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Preparation and Properties of Molybdenum- and Tungsten-Dinitrogen Complexes 7 [1]. The Molecular Structure of $MoCl(N_2COPh)(Ph_2PCH_2CH_2PPh_2)_2$.

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Summary

The structure of the complex $MoCl(N_2COPh)(Ph_2PCH_2CH_2PPh_2)_2$ has been determined from three-dimensional X-ray counter data collected on a single crystal. The material crystallizes in space group $P2_1/n$ of the monoclinic system with four formula units of the complex in a cell of dimensions $a = 21.17(1)$ Å, $b = 19.97(1)$ Å, $c = 12.56(2)$ Å, $\beta = 100.57(3)°$, $V = 5220.6(52)$ Å^3. The structure has been refined by block-diagonal least-squares techniques to a final R index 0.0715 based on 7386 reflections above background. The complex has an octahedral geometry with benzoyldiazenido and chloride ligands in a trans position and the benzoyldiazenido ligand is not chelating through the carbonyl oxygen. The bond orders of N-N, N-C, and C-O are estimated to be 1.85, 1.3, and 1.85, respectively, which indicate the mesomeric spread of a high electron density from the metal to the benzoyldiazenido ligand. However, this spread does not extend so far to the phenyl group.

Introduction

The formation of carbon-nitrogen bonds from coordinated dinitrogen is an important elementary step for the direct conversion of dinitrogen into organo-nitrogen compounds. In 1972, Chatt and his coworkers briefly reported that organic acid chlorides react with trans-$W(N_2)_2(dpe)_2$ (dpe = $Ph_2PCH_2CH_2PPh_2$) to produce complexes $WCl_2(N_2HCOR)(dpe)_2$ from which HCl can be removed to form chelated acyl- and aroyldiazenido complexes (equation 1) and that trans-$Mo(N_2)_2(dpe)_2$ reacts analogously with organic acid halides [2].

$$\underline{\text{trans}}\text{-}W(N_2)_2(dpe)_2 + RCOCl + H_2O \longrightarrow$$

$$WCl_2(dpe)_2(N_2HCOR) \underset{HCl}{\overset{NEt_3}{\rightleftarrows}} Cl(dpe)_2\overline{W(N_2CO}R) \qquad (1)$$

They proposed the coordination of the carbonyl oxygen to tungsten in these complexes since the $\nu(C{=}O)$ was observed in the region of 1550 - 1575 cm^{-1}. In 1975, we found that the benzoyldiazenido complex $MoCl(N_2COPh)(dpe)_2$ 1 is obtained by the reaction of trans-$Mo(N_2)(RCN)(dpe)_2$ with benzoyl chloride and showed by preliminary X-ray structural analysis that the complex has actually a carbon-nitrogen bond and the benzoyldiazenido ligand is not chelating through the carbonyl oxygen to the metal [3]. Here we wish to describe in detail the

$$\underline{\text{trans}}\text{-}Mo(N_2)(RCN)(dpe)_2 + PhCOCl \longrightarrow \underset{\underline{1}}{MoCl(N_2COPh)(dpe)_2} \qquad (2)$$

molecular structure of the complex 1.

Experimental

X-Ray analysis for $MoCl(N_2COPh)(dpe)_2$ [4]. The title complex was prepared according to the method described above

Table 1. Crystallographic Data of $MoCl(N_2COPh)(dpe)_2$

a	21.17(1) Å
b	19.97(1) Å
c	12.56(2) Å
β	100.57(3)°
V	5220.6(52) $Å^3$
Z	4
Density (by flotation in aqueous potassium carbonate)	1.354 g/cm^3 (calcd) 1.367 g/cm^3 (found)
Crystal dimensions	0.28 × 0.33 × 0.66 mm
Systematic absences	h0l: h + l = 2n + 1 0k0: k = 2n + 1
Space group	$P2_1/n$
μ	4.72 cm^{-1}
Maximum absorption effect (exp(-μR))	27 %
Scan	2θ - ω
2θ limits	$0° \leqq 2\theta \leqq 60°$
Backgrounds	Measd for 10 s at each end of the scan
Total data	12926
Unique data ($Fo^2 \geqq 3\sigma(Fo^2)$)	7386
Final R	0.0715

[3], and the orange crystals were obtained in the form of plates by recrystallization from toluene/n-hexane. Crystals were sealed in a glass capillary under a dinitrogen atmosphere. Intensity measurements were made with Mo Kα(0.7107 Å) radiation monochromatized by LiF, using a Rigaku automated four-circle

(Continued on p.245)

Table 2. Positional and Thermal Parameters for the Nonhydrogen Atoms of $MoCl(N_2COPh)(dpe)_2$.

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	1959(1)	1608(1)	1503(1)	135(1)	198(1)	453(3)	-8(1)	20(2)	16(2)
P(1)	1426(1)	761(1)	2554(2)	179(4)	221(5)	586(13)	-14(4)	72(6)	31(7)
P(2)	1477(1)	810(1)	6(1)	177(4)	256(5)	525(12)	-30(4)	18(6)	-38(7)
P(3)	2350(1)	2558(1)	434(1)	182(4)	231(5)	539(12)	-16(4)	49(6)	45(6)
P(4)	2343(1)	2455(1)	3001(1)	164(4)	212(5)	503(11)	-6(4)	2(5)	-2(6)
Cl	955(1)	2266(1)	1308(2)	160(4)	336(6)	640(12)	43(4)	8(5)	62(7)
N(1)	2694(3)	1125(3)	1621(4)	140(12)	306(19)	492(38)	-33(12)	0(17)	-14(22)
N(2)	3227(3)	850(3)	1619(6)	248(18)	267(20)	812(53)	35(15)	71(25)	69(26)
O	2919(3)	-83(4)	2496(7)	313(20)	415(26)	1749(88)	13(18)	215(34)	313(39)
C(1)	1324(4)	-15(4)	1729(7)	225(19)	224(21)	819(61)	-8(16)	80(28)	33(29)
C(2)	1006(4)	162(4)	570(7)	204(18)	297(24)	699(57)	-51(17)	11(26)	-15(30)
C(3)	2800(4)	3152(4)	1418(6)	245(19)	237(20)	586(50)	-61(16)	37(25)	11(26)
C(4)	2423(4)	3266(4)	2326(6)	310(23)	228(23)	615(54)	-10(18)	61(28)	9(27)
C(5)	3319(4)	233(4)	2096(7)	227(20)	290(25)	920(71)	16(18)	69(30)	-68(34)
C(51)	4011(4)	-11(4)	2187(7)	244(21)	237(22)	909(69)	51(18)	-30(30)	-72(32)
C(52)	4382(4)	189(6)	1450(9)	258(24)	409(35)	1143(92)	49(23)	28(37)	-160(46)
C(53)	5022(5)	-52(7)	1540(10)	244(25)	595(48)	1377(111)	2(28)	71(42)	-449(62)
C(54)	5252(6)	-496(7)	2354(12)	312(32)	526(46)	1688(136)	109(31)	-84(53)	-219(65)
C(55)	4889(7)	-695(7)	3064(12)	491(43)	423(42)	1659(140)	144(35)	-174(62)	25(61)
C(56)	4238(6)	-470(6)	2999(10)	381(34)	346(33)	1335(108)	99(27)	-75(48)	19(48)
C(111)	615(3)	947(4)	2800(6)	192(17)	261(22)	687(55)	-34(16)	94(25)	-23(28)
C(112)	75(4)	559(5)	2413(9)	211(21)	371(32)	1295(94)	-67(21)	194(36)	-82(44)

C(113)	-524(5)	745(6)	2660(12)	262(26)	370(35)	2063(151)	-105(25)	282(51)	-186(59)
C(114)	-574(5)	1288(6)	3314(11)	216(23)	403(35)	2063(147)	-15(23)	341(49)	-1(59)
C(115)	-35(4)	1653(5)	3709(10)	258(23)	313(29)	1465(104)	-1(22)	227(40)	-92(45)
C(116)	549(4)	1490(5)	3436(7)	267(22)	342(29)	850(67)	-43(20)	195(31)	-85(35)
C(121)	1791(4)	463(4)	3900(7)	309(24)	292(24)	655(57)	77(20)	142(30)	103(30)
C(122)	2388(5)	684(5)	4363(8)	393(31)	357(32)	826(72)	82(26)	-138(38)	62(39)
C(123)	2649(8)	487(8)	5455(11)	717(62)	573(55)	1252(123)	221(49)	-294(70)	-69(66)
C(124)	2319(10)	61(9)	5984(10)	1123(88)	734(67)	681(86)	333(64)	128(70)	219(62)
C(125)	1742(9)	-184(9)	5511(11)	916(74)	810(71)	1232(117)	267(59)	703(80)	604(78)
C(126)	1488(6)	30(7)	4469(10)	509(43)	639(53)	1294(109)	125(39)	474(58)	441(64)
C(211)	890(4)	1039(4)	-1219(6)	218(19)	279(23)	644(54)	-48(17)	-65(26)	-18(29)
C(212)	1021(5)	960(5)	-2264(7)	357(27)	315(27)	640(58)	-71(22)	-21(32)	51(32)
C(213)	544(5)	1152(6)	-3151(7)	413(34)	455(37)	653(65)	-29(28)	-35(37)	19(40)
C(214)	-37(5)	1415(6)	-2986(8)	348(29)	457(38)	818(75)	-55(27)	-134(38)	76(42)
C(215)	-165(5)	1485(5)	-1970(9)	250(23)	370(34)	1335(102)	-50(23)	-73(39)	-27(45)
C(216)	297(4)	1309(5)	-1070(7)	194(18)	381(29)	739(62)	-14(19)	-89(27)	-57(35)
C(221)	2085(3)	318(4)	-528(6)	202(17)	290(23)	474(46)	-8(16)	54(23)	-22(26)
C(222)	2575(5)	653(6)	-882(11)	335(30)	427(38)	1782(132)	-121(27)	387(52)	-409(59)
C(223)	3066(5)	303(7)	-1214(11)	306(29)	599(50)	1538(119)	-106(31)	288(49)	-415(64)
C(224)	3074(5)	-368(6)	-1235(8)	379(31)	517(42)	787(72)	100(29)	143(39)	47(44)
C(225)	2612(7)	-699(6)	-894(12)	656(54)	357(38)	1867(151)	197(37)	597(76)	257(62)
C(226)	2113(6)	-368(5)	-530(10)	487(40)	323(32)	1385(110)	29(28)	430(55)	85(47)
C(311)	1729(4)	3078(4)	-384(6)	224(19)	293(23)	559(50)	-24(17)	82(25)	114(28)
C(312)	1690(5)	3764(5)	-275(9)	341(28)	275(27)	1141(90)	-26(22)	-77(40)	116(40)
C(313)	1169(6)	4129(5)	-877(11)	417(35)	294(32)	1668(128)	45(27)	-82(54)	278(52)
C(314)	713(5)	3778(6)	-1590(9)	299(28)	497(42)	1239(100)	6(27)	-55(42)	381(54)
C(315)	743(4)	3101(6)	-1716(7)	286(25)	456(35)	701(64)	-12(24)	-13(32)	195(39)
C(316)	1249(4)	2751(5)	-1094(7)	263(22)	338(29)	775(63)	-24(20)	10(30)	66(35)

(Table continued)

Table 2 (Continued)

C(321)	2929(4)	2394(4)	-452(7)	228(19)	238(22)	781(60)	-36(16)	129(27)	17(29)
C(322)	2793(5)	2536(6)	-1567(7)	324(27)	490(38)	676(64)	-73(26)	131(34)	29(39)
C(323)	3232(6)	2371(7)	-2223(9)	400(34)	632(51)	873(80)	-67(33)	291(43)	-67(51)
C(324)	3802(5)	2060(6)	-1777(10)	401(34)	411(36)	1525(118)	-104(29)	458(53)	-88(53)
C(325)	3953(5)	1914(5)	-686(10)	282(26)	357(32)	1617(119)	-20(24)	351(47)	15(51)
C(326)	3502(4)	2078(5)	-15(8)	267(23)	326(28)	1091(84)	-44(21)	215(36)	28(39)
C(411)	3155(3)	2391(4)	3846(6)	171(17)	307(24)	616(52)	-0(16)	-15(23)	1(29)
C(412)	3351(4)	2871(5)	4634(7)	256(22)	377(30)	711(62)	-69(21)	15(30)	-96(35)
C(413)	3966(5)	2828(6)	5284(8)	286(26)	510(40)	894(76)	-194(27)	-61(35)	-2(45)
C(414)	4363(4)	2305(6)	5116(9)	192(22)	647(48)	1041(86)	-104(26)	-81(35)	124(53)
C(415)	4170(4)	1849(7)	4355(10)	194(22)	533(44)	1537(118)	57(25)	-79(41)	93(59)
C(416)	3555(4)	1882(5)	3709(7)	198(20)	386(29)	887(71)	20(20)	-21(30)	-52(38)
C(421)	1849(4)	2674(4)	3999(6)	209(18)	254(22)	633(52)	-45(16)	58(25)	-87(28)
C(422)	1942(4)	2354(5)	5001(6)	250(21)	355(28)	554(51)	-57(19)	30(26)	14(31)
C(423)	1539(5)	2502(6)	5730(7)	357(30)	535(41)	664(64)	-133(28)	133(35)	-50(42)
C(424)	1047(5)	2954(6)	5478(9)	314(27)	549(44)	993(83)	-71(28)	209(39)	-234(49)
C(425)	948(4)	3264(5)	4492(8)	274(24)	403(34)	1044(82)	39(22)	152(36)	-173(42)
C(426)	1346(4)	3125(5)	3757(7)	248(21)	368(28)	727(61)	59(20)	110(29)	-48(34)

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[a] The quantities given in the table are the positional coefficients x 10^4.

[b] The form of the anisotropic thermal ellipsoid is

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

The quantities given in the table are the thermal coefficients x 10^5.

diffractometer by 2θ-ω scan technique. Lorentz and polarization cerrections were applied, but no absorption correction was made since the maximum absorption effect (μR) is 0.62. Table 1 shows the crystallographic data. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares using anisotropic temperature factors for nonhydrogen atoms. The quantity minimized was $\underline{w}(|Fo|-k|Fc|)^2$ and the weighting scheme was $\underline{w} = 0.7$ for $|Fo|<12$, $\underline{w} = 1.0$ for $12\leq|Fo|\leq48$, and $\underline{w} = (48/|Fo|)^2$ for $|Fo|>48$. The atomic scattering factors were taken from the usual tabulation [5a] and the anomalous terms for Mo, Cl, and P were those of Cromer and Liberman [5b] and were included in Fc. At this stage, a difference-Fourier synthesis was computed to reveal clear peaks of hydrogen atoms. We carried out then the final cycle including the positional parameters of the above hydrogen atoms, the isotropic temperature parameters of which were fixed at 5.0 Å^2. No parameters shifted at this stage by more than 0.3 of their estimated standard deviations. The atomic parameters are shown in Tables 2 and 3.*

Results and Discussion

The perspective views of the complex 1 are shown in Figs. 1 and 2. This complex has an octahedral geometry with benzoyldiazenido and chloride ligands in a *trans* position. Selected bond distances and angles are shown in Table 4. There are no significant intra- and intermolecular contacts.

(Continued on p. 248)

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* The table of structure factors has been deposited as NAPS Document No.03236 (24 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10017. A copy may be secured by citing the document number, remitting $6.00 for photocopies or $3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications. Outside the U.S.A. and Canada, postage is $3.00 for photocopies and $1.00 for a fiche.

Table 3. Positional Parameters for the Hydrogen Atoms of $MoCl(N_2COPh)(dpe)_2$

Atom	x^a	y	z
H(11)	106(5)	-33(5)	211(8)
H(12)	184(5)	-8(5)	177(8)
H(21)	98(5)	-26(5)	10(8)
H(22)	56(5)	35(5)	56(8)
H(31)	280(5)	368(5)	108(8)
H(32)	329(5)	293(5)	169(8)
H(41)	261(5)	353(5)	298(8)
H(42)	197(5)	342(5)	204(8)
H(52)	419(5)	56(5)	91(8)
H(53)	542(5)	6(5)	96(8)
H(54)	578(5)	-72(5)	258(9)
H(55)	481(5)	-114(5)	333(9)
H(56)	392(5)	-60(6)	363(8)
H(112)	8(5)	8(5)	191(8)
H(113)	-93(5)	39(5)	220(8)
H(114)	-105(5)	149(5)	341(8)
H(115)	-16(5)	210(5)	398(8)
H(116)	97(5)	178(5)	373(8)
H(122)	265(5)	100(5)	391(8)
H(123)	319(5)	68(5)	572(9)
H(124)	249(5)	-24(5)	675(8)
H(125)	157(5)	-55(5)	588(8)
H(126)	106(5)	-1(6)	422(8)
H(212)	150(5)	74(5)	-236(8)
H(213)	64(5)	112(5)	-392(8)
H(214)	-37(5)	154(5)	-364(8)
H(215)	-63(5)	166(5)	-189(8)

H(216)	21(5)	133(5)	-28(8)
H(222)	256(5)	121(6)	-93(9)
H(223)	342(5)	58(5)	-145(8)
H(224)	329(5)	-69(5)	-166(8)
H(225)	265(5)	-127(5)	-85(8)
H(226)	175(5)	-63(5)	-28(8)
H(312)	206(5)	406(5)	14(8)
H(313)	121(5)	467(5)	-77(8)
H(314)	45(5)	407(5)	-220(8)
H(315)	24(5)	285(5)	-212(8)
H(316)	118(5)	228(5)	-107(8)
H(322)	235(5)	280(5)	-184(9)
H(323)	317(5)	247(5)	-312(9)
H(324)	414(5)	202(5)	-225(8)
H(325)	438(5)	168(5)	-33(8)
H(326)	361(5)	209(5)	85(8)
H(412)	301(5)	328(5)	489(8)
H(413)	414(5)	322(5)	568(8)
H(414)	480(5)	236(5)	542(8)
H(415)	442(5)	146(5)	434(9)
H(416)	342(5)	147(5)	315(8)
H(422)	225(5)	206(5)	519(8)
H(423)	154(5)	224(5)	625(8)
H(424)	72(5)	296(5)	602(8)
H(425)	56(5)	363(5)	434(8)
H(426)	125(5)	334(5)	295(8)

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[a] The quantites given in the table are the positional coefficients x 10^3.

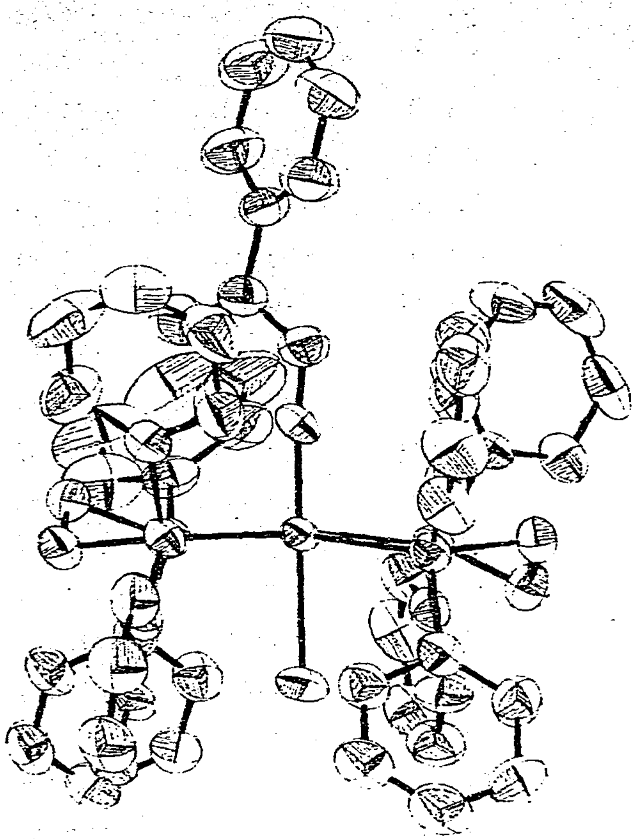


Fig. 1. Perspective of $MoCl(N_2COPh)(dpe)_2$.
The shapes of the atoms in this drawing represent 50% probability contours of thermal motions.

The maximum and minimum C–C bond distances of phenyl groups are 1.437(20) Å and 1.316(20) Å, and those of the C–C–C angles are 123.7(14)° and 116.7(10)°, respectively. The Mo...O distance of 4.019(9) Å clearly shows that the benzoyldiazenido ligand is not chelating through the carbonyl oxygen to molybdenum. Recently Chatt and his coworkers prepared the complex $[Mo_2O(PhCON_2)_2(S_2CNEt_2)_2]$ with bridging benzoyldiazenido ligand [6].

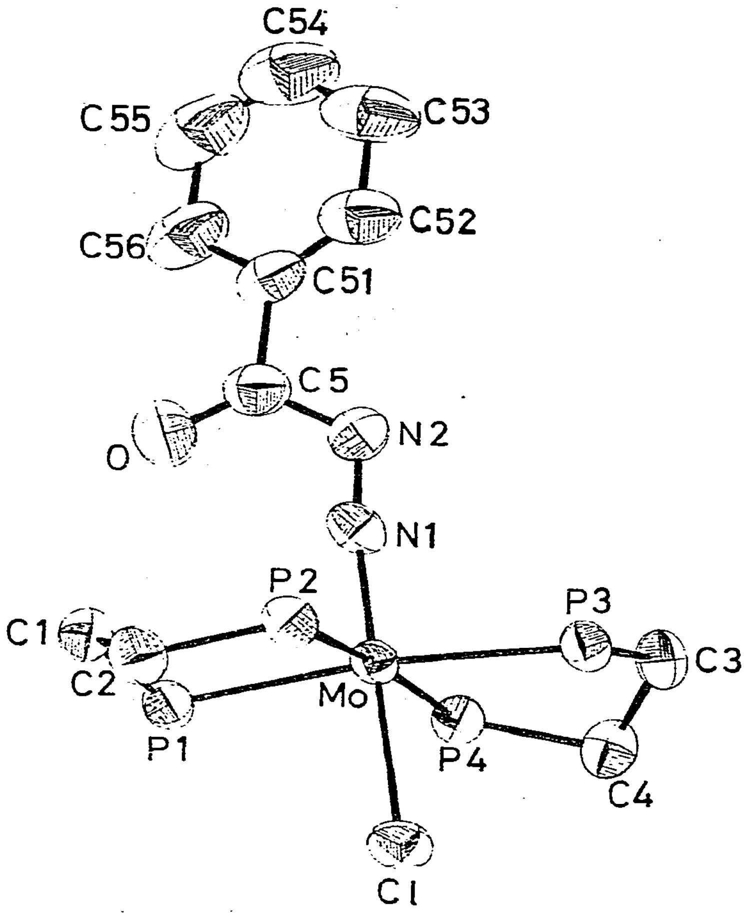


Fig. 2. Perspective view of MoCl(N_2COPh)(dpe)$_2$ with labeling scheme. The shapes of the atoms on this drawing represent 50% probability contours of thermal motions.

The average Mo-P distance of 2.542(5) Å found in <u>1</u> is nearly equal to that of 2.541(4) Å in [MoF(N_2H_2)(dpe)$_2$][BF_4]·CH_2Cl_2 [7] and that of 2.57 Å in [MoOCl(dpe)$_2$][$ZnCl_3${OC(CH_3)$_2$}] [8], but longer than that of 2.454(1) Å in <u>trans</u>-Mo(N_2)$_2$(dpe)$_2$

Table 4. Selected Bond Distances (Å) and Angles (deg.) of $MoCl(N_2COPh)(dpe)_2$

Mo – N(1)	1.813(7)	Mo – N(1) – N(2)	172.1(6)
Mo – Cl	2.472(2)	N(1) – N(2) – C(5)	116.7(7)
Mo – P(1)	2.535(2)	N(2) – C(5) – O	125.7(9)
Mo – P(2)	2.532(2)	N(2) – C(5) – C(51)	112.2(8)
Mo – P(3)	2.549(2)	O – C(5) – C(51)	121.9(9)
Mo – P(4)	2.551(2)	N(1) – Mo – Cl	179.0(2)
N(1) – N(2)	1.255(10)	N(1) – Mo – P(1)	93.4(2)
N(2) – C(5)	1.369(12)	N(1) – Mo – P(2)	87.1(2)
C(5) – O	1.235(13)	N(1) – Mo – P(3)	94.7(3)
C(5) – C(51)	1.526(13)	N(1) – Mo – P(4)	98.0(2)
C – C (phenyl)	1.382(24)*	C – C – C (phenyl)	120.0(13)*
Mo ... O	4.019(9)	(nonbonded distance)	

*average.

[9] and 2.448(4) Å in *trans*-$Mo(CO)(N_2)(dpe)_2 \cdot 1/2C_6H_6$ [1]. This is consistent with a weaker back donation from the high-valent metal to the phosphorus ligand, resulting in the lengthening of Mo-P distances.

The Mo-N-N linkage is essentially linear and the angle N-N-C is 116.7(7)°, indicating that *1* is a singly-bent benzoyldiazenido complex. In Table 5, there are shown pertinent bond angles and distances of several singly-bent benzoyl- and phenyldiazenido-complexes. The N-N distance of 1.255(10) Å found in *1* is longer than an ordinary N=N bond distance (1.24 Å). Accompaning the elongation of the N-N bond, the C-N bond possesses some double-bond character and the C-O bond has some single-bond character. Allman estimated

Table 5. Bond Distances and Angles for Singly-Bent Acyl- and Aryldiazenido Ligands

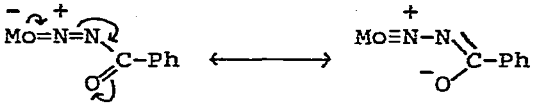
Complex	M - N (Å)	N - N (Å)	N - C (Å)	N - N - C (deg.)	M - N - N (deg.)	Reference
$MoCl(N_2COPh)(dpe)_2$	1.813(7)	1.255(10)	1.369(12)	116.7(7)	172.1(6)	a
$ReCl_2(N_2COPh)(PPhMe_2)_3$	1.74(2)	1.22(3)	1.42(3)	124(2)	170(2)	b
$Mo(HBPz_3)(CO)_2(N_2Ph)$	1.825(4)	1.211(6)	1.432(17)	121.1(2)	174.2(1)	c
$ReCl_2(N_2Ph)(PPhMe_2)_3$	1.77(2)	1.23(2)	1.43(2)	119(2)	173(2)	b
Ru(*p*-$N_2C_6H_4Me)Cl_3(PPh_3)_2$	1.796(9)	1.14(1)	1.40(1)	136(1)	171.2(9)	d
	1.784(5)	1.158(6)	1.376(6)	137.1(5)	171.9(5)	e
$[Fe(N_2Ph)(CO)_2(PPh_3)_2]^+$	1.702(6)	1.201(7)	1.404(8)	124.2(6)	179.2(5)	e,f
trans-PhNNPh		1.243(6)	1.433(3)	113.6(2)		g

Pz = 1-pyrazolyl

a) This work. b) R. Mason, K. M. Thomas, J. A. Zubieta, P. G. Douglas, A. T. Galbraith, and B. L. Show, *J. Am. Chem. Soc.*, 96(1974)260. c) G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Crystallogr.*, B27(1971)725. d) J. V. McArdle, A. J. Schultz, B. J. Corden, and R. Eisenberg, *Inorg. Chem.*, 12(1973)1676. e) J. A. Ibers and B. L. Haymore, *Inorg. Chem.*, 14(1975)1369. f) W. E. Carroll and F. J. Lalor, *J. Chem. Soc. Dalton*, (1973)1754. g) Reference [10].

bond lengths for atoms in sp^2-state for a given total bond order n (from simple VB, $n = 1 + p$) using Pauling's formula $r(n) = r(1) - k \times \log n$, where the constant k (in Å) was fixed to fit the assumed values for $n = 1.0$ and $n = 2.0$ (i.e., $k = (r(1) - r(2))/\log 2$) [10]. By using this method, the bond orders of N-N, N-C, and C-O in the complex 1 are calculated to be 1.85, 1.3, and 1.85, respectively. This means that the complex 1 may be expressed by the two resonance structures as shown below, where the canonical structures (ii), which may contribute about 20 %, results from the back-donation of a high electron density from molybdenum. The five atoms, Mo, N(1), N(2), C(5), and O, lie on a same plane (1) as shown in Table 6. However, it is very interesting to note that the phenyl group of the benzoyldiazenido ligand is twisted toward the plane (1) at an angle of 26.2° and the C(5)-C(51) distance of 1.526(13) Å corresponds to an ordinary single bond. This indicates that the conjugation does not extend so far to the phenyl group.

The exceedingly low ν(C=O) of the complex 1 observed at 1565 cm^{-1} may reflect this resonance. An acyl complex $[Mn(CO)_4(COCH_3)(COPh)][N(CH_3)_4]$ [11] shows two bands at 1550 and 1585 cm^{-1} due to ν(C=O). These low ν(C=O)'s are also compatible with long C-O distances of 1.203(13) Å and 1.218(13) Å which may reflect the mesomeric spread of a very high density from the metal. On the other hand, the ν(C=O) of an analogous benzoyldiazenido complex of rhenium, $ReCl_2(N_2COPh)(PPhMe_2)_3$, appears at 1630 cm^{-1} [12]. This indicates that the contribution



(i) ca. 80 % (ii) ca. 20 %

Table 6. Weighted Least-Square Planes[a]

Atom	Deviations from the planes (Å) Plane 1	 Plane 2
Mo	-0.000(16)	
N(1)	-0.006(17)	
N(2)	0.013(17)	
C(5)	-0.015(18)	0.005(10)*
O	0.008(18)	
C(51)		-0.004(10)
C(52)		-0.000(12)
C(53)		0.002(14)
C(54)		0.000(15)
C(55)		-0.005(16)
C(56)		0.005(13)

a) Plane equation: $AX + BY + CZ + D = 0$, where X,Y,Z are equal to the sirection cosines with respect to the axis a,b,c*, and A, B, C, and D in Å. * C(5) was excepted in the calculation of the plane 2.

	A	B	C	D
Plane 1	-0.1860	-0.4216	-0.8875	3.7098
Plane 2	-0.2337	-0.7667	-0.5980	3.4513

A dihedral angle between the planes. 26.2°

of a canonical structure corresponding to (ii) may be less important in the rhenium complex. This is substantiated by the shorter N-N distance and the longer N-C distance of the benzoyldiazenido ligand compared with those of the molybdenum complex 1 (Table 5).

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References and Notes

1 Part 6: M. Sato, T. Tatsumi, T. Kodama, M. Hidai, and Y.Uchida, to be published.

2 J. Chatt, G. A. Heath, G. J. Leigh, J. Chem. Soc. Chem. Commun., (1972)444.

3 T. Tatsumi, M. Hidai, and Y. Uchida, Inorg. Chem., 14(1975) 2530.

4 The UNICS program system for HITAC 8700/8800 computers was employed at Tokyo University Computer Centre.

5 (a) D. T. Cromer and J. T. waber, "International Tables for X-Ray Crystallography", Vol. IV. Kynoch Press, Birmingam, England, 1974, Table 2.2A; (b) D. T. Cromer and D. Liberman, ibid, Table 2.3.1.

6 M. Michael, W. Bishop, J. Chatt, J. R. Dilworth, G. Kaufman, S. Kim, J. Zubieta, J. Chem. Soc. Chem. Commun., (1977)70.

7 M. Hidai, T. Kodama, M. Sato, M. Harakawa, and Y. Uchida, Inorg. Chem., 15(1976)2694.

8 V. C. Adam, U. A. Gregory, and B. T. Kilbourn, J. Chem. Soc. (D), (1970)1400.

9 T. Uchida, Y. Uchida, M. Hidai, and T. Kodama, Acta Crystallogr., B31(1975)1197.

10 S. Patai, Ed., "The chemistry of the hydrazo, azo, and azoxy groups.", John Wiley & Sons, Part 1, London, Newyork, Sydney, and Toronto, P. 23, and references therein.

11 C. P. Casey and C. A. Bunnell, J. Am. Chem. Soc., 98(1976) 436.

12 J. Chatt, J. R. Dilworth, G. J. Leigh, and V. D. Gupta, J. Chem. Soc. (A), (1971)2631.