

Journal of Organometallic Chemistry, 399 (1990) 149–152
Elsevier Sequoia S.A., Lausanne
JOM 21216

Imido ligand exchange at a molybdenum(V) centre

Graeme Hogarth^{*,*} and Peter C. Konidaris

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR (UK)

(Received June 18th, 1990)

Abstract

Reaction of the dimolybdenum tetraimido complex $[(\text{MeC}_5\text{H}_4)\text{Mo}(\text{NPh})(\mu\text{-NPh})]_2$ with an excess of *para*-tolyl isocyanate results in the stepwise exchange of terminal imido ligands to yield $[(\text{MeC}_5\text{H}_4)_2\text{Mo}_2(\text{N-}p\text{-tolyl})(\text{NPh})(\mu\text{-NPh})_2]$ and $[(\text{MeC}_5\text{H}_4)\text{Mo}(\text{N-}p\text{-tolyl})(\mu\text{-NPh})]_2$. Prolonged heating does not, however, result in substitution of the bridging phenylimido ligands.

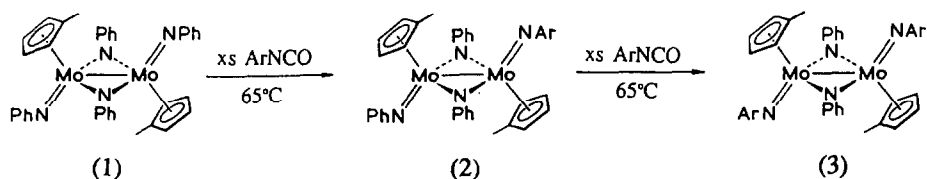
Introduction

The replacement of one multiply bonded ligand by another at a transition metal centre upon treatment with an unsaturated reagent is a well known process suggested to occur via a Wittig-like $(2 + 2)\pi$ rearrangement [1]. Reactions of this type have been extensively utilised in the synthesis of metal–ligand multiple bonds, being especially successful in the synthesis of organoimido functionalities starting from either alkylidene [2] or oxo [3] moieties. In this latter process, isocyanates have proved to be particularly versatile reagents, effecting the transformation at a large number of transition metal centres [4]. Indeed, we have recently been successful in utilising this approach to generate organoimido ligands at molybdenum(V) centres [5]. Other examples of this class of reaction include the catalytic metathesis of olefins [6], alkynes [7], and carbodiimides [8], the first two being of industrial importance. Surprisingly in this context, the metathesis of isocyanates by transition metal imido complexes has not been reported. Such a process will, however, result in the exchange of imido moieties at the transition metal centre. We report here preliminary studies which show that imido ligand exchange can be effected at a molybdenum(V) centre in the presence of isocyanates.

* Present address: Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ (UK)

Results and discussion

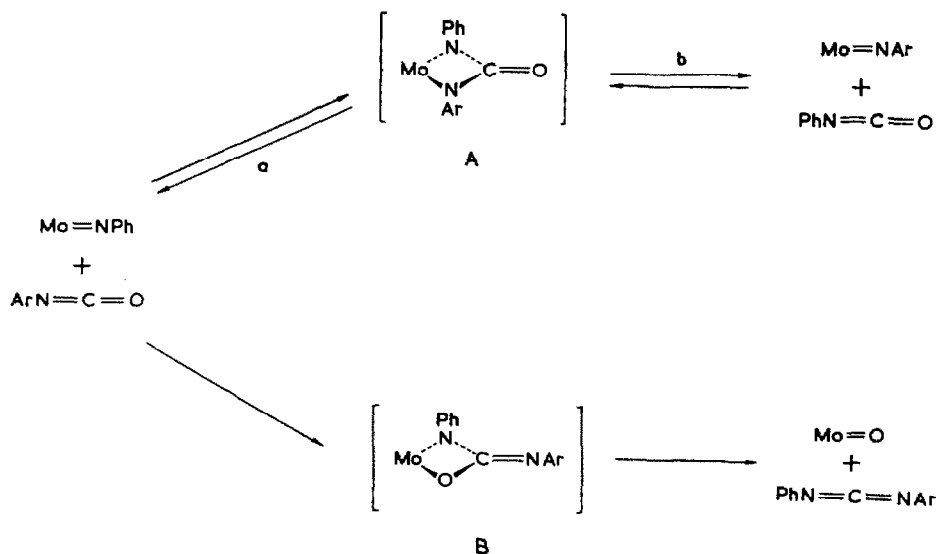
The thermolytic reaction of the tetraimido complex $[(\text{MeC}_5\text{H}_4)\text{Mo}(\text{NPh})(\mu\text{-NPh})]_2$ (**1**) with excess *para*-tolyl isocyanate in rigorously dried THF was monitored by ^1H NMR spectroscopy. Monitoring the high field region of the spectrum showed that over a period of two weeks, the methyl resonance of the cyclopentadienyli ligands of **1** at δ 1.15 gradually diminished whilst at δ 1.17 a new resonance attributed to the monosubstituted complex $[(\text{MeC}_5\text{H}_4)_2\text{Mo}_2(\text{N-}i>p\text{-tolyl})(\text{NPh})(\mu\text{-NPh})_2]$ (**2**) grew in. Over a period of four weeks, and before the resonance attributed to **1** had completely disappeared, a further new resonance at δ 1.19 developed. This signal, attributed to the disubstituted complex $[(\text{MeC}_5\text{H}_4)\text{Mo}(\text{N-}i>p\text{-tolyl})(\mu\text{-NPh})]_2$ (**3**), predominated after six weeks, and after approximately eight weeks conversion of **1** to **3** was complete.



Isolation of pure **3** from the reaction mixture did not prove possible due to contamination by isocyanate oligomers also formed during the reaction. The identities of **2** and **3** were, however, confirmed by their independent synthesis and characterisation. Thus, the monooxo complex $[(\text{MeC}_5\text{H}_4)_2\text{Mo}_2\text{O}(\text{NPh})(\mu\text{-NPh})_2]$ (**4**) and the bisoxo complex $[(\text{MeC}_5\text{H}_4)\text{MoO}(\mu\text{-NPh})]_2$ (**5**) react with excess *para*-tolyl isocyanate to yield **2** and **3** respectively in high yield. Both are orange air-stable crystalline solids readily characterised by analytical and spectroscopic techniques.

Further thermolysis of **3** with an excess of *para*-tolyl isocyanate did not, during an eight week period, lead to the exchange of bridging imido moieties, and **3** was recovered in high yield. The expected product of this transformation, namely the tetra-*para*-tolyl substituted complex $[(\text{MeC}_5\text{H}_4)\text{Mo}(\text{N-}i>p\text{-tolyl})(\mu\text{-N-}i>p\text{-tolyl})]_2$ has, however, been independently synthesised [5]. This pronounced difference in reactivity between the terminal and bridging imido moieties at molybdenum(V) centres has previously been noted with respect to their hydrolysis [5]. We have also previously addressed the possibility of terminal-bridge exchange in these complexes on the NMR timescale. High yield recovery of **3** after heating for eight weeks indicates that this process does not occur.

Whilst mechanistic details of the exchange process are not known, the reaction is assumed to proceed (as shown below) via a Wittig-like $(2+2)\pi$ transformation similar to that postulated for the exchange of oxo for imido ligands upon reaction with isocyanates [9]. The exchange of imido moieties via such a process is expected to be slower than that of oxo replacement since the $\text{M}=\text{O}$ fragment is more highly polarised than the $\text{M}=\text{NAr}$ moiety [1]. Addition of the imido moiety to the $\text{N}=\text{C}$ bond will result in a metallacycle **A** which can dissociate via two pathways, (a) and (b), the former resulting in regeneration of the starting imido complex and the latter producing the observed product. The presence of the excess of *para*-tolyl isocyanate (ArNCO) would drive the reaction to the right hand side. Indeed, a metallacycle of this type involving a rhenium centre has recently been isolated, its formation being



postulated to occur via addition of isocyanate to an intermediate imido complex [10]. We cannot however rule out a second process whereby addition of the isocyanate is across the carbonyl moiety. This metallacycle **B** may dissociate to give a carbodi-imide and a molybdenum oxide, the latter reacting further with *para*-tolyl isocyanate. We are currently trying to distinguish between these routes by attempting to detect phenylisocyanate or the carbodi-imide.

Experimental

All reactions were carried out under N_2 using predried solvents. ^1H NMR spectra were recorded on a Bruker AM300 spectrometer. IR spectra were recorded on a Perkin-Elmer 1710 FTIR spectrometer.

Reaction of $[(\text{MeC}_5\text{H}_4)_2\text{Mo}(\text{NPh})(\mu\text{-NPh})_2]$ (**1**) with *para*-tolyl isocyanate

A THF solution (30 cm^3) of **1** (0.2 g, 0.28 mmol) and *para*-tolyl isocyanate (0.4 cm^3 , 3.00 mmol) was heated to 70°C in a Young's ampoule. Samples, taken every week over an eight week period, were examined by ^1H NMR spectroscopy in C_6D_6 . After eight weeks, removal of solvent and excess isocyanate afforded, after washing with 40–60 petroleum ether, an orange powder identified as **3** by ^1H NMR and IR spectra. The NMR spectrum showed that the sample was contaminated with *para*-tolyl isocyanate oligomers ($\sim 20\%$).

Reaction of $[(\text{MeC}_5\text{H}_4)_2\text{Mo}_2\text{O}(\text{NPh})(\mu\text{-NPh})_2]$ (**4**) with *para*-tolyl isocyanate

Heating a THF solution (15 cm^3) of **4** (0.1 g, 0.16 mmol) and *para*-tolyl isocyanate (0.2 cm^3 , 1.50 mmol) at 70°C for 24 h resulted in a colour change from yellow to orange. Removal of solvent and excess isocyanate gave **2** (90 mg, 80%) as an orange powder. Crystallisation from 40–60 petroleum ether afforded an orange crystalline solid.

$[(\text{MeC}_5\text{H}_4)_2\text{Mo}_2(\text{N-}p\text{-tolyl})(\text{NPh})(\mu\text{-NPh}_2)]$ (**2**): Anal. Found: C,60.69; H,4.87; N,7.82. $\text{C}_{37}\text{H}_{36}\text{Mo}_2\text{N}_4$ calcd: C,61.15; H,4.96; N,7.71%. IR (CsI): 1321(s), 1265(s) cm^{-1} . ^1H NMR (C_6D_6) δ 8.10–6.70 (19H, m, C_6H_5 and $\text{C}_6\text{H}_4\text{Me}$), 5.84 (4H, t, J 3 Hz, MeC_5H_4), 5.15 (4H, t, J 3 Hz, MeC_5H_4), 1.98 (3H, MeC_6H_4), 1.17 (6H, MeC_5H_4).

*Reaction of $[(\text{MeC}_5\text{H}_4)\text{MoO}(\mu\text{-NPh})]_2$ (**5**) with para-tolyl isocyanate*

Heating a THF solution (20 cm^3) of **5** (0.1 g, 0.18 mmol) and *para*-tolyl isocyanate (0.2 cm^3 , 1.50 mmol) at 70 °C for 48 h resulted in a colour change from yellow to orange. Removal of solvent and excess isocyanate gave **3** (110 mg, 83%) as an orange powder. Crystallisation from 40–60 petroleum ether afforded an orange crystalline solid.

$[(\text{MeC}_5\text{H}_4)\text{Mo}(\text{N-}p\text{-tolyl})(\mu\text{-NPh})]_2$ (**3**): Anal. Found: C,61.41; H,5.19; N,7.37. $\text{C}_{38}\text{H}_{38}\text{Mo}_2\text{N}_4$ calcd: C,61.62; H,5.14; N,7.56%. IR (CsI): 1326(s), 1270(s) cm^{-1} . ^1H NMR (C_6D_6): δ 8.1–6.7 (18 H, m, C_6H_5 and $\text{C}_6\text{H}_4\text{Me}$), 5.86 (4H, t, J 3 Hz, MeC_5H_4), 5.18 (4H, t, J 3 Hz, MeC_5H_4), 2.07 (6H, MeC_6H_4), 1.19 (6H, MeC_5H_4).

*Reaction of $[(\text{MeC}_5\text{H}_4)\text{Mo}(\text{N-}p\text{-tolyl})(\mu\text{-NPh})]_2$ (**3**) with para-tolyl isocyanate*

A THF solution (20 cm^3) of **3** (0.1 g, 0.13 mmol) and *para*-tolyl isocyanate (1.0 cm^3 , 7.51 mmol) was heated at 70 °C for 8 weeks. Removal of solvent and excess isocyanate gave an orange powder shown to be unreacted **3** by ^1H NMR spectroscopy.

Acknowledgement

We thank Professor M.L.H. Green for support of this work.

References

- 1 W.A. Nugent and J.M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley-Interscience, New York, 1988, pp. 86–90 and references therein.
- 2 S.M. Rocklage and R.R. Schrock, *J. Am. Chem. Soc.*, 102 (1980) 7808; *idem*, *ibid*, 104 (1982) 3077.
- 3 J. Chatt and J.R. Dilworth, *J. Chem. Soc., Chem. Commun.*, (1972) 549; E.A. Maatta, B.L. Haymore, and R.A.D. Wentworth, *Inorg. Chem.*, 19 (1980) 1055.
- 4 I.S. Kolomnikov, Yu.D. Koreshkov, T.S. Lobeeva, and M.E. Volpin, *J. Chem. Soc., Chem. Commun.*, (1970) 1432; A.D. Horton, R.R. Schrock, and J.H. Freudenberger, *Organometallics*, 6 (1987) 893; D.C. Bradley, M.B. Hursthouse, K.M.A. Malik, A.J. Nielson, and R.L. Scott, *J. Chem. Soc., Dalton Trans.*, (1983) 2651; E.A. Maatta, *Inorg. Chem.*, 23 (1984) 2560.
- 5 M.L.H. Green, G. Hogarth, P.C. Konidaris, and P. Mountford, *J. Chem. Soc., Dalton Trans.*, in press.
- 6 S.M. Rocklage, J.D. Fellmann, G.A. Rupprecht, L.W. Messerle, and R.R. Schrock, *J. Am. Chem. Soc.*, 103 (1981) 1440; J. Kress, J.A. Osborn, R.M.E. Greene, K.J. Ivin, and J.J. Rooney, *J. Am. Chem. Soc.*, 109 (1987) 899.
- 7 T.J. Katz and J. McGinnis, *J. Am. Chem. Soc.*, 97 (1975) 1592; J.H. Wengrovius, J. Sancho, and R.R. Schrock, *J. Am. Chem. Soc.*, 103 (1981) 3932; J. Sancho and R.R. Schrock, *J. Mol. Catal.*, 15 (1982) 75.
- 8 I. Meisel, G. Hertel, and K. Weiss, *J. Mol. Catal.*, 36 (1986) 159.
- 9 P. Jernakoff, G.L. Geoffroy, A.L. Rheingold, and S.J. Geib, *J. Chem. Soc., Chem. Commun.*, (1987) 1610.
- 10 W.A. Herrmann, G. Weichselbaumer, R.A. Paciello, R.A. Fischer, E. Herdtweck, J. Okuda, and D.W. Marz, *Organometallics*, 9 (1990) 489.