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REACTIONS OF THE MOLYBDENUM COMPLEX $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ WITH ONE EQUIVALENT OF L $\{L = PPh_3, AsPh_3, SbPh_3, py, 3Br—py, 4Br—py$ AND $P(OPh)_3\}$ TO GIVE $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3L]_2$. BRIDGE CLEAVAGE REACTIONS OF $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(PPh_3)]_2$

PAUL K. BAKER* and **ADRIAN BURY**

Department of Chemistry, University College of North Wales, Bangor,
Gwynedd LL57 2UW, U.K.

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Abstract—The seven-coordinate molybdenum complex $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ reacts rapidly with 1 equivalent of L [L = PPh_3, $AsPh_3$, $SbPh_3$, py, 3Br—py, 4Br—py and $P(OPh)_3$], in acetone at room temperature, to afford the chloro-bridged compounds $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3L]_2$. The triphenylphosphine dimer $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(PPh_3)]_2$ reacts with 2 equivalents of L′ [L′ = PPh_3, $SbPh_3$, py and $P(OPh)_3$] to give the bridge-cleaved mononuclear compounds $[MoCl(SnCl_3)(CO)_3LL']$.

Recent interest in seven-coordinate complexes has been highlighted by Bencze *et al.*[1,2] They showed the seven-coordinate complexes $[MX_2(CO)_3L_2]$ (M = Mo or W; X = Cl or Br; L = PPh_3 or $AsPh_3$) to be active alkene metathesis catalysts for the ring-opening polymerization of norbornene and norbornadiene.[1,2] Although many examples of seven-coordinate dihalo complexes of the type $[MX_2(CO)_3L_2]$ (M = Mo or W; X = Cl, Br or I; L = neutral donor ligands) have been prepared,[3–11] very few analogous halotin compounds such as $[MX(SnX_3)(CO)_3L_2]$ have been reported.[12–14] Very recently we have described the preparation of the reactive seven-coordinate halotin complex, $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$, from reaction of the zero-valent complex $[Mo(CO)_3(NCMe)_3]$ *in situ* with an equimolar quantity of $SnCl_4$.[15]

In this paper we wish to describe the reactions of $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ with 1 equivalent of monodentate neutral donor ligand (L) to rapidly give the chloro-bridged complexes $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3L]_2$. The bridge cleavage reactions of $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3L]_2$ are also described herein.

EXPERIMENTAL

All reactions described in this paper were carried out under an atmosphere of dry nitrogen using standard Schlenk line techniques.

The complex $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ was prepared by the published method.[15] $[Mo(CO)_6]$ was generously donated by Amax Speciality Metals U.K. Ltd. All other chemicals were purchased from commercial sources.

Elemental analyses for carbon, hydrogen and nitrogen were recorded on a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas). IR spectra were recorded on a Perkin–Elmer 1430 ratio recording IR spectrophotometer. Magnetic susceptibilities of the complexes were measured on a Johnson-Matthey Magnetic Susceptibility balance. The molecular weight of $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(py)]_2$ (**4**) was determined by Rast's method[16] using camphor as the solvent.

$[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(PPh_3)]_2$ (1)

To $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ (4.03 g, 7.7 mmol) dissolved in acetone (50 cm^3) with continuous stirring under a stream of dry nitrogen, was added PPh_3 (2.02 g, 7.7 mmol). After stirring for 30 s, filtration and removal of the solvent *in vacuo* gave light brown crystals of $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(PPh_3)]_2$ (**1**) (yield = 5.31 g, 98%), which were recrystallized from acetone.

Similar reactions of $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ with 1 equivalent of L [L = $AsPh_3$, $SbPh_3$, py, 3Br—py, 4Br—py and $P(OPh)_3$] in ace-

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* Author to whom correspondence should be addressed.

Table 1. Physical and analytical[a] data for the complexes $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3L]_2$ and $[MoCl(SnCl_3)(CO)_3LL']$

Complex	Colour	Yield	C	H	N
$[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(PPh_3)]_2$ (**1**)	Orange–brown	98	36.1	3.1	—
			(35.9)	(2.2)	—
$[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(AsPh_3)]_2$ (**2**)	Light brown	75	34.2	2.7	—
			(33.8)	(2.0)	—
$[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(SbPh_3)]_2$ (**3**)	Light brown	80	31.5	2.1	—
			(31.8)	(1.9)	—
$[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(py)]_2$ (**4**)	Brown	92	18.3	1.4	2.9
			(18.5)	(1.0)	(2.7)
$[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(3Br\text{—}py)]_2$ (**5**)	Brown	78	16.4	1.0	2.2
			(16.1)	(0.7)	(2.3)
$[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(4Br\text{—}py)]_2$ (**6**)	Brown	80	15.3	0.8	2.2
			(16.1)	(0.7)	(2.3)
$[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3\{P(OPh)_3\}]_2$ (**7**)	Brown	64	34.2	2.6	—
			(33.6)	(2.0)	—
$[MoCl(SnCl_3)(CO)_3(PPh_3)_2]$ (**8**)	Yellow	69	48.4	3.4	—
			(48.5)	(3.1)	—
$[MoCl(SnCl_3)(CO)_3(PPh_3)(SbPh_3)]$ (**9**)	Orange–yellow	74	45.3	3.0	—
			(44.4)	(2.9)	—
$[MoCl(SnCl_3)(CO)_3(py)(PPh_3)]$ (**10**)	Orange–yellow	90	40.6	2.2	1.8
			(39.9)	(2.6)	(1.8)
$[MoCl(SnCl_3)(CO)_3(PPh_3)\{P(OPh)_3\}]$ (**11**)	Brown	88	45.7	3.2	—
			(46.2)	(3.0)	—

[a] Calculated values in parentheses.

tone at room temperature after stirring for 30 s, afforded the analogous chloro-bridged complexes $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3L]_2$ (**2**–**7**) (see Table 1 for colour and yields). Molecular weight determination for $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(py)]_2$: Found: 872, Calc: 1039.

Reaction of $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(PPh_3)]_2$ *with* 2 *equivalents of* PPh_3

To $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(PPh_3)]_2$ (0.70 g, 0.5 mmol) dissolved in acetone (15 cm^3) with continuous stirring under a stream of dry nitrogen, was added PPh_3 (0.26 g, 1 mmol). After stirring for 30 min, filtration and removal of the solvent *in vacuo* gave bright yellow crystals of $[MoCl(SnCl_3)(CO)_3(PPh_3)]_2$ (**8**) (yield = 0.66 g, 69%), which were recrystallized from acetone.

Similar reactions of $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(PPh_3)]_2$ with 2 equivalents of L′ [L′ = $SbPh_3$, py and $P(OPh)_3$] gave $[MoCl(SnCl_3)(CO)_3(PPh_3)L]$ (**8**–**11**) (see Table 1 for colours and yields).

RESULTS AND DISCUSSION

Equimolar quantities of the bisacetonitrile complex $[MoCl(SnCl_3)(CO)_3(NCMe)_2]$ and L [L = PPh_3, $AsPh_3$, $SbPh_3$, py, 3Br—py, 4Br—py and $P(OPh)_3$] react in acetone at room temperature to give good yields of the new chloro-bridged dimers $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3L]_2$ (**1**–**7**). The triphenylphosphine dimer $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(PPh_3)]_2$ (**1**) reacts with 2 equivalents of L′ [L′ = PPh_3, $SbPh_3$, py and $P(OPh)_3$] in acetone at room temperature, to give the symmetrical bridge-cleaved products $[MoCl(SnCl_3)(CO)_3LL']$ (**8**–**11**). The complexes, **1**–**11**, were characterized by elemental analysis (C, H and N) (Table 1) and IR spectroscopy (Table 2). All the complexes were found to be diamagnetic, which was expected since the complexes obey the effective atomic number rule. The dimers **1**–**7** are photosensitive and thermally unstable, however they can be stored in the dark under a nitrogen atmosphere at 0°C for several days. The monomeric complexes, **8**–**11**, are more stable than the dimers, but are still stored in Schlenk tubes under nitrogen. The complexes, **1**–**11**, are only slightly soluble in chlorinated solvents such as $CHCl_3$ or CH_2Cl_2, however they are much more soluble in acetone (see Experimental).

Reaction of $[MoCl(SnCl)_3(CO)_3(NCMe)_2]$ with 1 equivalent of L [L = PPh_3, $AsPh_3$, $SbPh_3$, py, 3Br—py, 4Br—py and $P(OPh)_3$] probably initially affords the monoacetonitrile complexes $[MoCl(SnCl_3)(CO)_3(NCMe)L]$. Several attempts

Table 2. IR data[a] for the complexes $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3L]_2$ and $[MoCl(SnCl_3)(CO)_3LL']$

Complex	ν(CO) (cm^{-1})
(1)	2077, 2051, 1959, 1941, 1873 and 1708
(2)	2050, 2040, 1966, 1959, 1945 and 1879
(3)	2040, 1937 and 1868
(4)	2034, 1948 and 1940
(5)	2025, 1946, 1940, 1927, 1919 and 1915
(6)	2025, 1947, 1940, 1929, 1927 and 1916
(7)	2002, 1959, 1929 and 1902
(8)	1964, 1950 and 1882
(9)	1947, 1941 and 1877
(10)	1958, 1946 and 1940
(11)	1980, 1945 and 1881

[a] Spectra recorded as $CHCl_3$ thin films between NaCl plates.

were made to isolate these monoacetonitrile intermediates by rapid work-up procedures without success. Evidence to support the initial formation of these monoacetonitrile intermediates comes from related work we have carried out on the related diiodo system $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W). The complexes $[MI_2(CO)_3(NCMe)_2]$, react with 1 equivalent of L [L = PPh_3, $AsPh_3$, $SbPh_3$, PPh_2Cy and $P(OPh)_3$] in CH_2Cl_2 to give the monoacetonitrile complexes $[MI_2(CO)_3(NCMe)L]$, which were isolated and fully characterized.[17] The apparent greater ease of dimerization of $[MoCl(SnCl_3)(CO)_3(NCMe)L]$ compared to the diiodo analogues, may be due to the steric bulk of the $SnCl_3$ group. Seven-coordinate complexes of molybdenum(II) and tungsten(II) are highly crowded and coordinatively saturated, hence it is highly likely that the substitution reactions go via a dissociative mechanism. Hence, the bulky $SnCl_3$ group attached to the metal should facilitate easy loss of acetonitrile from $[MoCl(SnCl_3)(CO)_3(NCMe)L]$ to give the dimers $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3L]_2$. The dimeric nature of the complexes $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3L]_2$ was confirmed by molecular weight measurements on $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(py)]_2$ (4) by Rast's method[16] (see Experimental).

It is highly likely that the dimeric complexes, 1–7, are bridged via the chloride ion rather than the $SnCl_3$ group, since $SnCl_3$ does not possess a dative lone pair on the tin (apart from the attached chlorine atoms) to coordinate to the other molybdenum atom. It is improbable that chloride groups on the tin bridge, since there are no precedents for this type of behaviour. Several attempts were made to grow a single crystal for X-ray crystallography of the dimers $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3L]_2$ (1–7), but due to the instability of these complexes no success was achieved. However, since the structure of the bromide-bridged dimer $[W(\mu\text{-}Br)Br(CO)_4]_2$ shows the two tungsten atoms to be in capped octahedral environments,[18] it is highly likely that these $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3L]_2$ (1–7) complexes have this type of geometry.

Symmetric cleavage of the chloride bridges in the complexes $[Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3(PPh_3)]_2$ (1), by L′ to give monomeric seven-coordinate complexes of the type $[MoCl(SnCl_3)(CO)_3(PPh_3)L']$, are similar to the symmetric bridge cleavage reactions carried out on the octacarbonyl halo-bridged dimers of the type $[M(\mu\text{-}X)X(CO)_4]_2$ (M = Mo or W; X = Cl, Br or I) described by Colton and his coworkers.[19] Since the IR spectra of the compounds $[MoCl(SnCl_3)(CO)_3(PPh_3)L']$ (**8–11**) show three carbonyl stretching bands (Table 2) with a similar pattern to analogous dihalo complexes of the type $[MX_2(CO)_3L_2]$ which have been shown to have capped octahedral geometry by X-ray crystallography,[20–28] it is likely that complexes **8–11** have this geometry.

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