

Inorganica Chimica Acta

LETTER

The preparation of the novel seven-coordinate compound $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})_2]$ and its reactions with one equivalent of L ($\text{L} = \text{PPh}_3$, AsPh_3 or SbPh_3) to give $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})\text{L}]$ or $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_2(\text{NCMe})_2\text{L}]$ depending upon the solvent

Paul K. Baker* and Dafydd ap Kendrick
Department of Chemistry, University of Wales, Bangor,
Gwynedd LL57 2UW (U.K.)

(Received May 31, 1991; revised July 21, 1991)

Many seven-coordinate dihalocarbonyl complexes of the type $[\text{MX}_2(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mo}$ or W ; $\text{X} = \text{Cl}$, Br or I ; $\text{L} = \text{Group 5 donor ligand}$) have been prepared [1]. The importance of these compounds has been highlighted by the catalytic activity of $[\text{MX}_2(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mo}$ or W ; $\text{X} = \text{Cl}$ or Br ; $\text{L} = \text{PPh}_3$ or AsPh_3) for the ring-opening polymerisation of norbornene and norbornadiene [2]. However, analogous halogermanium compounds are scarce; some early examples of this type which have been reported are $[\text{MoX}(\text{GeX}_3)(\text{CO})_3(\text{bipy})]$ ($\text{X} = \text{Cl}$ or I) [3]. In this communication we describe the synthesis of the novel highly reactive seven-coordinate compound $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})_2]$ (1), and report its reactions with 1 equiv. of L ($\text{L} = \text{PPh}_3$, AsPh_3 or SbPh_3) in CH_2Cl_2 and NCMe .

Results and discussion

Equimolar quantities of $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ (prepared *in situ* by reacting $[\text{Mo}(\text{CO})_6]$ in refluxing acetonitrile for 24 h [4]) and GeCl_4 react *in situ* to afford an orange solution which after removal of the solvent *in vacuo* gives the golden yellow solid $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})_2]$ (1) in high yield. This reaction presumably occurs by oxidative-addition of the zero-valent complex $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$ with

GeCl_4 to give via cleavage of a $\text{Ge}-\text{Cl}$ bond and elimination of an acetonitrile molecule the oxidized product 1. Compound 1 is very air-sensitive in the solid state and extremely air-sensitive in solution, however it can be stored under nitrogen for prolonged periods of time. Compound 1 is soluble in polar solvents such as CHCl_3 , CH_2Cl_2 , NCMe or $\text{OC}(\text{Me})_2$, however it is only very slightly soluble in hydrocarbon solvents and Et_2O . Complex 1 has been characterised by IR (Table 1), ^1H NMR spectroscopy (Table 2) and elemental analysis (C, H and N) (Table 3). The structure of 1 is likely to be capped octahedral since most seven-coordinate $[\text{MX}_2(\text{CO})_3\text{L}_2]$ complexes have this geometry [5]. The related diido compound $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ has been shown by X-ray crystallography [6] to have the structure shown in Fig. 1, where the two iodide ligands have been replaced by a chloride ligand on the capping face and the considerably larger GeCl_3 group on the uncapped face, which may be the structure of 1.

The reactions of $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})_2]$ (1) with an equimolar amount of L ($\text{L} = \text{PPh}_3$, AsPh_3 or SbPh_3) in CH_2Cl_2 at room temperature gave the acetonitrile displaced products $[\text{MoCl}(\text{GeCl}_3)-$

TABLE 1. IR data* for the complexes $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})_2]$, $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})\text{L}]$ and $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_2(\text{NCMe})_2\text{L}]$

Complex	$\nu(\text{C}\equiv\text{O})$ (cm^{-1})	$\nu(\text{N}\equiv\text{C})$ (cm^{-1})
1	2040(s), 1953(s), 1877(m)	2314(m), 2286(m)
2	2025(m), 1940(s), 1870(s)	2300(w), 2280(w)
3	2020(m), 1930(s), 1875(s)	2300(w), 2280(w)
4	2020(s), 1925(s), 1860(s)	2300(w), 2280(w)
5	1945(s), 1870(s)	2300(w), 2280(w)
6	1945(s), 1875(s)	2300(w), 2285(w)
7	1945(s), 1880(s)	2300(w), 2285(w)

*Spectra recorded as thin films in CHCl_3 between NaCl plates; s, strong; m, medium; w, weak.

TABLE 2. ^1H NMR data for the complexes $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})_2]^a$, $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})\text{L}]^a$ and $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_2(\text{NCMe})_2\text{L}]^b$

Complex	^1H NMR (δ) (ppm)
1	2.45 (s, Me)
2	7.4 (m, 15H, Ph); 2.4 (s, 3H, Me)
3	7.35 (m, 15H, Ph); 2.4 (s, 3H, Me)
4	7.6, 7.45, 7.35 (m, 15H, Ph); 2.2 (s, 3H, Me)
5	7.40 (m, 15H, Ph); 2.35 (s, 6H, Me)
6	7.35 (m, 15H, Ph); 2.3 (s, 6H, Me)
7	7.6, 7.45, 7.35 (m, 15H, Ph); 2.3 (s, 6H, Me)

^aSpectra recorded in CDCl_3 (25 °C) and referenced to Me_4Si . ^bSpectra recorded in CD_3COCD_3 (25 °C).

*Author to whom correspondence should be addressed.

TABLE 3. Physical and analytical data for the complexes $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})_2]$, $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})\text{L}]$ and $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_2(\text{NCMe})_2\text{L}]$

Compound	Colour	Yield (%)	Analysis (%) ^a			Reaction times
			C	H	N	
$[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})_2]$ (1)	golden brown	94	17.2 (17.6)	1.5 (1.3)	6.1 (5.9)	
$[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})(\text{PPh}_3)]$ (2)	golden brown	53	39.2 (39.6)	2.7 (2.6)	1.5 (2.0)	1 min
$[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})(\text{AsPh}_3)]$ (3)	golden brown	53	37.6 (37.2)	2.5 (2.4)	1.5 (1.9)	3 min
$[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})(\text{SbPh}_3)]$ (4)	orange	50	34.7 (35.0)	2.4 (2.3)	1.4 (1.8)	5 min
$[\text{MoCl}(\text{GeCl}_3)(\text{CO})_2(\text{NCMe})_2(\text{PPh}_3)]$ (5)	yellow	47	40.1 (40.6)	2.4 (3.0)	3.7 (3.9)	18 h ^b
$[\text{MoCl}(\text{GeCl}_3)(\text{CO})_2(\text{NCMe})_2(\text{AsPh}_3)]$ (6)	yellow	41	37.7 (38.2)	2.7 (2.8)	3.4 (3.7)	18 h ^b
$[\text{MoCl}(\text{GeCl}_3)(\text{CO})_2(\text{NCMe})_2(\text{SbPh}_3)]$ (7)	yellow	44	36.0 (36.0)	2.6 (2.6)	3.2 (3.5)	18 h ^b

^aCalculated values in parentheses. ^bA precipitate of the products started to form after 1, 3 and 5 min for 5 and 6 and 7, respectively; however, these reactions were left overnight to obtain a higher yield.

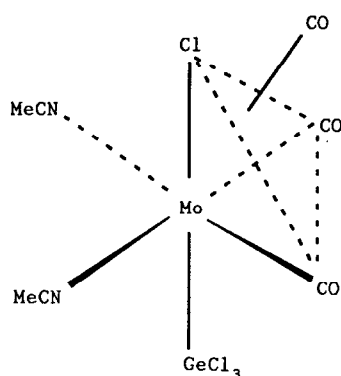


Fig. 1. Proposed structure of the seven-coordinate complex $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_3(\text{NCMe})_2]$ (1).

$(\text{CO})_3(\text{NCMe})\text{L}]$ (2–4) in good yield. Compounds 2–4 have been characterised by elemental analysis, IR and ^1H NMR spectroscopy (Tables 1–3). However, equimolar quantities of 1 and L ($\text{L} = \text{PPh}_3$, AsPh_3 or SbPh_3) react in NCMe to give, after initial effervescence of CO, the bis-acetonitrile complexes $[\text{MoCl}(\text{GeCl}_3)(\text{CO})_2(\text{NCMe})_2\text{L}]$ (5–7). Complexes 5–7 have also been characterised by elemental analysis (Table 3), IR (Table 1) and ^1H NMR spectroscopy (Table 2). Compounds 2–7 are all considerably more stable than 1. The mono-acetonitrile compounds 2–4

are more soluble in polar solvents than the bis-acetonitrile complexes 5–7.

References

- (a) F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, **3** (1964) 1609; (b) W. S. Tsang, D. W. Meek and A. Wojcicki, *Inorg. Chem.*, **7** (1968) 1263; (c) R. Colton and G. P. Scollary, *Aust. J. Chem.*, **21** (1968) 1435; (d) J. R. Moss and B. L. Shaw, *J. Chem. Soc. A.*, (1970) 595; (e) R. Colton, *Coord. Chem. Rev.*, **6** (1971) 269; (f) A. D. Westland and N. Muriithi, *Inorg. Chem.*, **12** (1973) 2356; (g) P. K. Baker, S. G. Fraser and E. M. Keys, *J. Organomet. Chem.*, **309** (1986) 319; (h) P. K. Baker and S. G. Fraser, *Inorg. Chim. Acta*, **130** (1987) 61; (i) P. K. Baker and S. G. Fraser, *Transition Met. Chem.*, **12** (1987) 560; (j) P. K. Baker, S. G. Fraser and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, (1988) 2729; (k) K. -B. Shu, K. S. Lion, S. L. Wang and S. C. Wei, *Organometallics*, **9** (1990) 669.
- (a) L. Bencze and A. Kraut-Vass, *J. Mol. Catal.*, **28** (1985) 369; (b) L. Bencze, A. Kraut-Vass and L. Prókai, *J. Chem. Soc., Chem. Commun.*, (1985) 911.
- R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7** (1968) 310.
- D. P. Tate, W. R. Knipple and J. M. Augl, *Inorg. Chem.*, **1** (1962) 433.
- M. G. B. Drew, *Prog. Inorg. Chem.*, **23** (1977) 67, and refs. therein.
- M. G. B. Drew, P. K. Baker, E. M. Armstrong and S. G. Fraser, *Polyhedron*, **7** (1988) 245.