# Chlorobis[1,1'-diphenylhydrazido(2–)-$N^2$]-[hydridotris(pyrazolyl-$N^2$)borato]molybdenum(VI)

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## Abstract

The Mo$^{VI}$ atom in the title complex, [MoCl($C_9H_{10}BN_6$)-($C_{12}H_{10}N_2$)$_2$] or TpMo(NNPh$_2$)$_2$Cl, where Tp = HB-($C_3H_3N_2$)$_3^-$, has a distorted octahedral environment afforded by the facially coordinated Tp ligand, two terminal NNPh$_2$ ligands and the chloro ligand. The bond distances Mo—N of 1.773 (3) and 1.780 (3) Å, N—N of 1.319 (4) and 1.312 (4) Å, and bond angles Mo—N—N of 167.1 (2) and 170.9 (3)°, in the Mo(NNPh$_2$)$_2$ moiety, together with the absence of pyramidalization on the N atoms remote from the Mo atom, are indicative of an extensive delocalization of the $\pi$-electron density throughout the Mo—N—N system.

## Comment

The NN$RR'$ group ($RR'$ = Me,Me; Me,Ph; Ph,Ph) is of interest as a potential model of NNH$_2$ which is an intermediate observed in the conversion of ligated dinitrogen into ammonia (Chatt, Pearman & Richards, 1978; Anderson, Fakley, Richards & Chatt, 1981). Thus, studies have been reported concerning the N—N$R_2$ bond cleavage (Henderson, Leigh & Pickett, 1991; Walsh, Carney & Bergman, 1991; DeBord, George, Chang & Zubieta, 1993; Vale & Schrock, 1993; Redböll, Moller, Hazell & Jörgensen, 1995) and NN$R_2$-alkylation (Vale & Schrock, 1993). Our efforts have focused on developing new organohydrazido and bis-organohydrazido complexes containing a variety of co-ligands, *e.g.* acetylacetonato (Bustos *et al.*, 1991; Carrillo, Robert & Gouzerh, 1992; Manzur, Bustos, Carrillo, Robert & Gouzerh, 1996; Manzur, Carrillo, Baggio & Garland, 1997), phosphines (Bustos, Manzur, Carrillo, Robert & Gouzerh, 1994*b*; Manzur, Carrillo, Baggio & Garland, 1997), di-imines (Manzur, Bustos, Carrillo, Boys & Hamon, 1997) and mercaptobenzoato (Li-Kao *et al.*, 1995). Special attention has been paid to the *trans* effect of these ancillary ligands on the organohydrazido groups. Likewise, we have studied the deprotonation

and protonation of the NHN$RR'$ ($RR'$ = Me,Ph; Ph,Ph) and NN$RR'$ moieties, respectively (Bustos, Manzur, Carrillo, Robert & Gouzerh, 1994*a*), and the hydrolysis of the Mo—NN$RR'$ bond to give the Mo=O group (Manzur, Bustos, Carrillo, Boys & Hamon, 1997). The purpose of this work was the synthesis of a new complex, [TpMo(NNPh$_2$)$_2$Cl], containing the *cis*-Mo(NNPh$_2$)$_2$ core and the tridentate nitrogenate anion hydridotris(pyrazolyl)borate, Tp$^-$, as ancillary ligand.



(I)
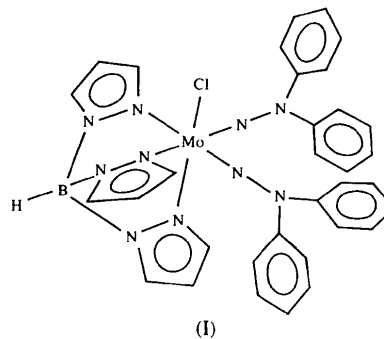
The complex is neutral in nature and the tridentate Tp$^-$ ligand occupies one face of the distorted octahedron about the Mo atom, while the two organohydrazido(2–) ligands, with an end-on configuration, and the covalent chloro ligand occupy the other three mutually *cis* coordination sites (Fig. 1). The best mean coordination plane is defined by the N1 and N3 atoms of the organohydrazido(2–) ligands and the N5 and N7 donor atoms of two pyrazolyl rings. The central Mo atom deviates by 0.092 (1) Å from this best plane towards the Cl atom. Atom N6 of the third pyrazolyl ring and the Cl atom are *trans* to each other occupying the remaining octahedral sites. Distortions from ideal octahedral geometry are evidenced by the non-linear *trans* bond angles
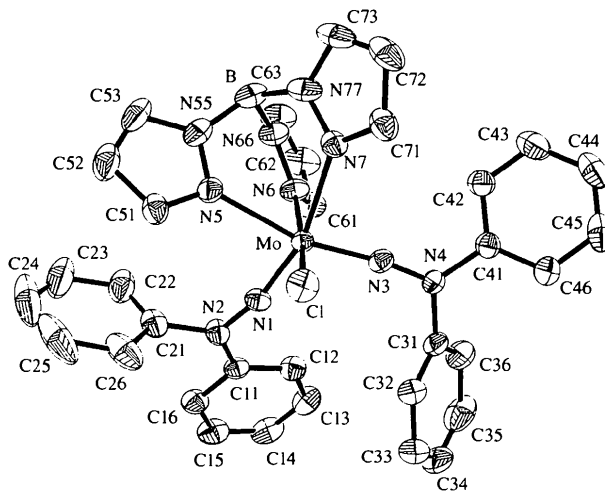


Fig. 1. The structure of the title complex with the atom labelling. Displacement ellipsoids are drawn at the 40% probability level.

ranging from 162.0(1) to 167.9(1)° and the *cis* bond angles ranging from 74.6(1) to 105.3(1)° (Table 1).

The molecule has no mirror symmetry due to the different orientations exhibited by the phenyl groups of the hydrazido ligands in order to diminish their mutual electronic repulsions. As a consequence of steric interactions of phenyl groups Ph2 and Ph4 with the pyrazolyl rings containing N5 and N7, there is a larger opening of the N5—Mo—N6 and N6—Mo—N7 angles compared with the N5—Mo—N7 angle. The bond distance Mo—N6 is in the normal range for a single bond, while the larger values found for Mo—N5 and Mo—N7 are consistent with a strong *trans* effect of both organohydrazido(2−) ligands. Finally, the most relevant structural features of the Mo(NNPh$_2$)$_2$ core are: (i) the short Mo—N and N—N bond distances, and almost linear Mo—N—N bond angles (Table 1), and (ii) the absence of pyramidalization on the N atoms remote from the Mo centre, N2 and N4; bond angles having N2 and N4 as central atoms add to 360°, within error, indicating an N—N—C—C planar system (Table 1). These features indicate the presence of multiple bonds and an extensive electronic delocalization throughout the Mo—N—N units, and are consistent with the description of the organohydrazido ligand as the six-electron-donating diphenylhydrazido ligand attaining the Mo centre a formal 20-electron shell.

## Experimental

Synthesis of the complex was carried out by reaction of NaTp on the precursor Mo(NHNPh$_2$)(NNPh$_2$)(acac)Cl (Bustos *et al.*, 1994*a*). The precursor (3.00 g, 4.75 mmol) and NaTp (1.12 g, 4.75 mmol) were dissolved in acetonitrile (25 ml) and refluxed for 0.5 h under dinitrogen. The deep-orange solid obtained was filtered off and washed with diethyl ether and dried *in vacuo*. The recrystallized product was obtained from a filtered dichloromethane solution layered with *n*-hexane (1:1). Single crystals suitable for X-ray analysis were obtained from acetonitrile (yield 2.01 g, 59%).

### Crystal data

[MoCl(C$_9$H$_{10}$BN$_6$)-(C$_{12}$H$_{10}$N$_2$)$_2$]
$M_r$ = 708.87
Monoclinic
$P2_1$
$a$ = 9.504 (3) Å
$b$ = 18.536 (5) Å
$c$ = 10.305 (3) Å
$\beta$ = 112.76 (2)°
$V$ = 1674.0 (8) Å$^3$
$Z$ = 2
$D_x$ = 1.406 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 32 reflections
$\theta$ = 7.5–15.0°
$\mu$ = 0.511 mm$^{-1}$
$T$ = 295 (2) K
Parallelepiped
0.40 × 0.30 × 0.28 mm
Deep orange

### Data collection

Siemens $R3m/V$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction:
$\psi$ scans (*XEMP* in *SHELXTL/PC*; Sheldrick, 1991)
$T_{min}$ = 0.681, $T_{max}$ = 0.766
5327 measured reflections
5056 independent reflections

4449 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.030
$\theta_{max}$ = 30.06°
$h$ = 0 → 13
$k$ = 0 → 26
$l$ = −14 → 13
2 standard reflections
every 98 reflections
intensity decay: none

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.075
$S$ = 1.008
5056 reflections
415 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.001

$\Delta\rho_{max}$ = 0.533 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.418 e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.00 (3)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Mo—Cl | 2.4516 (10) | N2—C21 | 1.419 (5) |
| Mo—N1 | 1.773 (3) | N4—C31 | 1.438 (4) |
| Mo—N3 | 1.780 (3) | N4—C41 | 1.431 (5) |
| Mo—N5 | 2.285 (3) | N5—N55 | 1.358 (4) |
| Mo—N6 | 2.170 (3) | N55—B | 1.530 (6) |
| Mo—N7 | 2.290 (3) | N6—N66 | 1.364 (4) |
| N1—N2 | 1.319 (4) | N66—B | 1.549 (5) |
| N3—N4 | 1.312 (4) | N7—N77 | 1.370 (5) |
| N2—C11 | 1.422 (4) | N77—B | 1.511 (7) |
| N6—Mo—Cl | 167.87 (8) | C21—N2—C11 | 121.5 (3) |
| N1—Mo—N7 | 161.99 (12) | N4—N3—Mo | 170.9 (3) |
| N3—Mo—N5 | 165.25 (12) | N3—N4—C31 | 118.7 (3) |
| N2—N1—Mo | 167.1 (2) | N3—N4—C41 | 119.4 (3) |
| N1—N2—C11 | 120.6 (3) | C41—N4—C31 | 121.6 (3) |
| N1—N2—C21 | 117.6 (3) | | |

A riding model was applied to all H atoms placed at idealized positions, with $U_{iso}$ = $U_{eq}$ of their respective parent atoms. The Flack parameter was refined in order to establish the correct direction of the polar axis in the crystal studied.

Data collection: *P3/P4-PC* (Siemens, 1991). Cell refinement: *P3/P4-PC*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *XS* in *SHELXTL/PC*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *CIFTAB* in *SHELXL93*.

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# Carbonyl(1,3-diphenyl-1,3-propanedionato-O,O')(triphenylphosphine-P)rhodium(I)

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## Abstract

One carbonyl group in dicarbonyl(1,3-diphenyl-1,3-propanedionato-O,O')rhodium(I) was substituted by triphenylphosphine to yield the title compound, [Rh(C$_{15}$H$_{11}$O$_2$)(C$_{18}$H$_{15}$P)(CO)], which has a square-planar

geometry about the Rh atom. There are two crystallographically independent molecules in the asymmetric unit.

## Comment

The title compound, [Rh(DBM)(CO)(PPh$_3$)] (DBM is the 1,3-diphenyl-1,3-propanedionate anion), (I), was prepared and its crystal structure solved as part of our study of the relationship between the chemical oxidation of Rh$^I$ to Rh$^{III}$ in these compounds by iodomethane, and the electrochemical oxidation by means of cyclic voltametry. To minimize the effect of different groups on the monocharged $\beta$-diketonate ligand, we have chosen the symmetrical $\beta$-diketone 1,3-diphenyl-1,3-propandione.
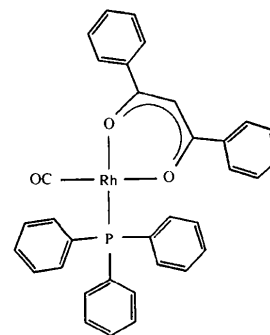


(I)

The asymmetric unit consists of two crystallographically independent molecules of the title compound. These molecules form a very closely centrosymmetric pair, but this is not a crystallographic inversion center. One of the molecules of (I) is illustrated in Fig. 1. The square-planar coordination of the Rh atom is clear from the bond angles in Table 1. The partial overlapping of the chelate ring of one molecule with a phenyl ring of the other molecule can be attributed to $\pi$–$\pi$ interactions by considering the intermolecular distances in Table 2.

The Rh1 and Rh2 atoms lie 0.012 and $-0.015$ Å from their respective coordination planes. The distances Rh1—O2 [2.081 (9) Å] and Rh2—O5 [2.072 (7) Å] when compared with Rh1—O1 [2.038 (10) Å] and Rh2—O4 [2.040 (7) Å] illustrate clearly the larger *trans* influence of triphenylphosphine compared with a carbonyl group. The same tendency with similar bond lengths was found in structures of the following compounds which also contain symmetrical $\beta$-diketones: [Rh(acac)(CO)(PPh$_3$)] (acac is acetylacetonate) (Leipoldt, Basson, Bok & Gerber, 1978) and [Rh(TROP)(CO)(PPh$_3$)] (TROP is tropolonate) (Leipoldt, Bok, Basson & Meyer, 1980). In a previous paper (Graham, Lamprecht, Potgieter, Roodt & Leipoldt, 1991), the authors claimed that the Rh—P distance could be used to estimate the relative *trans* influence of different donor atoms in the chelate rings. In this case,