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Transition Metal Complexes with Sulfur Ligands. XXXI.* Six and Seven Coordinate CO, NO, PMe_3 and Phosphineiminato Molybdenum Complexes with $[Mo\{S_4\}]$ Frameworks ($\{S_4\}$ = 2,3; 8,9-dibenzo-1,4,7,10-tetrathiadecane(2–))**

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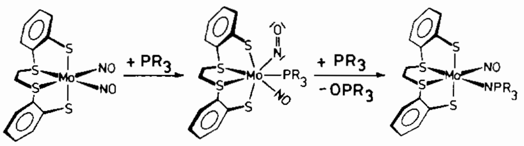
Abstract

In order to explain the high reactivity of $[Mo(NO)_2(dttd)]$ towards phosphines the structures of $[Mo(CO)_2(PMe_3)(dttd)]$ and $[Mo(NO)(NPMePh_2)(dttd)]$ have been determined by X-ray structure analysis and compared with the structures of other [M(dttd)] complexes ($dttd^{2-}$ = 2,3; 8,9-dibenzo-1,4,7,10-tetrathiadecane(2–)). In $[Mo(CO)_2(PMe_3)(dttd)]$ the seven coordinate Mo center is ligated by one P, two C and four sulfur atoms. $[Mo(NO)(NPMePh_2)(dttd)]$ contains a six coordinate molybenum atom pseudooctahedrally surrounded by two N and four S atoms and possesses a bent [MNP] entity with an exceedingly small angle of 129.7(4)°; the pseudooctahedral $[MS_4]$ core in [M(dttd)] fragments is flexible enough to accommodate the coordination of two as well as three further coligands. The reaction between $[Mo(NO)_2(dttd)]$ and phosphines PR_3 yielding the phosphineiminato complexes $[Mo(NO)(NPR_3)(dttd)]$ is dominated by the nucleophilicity of PR_3 as is shown by the fast reactions with PMe_3 and PCy_3 and the slow reactions with arylphosphines. [MNP] angles and $\nu_{as}(MNP)$ frequencies in [M(phosphineiminato)] complexes correlate: small angles compare with low frequencies. ^{13}C, ^{95}Mo and ^{14}N NMR data of the complexes are discussed and indicate the oxidation of Mo and the reduction of the nitrogen of one NO ligand, when $[Mo(NO)_2(dttd)]$ is converted into $[Mo(NO)(NPR_3)(dttd)]$; NPR_3 ligands act as strong $4e^-$ donors.

1. Introduction

Molybdenum in a coordination sphere of sulfur ligands is considered to be an essential constituent of the active centers of oxido-reductases, e.g. nitrate reductase, xanthine, sulfite and aldehyde oxidase as well as nitrogenase [2]. In search of sulfur coordinate molybdenum centers at which reactions of small nitrogen compounds can occur we have recently observed the formation of phosphineiminato complexes $[Mo(NO)(NPR_3)(dttd)]$, (R = e.g. Me, Et, Ph; dttd = 2,3; 8,9-dibenzo-1,4,7,10-tetrathiadecane(2–)), when $[Mo(NO)_2dttd]$ is reacted with PR_3 [3]. For the reaction mechanism we have discussed the sequence according to eqn. (1)



(1)

In the primary step the phosphine coordinates to the Mo center and generates an intermediate with a seven coordinate molybdenum and one bent nitrosyl ligand acting as $1e^-$ donor. In a rapid consecutive reaction this intermediate is desoxygenated by a second phosphine yielding the $[Mo(NO)(NPR_3)(dttd)]$ derivative. The reactions which occur very fast in several cases were unexpected because $[Mo(NO)_2(dttd)]$ has low ν(NO) frequencies (1760/1665 cm^{-1}) and such nitrosyl complexes are considered to be unreactive towards nucleophiles [4, 5]. In order to elucidate the cause of the unexpectedly high reactivity and to gain further insight into the reaction we have determined the structures of the six coordinate $[Mo(NO)(NPMePh_2)(dttd)]$ and of the seven coordinate $[Mo(CO)_2(PMe_3)(dttd)]$

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*For Part XXX see ref. 1.

**Dedicated to Prof. Dr. Gottfried Huttner, Heidelberg, on the occasion of his 50th birthday.

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[6] by single crystal X-ray diffraction to obtain information *inter alia* about the rigidity or flexibility of the [Mo(dttd)] framework. Reactions of [Mo(NO_2)(dttd)] with P(n-bu)$_3$, PCy$_3$ and diphos (=1,2-bis(diphenylphosphino)ethane) were expected to give a better estimate whether steric or electronic properties of the phosphines dominate the reductive desoxygenation of the NO ligand.

2. Experimental

General

All reactions were carried out in absolute solvents under nitrogen using the Schlenk tube technique and monitored by IR spectroscopy. The solution IR spectra were run in CaF_2 cuvettes with compensation of the solvent absorptions. Spectra were obtained on the following instruments: IR: Zeiss IR spectrometer IMR 25; NMR: JEOL JNM-GX 270 FT; mass spectra: VARIAN MAT 212.

[Mo(NO)$_2$(dttd)] [3], [Mo(NO)(NPMePh$_2$)(dttd)] [3] and [Mo(CO)$_2$(PMe$_3$)(dttd)] [6] were prepared as described in the literature. P(n-bu)$_3$, PCy$_3$ and diphos were purchased from Ventron GmbH, Karlsruhe.

Syntheses and Reactions

[Mo(NO)(NP{n-bu}$_3$)(dttd)]

404 mg (≙ 0.5 ml = 2 mmol) of P(n-bu)$_3$ are added to a solution of 464 mg (1 mmol) of [Mo(NO)$_2$(dttd)] in 40 ml of THF at 20 °C yielding within 5 min a red–brown solution with a ν(NO) IR band at 1610 cm^{-1}. The solution is evaporated to dryness, the residue is redissolved in 80 ml of Et_2O and filtered. The volume is reduced to *ca.* 30 ml; cooling to −30 °C for 7 d yields green–brown crystals, which are separated and recrystallized from Et_2O at 20 → −30 °C. Yield: 340 mg (52%). *Anal.* Calc. for $C_{26}H_{39}N_2OPS_4Mo$ (650.78): C, 47.98; H, 6.04; N, 4.30. Found: C, 47.74; H, 6.00; N, 4.16%. M^+: $m/e = 652$ (^{98}Mo, FD).

[Mo(NO)(NPCy$_3$)(dttd)]

A solution of 560 mg (2 mmol) of PCy$_3$ and 464 mg (1 mmol) of [Mo(NO)$_2$(dttd)] in 40 ml THF shows after 5 min at 20 °C a ν(NO) band at 1600 cm^{-1}. After evaporation to dryness OPCy$_3$ is extracted with 2 × 40 ml of Et_2O; the resulting brown solid material is recrystallized from CH_2Cl_2/Et_2O (1:3) at +20 → −30 °C. Yield: 620 mg (85%) of brown crystals. *Anal.* Calc. for $C_{32}H_{45}N_2OPS_4Mo$ (728.88): C, 52.73; H, 6.22; N, 3.84: Found: C, 52.74; H, 6.30; N, 3.85%. M^+: $m/e = 730$ (^{98}Mo, FD).

[Mo(NO)(NPPh$_2$C$_2$H$_4$PPh$_2$O)(dttd)]

A solution of 464 mg (1 mmol) of [Mo(NO)$_2$(dttd)] and 398 mg (1 mmol) of diphos in 50 ml of THF is heated under reflux for 60 min and evaporated to dryness. The residue is recrystallized from CH_2Cl_2/Et_2O (1:1) at +20 → −30 °C yielding black–red crystals. Yield: 515 mg (60%). *Anal.* Calc. for $C_{40}H_{36}N_2O_2P_2S_4Mo$ (862.89): C, 55.68; H, 4.21; N, 3.25. Found. C, 55.65; H, 4.24; N, 3.30%. M^+: $m/e = 864$ (^{98}Mo, FD). IR (KBr, cm^{-1}): 1055s (ν(MoNP)), 1115m-s (ν(P=O)), 1605ss (ν(NO)).

X-ray Structure Analyses of [Mo(CO)$_2$(PMe$_3$)(dttd)] and [Mo(NO)(NPMePh$_2$)(dttd)]

Yellow–orange single crystals of [Mo(CO)$_2$(PMe$_3$)(dttd)] were obtained at −30 °C by slow diffusion of Et_2O into a CH_2Cl_2 solution which was saturated at +20 °C. Cooling of a saturated CH_2Cl_2 solution of [Mo(NO)(NPMePh$_2$)(dttd)] from +20 to −30 °C yielded dark brown single crystals. The crystals were sealed in glass capillaries; determination of space groups, collection of datas, solution as well as refinement of the structures are tabulated in Table I. Tables II and III show the final atomic coordinates.

Restrictions

[Mo(CO)$_2$PMe$_3$(dttd)]: the phenyl H atoms were calculated for ideal geometry and fixed during the refinement. H atoms of the CH_3 and CH_2 groups were calculated for ideal tetrahedra and rotated around the central C atoms during refinement. Common isotropic temperature factors for C_6H_5, CH_2 and six CH_3 H-atoms; individual isotropic temperature factors for three CH_3 H-atoms.

[Mo(NO)(NPMePh$_2$(dttd)]: all H atoms were calculated as rigid groups and not refined; isotropic temperature factors.

3. Results and Discussion

3.1. Structure of [Mo(CO)$_2$(PMe$_3$)(dttd)]

Since the postulated seven coordinate intermediate of eqn. (1) could not be isolated we have determined the structure of the easily accessible [Mo(CO)$_2$(PMe$_3$)(dttd)] as 'model compound' of a seven coordinate [Mo(dttd)] complex. As example of a six coordinate [Mo(dttd)] complex [Mo(NO)(NPMePh$_2$)(dttd)] was investigated in addition to [Mo(NO)$_2$(dttd)], which has been described recently [3], especially in order to obtain the angle of the [MoNP] entity.

[Mo(CO)$_2$(PMe$_3$)(dttd)] (Fig. 1) contains a seven coordinate Mo center surrounded by one P, two C and four S atoms. The P atom is located in the S1–Mo–S4 plane which bisects the C15–Mo–C16 angle. An idealized geometry as for example the one of a capped octahedron or trigonal prism cannot be

TABLE I. Crystal Data

Compound	[Mo(CO)$_2$(PMe$_3$)(dttd)]	[Mo(NO)(NPMePh$_2$)(dttd)]
Formula	$C_{19}H_{21}O_2PS_4Mo$	$C_{27}H_{25}N_2OPS_4Mo$
Mass	536.64	648.71
a (Å)	13.126(3)	9.920(2)
b (Å)	12.598(3)	12.204(3)
c (Å)	13.623(3)	22.663(5)
β (°)	103.57(2)	90.62(2)
V (Å^3)	2189.8(9)	2743.5(8)
Z	4	4
ρ_{calc} (g cm^{-3})	1.64	1.57
Space group	$P2_1/c$	$P2_1/c$
Diffractometer	Nicolet R3	Siemens AED2
Radiation (Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
Temperature (°C)	23	−137
Scan range (°)	$3 < 2\theta < 45$	$5 < 2\theta < 45$
Scan made	Wychkhoff ω-scan	Wyckhoff ω-scan
Data collected	3173	4932
Unique data	2871	4536
Observed data	2686 ($F \geqslant 3\sigma(F)$)	4242 ($F \geqslant 5\sigma(F)$)
L.S. parameters	249	326
μ (cm^{-1})	10.42	8.03
Structure solution	direct methods	direct methods
Programm	SHELXTL	SHELX 76
R (%)	2.64	2.81
R_w (%)	2.87	3.31

TABLE II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) of the Non-hydrogen Atoms of [Mo(CO)$_2$(PMe$_3$)(dttd)]

	x	y	z	U_{eq}
Mo	2920(1)	5065(1)	1213(1)	30(1)
S(1)	2214(1)	6735(1)	247(1)	39(1)
S(2)	2016(1)	5999(1)	2468(1)	39(1)
S(3)	4354(1)	6424(1)	1872(1)	36(1)
S(4)	3814(1)	4149(1)	2795(1)	43(1)
P(1)	2179(1)	4563(1)	−577(1)	34(1)
C(1)	1348(2)	7361(2)	869(2)	36(1)
C(2)	728(2)	8203(2)	397(2)	46(1)
C(3)	56(3)	8730(3)	868(3)	53(1)
C(4)	−18(2)	8446(3)	1821(3)	51(1)
C(5)	573(2)	7622(3)	2311(2)	45(1)
C(6)	1263(2)	7081(2)	1836(2)	36(1)
C(7)	3121(2)	6725(2)	3245(2)	41(1)
C(8)	3761(2)	7315(2)	2633(2)	40(1)
C(9)	5277(2)	5772(2)	2859(2)	38(1)
C(10)	6223(2)	6272(3)	3261(2)	46(1)
C(11)	6951(3)	5785(3)	4025(3)	56(1)
C(12)	6734(3)	4803(3)	4382(3)	55(1)
C(13)	5792(3)	4314(3)	3999(2)	49(1)
C(14)	5041(3)	4781(2)	3221(2)	41(1)
C(15)	4036(2)	4322(2)	746(2)	37(1)
O(1)	4729(2)	3901(2)	525(2)	55(1)
C(16)	1941(2)	3895(2)	1234(2)	41(1)
O(2)	1393(2)	3206(2)	1321(2)	62(1)
C(17)	2372(3)	3183(3)	−888(3)	56(1)
C(18)	2673(3)	5248(3)	−1541(2)	48(1)
C(19)	769(2)	4709(3)	−1019(3)	51(1)

ascribed to the [MoS$_4$C$_2$P] core [7, 8]; the coordination geometry may rather be described as a combination of [MoS$_4$] octahedron and [MoC$_2$P] tetrahedron fragments. Thus the two thiolate S atoms are in *trans* positions as found in other octahedral [M(dttd)] complexes, (see Table IX), however, the S(thiolate)–Mo–S(thiolate) angle of only 151.1(2)° is much smaller. Since the S1–Mo–S4 and S2–Mo–S3 planes are nearly orthogonal (89.3°) the relatively large deviation from 180 °C of the S1–Mo–S4 angle cannot be caused by a planarization of the dttd ligand. As it follows from Fig. 1 and angles as well as distances (Table IV) [Mo(CO)$_2$(PMe$_3$)(dttd)] possesses only C_1 symmetry. The mean MoS distance (2.533 Å) compares with the ones found in [Mo(NO)$_2$(dttd)] (2.494 Å) or [Mo(NO)(NPMePh$_2$)(dttd)] (2.535 Å); the other distances show normal values as well.

3.2. Structure of [Mo(NO)(NPMePh$_2$)(dttd)]

In [Mo(NO)(NPMePh$_2$)(dttd)] the Mo center is pseudooctahedrally surrounded by four S and two N atoms (Fig. 2). The thiolate S atoms are in *trans* positions. The mutually two *cis* N and thioether S atoms occupy *trans* positions; the corresponding N1–Mo–S2 and N2–Mo–S3 angles are 161.7(2)° and 166.8(2)° respectively (Table V). Whereas the N1–Mo–N$_2$ angle of 104.1(3)° is larger than 90°; the opposite S2–Mo–S3 angle of 79.5(1)° is compressed. N, S(thioether) and Mo atoms form a plane which is nearly orthogonal (85.4°) to the S1–Mo–S4

TABLE III. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) of the Non-hydrogen Atoms of [Mo(NO)(NPMePh$_2$)(dttd)]

	x	y	z	U_{eq}
Mo	2410(0)	699(0)	1890(0)	15
N1	2408(2)	2156(2)	1588(1)	18
P2	3646(1)	2979(1)	1483(0)	16
C1	4451(3)	2728(2)	782(1)	18
C2	4447(3)	3518(2)	343(1)	24
C3	5044(3)	3306(3)	−196(1)	28
C4	5654(3)	2302(3)	−294(1)	24
C5	5678(3)	1515(2)	145(1)	25
C6	5072(3)	1726(2)	683(1)	24
C41	3039(3)	4368(2)	1445(1)	18
C42	3772(3)	5254(3)	1671(1)	25
C43	3251(4)	6311(3)	1617(1)	34
C44	2034(4)	6479(2)	1327(1)	33
C45	1320(3)	5612(3)	1092(1)	30
C46	1808(3)	4552(2)	1157(1)	23
C47	4936(3)	2931(3)	2045(1)	24
N2	4131(2)	355(2)	1942(1)	20
O2	5306(2)	57(2)	1949(1)	29
S1	2129(1)	1488(1)	2895(0)	22
C14	2087(3)	423(2)	3409(1)	20
C15	2219(3)	673(3)	4013(1)	28
C16	2111(3)	−140(3)	4434(1)	35
C17	1896(3)	−12223(3)	4276(1)	33
C18	1788(3)	−1495(3)	3684(1)	26
C19	1872(3)	−674(2)	3255(1)	19
C20	−48(3)	−1219(2)	2397(1)	22
C21	−809(3)	−158(3)	2365(1)	23
S2	1764(1)	−1059(1)	2500(0)	18
S3	−238(1)	728(1)	1768(0)	19
C22	−562(3)	−132(2)	1145(1)	22
C23	−1890(3)	−317(3)	964(1)	29
C24	−2162(4)	−979(3)	486(2)	37
C25	−1105(4)	−1452(3)	174(1)	37
C26	218(3)	−1279(3)	355(1)	30
C27	506(3)	−626(2)	851(1)	22
S4	2209(1)	−501(1)	1069(0)	21

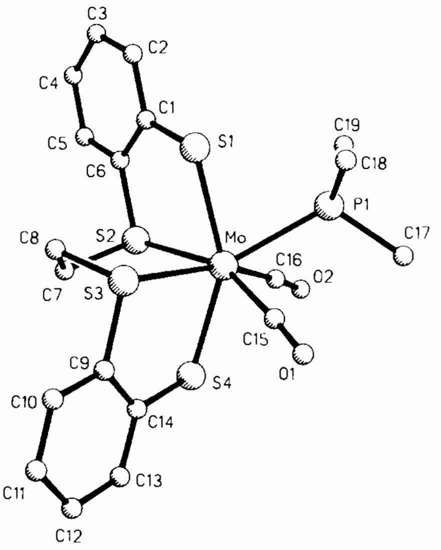


Fig. 1. Molecular structure of [Mo(CO)$_2$(PMe$_3$)(dttd)] (H atoms omitted).

TABLE IV. Selected Distances (Å) and Angles (°) of [Mo(CO)$_2$(PMe$_3$)(dttd)]

Mo–S1	2.534(1)	S1–Mo–S2	78.3(1)
Mo–S2	2.576(1)	S1–Mo–S3	77.0(1)
Mo–S3	2.542(1)	S1–Mo–S4	151.1(2)
Mo–S4	2.478(1)	S2–Mo–S3	82.9(1)
Mo–P1	2.482(1)	S1–Mo–P1	72.0(1)
Mo–C15	1.963(3)	S2–Mo–P1	129.1(2)
Mo–C16	1.956(3)	S4–Mo–P1	136.8(1)
S3–C8	1.817(3)	S1–Mo–C15	115.8(1)
C7–C8	1.508(5)	S2–Mo–C15	157.6(1)
S2–C7	1.824(3)	S4–Mo–C15	79.8(1)
S1–C6	1.779(3)	S2–Mo–C16	85.9(1)
S1–C1	1.752(3)	P1–Mo–C15	73.2(1)
C1–C2	1.396(4)	C15–Mo–C16	100.8(1)
C2–C3	1.373(5)	Mo–S1–C1	108.7(1)
C3–C4	1.369(5)	Mo–S2–C7	100.8(1)
C4–C5	1.370(4)	Mo–S2–C6	108.5(1)
C5–C6	1.404(5)	S1–C1–C6	123.2(2)
C1–C6	1.390(4)	S2–C7–C8	113.2(2)
C15–O1	1.150(4)	Mo–C15–O1	176.0(2)
C16–O2	1.485(4)	Mo–C16–O2	175.0(3)

plane; the S1–Mo–S4 entity is bent and shows an angle of 161.0(1)°. It is remarkable that the mean Mo–S(thiolate) distance (2.434 Å) is about as long as in [Mo(NO)$_2$(dttd)] (2.450 Å); however, the mean Mo–S(thioether) distance is distinctly longer (2.636 Å *versus* 2.536 Å; see also Table IX) indicating a large *trans* effect of the [NPMePh$_2$] ligand.

The most important structural property of [Mo(NO)(NPMePh$_2$)(dttd)] is the non-linear Mo–N–P angle of 129.7(4)°; it is the smallest M–N–P angle hitherto observed in phosphineiminato complexes and indicates sp^2 hybridization of the N atom.

Phosphineiminato complexes usually show linear [MNP] units [9–11] which are described as $\overset{-}{M}=\overset{+}{N}=PR_3$ with sp-hybridized nitrogen; slightly bent geometries have been observed in [Re(NPPh$_3$)(SPh)$_4$] [12] and [WF$_4$(NPPh$_3$)$_2$] [13] but so far only in [Re(NO)Cl$_3$(NPPh$_3$)(OPPh$_3$)] [14] an MNP angle of 138.5° has been observed which is closer to 120° than to 180° (see also Table VIII). In [Re(NO)Cl$_3$(NPPh$_3$)(OPPh$_3$)] the [ReNP] geometry has been attributed to favourable overlap of an occupied p orbital of nitrogen with the vacant $d_{x^2-y^2}$ orbital of phosphorus [14].

It cannot be decided so far to what extent the M–N–P angles depend on electronic or sterical reasons. It follows from molecular models that a linear Mo–N–P entity in [Mo(NO)(NPMePh$_2$)(dttd)] would lead to a strong mutual steric hin-

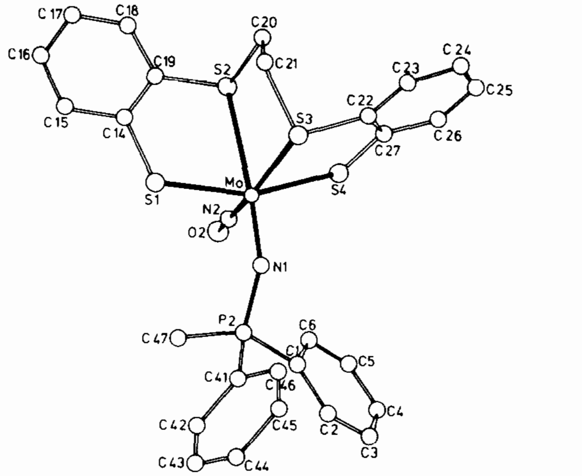


Fig. 2. Molecular structure of [Mo(NO)(NPMePh$_2$)(dttd)] (H atoms omitted).

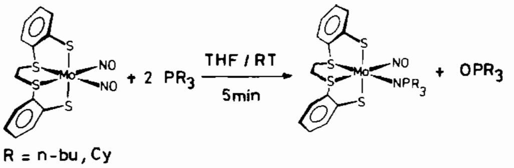
TABLE V. Selected Distances (Å) and Angles (°) of [Mo(NO)(NPMePh$_2$)(dttd)]

Mo–S1	2.492(2)	S1–Mo–S4	161.0(1)
Mo–S2	2.635(2)	S2–Mo–S3	79.5(1)
Mo–S3	2.638(2)	S1–Mo–S2	78.7(1)
Mo–S4	2.375(2)	S1–Mo–S3	88.2(1)
Mo–N1	1.904(6)	N1–Mo–N2	104.1(3)
Mo–N2	1.761(7)	N1–Mo–S2	161.7(2)
N2–O2	1.221(9)	N2–Mo–S3	166.8(2)
N1–P2	1.606(6)	S1–Mo–N2	98.6(2)
P2–C47	1.797(8)	S1–Mo–N1	88.2(2)
P2–C47	1.801(8)	N1–Mo–S3	87.3(2)
P2–C1	1.813(7)	N2–Mo–S2	90.7(2)
S1–C14	1.746(8)	Mo–S1–C14	109.0(3)
C14–C19	1.399(11)	Mo–S2–C19	106.1(3)
S2–C19	1.775(8)	Mo–S2–C20	105.4(3)
S2–C20	1.822(8)	C19–S2–C20	101.6(4)
C20–C21	1.500(12)	Mo–N2–O2	175.3(6)
		Mo–N1–P2	129.7(4)

drance of the aromatic rings of the dttd and [NPMePh$_2$] ligands in any conformation. This hindrance alone would already favour a bending of the Mo–N–P bond and possibly encourage the observed conformation in the solid state in which the least demanding methyl substituent of the [NPMePh$_2$] entity points to the *cis* NO ligand.

3.3. Reactions of [Mo(NO)$_2$(dttd)] with Bulky Phosphines

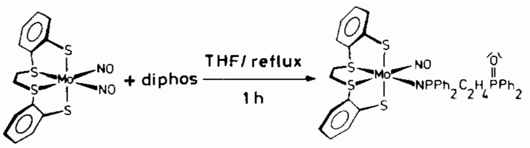
The nucleophilic attack of the phosphine at the Mo center was postulated to be the primary step in the reaction according to eqn. (1); the very slow reaction (~1 h) with PPh$_3$ indicated additional steric influences. In order to decide whether nucleophilic or steric properties of the phosphines dominate the reaction rates, we have also reacted the strongly nucleophilic but bulky P(n-bu)$_3$ and PCy$_3$ with [Mo(NO)$_2$(dttd)] (eqn. (2)).



(2)

They react at ambient temperature practically as fast (5 min) as PMe$_3$. Along with the cone angles [15] (PMe$_3$: 118°; P(n-bu)$_3$: 130°; PPh$_3$: 145°; PCy$_3$: 179°) it follows that the bulkiness of the phosphines plays only a minor role and the nucleophilicity dominates, as is shown in particular by PCy$_3$.

The reaction with diphos, (=1,2-bis(diphenylphosphino)ethane), takes about as much time as the reaction with PPh$_3$, but in this case a phosphineiminato complex forms which carries the simultaneously generated phosphine oxide at the 'free' end of the NPR$_3$ ligand; it is obvious to assume an intramolecular reaction.



(3)

3.4. Spectroscopic Investigations and Discussion of Bonding

The structures of [Mo(NO)(NPMePh$_2$)(dttd)], [Mo(CO)$_2$(PMe$_3$)(dttd)] as well as [Mo(NO)$_2$(dttd)] are reflected by their $^{13}C\{^1H\}$ NMR spectra (Table VI and Fig. 3).

The six coordinate [Mo(L$_1$)(L$_2$)(dttd)] complexes with two identical ligands $L_1 = L_2$ show only seven ^{13}C signals for the C atoms of the dttd ligand since the C atoms are pairwise homotopical because of the molecular C_2 symmetry. If $L_1 \neq L_2$ the complexes possess only C_1 symmetry and consequently fourteen ^{13}C signals are observed for the dttd ligand. The seven coordinate [Mo(CO)$_2$(PMe)$_3$(dttd)] possesses also C_1 symmetry only and consequently two ^{13}C doublets (*J*(PC) 35 Hz and 38 Hz respectively; $\delta = 238.9$ and 237.6 ppm respectively) are observed for the CO ligands; unexpectedly, however, the dttd ligand shows only seven instead of fourteen ^{13}C signals. It could not be decided yet whether for example the perturbation of the C_2 symmetry of the [Mo(dttd)] core by the [(CO)$_2$PMe$_3$] entity is so low that the ^{13}C signals of [Mo(dttd)] are not resolved or whether this effect is due to fluxional processes.

The ^{95}Mo along with the ^{14}N chemical shifts (Table VII) indicate that the conversion of [Mo-

TABLE VI. Selected $^{13}C\{^1H\}$ NMR Data of [Mo(dttd)] Complexes[a]

Complex	Signals of the aromatic rings of dttd	C_2H_4 signals of dttd
$[Mo(NO)_2(dttd)]$	124.8, 129.3, 131.3, 132.6, 133.9, 155.8	42.7
$[Mo(NO(NPCy_3)(dttd)]$	123.5, 125.3, 130.1, 130.5, 130.6, 131.1, 131.3 132.3, 133.8, 135.4, 155.4, 157.4	42.6, 44.2
$[Mo(CO)_2(PMe_3)(dttd)]$	124.2, 130.2, 132.0, 132.2, 133.7, 157.4	42.0

[a] Shifts in ppm relative to TMS in CD_2Cl_2.

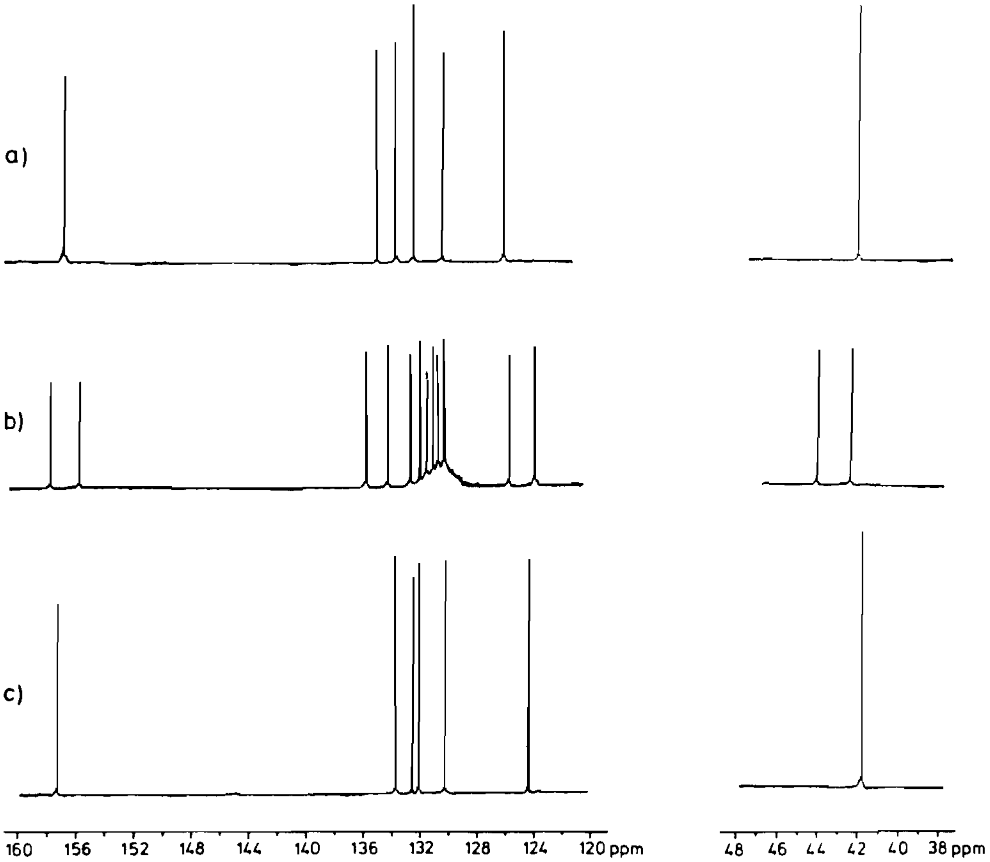


Fig. 3. Aromatic and C_2H_4 range respectively of the $^{13}C\{^1H\}$ NMR spectra of (a) $[Mo(NO)_2(dttd)]$, (b) $[Mo(NO)(NPCy_3)dttd]$ and (c) $[Mo(CO)_2(PMe_3)(dttd)]$ in CD_2Cl_2.

$(NO)_2(dttd)]$ into $[Mo(NO)(NPR_3)(dttd)]$ complexes involves the oxidation of the Mo center and the reduction of one N ligand as has been discussed in greater detail recently [3]. The similar ^{95}Mo shifts of $[Mo(NO)_2(dttd)]$ and $[Mo(CO)_2(PMe_3)(dttd)]$ for example indicate furthermore the same oxidation state (+II) of the Mo centers in both complexes.

Surprisingly $[Mo(NO)_2(dttd)]$ and $[Mo(NO)_2(C_6H_4S_2)_2]^{2-}$ have practically identical ^{95}Mo shifts. The negative charge of the dianion obviously does not influence the ^{95}Mo shift although the $\nu(NO)$ frequencies of both complexes distinctly differ in the familiar way and point to an enhanced Mo → NO backbonding in the dianion. Comparing the $\nu(NO)$ frequencies of $[Mo(NO)_2(dttd)]$ and $[Mo(NO)(NPR_3)(dttd)]$ complexes such an enhanced backbonding must also be deduced for $[Mo(NO)(NPR_3)(dttd)]$ despite the ^{95}Mo shifts indicating Mo(III) centers. The shortened Mo–N and elongated N–O distances as well point to such an enforced Mo → NO backbonding in $[Mo(NO)(NPMePh_2)(dttd)]$ (Table VII).

TABLE VII. Selected Spectroscopic and Structural Data of [Mo(dttd)] Complexes

Complex	^{95}Mo NMR[a, b]	^{31}P NMR[a, c] (ppm)	^{14}N NMR[a, d] (ppm)	IR (in KBr) (cm^{-1})	Mo–NO[d] (Å)	N–O[d] (Å)	∢Mo–N–O (°)
[Mo(NO)(NPCy$_3$)(dttd)]	340(858)	35.4	45(NO) −332(NPCy$_3$)	1580 ν(NO) 1065 ν(MoNP)			
[Mo(NO)(NPMePh$_2$)(dttd)]	390(490)	29.6	44(NO) −330(NPMePh$_2$)	1605 ν(NO) 1050 ν(MoNP)	1.761	1.221	175.3
[Mo(NO)$_2$(dttd)]	−512(38)		190	1760 1665 } ν(NO)	1.833 1.842	1.134 1.156	176.4 177.1
(NMe$_4$)$_2$[Mo(NO)$_2$(C$_6$H$_4$S$_2$)$_2$]	−520(133)[e]		161[e]	1695 1590 } ν(NO)			
[Mo(CO)$_2$PMe$_3$(dttd)]	−550(255)	19.1					
[Mo(CO)$_3$(dttd)]	−717(89)						

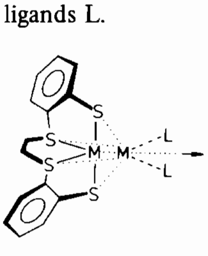
[a] NMR shifts in ppm and $CDCl_2$ solutions, if not otherwise noted. [b] Relative to $(NH_4)_6(Mo_7O_{24})$, half width in Hz in brackets. [c] Relative to ext. H_3PO_4. [d] Relative to ext. NH_4NO_3. [e] In D_2O.

Thus bond distances, ν(NO) frequencies and ^{14}N NMR shifts characterize NPR$_3$ ligands as strong electron donors, however, according to the ^{95}Mo shifts they do not raise the electron density at the Mo centers. This may be explained by the bonding model of Dehnicke *et al.* [14], according to which NPR$_3$ ligand can act as 4e$^-$ donors in the linear as well as in the bent state. [NPR$_3$] ligands acting as 4e$^-$ donors would allow the Mo centers in [Mo(NO)(NPR$_3$)(dttd)] complexes to retain a 18e$^-$ configuration and the observed effects which were discussed here would then be due mainly to changes in the π-bond system [P$\overset{..}{-}$N$\overset{..}{-}$Mo$\overset{..}{-}$N$\overset{..}{-}$O].

As Table VIII shows a clear correlation exists between M–N–P angles and the ν_{as}(MNP) frequencies of phosphineiminato complexes: small angles correspond with low ν_{as}(MNP) frequencies. In contrast the M–N and N–P distances show no correlation neither among each other nor with the M–N–P angles or ν_{as}(MNP) frequencies.

3.5. Is the [M(dttd)] Fragment in dttd Complexes Stereochemically Rigid or Flexible?

A comparison of [M(dttd)] complexes which have been characterized by X-ray structure analysis (Table IX) shows that they can contain six coordinate as well as seven coordinate metal centers. Bond distances and angles vary, but apparently only within relatively narrow limits, since open chain ligands as dttd^{2-} should principally be able to form even planar metal complexes. The complexes of Table IX, however rather show a relatively rigid pseudooctahedral [M(dttd)] fragment. The analysis of S(thiolate–M–S(thiolate) and S(thioether)–M–S(thioether) angles along with the corresponding distances shows short M–S distances to be connected with nearly linear or right angles respectively. Increasing distances, e.g. from the Fe via the Ru to the Mo complexes, causes a decrease of the angles, and in the seven coordinate [Mo(CO)$_2$(PMe$_3$)(dttd)] with the particularly long M–S(thiolate) distances of $\bar{d}$ = 2.506 Å the [S1MoS4] angle finally shows a value of only 151.1°. In these terms the individual structures can be derived from octahedral complexes by moving the metal from the center of the octahedron towards the edge which is defined by the two coligands L.

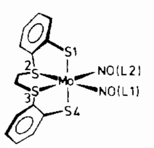
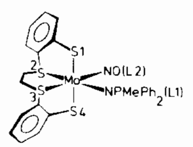
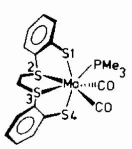
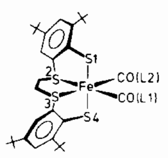
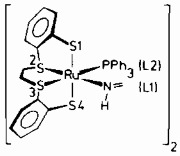


The different distances themselves – and consequently angles – can be traced back to purely geometrical causes: distances and angles depend on different

TABLE VIII. Distances (Å), Angles (°) and Frequencies (cm^{-1}) in Metal Phosphineiminato Complexes

Complex	∢M–N–P (°)	ν_{as}(MNP) (cm^{-1})	M–NP (pm)	N–P (pm)	Reference
[$RuCl_3(NPEt_2Ph)(PEt_2Ph)_2$]	175.0	1165	185.5	157.1	9
[$NbCl_4(NPPh_3)$]$_2$	171.1	1117	177.6	163.7	10
[$TaCl_4(NPPh_3)$]$_2$	176.8	1121	180.1	159.3	11
[$Re(NPPh_3)(SPh)_4$]	163.1	1120	174.3	163.4	12
[$Re(NO)Cl_3(NPPh_3)(OPPh_3)$]	138.5	1017	185.5	163.0	14
[$Mo(NO)(NPMePh_2)$(dttd)]	129.7	1050	190.4	160.6	this work
[$WF_4(NPPh_3)_2$]	157.2	not reported	182.5	159.4	13

TABLE IX. Angles and Distances in [M(dttd)] Complexes

Angle (°)	Distance (Å)	Complex				
						
S1–M–S4	(M–S1)	160.1(2.446)	161.0(2.492)	151.1(2.534)	172.7(2.276)	168.7(2.372)
S2–M–S3	(M–S2)	83.9(2.538)	79.5(2.635)	82.9(2.576)	91.4(2.245)	88.4(2.344)
S1–M–S2	(M–S3)	81.5(2.534)	78.7(2.638)	78.3(2.542)	88.2(2.245)	86.1(2.282)
S1–M–S3	(M–S4)	83.8(2.456)	88.2(2.375)	77.0(2.478)	86.6(2.276)	93.1(2.374)
Mean M–S		(2.494)	(2.535)	(2.533)	(2.261)	(2.343)
L1–M–L2		91.4	104.1		90.3	92.2
L1–M–S2		173.1	161.7		179.4	178.1
Reference		3	this work	this work	16	17

metal radii (as well as on influences of the coligands). Vice versa, however, the dttd^{2-} ligand is flexible by allowing changes in distances and angles in the [M(dttd)] fragment without the necessity of significantly weakening or even breaking M–S bonds. The unusual reactivity of [$Mo(NO)_2$(dttd)] towards phosphines can then be attributed to the easy conversion of six into seven coordinate [M(dttd)] complexes according to eqn. (1).

4. Conclusions

The results show that the reaction between [$Mo(NO)_2$(dttd)] and phosphines is dominated by the nucleophilicity of the phosphines. PCy_3, which combines the steric and electronic properties of PPh_3 and PMe_3, reacts comparably as fast as PMe_3.

The spectroscopic results corroborate the previous findings that the reductive desoxygenation of NO to give NPR_3 ligands is connected with an oxidation of the metal center from Mo(II) to Mo(III). The NPR_3 ligand functions as a 4e$^-$ donor also in strongly bent [M–N–P] entities as found in [$Mo(NO)(NPMePh_2)$(dttd)]. Distances and angles in pseudo-octahedral [M(dttd)] complexes are primarily determined by geometrical factors such as metal radii. [M(dttd)] fragments are flexible by allowing changes in distances (and angles) without a significant weakening of M–S bonds. The unusual reactivity of [$Mo(NO)_2$dttd] towards phosphines can then be attributed to the easy interconversion of six and seven coordinate [M(dttd)] complexes.

Supplementary Material

Further details of the X-ray crystal structure analyses have been deposited and can be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2 by citing the deposition No. CSD 52 404, the authors and the reference.

Acknowledgements

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