metal-organic compounds

Dichloro(1,2-dimethoxyethane)-bis(tosylimido)molybdenum(VI), a versatile nitrene transfer reagent

Konstantin A. Rufanov*‡ and Burkhard Ziemer

Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, D-12489 Berlin, Germany
Correspondence e-mail: k_rufanov@gmx.de

In the title compound, [Mo$(C_7H_7NO_2S)_2Cl_2(C_4H_{10}O_2)$], the Mo—Cl bond lengths are 2.3730 (8) and 2.3842 (8) Å, the former being the shortest within the series of analogous structurally characterized bis(imido) Mo complexes. This fact clearly explains the very strong Lewis acidity of the metal centre in this complex and, as a result, its synthetic versatility as a nitrene transfer reagent towards different phosphanes and strained cycloolefins.

Comment

The title compound, (I), was first reported in 1999 (Korn *et al.*, 1999). The authors reported its reaction with P$(CH_3)_3$, when one tosylimide group is transferred to the P atom. We have recently found that compound (I) reacts readily with different alkyl- and arylphosphanes and also with some strained cycloalkenes, easily transferring the nitrene group (Rufanov, 2006). Analogous bis(arylimido) complexes do not react in this way. In order to explain the reactivity of (I), we have studied its crystal structure (Fig. 1) and present the results here.
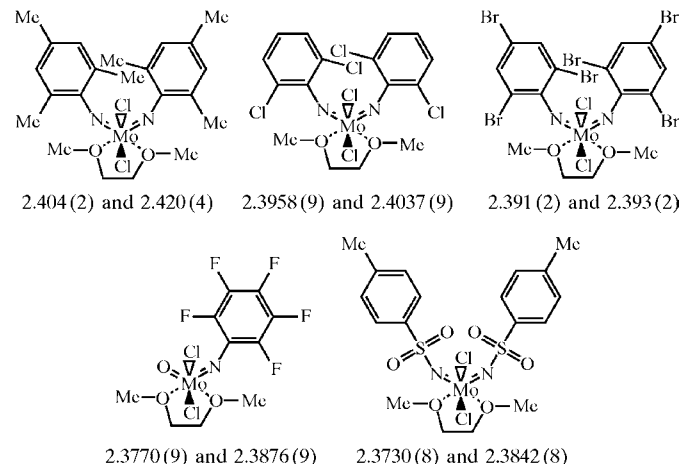

(I)
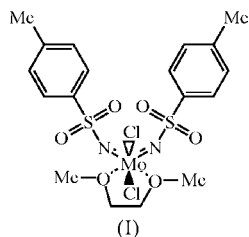
We assumed that the reactivity of bis(imido) complexes in nitrene transfer strongly depends on the Lewis acidity of the Mo centre. As the 'probe' for this, we have used the range of the Mo—Cl bond lengths. For the title Mo complex, we found values of 2.3730 (8) and 2.3842 (8) Å, which are almost equal to the Mo—Cl bond lengths in the structure of the mixed oxo–

‡ Current address: Leibniz-Institut für Organische Katalyse an der Universität Rostock, Albert-Einstein-Straße 29A, D-18059 Rostock, Germany.

imido Mo complex $(C_6F_5N)Mo(O)Cl_2$(dme) [2.3770 (9) and 2.3876 (9) Å; dme is 1,2-dimethoxyethane; Rufanov *et al.*, 2001] and very close to the values of 2.347 (4) and 2.340 Å found in the molecular structure of the dioxo analogue MoO_2Cl_2(dme) (Kamenar *et al.*, 1982). Comparison of this parameter with the known structures of similar bis(arylimido) Mo complexes confirms that the Mo—Cl bond lengths in (I) are the shortest in the whole series (Fig. 2). Therefore, we have confirmed our initial assumption about the role of the Lewis acidity of the Mo centre for the reactivity of bis(imido) Mo complexes in the nitrene transfer reaction. We have found that the title complex has the highest Lewis acidity within this series of complexes, *i.e.* comparable with Mo–oxo complexes, which are well known as efficient oxo-group transfer reagents.
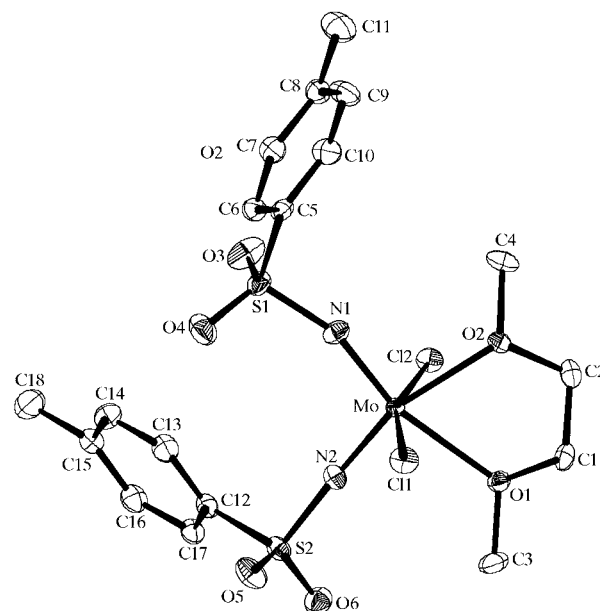
Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

2.404 (2) and 2.420 (4) 2.3958 (9) and 2.4037 (9) 2.391 (2) and 2.393 (2)

2.3770 (9) and 2.3876 (9) 2.3730 (8) and 2.3842 (8)

Figure 2
The series of Mo complexes and the Mo—Cl bond lengths (Å) used as the probe for comparison of molybdenum Lewis acidity in this series.

This clearly explains the high reactivity of (I) and its versatility as a nitrene transfer reagent.

Experimental

The title compound was synthesized according to the procedure of Korn *et al.* (1999). Crystallization was achieved by very slow cooling of a hot saturated toluene solution to room temperature.

Crystal data

[Mo(C7H7NO2S)2Cl2(C4H10O2)]
$M_r = 595.35$
Monoclinic, $P2_1/n$
$a = 11.895 (2)$ Å
$b = 13.124 (2)$ Å
$c = 15.564 (3)$ Å
$\beta = 104.66 (2)°$
$V = 2350.7 (7)$ Å^3
$Z = 4$

$D_x = 1.682$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5000 reflections
$\theta = 2.5–25.0°$
$\mu = 1.00$ mm^{-1}
$T = 150 (2)$ K
Block, dark yellow
$0.60 \times 0.32 \times 0.16$ mm

Data collection

Stoe IPDS diffractometer
φ oscillation scans (increment 1.2°, 200 exposures)
Absorption correction: part of the refinement model (ΔF) [*ABSCOR* (Higashi, 1995), a modification of *DIFABS* (Walker & Stuart, 1983); in contrast with *DIFABS*, *ABSCOR* loads F^2

values instead of F values.
$T_{min} = 0.585$, $T_{max} = 0.856$
15274 measured reflections
4329 independent reflections
3598 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 25.5°$
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.071$
$S = 1.05$
4329 reflections
284 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

H atoms were positioned geometrically and treated as riding, with C—H distances in the range 0.95–0.99 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

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

References

Brandenburg, K. & Berndt, M. (1999). *DIAMOND*. Release 2.1b. Crystal Impact GbR, Bonn, Germany.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Kamenar, B., Penavic, M., Korpar-Colig, B. & Markovic, B. (1982). *Inorg. Chim. Acta*, **65**, L245–L247.
Korn, K., Schorm, A. & Sundermeyer, J. (1999). *Z. Anorg. Allg. Chem.* **625**, 2125–2132.
Rufanov, K. A. (2006). In preparation.
Rufanov, K. A., Zarubin, D. N., Ustynyuk, N. A., Gourevitch, D. N., Sundermeyer, J., Churakov, A. V. & Howard, J. A. K. (2001). *Polyhedron*, **20**, 379–385.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Stoe & Cie (1997). *IPDS*. Version 2.79. Stoe & Cie, Darmstadt, Germany.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.