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Syntheses of 1,2-diamidobenzene complexes of molybdenum. Crystal structure of the complex *cis*-dicarbonyl 1,2-diamidobenzenebis(triphenylphosphine)molybdenum $[Mo\{(NH)_2C_6H_4\}(CO)_2(PPh_3)_2]$

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Abstract

The complex $[Mo(dib)(CO)_2(PPh_3)_2]$ (**1**) [dib = $1,2\text{-}(NH)_2C_6H_4$] is obtained from $[MoBr_2(CO)_2(PPh_3)_2]$, $1,2\text{-}(NH_2)_2C_6H_4$ and KOH dissolved in a mixture of tetrahydrofuran and water; its X-ray structure and properties are described. Substitution derivatives of this complex are obtained by reaction of **1** with P donors to give $[Mo(dib)(CO)_2L_2]$ (L = PEt_3 (**2**), $P(OEt)_3$ (**3**)] and $[Mo(dib)(CO)_2(dppe)]$ (**4**) [deppe = $Ph_2P(CH_2)_2PPh_2$], and their spectroscopic properties are reported. Attempted reactions of **1** with CO or dppm [dppm = $Ph_2PCH_2PPh_2$] were unsuccessful and the starting complex was recovered unchanged.

1. Introduction

The $1,2\text{-}(NH)_2C_6H_4$ ligand (dib) and related species form stable complexes with transition metals [1], where π-acid ligands can also be bound to the "$M(NH)_2C_6H_4$" moiety to give complexes with low oxidation numbers for M [2]. The diamido-ligand is non-innocent and can be considered formally as neutral (benzoquinone diimide), monoanionic (semibenzoquinone diimide) or dianionic (diamide) [3]. The complex $[Ru(dib)(PPh_3)_3]$, crystallographically characterized [4*], is described as a ruthenacycle with electron delocalization in its π-extended system, and is diamagnetic, with "short" C–N bond distances consistent with the diamide form (benzo- or semibenzoquinone). It gives other five-coordinate complexes when it reacts with π-acids. When quinones such as $C_6X_4O_2$ (X = Cl or Br), with high electron-withdrawing ability, and good π-acceptors such as CO are bonded, six-coordinate ruthenium(II) complexes are formed [5]. Six-coordinate complexes of molybdenum(II) are well known but scarce [6], and from the seven-coordinate 18-electron species they can be easily obtained. We have extended the study of this type of 1,2-diamido complexes to other metals with low oxidation states, and molybdenum offers the appropriate versatility in oxidation and coordination number.

2. Results and discussion

2.1. Synthesis of $[Mo(dib)(CO)_2(PPh_3)_2]$ (1)

The reaction between $[MoBr_2(CO)_2(PPh_3)_2]$ and $1,2\text{-}(NH_2)_2C_6H_4$ in a basic medium (see Experimental details) yielded $[Mo\{1,2\text{-}(NH)_2C_6H_4\}(CO)_2(PPh_3)_2]$ (**1**) as dark brown crystals from toluene–hexane solutions. It has an IR band at 3335 cm^{-1}, which can be attributed to ν(NH) (diimine), and two absorptions (toluene solution) at 1913 cm^{-1} and 1826 cm^{-1} suggesting a *cis*-dicarbonyl arrangement. These low values are comparable to those found for other dicarbonyl molybdenum(II) complexes [7]. Further structural in-

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formation was obtained from ^{1}H and ^{31}P NMR spectroscopy: a singlet at 71.92 ppm [^{31}P{^{1}H}] (unchanged at 203 K) and a multiplet at 7.85 ppm (^{1}H) (tentatively attributed to amide protons) show equivalence of the phosphines and of the nitrogen atoms, which led us to the conclusion that molybdenum in this complex, and ruthenium in [Ru(dib)L$_3$] [2,4], are isoelectronic.

2.2. Crystal structure of [Mo(dib)(CO)$_2$(PPh$_3$)$_2$] (1)

The structure of complex **1**, determined by X-ray diffraction methods, is depicted in Fig. 1. Selected bond distances and angles are given in Table 1. The complex, with approximate C_2 symmetry, has a molybdenum atom with a very distorted octahedral arrangement, like those found in other six-coordinate molybdenum(II) complexes [6d–6g]. The values of the bond angles are as expected for a dodecahedral coordination [8] with two vacant sites, roughly centred on the two faces N(1)N(2)P(1)C(1) and N(1)N(2)C(2)P(2). Two hydrogen atoms from two phenyl rings of the PPh$_3$, H(26) and H(38), are close to the vacant sites. Even if rather distant, (3.21(3) Å and 3.04(3) Å) from the Mo atom, they can be considered as acting as "token ligands" [9]. In the starting compound [MoBr$_2$(CO)$_2$(PPh$_3$)$_2$] [6f] the bond angles around the molybdenum atom are those expected for a cubic coordination with two vacant sites. The substitution of two Br atoms by two N atoms from the dib ligand causes an increase of the P–Mo–P angle from 127.8(4)° to 140.8(2)°, a decrease of the C–Mo–C angle from 119.5(4)° to 106.3(10)°, and a decrease of the Br–Mo–Br angle compared to the N–Mo–N angle from 83.1(2)° to 74.8(7)°. The P–Mo–P and C–Mo–C angles in **1** are comparable to those found in the analogous complexes [MoBr$_2$(CO)$_2$(PEt$_3$)$_2$], 138.8(2)° and 102.3° [6d], and [Mo{(C$_5$H$_{10}$N)$_2$C$_2$S$_2$}(CO)$_2$(PBu$^n_3$)$_2$], 146.8(2)° and 106(1)° [6e], in which hydrogen atoms from ethyl and n-butyl groups also point towards the Mo atom in such a way to act as "token ligands".

TABLE 1. Selected bond distances (Å) and angles (°) for **1**

Mo–P(1)	2.452(7)	P(2)–C(39)	1.82(3)
Mo–P(2)	2.492(6)	O(1)–C(1)	1.21(4)
Mo–N(1)	2.15(2)	O(2)–C(2)	1.06(4)
Mo–N(2)	2.02(2)	N(1)–C(3)	1.36(3)
Mo–C(1)	1.90(3)	N(2)–C(8)	1.39(3)
Mo–C(2)	2.11(3)	C(3)–C(4)	1.43(4)
P(1)–C(9)	1.78(2)	C(3)–C(8)	1.44(3)
P(1)–C(15)	1.87(3)	C(4)–C(5)	1.36(4)
P(1)–C(21)	1.83(3)	C(5)–C(6)	1.40(3)
P(2)–C(27)	1.86(3)	C(6)–C(7)	1.39(4)
P(2)–C(33)	1.83(3)	C(7)–C(8)	1.37(3)
C(1)–Mo–C(2)	106(1)	Mo–P(2)–C(39)	115.2(8)
N(2)–Mo–C(2)	91(1)	Mo–P(2)–C(33)	114.2(9)
N(2)–Mo–C(1)	151(1)	Mo–P(2)–C(27)	118.6(9)
N(1)–Mo–C(2)	152(1)	C(33)–P(2)–C(39)	101(1)
N(1)–Mo–C(1)	96(1)	C(27)–P(2)–C(39)	102(1)
N(1)–Mo–N(2)	74.8(7)	C(27)–P(2)–C(33)	103(1)
P(2)–Mo–C(2)	80.1(8)	Mo–N(1)–C(3)	116(2)
P(2)–Mo–C(1)	78.6(8)	Mo–N(2)–C(8)	122(2)
P(2)–Mo–N(2)	127.7(6)	Mo–C(1)–O(1)	175(2)
P(2)–Mo–N(1)	89.8(6)	Mo–C(2)–O(2)	173(3)
P(1)–Mo–C(2)	77.3(8)	N(1)–C(3)–C(8)	116(2)
P(1)–Mo–C(1)	77.7(9)	N(1)–C(3)–C(4)	127(2)
P(1)–Mo–N(2)	84.6(6)	C(4)–C(3)–C(8)	118(2)
P(1)–Mo–N(1)	123.3(5)	C(3)–C(4)–C(5)	120(2)
P(1)–Mo–P(2)	140.8(2)	C(4)–C(5)–C(6)	122(2)
Mo–P(1)–C(21)	113.0(9)	C(5)–C(6)–C(7)	121(3)
Mo–P(1)–C(15)	119.1(9)	C(6)–C(7)–C(8)	119(2)
Mo–P(1)–C(9)	113.8(9)	C(3)–C(8)–C(7)	121(2)
C(15)–P(1)–C(21)	101(1)	N(2)–C(8)–C(7)	127(2)
C(9)–P(1)–C(21)	104(1)	N(2)–C(8)–C(3)	111(2)
C(9)–P(1)–C(15)	104(1)		

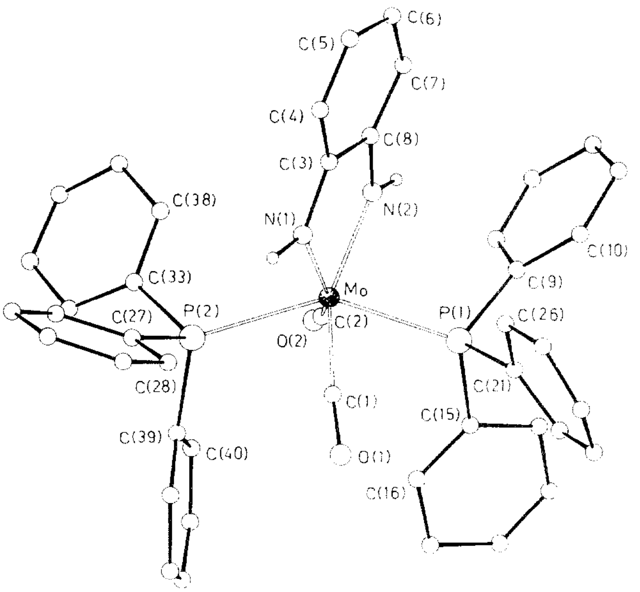


Fig. 1. View of the structure of [Mo(dib)(CO)$_2$(PPh$_3$)$_2$] (1) with the atomic numbering scheme.

The lengths of the C–N bonds in **1**, 1.36(3) Å and 1.39(3) Å (similar values have been found in the ruthenium compound [4]) suggest partial double-bond character, as found for the NH$_2$–C$_{\text{aryl}}$ bonds, 1.355(20) Å [10] and are consistent with a mono- (17-electron) or di-anionic (16-electron) form of the ligand. The neutral (18-electron) form would require greater double-bond character and therefore shorter bond distances.

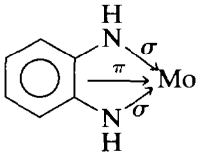
2.3. Substitution reactions

Compound **1** has proved to be a very stable complex, as it can be recovered unchanged when heated in boiling aromatic solvents, such as mesitylene, for a few minutes. When CO was bubbled through a toluene solution (cold or hot), a further CO was not added to the complex (as would be expected for a six-coordinate 16-electron molybdenum species [6]), and **1** remained unchanged.

Phosphorus ligands, less π-acid than CO, did not give any addition product when mixed with complex **1**, but the derivatives $[Mo(dib)(CO)_2(L)_2]$ [L = PEt_3 or $P(OEt)_3$] and $[Mo(dib)(CO)_2(dppe)]$ were obtained when reaction solutions were boiled (see Experimental details). The new complexes showed similar infrared spectra in solution in the CO stretching region, having two bands that suggest a *cis*-dicarbonyl coordination. In addition, their ^{31}P NMR spectra (one singlet) confirm the equivalence of the phosphines and the complete replacement of the original PPh_3. The stretching ν(CO) values are lower than those of the starting compound, with the weaker π-acid, (PEt_3) and higher for the stronger π-acid, ($P(OEt)_3$). They are also raised for dppe.

The attempted reaction between **1** and dppm did not produce a new complex, even in boiling mesitylene, and the starting complex was recovered unchanged. When the reaction was carried out under ultraviolet (UV) light in aromatic solvents, extensive decomposition occurred, to give solutions in which no IR ν(CO) absorptions were detected.

It is concluded that **1** is formally a molybdenum(II) complex. Its lack of reactivity with π-acids, not a characteristic of six-coordinate molybdenum(II) complexes, can be explained by assuming that dib is a six-electron donor, through two σ and one π bonds, as shown below, and that the metal atom thus achieves a stable configuration of 18 electrons.



3. Experimental details

All reactions were carried out under dinitrogen, using freshly distilled solvents. $1,2-(NH_2)_2C_6H_4$, PEt_3, $P(OEt)_3$, dppm, dppe, CO and KOH were used as supplied and $[MoBr_2(CO)_2(PPh_3)_2]$ was prepared according to the published procedure [11]. IR spectra were recorded as Nujol mulls (KBr discs) or solutions (CaF_2 discs) on a Perkin Elmer 1720-XFT spectrometer. ^1H and ^{31}P NMR spectra were recorded on a Bruker AC-300 instrument. Microanalytical data (C, H and N) were obtained with a Perkin Elmer 240-B elemental analyser.

3.1. $[Mo(dib)(CO)_2(PPh_3)_2]$ (1)

$[MoBr_2(CO)_2(PPh_3)_2]$ (0.50 g, 0.60 mmol) and $1,2-(NH_2)_2C_6H_4$ (0.065 g, 0.60 mmol) were heated under reflux for 1 h in a mixture of THF (5 cm^3) and a solution of KOH (1.50 g) in water (5 cm^3). The THF was evaporated *in vacuo* and the water decanted, leaving an oily product that was washed with EtOH and with hexane, and then vacuum dried. The brown residue was dissolved in hot toluene (10 cm^3). From this solution a crystalline solid or precipitate was obtained within 1 d at 20°C after adding hexane. Yield about 50%. Anal. Found: C, 66.98; H, 4.72; N, 3.53. $C_{44}H_{36}MoN_2O_2P_2$ calc.: C, 67.52; H, 4.60; N, 3.58%. IR: [ν(NH), nujol mull]; 3335w [ν(CO), toluene]. 1913m and 1826s cm^{-1}. ^{31}P NMR (C_6D_6): 71.92 (s, 2P, PPh_3) ppm. ^{31}P NMR (203 K): 72.61 (s) ppm; ^1H NMR: 7.85 (s, 2H, NH) ppm.

3.2. $[Mo(dib)(CO)_2(PEt_3)_2]$ (2)

$[Mo(dib)(CO)_2(PPh_3)_2]$ (0.020 g, 0.025 mmol) and triethylphosphine (2 drops) were heated in boiling THF (8 cm^3) for 15 h. The oily residue, after solvent evaporation, was dissolved in hexane (50 cm^3) and the solution filtered after 1 d at room temperature. The brown oil obtained from hexane evaporation *in vacuo* is a mixture of the bis(triethylphosphine) complex and triphenylphosphine. IR: [ν(CO), (THF)] 1897s and 1806vs cm^{-1}. ^{31}P NMR 50.8 (s, PEt_3); −4.6 (s, free PPh_3) ppm. Trace amounts of free PEt_3 are also detected by ^{31}P NMR (THF/D_2O): −18.9 (s) ppm.

3.3. $[Mo(dib)(CO)_2\{P(OEt)_3\}_2]$ (3)

$[Mo(dib)(CO)_2(PPh_3)_2]$ (0.040 g, 0.051 mmol) and triethylphosphite (0.017 g, 0.102 mmol) were heated under reflux in toluene (6 cm^3). After 1 h the reaction was almost complete (traces of the starting complex were detected by IR), yielding a brown solution [IR ν(CO): 1937m, 1852s cm^{-1}] which decomposed before crystal and spectroscopic data could be obtained.

3.4. $[Mo(dib)(CO)_2(dppe)]$ (4)

$[Mo(dib)(CO)_2(PPh_3)_2]$ (0.035 g, 0.045 mmol) and 1,2-bis(diphenylphosphino)ethane (0.036 g, 0.090 mmol) were heated under reflux in toluene (10 cm^3) for 90 min. The volume of the filtered solution was reduced to 3 cm^3 and hexane (10 cm^3) added. After 1 d at 20°C brown-red crystals were collected, washed with hexane and then dried *in vacuo*. Yield about 50%. Anal. Found: C, 61.7; H, 4.8; N, 4.1. $C_{34}H_{30}MoN_2O_2P_2$ calc.: C, 62.2; H, 4.6; N, 4.3%. IR: [ν(NH), nujol mull] 3325w cm^{-1}; [ν(CO), nujol mull] 1930vs, 1846vs cm^{-1}; [ν(CO), toluene] 1929vs, 1851s cm^{-1}. ^{31}P NMR (C_6D_6): 86.7 (s, 2P, dppe) ppm; ^1H NMR: 8.40 (s, 2H, NH) ppm.

3.5. Reaction with bis(diphenylphosphino)methane (dppm)

No reaction was observed in boiling solvents like toluene, xylene or mesitylene. When xylene solutions were irradiated (UV) only a mixture of decomposition products without CO ligands was obtained.

3.6. *X-ray data collection, structure determination and refinement for [Mo(dib)(CO)$_2$(PPh$_3$)$_2$] (1)*

Crystal data for **1**: $C_{44}H_{36}MoN_2O_2P_2$, M = 782.67, triclinic, space group $P_{\bar{1}}$, a = 11.473(6) Å, b = 12.999(7) Å, c = 14.073(3) Å, α = 72.97(3)°, β = 86.40(4)°, γ = 71.06(5)°, V = 1897(2) Å^3, Z = 2, D_c = 1.370 g cm^{-3}, F (000) = 804, graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å, μ = 4.57 cm^{-1}.

TABLE 2. Fractional atomic coordinates ($\times 10^4$) for **1**

Atom	x	y	z
Mo	2389(2)	192(2)	2962(2)
P(1)	3346(6)	−1740(5)	2828(5)
P(2)	1364(6)	2170(5)	1912(5)
O(1)	348(17)	−210(15)	1904(13)
O(2)	4481(18)	537(17)	1444(15)
N(1)	1300(17)	566(16)	4192(13)
N(2)	3610(17)	−320(15)	4112(13)
C(1)	1133(27)	−6(22)	2286(17)
C(2)	3773(27)	379(21)	1923(20)
C(3)	1926(23)	254(19)	5073(20)
C(4)	1413(24)	393(20)	5996(19)
C(5)	2162(23)	34(19)	6816(19)
C(6)	3432(25)	−512(21)	6793(20)
C(7)	3971(23)	−675(19)	5910(17)
C(8)	3241(21)	−273(18)	5060(18)
C(9)	4774(22)	−2481(19)	3506(17)
C(10)	4997(26)	−3413(23)	4354(20)
C(11)	6085(31)	−3885(27)	4953(25)
C(12)	7031(28)	−3424(24)	4639(22)
C(13)	6856(26)	−2538(23)	3811(21)
C(14)	5813(23)	−2090(21)	3235(18)
C(15)	3679(25)	−1951(23)	1569(20)
C(16)	3018(26)	−1222(24)	759(21)
C(17)	3221(29)	−1457(26)	−177(24)
C(18)	4254(27)	−2435(25)	−171(23)
C(19)	4943(26)	−3120(23)	584(21)
C(20)	4733(24)	−2935(22)	1518(20)
C(21)	2397(21)	−2660(19)	3321(18)
C(22)	2212(22)	−3398(20)	2915(18)
C(23)	1367(25)	−3986(22)	3296(20)
C(24)	766(26)	−3794(23)	4109(21)
C(25)	942(26)	−3158(23)	4606(22)
C(26)	1808(24)	−2527(22)	4199(20)
C(27)	−176(24)	2980(23)	2264(18)
C(28)	−982(26)	2376(24)	2599(19)
C(29)	−2173(26)	2978(24)	2900(20)
C(30)	−2487(29)	4104(26)	2860(21)
C(31)	−1668(31)	4714(29)	2517(22)
C(32)	−509(25)	4123(23)	2207(19)
C(33)	2262(22)	3130(20)	1800(19)
C(34)	2149(27)	4084(25)	1003(22)
C(35)	2964(25)	4752(22)	961(21)
C(36)	3732(25)	4404(23)	1703(21)
C(37)	3898(25)	3529(24)	2488(21)
C(38)	3122(23)	2838(21)	2530(18)
C(39)	1087(23)	2317(19)	612(17)
C(40)	2091(23)	2150(20)	−10(18)
C(41)	1898(27)	2107(22)	−954(21)
C(42)	837(30)	2132(24)	−1266(24)
C(43)	−199(30)	2253(24)	−699(23)
C(44)	−59(26)	2311(21)	287(22)

The intensity data were collected on a CAD-4 Enraf Nonius diffractometer, using the ω-2θ scan technique at room temperature. 4624 unique reflections were measured with θ in the range 2.5–22°; 1211, having $I > 3\sigma(I)$, were used in the refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures, with anisotropic thermal parameters in the last cycles of refinement for Mo, P, N, O and C (only of CO groups) atoms. The hydrogen atoms were introduced in calculated positions and refined "riding" on the corresponding carbon atoms. The R and R_w values were 0.0679 and 0.0828. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref. 12. All calculations were carried out on the GOULD POWERNODE 6040 of the "Centro di Studio per la Strutturistica Diffrattometrica" del C.N.R., Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs [13]. The final atomic coordinates for the non-hydrogen atoms are given in Table 2. Additional data (atomic coordinates of the hydrogen atoms, thermal parameters) are available from the Cambridge Crystallographic Data Centre.

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