Prog. Inorg. Chem.* **1981**, *28*, 239.

(34) Chatt, J.; Leigh, G. J.; Neukomm, H.; Pickett, C. J.; Stanley, D. R. *J. Chem. Soc., Dalton Trans.* **1980**, 121.

Contribution from the Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
Calcutta 700032, India, and the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

Trinucleation of Arylazo Oxime Ensembles: Structure and Reactions of Novel Linear $Fe^{II}Fe^{III}Fe^{II}$ Species

SAMUDRANIL PAL,[1a] TAMMY MELTON,[1b] RABINDRANATH MUKHERJEE,[1a] AKHIL R. CHAKRAVARTY,[1a]
MILAGROS TOMAS,[1b,c] LARRY R. FALVELLO,[1b] and ANIMESH CHAKRAVORTY*[1a]

Received July 19, 1984

The reaction of phenylazo aldoximes, RC(=NOH)N=NPh (HRL; R = Me, Ph), with iron(II) perchlorate hexahydrate in ethanol affords $[Fe_3(RL)_6]ClO_4$ (**1**) crystallizing with or without solvent molecules. The structure of one solvate, viz., $[Fe_3(PhL)_6]ClO_4\cdot 2CHCl_3$, has been determined X-ray crystallographically. The compound forms monoclinic crystals in the space group $P2_1/n$ with $Z = 2$ and unit cell dimensions $a = 15.521$ (4) Å, $b = 12.743$ (5) Å, $c = 21.788$ (5) Å, $\beta = 104.35$ (2)°, and $V = 4175$ (2) Å^3. The structure was refined to $R = 0.0881$ and $R_w = 0.1281$. The trinuclear cation $Fe_3(PhL)_6{}^+$ sits on a crystallographic center of symmetry. The central iron(III) atom is surrounded by an octahedron of six oximato oxygen atoms. Each of the two terminal iron(II) atoms is held in the facial tris chelate environment of azo and oxime nitrogen atoms. The FeN_6 coordination sphere is trigonal antiprismatic. Each oximato function acts as a bridge between iron(III) and iron(II) atoms. Both the $ClO_4{}^-$ anion and the $CHCl_3$ molecules are disordered in the crystal. The reaction of iron(III) chloride with HRL furnishes $[Fe_3(RL)_6]FeCl_4$ (**2**). The iron(III) and iron(II) atoms of $Fe_3(RL)_6{}^+$ are high spin ($S = {}^5/_2$) and low spin ($S = 0$), respectively. Subtle rhombic distortion of the $Fe^{III}O_6$ sphere in $Fe_3(RL)_6{}^+$ is revealed by strong EPR lines near $g = 4$ in both **1** and **2**. The observation of intervalence band(s) in **1** and **2** has been vitiated by the strong visible and near-UV bands localized on the FeN_6 chromophore. Hydroxide ions selectively and quantitatively extrude iron(III) from both **1** and **2**, liberating the green anion $Fe(RL)_3{}^-$ (isolated as Na^+ and Ph_4As^+ salts), which retains the facial stereochemistry characteristic of the parent aggregate. Reaction with iron(III) salts causes reaggregation into $Fe_3(RL)_6{}^+$. The $Fe(RL)_3{}^-$ anion is electrochemically oxidized to axially symmetric (EPR data) low-spin $Fe(RL)_3$, the $Fe^{III}N_6/Fe^{II}N_6$ formal potential being in the range 0.2–0.4 V vs. SCE. In $Fe_3(RL)_6{}^+$, the couple $Fe^{III}O_6/Fe^{II}O_6$ due to the central iron atom occurs near 0.0 V but the terminal $Fe^{III}N_6/Fe^{II}N_6$ couple is shifted to potentials above 1.5 V and is not directly observable. In the case of **2** the $FeCl_4{}^-/FeCl_4{}^{2-}$ couple is exactly superposed on the $Fe^{III}O_6/Fe^{II}O_6$ couple of the cation. These redox patterns have been used to rationalize the formation of **1** and **2** by the chelative redox reactions of iron salts with HRL. The possible role of $Fe(RL)_3{}^-$ as a translocator of metal ions via the reaggregation–extrusion sequence and its similarity to ferroverdin, the green pigment of a *Streptomyces* species, are noted.

Introduction

The binding of iron by nitrogen and oxygen donors is of widespread chemical interest. Unsaturated nitrogenous groups are good donors for low-spin iron(II). Anionic oxygen functions, on the other hand, commonly display pronounced affinity toward high-spin iron(III). The α-diimines[2] and β-diketones[3] are good examples of these simple rules that find elegant expression in the binding of iron in nature.[4]

---

(1) (a) Indian Association for the Cultivation of Science. (b) Texas A&M University. (c) Permanent address: University of Zaragoza, Zaragoza, Spain.

(2) Batschelet, W. H.; Rose, N. J. *Inorg. Chem.* **1983**, *22*, 2078. Krumholz, P. *Struct. Bonding* (*Berlin*) **1971**, *9*, 139.

(3) Mehrotra, R. C.; Bohra, R.; Gaur, D. P. "Metal β-Diketonates and Allied Derivatives"; Academic Press: New York, 1978.

0020-1669/85/1324-1250$01.50/0