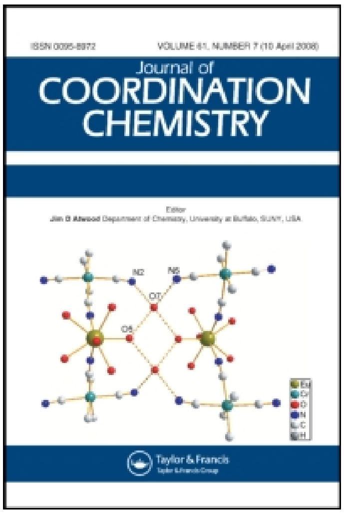


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 30.[1] Syntheses of Zero-Valent Molybdenum Complexes with the DMF Ligand: The Crystal Structure of *Trans*-[Mo(CO)(DMF)$(Ph_2PCH_2CH_2PPh_2)_2$]

Yasushi Mizobe[a]; Toyohisa Ishida[a]; Yumiko Egawa[a]; Kenshi Ochi[a]; Tomoaki Tanase[a]; Masanobu Hidai[a]
[a] Department of Synthetic Chemistry, The University of Tokyo, Hongo, Tokyo, Japan

To cite this Article Mizobe, Yasushi , Ishida, Toyohisa , Egawa, Yumiko , Ochi, Kenshi , Tanase, Tomoaki and Hidai, Masanobu(1991) 'Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 30.[1] Syntheses of Zero-Valent Molybdenum Complexes with the DMF Ligand: The Crystal Structure of *Trans*-[Mo(CO)(DMF)$(Ph_2PCH_2CH_2PPh_2)_2$]', Journal of Coordination Chemistry, 23: 1, 57 — 66
To link to this Article: DOI: 10.1080/00958979109408242
URL: http://dx.doi.org/10.1080/00958979109408242

J. Coord. Chem. 1991, Vol. 23, pp. 57–66
Reprints available directly from the publisher
Photocopying permitted by license only

PREPARATION AND PROPERTIES OF MOLYBDENUM AND TUNGSTEN DINITROGEN COMPLEXES. 30.[1] SYNTHESES OF ZERO-VALENT MOLYBDENUM COMPLEXES WITH THE DMF LIGAND: THE CRYSTAL STRUCTURE OF *TRANS*-$[Mo(CO)(DMF)(Ph_2PCH_2CH_2PPh_2)_2]$†

YASUSHI MIZOBE, TOYOHISA ISHIDA, YUMIKO EGAWA,
KENSHI OCHI, TOMOAKI TANASE, and MASANOBU HIDAI*

Department of Synthetic Chemistry, The University of Tokyo, Hongo, Tokyo 113, Japan

(Received July 3, 1990)

Treatment of *trans*-$[Mo(N_2)_2(dpe)(dpm)]$ (dpe = $Ph_2PCH_2CH_2PPh_2$, dpm = $Ph_2PCH_2PPh_2$) or *trans*-$[Mo(N_2)_2(dpe)(dpp)]$ (dpp = $Ph_2PCH_2CH_2CH_2PPh_2$) with excess DMF in benzene at reflux under Ar resulted in the formation of *trans*-[Mo(CO)(DMF)(dpe)(dpm)] or *trans*-[Mo(CO)(DMF)(dpe)(dpp)]. X-ray structural analysis of *trans*-$[Mo(CO)(DMF)(dpe)_2]$ was performed using single crystals isolated as the minor product from the reaction mixture of *trans*-$[Mo(N_2)_2(dpe)(dpp)]$ and DMF. Crystal data: $C_{56}H_{55}O_2NP_4Mo$, monoclinic, space group $P2_1$, $a = 11.145(4)$, $b = 23.425(5)$, $c = 10.516(3)$ Å, $\beta = 117.17(2)°$, $V = 2442.6(13)$ Å^3, $D_{calcd} = 1.35$ g/cm^3 for $Z = 2$. This disclosed the relatively long C≡O bond distance of the carbonyl ligand and the significantly short C=O bond length in the DMF ligand. When recrystallized from benzene/hexane under N_2, *trans*-[Mo(CO)(DMF)(dpe)(dpm)] was converted into *trans*-$[Mo(CO)(N_2)(dpe)(dpm)]$.

Keywords: Molybdenum, *N,N*-dimethylformamide, carbonyl, dinitrogen, complex, X-ray structure

INTRODUCTION

We previously reported the decarbonylation of DMF by *trans*-$[Mo(N_2)_2(dpe)_2]$ (IA; dpe = $Ph_2PCH_2CH_2PPh_2$) to give $[Mo(CO)(DMF)(dpe)_2]$ (IIA) and $HNMe_2$.[2] Interestingly, IIA can easily be converted into a carbonyl-dinitrogen complex, *trans*-$[Mo(CO)(N_2)(dpe)_2]$ (IIIA), under N_2 and then into a coordinatively unsaturated complex, $[Mo(CO)(dpe)_2]$. (IVA), under Ar. An attractive feature of IVA is that it can bind a wide range of substrates including common Lewis bases, ethene, and N_2.[2,3] More recently, Kubas and coworkers have reported that IVA reacts with H_2 to give a molecular hydrogen complex, *trans*-$[Mo(CO)(\eta^2\text{-}H_2)(dpe)_2]$.[4] Thus we have started to prepare a series of five coordinate Mo and W complexes using various diphosphine ligands. In this context, we have carried out the reaction of *trans*-$[W(N_2)_2(dpe)_2]$ with DMF and have isolated *trans*-$[W(CO)(DMF)(dpe)_2]$ together with $[WH(\eta^2\text{-}CONMe_2)(dpe)_2]$ as an intermediate of this decarbonylation.[5] It is noteworthy that the five-coordinate complex $[W(CO)(dpe)_2]$, derived from the former *via* $[W(CO)(N_2)(dpe)_2]$, reacts with H_2 to give a dihydrido complex

---

* Author for correspondence.

† Dedicated to Professor Arthur Martell on the occasion of his 75th birthday.

$[WH_2(CO)(dpe)_2]$,[6] presenting a sharp contrast to the corresponding Mo complex with the η^2-H_2 ligand. Here we describe preparation and some reactivities of Mo complexes *trans*-$[Mo(CO)(DMF)(dpe)(dpm)]$ (IIB; dpm = $Ph_2PCH_2PPh_2$) and *trans*-$[Mo(CO)(DMF)(dpe)(dpp)]$ (IIC; dpp = $Ph_2PCH_2CH_2CH_2PPh_2$), as well as the structure of *trans*-$[Mo(CO)(DMF)(dpe)_2]$ determined by X-ray methods.

$$\underset{\text{IA}}{trans\text{-}[Mo(N_2)_2(dpe)_2]} \xrightarrow[C_6H_6/\text{reflux}]{\text{DMF}} \underset{\text{IIA}}{trans\text{-}[Mo(CO)(DMF)(dpe)_2]}$$

$$\xrightarrow[C_6H_6]{N_2} \underset{\text{IIIA}}{trans\text{-}[Mo(CO)(N_2)(dpe)_2]} \xrightarrow[C_6H_6/50°C]{\text{Ar}} \underset{\text{IVA}}{[Mo(CO)(dpe)_2]}$$

EXPERIMENTAL

General

All experiments were carried out under N_2 or Ar, as appropriate. Solvents were dried, distilled under an inert atmosphere and degassed just before use. Diphosphines[7] and $[MoCl_4(dpe)]$[8] were prepared according to published methods. The IR spectra were recorded on a Shimadzu IR-408 spectrometer.

trans-*[Mo(N$_2$)$_2$(dpe)(dpm)] (IB)*

A mixture of $[MoCl_4(dpe)]$ (4.27 g, 6.71 mmol), dpm (2.56 g, 6.71 mmol) and Mg turnings (4.0 g, 0.16 mol) in THF (80 cm^3) was stirred overnight under N_2. The resultant dark brown solution was separated from Mg by filtration and the filtrate was concentrated *in vacuo* until the yellow solid started to precipitate. The crude product deposited by the addition of ether to this mixture was recrystallized from toluene/hexane. Yield, 1.76 g (28%). *Anal.*: Calcd. for $C_{51}H_{46}N_4P_4Mo$: C, 65.5; H, 4.97; N, 5.99%. Found: C, 65.4; H, 4.84; N, 5.82%.

trans-*[Mo(N$_2$)$_2$(dpe)(dpp)] (IC)*

Onto 1% Na–Hg (70 g, 0.03 g-atom Na) were charged $[MoCl_4(dpe)]$ (4.4 g, 6.9 mmol), dpp (2.9 g, 7.0 mmol), and THF (95 cm^3). The mixture was stirred overnight under N_2. The dark reddish brown suspension obtained was filtered and the filtrate dried *in vacuo*. The residue was crystallized from toluene/methanol. The solid remaining in the reaction flask was extracted with toluene and crystallized by addition of methanol. The combined yield was 1.99 g (30%). *Anal.*: Calcd. for $C_{53}H_{50}N_4P_4Mo$: C, 66.1; H, 5.23, N, 5.82%. Found: C, 65.9; H, 4.88; N, 5.23%.

trans-*[Mo(CO)(DMF)(dpe)(dpm)] (IIB)*

This experiment was carried out under Ar. A solution of IB (150 mg, 0.160 mmol) and DMF (1 cm^3) in benzene (5 cm^3) was refluxed for 20 min with stirring. After cooling, hexane (8 cm^3) was added to the dark red product solution. Red crystals were deposited and were filtered off, washed with hexane and dried *in vacuo*. Yield, 104 mg (66%). *Anal.*: Calcd. for $C_{55}H_{53}O_2NP_4Mo$: C, 67.4; H, 5.45: N, 1.43%. Found: C, 67.2; H, 5.35; N, 1.10%.

trans-*[Mo(CO)(DMF)(dpe)(dpp)] (IIC)*

This experiment was also performed under Ar. A suspension of IC (320 mg, 0.322 mmol) in DMF (1.6 cm^3)/benzene (33 cm^3) mixture was refluxed slowly for 40 min with stirring. The resultant red solution was concentrated to about 1/4 volume and hexane (15 cm^3) was added. The orange crystals obtained were filtered off and dried *in vacuo*. Yield, 221 mg (66%). *Anal.*: Calcd. for $C_{57}H_{57}O_2NP_4Mo$: C, 67.9; H, 5.71; N, 1.39%. Found: C, 65.4; H, 5.50; N, 1.34%. In addition to the orange crystals of IIC above, dark red crystals of *trans*-[Mo(CO)(DMF)(dpe)$_2$] (IIA) were also obtained in quite low yield.

Preparation of trans-*[Mo(CO)(N_2)(dpe)(dpm)] (IIIB) from* trans-*[Mo(N_2)$_2$ (dpe)(dpm)] (IB) and MeOH*

A solution of IB (82 mg, 0.088 mmol) in benzene (4 cm^3) and MeOH (1 cm^3) was refluxed for 20 min under N_2 and the resultant solution was concentrated to about half volume. Addition of hexane (5 cm^3) deposited the title compound as orange-red crystals containing two benzene molecules of solvation (30 mg, 31%). *Anal.*: Calcd. for $C_{64}H_{58}ON_2P_4Mo$: C, 70.5; H, 5.37; N, 2.57%. Found: C, 70.1; H, 5.42; N, 2.14%.

Preparation of trans-*[Mo(CO)(N_2)(dpe)(dpm)] (IIIB) from* trans-*[Mo(CO)(DMF)(dpe)(dpm)] (IIB)*

To a solution of IIB (120 mg, 0.122 mmol) in benzene (12 cm^3) under N_2 was added hexane (24 cm^3). Orange-red crystals deposited and were filtered off and dried *in vacuo* (50 mg, 38%).

X-ray structure of trans-*[Mo(CO)(DMF)(dpe)$_2$] (IIA)*

Dark red crystals of IIA grown as a minor component together with orange crystals of IIC were collected and sealed in glass capillaries under Ar. Data collection was performed at room temperature on a Rigaku AFC-5 four-circle diffractometer equipped with a Mo X-ray source and a graphite monochromator. Crystal and data collection parameters are summarized in Table 1. The orientation matrix and unit cell parameters were derived from a least-squares fit of 18 machine-centred reflections with 2θ values between 20 and 25°. No significant decay of three check reflections measured every 100 reflections was observed during the data collection. Intensity data were corrected for Lorentz, polarization and absorption effects. A preliminary measurement showed a systematic absence of $0k0$ ($k = 2n + 1$), which corresponds to space group $P2_1$ or $P2_1/m$. However, the space group $P2_1$ is more appropriate because IIA has no mirror plane in the molecule. This was confirmed by successful solution and refinement of the structure using $P2_1$ rather than $P2_1/m$.

Structure solution and refinement were performed using the UNIX-III program package[9] at the Computer Centre of the University of Tokyo. The Mo atom was found by the direct methods program MULTAN 78. Subsequent difference Fourier

TABLE I
Summary of crystallographic data for *trans*-[Mo(CO)(DMF)(dpe)$_2$].

Formula	$C_{56}H_{55}O_2NP_4Mo$
Molecular weight	993.94
Colour	dark red
Space group (crystal system)	$P2_1$ (monoclinic)
a, Å	11.145(4)
b, Å	23.425(5)
c, Å	10.516(3)
β, deg	117.17(2)
Cell volume, Å^3	2442.6(13)
Z	2
D_{calcd}, g/cm^3	1.35
Radiation	Mo$K\alpha$ ($\lambda = 0.7107$ Å)
μ, cm^{-1}	4.32
$F(000)$, electrons	1032
2θ Range, deg	$2 < 2\theta < 60$
Scan mode	ω ($2 < 2\theta < 30°$), ω–2θ ($30 < 2\theta < 60°$)
Scan speed, deg/min	2
Reflections measured	4583
Reflections used ($\lvert F_o \rvert > 5\sigma(F_o)$)	2981
Parameters refined	578
R	0.067
R_w	0.076
Max residual, e/Å^3	1.0 (around Mo)

syntheses revealed the positions of all other non-hydrogen atoms, which were refined anisotropically by block-diagonal least-squares techniques. Hydrogen atoms were placed at the calculated positions and included in the final stage of refinement with fixed positional and isotropic thermal parameters. The atomic scattering factors were taken from Ref. 10 and the absolute configuration was not determined. Final atomic parameters of non-hydrogen atoms are summarized in Table II.

TABLE II
Positional parameters and equivalent temperature factors (Å^2) for the non-hydrogen atoms in *trans*-[Mo(CO)(DMF)(dpe)$_2$].

Atom	x/a	y/b	z/c	B_{eq}
Mo	0.0183(1)	0.2500(1)	0.3102(1)	2.2
P(1)	0.0608(4)	0.1603(2)	0.2110(5)	2.9
P(2)	0.0341(5)	0.2880(2)	0.1014(5)	3.0
P(3)	−0.0284(4)	0.3397(2)	0.3927(5)	2.8
P(4)	0.0038(4)	0.2177(2)	0.5218(5)	3.0
O(1)	−0.292(1)	0.244(1)	0.159(1)	4.2
O(2)	0.255(1)	0.252(1)	0.419(1)	4.4
N	0.467(1)	0.220(1)	0.519(2)	5.1
C(1)	−0.173(1)	0.246(1)	0.214(2)	2.8
C(2)	0.338(2)	0.222(1)	0.500(2)	3.8
C(3)	0.512(2)	0.251(2)	0.437(3)	8.8
C(4)	0.564(3)	0.181(1)	0.627(3)	7.7
C(5)	0.132(2)	0.181(1)	0.089(2)	3.9

TABLE II (continued)

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
C(6)	0.048(2)	0.229(1)	−0.007(2)	3.6
C(7)	−0.140(2)	0.321(1)	0.475(2)	4.1
C(8)	−0.070(2)	0.275(1)	0.592(2)	4.1
C(111)	−0.072(2)	0.111(1)	0.092(2)	2.8
C(112)	−0.208(2)	0.126(1)	0.030(2)	4.2
C(113)	−0.304(2)	0.087(1)	−0.054(3)	6.6
C(114)	−0.274(2)	0.035(1)	−0.086(2)	4.4
C(115)	−0.138(2)	0.021(1)	−0.032(2)	4.7
C(116)	−0.041(2)	0.058(1)	0.055(2)	3.6
C(121)	0.183(2)	0.107(1)	0.327(2)	4.1
C(122)	0.302(2)	0.095(1)	0.321(3)	6.3
C(123)	0.392(2)	0.053(1)	0.414(3)	8.3
C(124)	0.361(3)	0.025(1)	0.508(3)	8.1
C(125)	0.243(3)	0.036(1)	0.516(3)	6.9
C(126)	0.151(2)	0.076(1)	0.420(2)	5.7
C(211)	−0.100(2)	0.330(1)	−0.047(2)	4.5
C(212)	−0.073(2)	0.379(1)	−0.099(2)	4.2
C(213)	−0.181(2)	0.406(1)	−0.214(2)	5.4
C(214)	−0.305(2)	0.385(1)	−0.274(2)	5.0
C(215)	−0.333(2)	0.336(1)	−0.220(3)	6.3
C(216)	−0.230(2)	0.309(1)	−0.104(2)	4.4
C(221)	0.187(2)	0.329(1)	0.140(2)	3.9
C(222)	0.275(2)	0.319(1)	0.086(2)	5.4
C(223)	0.397(3)	0.350(1)	0.131(3)	7.0
C(224)	0.428(2)	0.391(1)	0.231(2)	5.1
C(225)	0.343(2)	0.403(1)	0.288(2)	4.5
C(226)	0.225(2)	0.373(1)	0.241(2)	3.7
C(311)	−0.123(2)	0.398(1)	0.269(2)	3.6
C(312)	−0.254(2)	0.386(1)	0.166(2)	4.8
C(313)	−0.320(2)	0.429(1)	0.068(3)	5.6
C(314)	−0.266(3)	0.480(1)	0.064(3)	6.5
C(315)	−0.133(2)	0.490(1)	0.166(3)	5.1
C(316)	−0.064(2)	0.450(1)	0.267(2)	4.1
C(321)	0.097(2)	0.382(1)	0.542(2)	3.0
C(322)	0.065(2)	0.422(1)	0.618(2)	4.7
C(323)	0.162(2)	0.452(1)	0.733(2)	5.5
C(324)	0.295(2)	0.441(1)	0.773(2)	5.8
C(325)	0.333(2)	0.405(1)	0.696(2)	5.2
C(326)	0.234(2)	0.376(1)	0.582(2)	4.0
C(411)	0.161(2)	0.201(1)	0.687(2)	3.4
C(412)	0.249(2)	0.246(1)	0.756(2)	4.5
C(413)	0.374(2)	0.238(1)	0.869(2)	5.2
C(414)	0.412(2)	0.183(1)	0.917(2)	5.6
C(415)	0.332(2)	0.137(1)	0.855(3)	5.9
C(416)	0.204(2)	0.146(1)	0.738(2)	4.4
C(421)	−0.102(2)	0.158(1)	0.518(2)	3.6
C(422)	−0.107(2)	0.137(1)	0.641(2)	4.7
C(423)	−0.178(2)	0.086(1)	0.636(3)	6.4
C(424)	−0.247(2)	0.060(1)	0.506(3)	6.8
C(425)	−0.248(2)	0.079(1)	0.386(3)	5.8
C(426)	−0.171(2)	0.129(1)	0.394(2)	4.8

RESULTS AND DISCUSSION

Preparation of trans-*[Mo(CO)(DMF)(dpe)(dpm)] (IIB) and* trans-*[Mo(CO)(DMF)(dpe)(dpp)] (IIC)*

Previously we reported the synthesis of dinitrogen complexes *trans*-[Mo(N_2)$_2$(dpm)$_2$], IA, and *trans*-[Mo(N_2)$_2$(dpp)$_2$].[11] For these complexes, as the number of methylene groups in the diphosphine ligands increases, the ν(N≡N) value shifts lower as shown in Table III, indicating that the electron density on the molybdenum atom increases due to the increasing basicity of the diphosphine ligands. To examine the effect of the nature of the diphosphine ligands on the decarbonylation and properties of the carbonyl-DMF complexes produced by the decarbonylation, the reactions of *trans*-[Mo(N_2)$_2$(dpp)$_2$] and *cis*-[Mo(N_2)$_2$(dpm)$_2$]* with DMF were first carried out. However, the expected carbonyl-DMF complexes were not isolated, although the formation of uncharacterizable carbonyl complexes was observed. On the other hand, the dinitrogen complexes IIB and IIC, prepared from [$MoCl_4$(dpe)] and dpm or dpp in the presence of Mg turnings or Na–Hg under N_2, reacted with DMF in benzene at reflux under Ar to give *trans*-[Mo(CO)(DMF)(dpe)(dpm)] (IIB) and *trans*-[Mo(CO)(DMF)(dpe)(dpp)] (IIC) in moderate yields, after the addition of hexane to the product solutions. When these reactions were performed under N_2, the products were a mixture of *trans*-[Mo(CO)(N_2)(dpe)(dpm)] (IIIB) and IIB, or a mixture of *trans*-[Mo(CO)(N_2)(dpe)(dpp)] (IIIC), *trans*-[Mo(CO)$_2$(dpe)(dpp)], and IIC, despite the presence of excess DMF. In contrast, IA afforded IIA exclusively even by reaction under N_2, indicating that the DMF ligand in IIB and IIC is more weakly coordinated to the Mo atom and more replaceable by N_2 than that in IIA.

$$\textit{trans}\text{-[Mo(N}_2)_2\text{(dpe)(L)]} \xrightarrow[\text{C}_6\text{H}_6\text{/reflux}]{\text{DMF/Ar}} \textit{trans}\text{-[Mo(CO)(DMF)(dpe)(L)]}$$

IB: L = dpm; IIB: L = dpm;
IC: L = dpp. IIC: L = dpp.

TABLE III
IR data for the molybdenum complexes.[a]

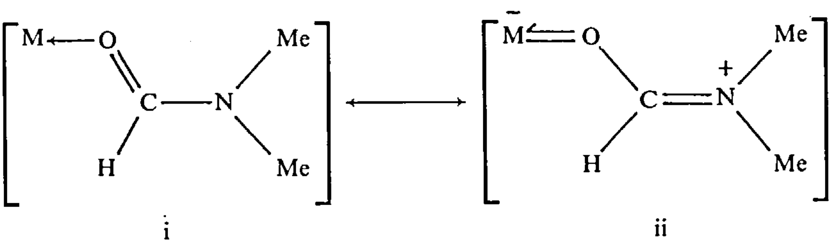
Complex	ν(C≡O)	ν(C=O)	ν(N≡N)
trans-[Mo(CO)(DMF)(dpe)(dpm)]	1715s	1640s	
trans-[Mo(CO)(DMF)(dpe)$_2$][b]	1685s	1640s	
trans-[Mo(CO)(DMF)(dpe)(dpp)]	1695s	1650s	
trans-[Mo(N_2)$_2$(dpm)$_2$][c]			1995s[d]
trans-[Mo(N_2)$_2$(dpe)(dpm)]			2050w, 1990s
trans-[Mo(N_2)$_2$(dpe)$_2$][c]			2020w, 1970s
trans-[Mo(N_2)$_2$(dpe)(dpp)]			2010w, 1940s
trans-[Mo(N_2)$_2$(dpp)$_2$][c]			2010w, 1925s
trans-[Mo(CO)(N_2)(dpe)(dpm)]	1820s		2100m
trans-[Mo(CO)(N_2)(dpe)$_2$][b]	1812s, 1739s		2110m, 2080m
trans-[Mo(CO)(N_2)(dpe)(dpp)]	1790s, 1760s		2120m

[a] KBr disks; cm^{-1}. [b] Ref. 2. [c] Ref. 11. [d] Toluene solution.

---

* The *cis* isomer was used because this isomer was prepared in much higher yield than the *trans* isomer.

IR data for these carbonyl–DMF complexes are also shown in Table III. A distinct correlation was not observed between ν(C≡O) or ν(C=O) and the number of methylene groups in the diphosphines. Interestingly, all these complexes show the ν(C≡O) band in an unusually low frequency region for terminal CO ligands and the ν(C=O) band in the DMF ligands also shifted lower by 20–40 cm^{-1} from that of neat DMF. In a previous paper,[2] we tentatively explained the shift of these bands in IIA to lower frequencies by taking the canonical structure ii into account in addition to structure i. Cotton also claimed the presence of the contribution of structure ii to explain the shift of ν(C≡O) to lower frequency in [Mo(CO)$_5$(DMF)].[12] To clarify this contribution, attempts were made to prepare single crystals of IIA and IIB suitable for X-ray analysis, but these were unsuccessful in spite of repeated trials. On the other hand, from the reaction mixture of IC and DMF, dark red single crystals of IIA were isolated as a very minor component together with orange crystals of IIC. Presumably IIA obtained here resulted from the disproportionation of IIC initially formed under refluxing conditions.



X-ray structure of trans-[Mo(CO)(DMF)(dpe)$_2$] (IIA)

The X-ray analysis was performed using a single crystal of IIA. The ORTEP diagram and atom numbering for IIA are illustrated in Figure 1. Table IV summarizes selected bond lengths and angles. Complex IIA has an octahedral configuration with CO and DMF ligands in the mutually *trans* position. The Mo–C(1)–O(1) linkage is essentially linear and, as expected from the IR data in Table III, the C(1)–O(1) distance of 1.18(2) Å is slightly elongated if compared with that of IIIA (1.13(2) Å); the Mo–C(1) distance shortens (IIA: 1.90(1) Å; IIIA: 1.97(2) Å).[2] This may be explained by the stronger π back donation from the Mo atom to the CO ligand in IIA than in IIIA, resulting from the weaker π acidity of DMF molecule than N$_2$ in a position *trans* to the CO ligand.

As observed in the free DMF molecule[13,14] and coordinated DMF in almost all DMF complexes reported to date, the five non-hydrogen atoms in IIA lie almost in the same plane (to within 0.012 Å). This plane is not perpendicular to the basal plane including the Mo and the four P atoms, the dihedral angle being 64°. If there exists a substantial pπ donation from the O atom to the Mo atom as in ii, the planar DMF ligand should become perpendicular to the basal plane and therefore this indicates that there is little or no such pπ–dπ interaction between the O and Mo atoms. This is strongly supported by the fact that the Mo–O(2) bond length of 2.35(1) Å is much larger than the sum of the covalent radii of 2.20 Å,[15] which correlates well with the observation that the DMF ligand is coordinated so weakly as to be replaced easily by N$_2$. Thus it may be concluded that the DMF molecule is bonded to the metal only by the σ donation of a lone pair of the O atom as shown in resonance structures i and iii.

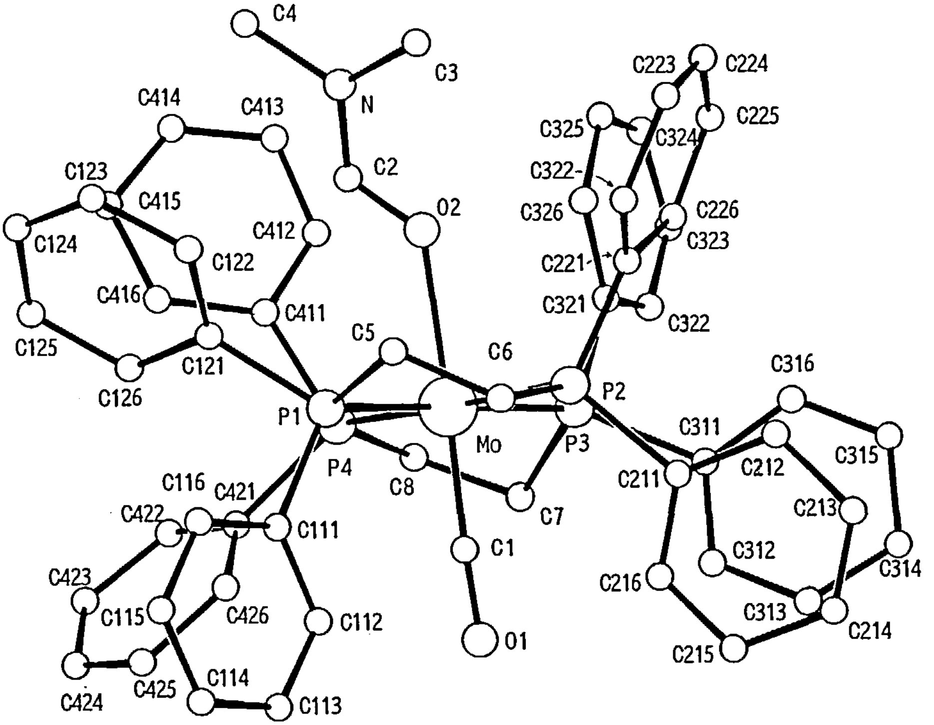
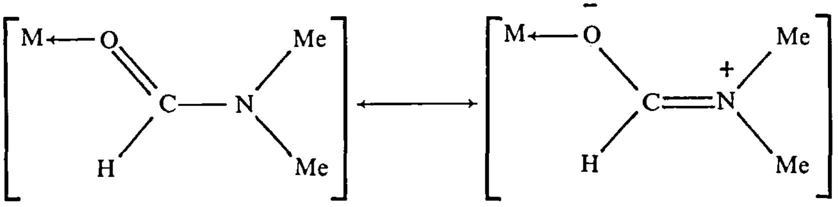


FIGURE 1 An ORTEP drawing of and the atom numbering scheme for *trans*-[Mo(CO)(DMF)(dpe)$_2$] (IIA).

TABLE IV
Selected bond distances and angles in *trans*-[Mo(CO)(DMF)(dpe)$_2$].

Distances, Å			
Mo–P(1)	2.485(6)	Mo–P(2)	2.449(6)
Mo–P(3)	2.419(5)	Mo–P(4)	2.425(6)
Mo–O(2)	2.35(1)	Mo–C(1)	1.90(1)
O(2)–C(2)	1.16(2)	C(2)–N	1.36(3)
N–C(3)	1.39(4)	N–C(4)	1.47(3)
C(1)–O(1)	1.18(2)	P(1)–C(5)	1.86(3)
P(2)–C(6)	1.84(2)	P(3)–C(7)	1.86(3)
P(4)–C(8)	1.90(2)	C(5)–C(6)	1.51(2)
C(7)–C(8)	1.54(3)		
Angles, deg			
P(1)–Mo–P(2)	80.0(2)	P(1)–Mo–P(3)	176.6(2)
P(1)–Mo–P(4)	103.1(2)	P(2)–Mo–P(3)	97.0(2)
P(2)–Mo–P(4)	176.9(2)	P(3)–Mo–P(4)	80.0(2)
P(1)–Mo–C(1)	96.4(7)	P(1)–Mo–O(2)	80.2(4)
P(2)–Mo–C(1)	93.7(6)	P(2)–Mo–O(2)	84.7(4)
P(3)–Mo–C(1)	82.4(7)	P(3)–Mo–O(2)	101.0(5)
P(4)–Mo–C(1)	86.8(5)	P(4)–Mo–O(2)	95.1(4)
Mo–C(1)–O(1)	177(2)	Mo–O(2)–C(2)	134(2)
O(2)–C(2)–N	125(2)	C(2)–N–C(3)	123(2)
C(2)–N–C(4)	119(2)		

Since the planar DMF ligand leans in the direction of the dpe ligand consisting of P(1) and P(2) atoms, the Mo–P(1) and Mo–P(2) bonds, especially the former, are substantially longer than the Mo–P(3) and Mo–P(4) bonds and the benzene ring (C(121)–C(126)) closest to the DMF ligand lies almost parallel to it (with a dihedral angle of 12°), thus avoiding steric interactions.



i iii

Complex IIA has a DMF ligand with a much shorter C=O bond and a relatively longer C–N bond than DMF complexes reported previously including $[(\pi\text{-}C_5Me_5)_2Ti(DMF)Cl][CF_3SO_3]$ (d(C=O): 1.28(1); d(C–N): 1.30(1) Å),[16] $[Mo_2O_5(PB)_2(DMF)_2]$ (1.23(av); 1.32(av) Å; PB = phenylbenzimidazole-2-olate),[17] $[CrCl_3(Phen)(DMF)]$ (1.28(2); 1.34(2) Å; Phen = *o*-phenanthroline),[18] and $[Mn(TPP)(DMF)_2][ClO_4]$ (1.27(1); 1.32(1) Å; TPP = tetraphenylporphyrinato).[19] This obviously arises from the zero-valent and electron-rich nature of the Mo atom in IIA, where the canonical structure iii is less favourable due to electronic repulsion between filled dπ and pπ orbitals of the Mo and O atoms, respectively.

Reaction of trans-*[Mo(CO)(DMF)(dpe)(dpm)] (IIB)*

When recrystallized from benzene/hexane under N_2, IIB was converted into the carbonyl-dinitrogen complex *trans*-$[Mo(CO)(N_2)(dpe)(dpm)]$ (IIIB), as observed for IIA.* The IR spectrum of IIIB is quite analogous to that of IIIA except for the absence of the splitting of the ν(C≡O) and ν(N≡N) bands by the crystal effect observed for IIIA. IIIB can also be prepared directly from IB and excess MeOH in benzene at reflux in 31% yield. It is noteworthy that the reaction of IA with MeOH results in the formation of a mixture of IIIA (46%) and $[MoH_4(dpe)_2]$ (25%), as previously reported.[20]

In contrast to the formation of IVA from IIIA, IIIB did not give a five coordinate complex by bubbling Ar gas through the benzene solution at 50°C. The only characterizable product isolated from the reaction mixture was *cis*-$[Mo(CO)_2(dpe)(dpm)]$. Presumably, the five-coordinate complex once formed was so unstable that this species was quickly converted into the dicarbonyl complex and the other Mo complexes by disproportionation.

---

* Recrystallization of IIC from benzene/hexane under N_2 also gave *trans*-$[Mo(CO)(N_2)(dpe)(dpp)]$ as an orange crystalline solid, as confirmed by the IR spectrum (Table III). However, the product could not be purified satisfactorily.

ACKNOWLEDGEMENTS

The financial support of the Ministry of Education of Japan and the Asahi Gl Foundation for Industrial Technology is greatly appreciated. We thank Kazuyuki Tatsumi of Osaka University for helpful discussion.

SUPPLEMENTARY MATERIAL

Tables of atomic coordinates for hydrogen atoms, complete bond distances angles, and anisotropic temperature factors for non-hydrogen atoms in IIA (6 pag and a listing of observed and calculated structure factors (17 pages) are availa from M.H. upon request.

REFERENCES

1. Part 29: Y. Ishii, H. Miyagi and M. Hidai, *Chem. Comm.*, 1569 (1990).
2. M. Sato, T. Tatsumi, T. Kodama, M. Hidai, T. Uchida and Y. Uchida, *J. Am. Chem. Soc.*, **100**, (1978).
3. T. Tatsumi, H. Tominaga, M. Hidai and Y. Uchida, *J. Organomet. Chem.*, **114**, C27 (1976); *id ibid.*, **199**, 63 (1980).
4. G.J. Kubas, R.R. Ryan and D.A. Wrobleski, *J. Am. Chem. Soc.*, **108**, 1339 (1986).
5. T. Ishida, Y. Mizobe, T. Tanase and M. Hidai, *Chem. Lett.*, 441 (1988).
6. T. Ishida, Y. Mizobe and M. Hidai, *Chem. Lett.*, 2077 (1989).
7. K. Sommer, *Z. Anorg. Allg. Chem.*, **376**, 37 (1970).
8. A.V. Butcher and J. Chatt, *J. Chem. Soc.*, 2652 (1970).
9. T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res.*, **55**, 69 (1979).
10. D.T. Cromer and J.T. Waber, *"International Tables for X-ray Crystallography,"* Vol IV, (Kyn Press, Birmingham, England, 1974).
11. M. Hidai, K. Tominari and Y. Uchida, *J. Am. Chem. Soc.*, **94**, 110 (1972).
12. F.A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).
13. H. Ohtaki, S. Itoh, T. Yamaguchi, S. Ishiguro and B.M. Rode, *Bull. Chem. Soc. Jpn.*, **56**, (1983).
14. L.V. Vilkov, P.A. Akishin and V.M. Presnyakova, *J. Struct. Chem. USSR.*, **3**, 3 (1962).
15. L. Pauling, *"The Nature of the Chemical Bond,"* 3rd Ed., (Cornel University Press, Cornel, pp. 246 and 256.
16. B. Honold and U. Thewalt, *J. Organomet. Chem.*, **316**, 291 (1986).
17. M.V. Caparelli, B. Piggott, S.D. Thorpe and R.N. Sheppard, *Inorg. Chim. Acta*, **98**, L53 (1985
18. J.A. Broomhead, J. Evans, W.D. Grumley and M. Sterns, *J. Chem. Soc., Dalton Trans.*, 173 (19
19. C.L. Hill and M.M. Williamson, *Inorg. Chem.*, **24**, 2836 (1985).
20. T. Tatsumi, H. Tominaga, M. Hidai and Y. Uchida, *J. Organomet. Chem.*, **215**, 67 (1981).