Polyhedron Vol. 8, No. 13/14, pp. 1786–1787, 1989
Printed in Great Britain

0277–5387/89 \$3.00+.00

REACTIVITY OF SEVEN-COORDINATE MOLYBDENUM(II) AND TUNGSTEN(II) ISOCYANIDE COMPLEXES: THE CRYSTAL STRUCTURE OF $[\mathrm{MoCl(CNBu}^t)_4(\mathrm{PMe}_3)_2]\mathrm{Cl}$

M. J. FERNANDEZ-TRUJILLO, M. JIMENEZ-TENORIO and M. C. PUERTA

Departamento de Quimica Inorganica, Facultad de Ciencias, Universidad de Cadiz,
Puerto Real, Cadiz, Spain

and

D. L. HUGHES*

AFRC Institute of Plant Science Research, Nitrogen Fixation Laboratory,
University of Sussex, Brighton BN1 9RQ, U.K.

Abstract—The seven-coordinate isocyanide complexes $[\mathrm{MCl}_2(\mathrm{CNBu}^t)_3(\mathrm{PMe}_3)_2]$ (M = Mo or W), react with additional CNBu^t yielding the derivatives $[\mathrm{MCl(CNBu}^t)_4(\mathrm{PMe}_3)_2]\mathrm{Cl}$. The crystal structure of the $[\mathrm{MoCl(CNBu}^t)_4(\mathrm{PMe}_3)_2]\mathrm{Cl}$ complex shows an almost perfect two-fold symmetry for the cation $[\mathrm{MoCl(CNBu}^t)_4(\mathrm{PMe}_3)_2]^+$ along the Mo—Cl bond, and two different possible orientations for the *t*-butyl groups. The reaction of $[\mathrm{MCl}_2(\mathrm{CNBu}^t)_3(\mathrm{PMe}_3)_2]$ (M = Mo or W) with anhydrous SnCl_2 yields complexes containing the SnCl_3^- ligand, derived from the insertion of SnCl_2 into the metal–halide bond.

We have been studying the reactivity of 16-electron six-coordinate molybdenum(II) and tungsten(II) species towards organic isocyanides, which allowed us to isolate $[\mathrm{MCl}_2(\mathrm{CNBu}^t)_3(\mathrm{PMe}_3)_2]$ (M = Mo or W).[1] Spectroscopic data for these complexes supported a capped-octahedral structure, with *trans*-phosphines for the molybdenum complex and *cis*- for the tungsten derivative, although fluxional behaviour was also observed.

These complexes react with additional CNBu^t to give $[\mathrm{MCl(CNBu}^t)_4(\mathrm{PMe}_3)_2]\mathrm{Cl}$. Spectroscopic data for these derivatives suggest a capped trigonal prismatic structure, with the chloride ligand in the capping position, as was found for the parent derivatives $[\mathrm{MX(CNR)}_6]\mathrm{X}$.[2] This has been confirmed by an X-ray structure analysis for the $[\mathrm{MoCl(CNBu}^t)_4\ (\mathrm{PMe}_3)_2]\mathrm{Cl}$ complex, which crystallizes as $[\mathrm{MoCl(CNBu}^t)_4(\mathrm{PMe}_3)_2]\mathrm{Cl}\cdot 2\mathrm{Me}_2\mathrm{CO}$ in the monoclinic system, space group $P2_1$, with $a = 11.563(6)$, $b = 18.722(2)$, $c = 11.202(2)$ Å, $\beta = 103.67(1)^\circ$ and $Z = 2$.

The crystal is composed of a lattice of molybdenum-complex cations and chloride anions. There are also large regions which, at the time of crystallization, contain acetone(solvent) molecules. There are two distinct solvent sites, each occupied by an acetone molecule, but these solvent molecules do not appear to have any well-defined positions or orientations in these regions.

The molybdenum complex cation $[\mathrm{MoCl(CNBu}^t)_4(\mathrm{PMe}_3)_2]^+$ has seven-fold coordination in a capped trigonal prismatic pattern. The chloro ligand is the capping atom on the rectangular face formed by two *trans*-phosphines and two *trans*-isocyanides. The opposite edge of the prism has the two remaining isocyanides at its ends. The cation has an almost perfect two-fold symmetry axis along the Mo—Cl bond. As is quite common in related $\mathrm{Mo(CNBu}^t)_n$ complexes, there are two possible orientations for each of the *t*-butyl groups, although only one is shown in the figure for clarity.

The reaction of $[\mathrm{MCl}_2(\mathrm{CNBu}^t)_3(\mathrm{PMe}_3)_2]$ with an excess of SnCl_2 allows the isolation of yellow–orange $[\mathrm{M(SnCl}_3)(\mathrm{CNBu}^t)_3(\mathrm{PMe}_3)_3](\mathrm{SnCl}_3)$ (M = Mo or W). These compounds are formally

---

* Author to whom correspondence should be addressed.

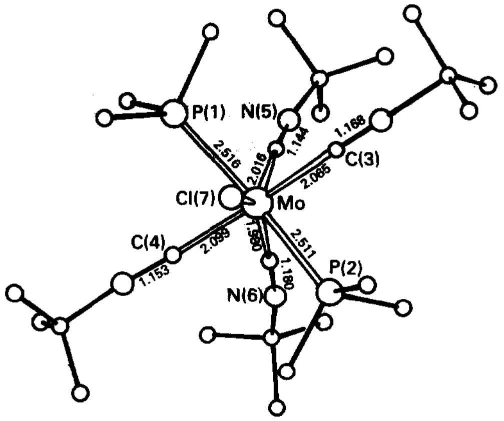

Fig. 1. Diagrammatic representation of the molecular structure of the cation $[MoCl(CNBu^t)_4(PMe_3)_2]^+$, showing selected bond lengths.

derived from the insertion of $SnCl_2$ into the metal–halide bond. ^{119}Sn NMR spectroscopy shows a quartet for coordinated $SnCl_3^-$ coupled with three phosphorus atoms, and a singlet for $SnCl_3^-$ in the external coordination sphere. This, together with ^1H and $^{31}P\{^1H\}$ NMR data, supports a capped-octahedral structure, with $SnCl_3^-$ as the capping ligand, and *fac*-arrangement of phosphines and isocyanides.

REFERENCES

1. M. Jimenez-Tenorio and M. C. Puerta-Vizcaino, *XVIII I.C.C.C.*, B12. Oporto, Portugal (1988).
2. S. J. Lippard, P. A. Bianconi, I. D. Williams and M. P. Engeler, *J. Am. Chem. Soc.* 1986, **108**, 311.