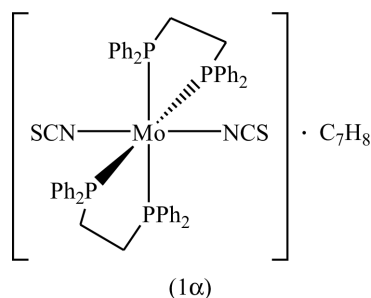


trans*-Bis[ethane-1,2-diylbis(diphenylphosphane)- κ 2*P,P'*]bis(thiocyanato- κ N)-molybdenum(II) toluene solvate*Athanasios I. Philippopoulos,
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GermanyCorrespondence e-mail:
filippou@chemie.hu-berlin.de**Key indicators**Single-crystal X-ray study
 $T = 180$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
Disorder in solvent or counterion
 R factor = 0.040
 wR factor = 0.101
Data-to-parameter ratio = 15.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The complex *trans*-[Mo(NCS)₂(dppe)₂] [dppe is ethane-1,2-diylbis(diphenylphosphane), C₂₆H₂₄P₂] was obtained upon air oxidation of [N(*n*-Bu)₄][Mo(NCS)(dppe)₂(N₂)] and the crystal structure of its toluene solvate, [Mo(NCS)₂(C₂₆H₂₄P₂)₂]·C₇H₈, has been determined. The complex molecule reveals a distorted octahedral coordination geometry, with two *trans*-oriented N-bonded thiocyanate ligands. The Mo atom resides on a crystallographic center of symmetry.

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Recently, we have shown that the reactions of the dinitrogen complexes *trans*-[M(dppe)₂(N₂)₂] [M = Mo, W; dppe is ethane-1,2-diylbis(diphenylphosphane), Ph₂PCH₂CH₂PPh₂] with the germanium(II) halides Cp*GeX (Cp* = C₅Me₅; X = Cl, Br, I) afford the germylyne complexes *trans*-[X(dppe)₂M≡Ge-(η^1 -Cp*)] (Filippou, Philippopoulos *et al.*, 2000; Filippou, Portius & Philippopoulos, 2002). Furthermore, the tungsten derivative *trans*-[I(dppe)₂W≡Ge-(η^1 -Cp*)] was shown to undergo iodide/pseudohalide ligand exchange with an excess of *M'Y* (M' = Na, K; Y = CN, NCO, N₃, NCS) to yield the germylyne complexes *trans*-[Y(dppe)₂W≡Ge-(η^1 -Cp*)] (Filippou, Philippopoulos *et al.*, 2002). Looking for an alternative approach to the analogous molybdenum compounds, we prepared the anionic dinitrogen complex [N(*n*-Bu)₄][Mo(NCS)(dppe)₂(N₂)], following the method of Chatt *et al.* (1980). Exposure of this complex to air was reported to give *trans*-[Mo(NCS)₂(dppe)₂], (1), which was characterized by IR spectroscopy and elemental analysis (Chatt *et al.*, 1980). However, the molecular structure of (1) remained unknown until now. Dark-green single crystals of the toluene solvate of (1), *viz.* (1 α), were obtained from a THF/toluene solution, upon cooling from 293 to 238 K. The title compound, (1 α), crystallizes in the same space group (*P*2₁/*c*) as the chloro complex *trans*-[MoCl₂(dppe)₂]·2C₄H₈O (Filippou, Portius *et al.*, 2000).



The 16 valence-electron complex (1) reveals a distorted octahedral geometry at the Mo atom, which bears two *trans*-arranged N-bonded thiocyanate ligands and lies on a crystal-

lographic center of symmetry. Distortion is evidenced in the tilt of the axial isothiocyanate ligands with respect to the equatorial plane spanned by the four P atoms, the angle between the N—Mo—N' axis and the P₄ plane being 82.9 (1)°. A similar tilt of the axial chloro ligands (80.5°) was observed in *trans*-[MoCl₂(dppe)₂] \cdot 2C₄H₈O (Filippou, Portius *et al.*, 2000). The isothiocyanate ligands feature an almost linear Mo—N—C1—S array in (1α), with Mo—N—C1 and N—C1—S angles of 176.2 (3) and 178.0 (4)°, respectively. The Mo—N bonds of (1α) [2.086 (3) Å] are slightly shorter than those of the few other structurally characterized molybdenum(II) isothiocyanate complexes (Bino & Cotton, 1979; Müller & Mohan, 1981) and the mean Mo—P bond length of (1α) (2.503 Å) compares well with that of *trans*-[MoCl₂(dppe)₂] \cdot 2C₄H₈O (average Mo—P = 2.499 Å; Filippou, Portius *et al.*, 2000) or *trans*-[MoCl₂(dppe)₂] \cdot CH₂Cl₂ (average Mo—P = 2.497 Å; Nardelli *et al.*, 1980).

Experimental

A Schlenk tube was charged with a mixture of *trans*-[Mo(dppe)₂(N₂)₂] (663 mg, 0.699 mmol) and [N(*n*-Bu)₄](NCS) (211 mg, 0.702 mmol). THF (40 ml) was added to the mixture and the resulting clear orange solution was stirred at ambient temperature overnight under an N₂ atmosphere. Within *ca* 20 min, the color of the solution changed to deep red. At the end of the reaction, the solution was concentrated to half its volume and stored for 2 h at 238 K, to afford a mixture of yellow and red–black crystalline material. The supernatant dark-red solution was decanted, treated with toluene (35 ml) and then stirred for 1–2 minutes in air. Dark-green single crystals of (1α) were obtained upon cooling the resulting yellow solution for 3 d at 238 K.

Crystal data

[Mo(NCS) ₂ (C ₂₆ H ₂₄ P ₂) ₂] \cdot C ₇ H ₈	$D_x = 1.374 \text{ Mg m}^{-3}$
$M_r = 1101.02$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 72 reflections
$a = 9.6277 (13) \text{ \AA}$	$\theta = 14.0\text{--}14.8^\circ$
$b = 17.017 (2) \text{ \AA}$	$\mu = 0.49 \text{ mm}^{-1}$
$c = 16.755 (2) \text{ \AA}$	$T = 180 (2) \text{ K}$
$\beta = 104.172 (11)^\circ$	Block, dark green
$V = 2661.5 (6) \text{ \AA}^3$	$0.68 \times 0.62 \times 0.48 \text{ mm}$
$Z = 2$	

Data collection

Stoe Stadi-4 diffractometer	$R_{\text{int}} = 0.098$
$2\theta/\omega$ scans	$\theta_{\text{max}} = 25.3^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -11 \rightarrow 11$
$T_{\text{min}} = 0.733$, $T_{\text{max}} = 0.800$	$k = 0 \rightarrow 20$
4828 measured reflections	$l = -2 \rightarrow 20$
4820 independent reflections	3 standard reflections
3796 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 3.8%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 3.8899P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.74 \text{ e \AA}^{-3}$
4820 reflections	$\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$
306 parameters	
H-atom parameters constrained	

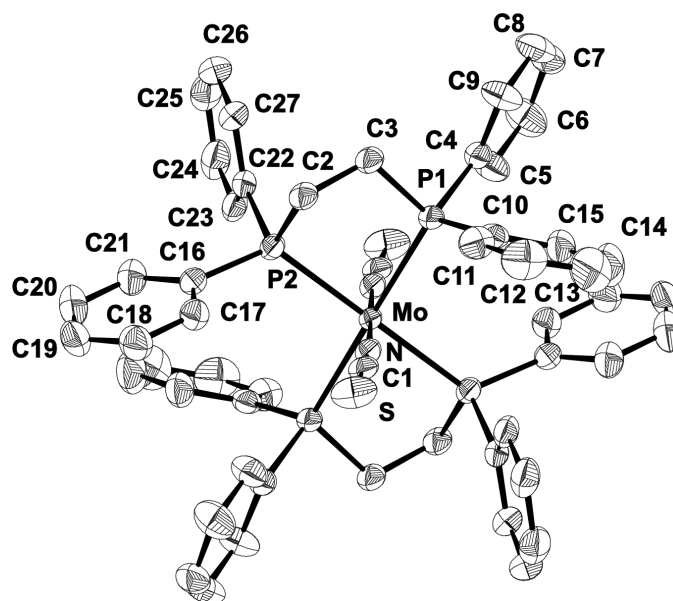


Figure 1

The molecular structure of (1α), showing 50% probability displacement ellipsoids (DIAMOND; Brandenburg, 1999). Labels of atoms related by symmetry, all H atoms and the disordered solvent molecule have been omitted for clarity.

The disordered toluene solvent molecule occupies two close positions with half-occupancy; these are related by inversion symmetry. Only five resolved atomic positions could be localized and refined isotropically with an adequate site-occupancy model. Restraints for distances and angles in the molecule were applied.

Data collection: STADIA (Stoe & Cie, 1997); cell refinement: STADIA; data reduction: XRED (Stoe & Cie, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: SHELXL97.

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