Journal of Organometallic Chemistry, 284 (1985) 327-335
Elsevier Sequoia S.A., Lausanne - Printed in The Netherlands

TRANSITION METAL DERIVATIVES OF ARENEDIAZONIUM IONS

XIV *. REACTIONS OF ARENEDIAZOMOLYBDENUM(II) COMPLEXES WITH NEUTRAL AND ANIONIC LEWIS BASES

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(Received October 12th, 1984)

Summary

The reactions of arenediazomolybdenum(II) complexes such as $[(\eta\text{-}C_5H_5)Mo(N_2C_6H_4CH_3\text{-}p)I_2]_2$, $(\eta\text{-}C_5H_5)Mo(CO)(N_2C_6H_4CH_3\text{-}p)(SnI_3)I$ and related species with neutral and anionic monodentate or chelating ligands have been investigated. The new arenediazo complexes isolated from these reactions include neutral species such as $(\eta\text{-}C_5H_5)Mo(PPh_3)(N_2C_6H_4CH_3\text{-}p)I_2$ and $(\eta\text{-}C_5H_5)Mo(N_2C_6H_4CH_3\text{-}p)[\eta^2\text{-}S_2CN(C_2H_5)_2]I$, cations of the type $[(\eta\text{-}C_5H_5)Mo(bipy)(N_2C_6H_4CH_3\text{-}p)I]^+$ and the anion $[(\eta\text{-}C_5H_5)Mo(N_2C_6H_4CH_3\text{-}p)I_3]^-$. The structures of the new complexes are discussed.

Introduction

In a recent communication [1] we reported that arenediazomolybdenum(0) complexes of the type $(\eta\text{-}C_5H_5)Mo(CO)_2(N_2Ar)$ undergo oxidative displacement of CO when treated with halogens. They yield initially the molybdenum(II) monocarbonyl complexes $(\eta\text{-}C_5H_5)Mo(CO)(N_2Ar)X_2$ and ultimately the fully decarbonylated species $[(\eta\text{-}C_5H_5)Mo(N_2Ar)X_2]_2$ (X = Cl, Br, I). Similar reactions were observed to take place between I and stannic halides. Only in the case of the reactions of I with I_2 and SnI_4 could stable solid complexes be isolated although products from the other reactions were detected spectroscopically. In this paper we describe the reactions of the arenediazomolybdenum(II) complexes with various neutral and anionic Lewis bases and the isolation of stable derivatives of species previously only detectable in solution.

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* For part XIII see ref. 9.

0022-328X/85/$03.30

Results and discussion

The dimeric halogen-bridged nitrosylmetal(II) complexes $[(\eta\text{-}C_5H_5)M(NO)X_2]_2$ (M = Mo, W) are known to undergo facile bridge-cleavage reactions with Lewis bases such as PPh_3 or $[I]^-$ [2–5]. We have found that the related arenediazo complex * $[(\eta\text{-}C_5H_5)Mo(N_2C_6H_4CH_3\text{-}p)I_2]_2$(I) also undergoes reaction with PPh_3 to yield the new arenediazo complex $(\eta\text{-}C_5H_5)Mo(PPh_3)(N_2C_6H_4CH_3\text{-}p)I_2$ (II). Complex II could also be obtained by iodine-induced oxidative displacement of CO from $(\eta\text{-}C_5H_5)Mo(CO)(PPh_3)(N_2C_6H_4CH_3\text{-}p)$ (III). The latter route gives a cleaner product due, perhaps, to the ability of II itself to undergo further reaction with PPh_3. Thus I reacts with ca. 2 equivalents of PPh_3 to yield a disubstituted cationic complex which was isolated as the hexafluorophosphate salt $[(\eta\text{-}C_5H_5)Mo(PPh_3)_2(N_2C_6H_4CH_3\text{-}p)I]PF_6$ (IV). With a large excess of PPh_3 I yields a second cationic complex for which microanalytical data suggest the formulation $[(\eta\text{-}C_5H_5)Mo(PPh_3)_3(N_2C_6H_4CH_3\text{-}p)][PF_6]_2$ (V) but this species could not be fully purified. In a similar fashion reaction of $(\eta\text{-}C_5H_5)Mo(CO)(N_2C_6H_4CH_3\text{-}p)(SnI_3)I$ (VI) with PPh_3 or of $(\eta\text{-}C_3H_5)Mo(CO)(PPh_3)(N_2C_6H_4CH_3\text{-}p)$ (III) with SnI_4 yields the arenediazo complex $(\eta\text{-}C_5H_5)Mo(PPh_3)(N_2C_6H_4CH_3\text{-}p)(SnI_3)I$ (VII). Complexes II, IV and VII are reddish-brown solids, moderately stable in the solid state but unstable in solution. They are assumed to adopt square-pyramidal "four-legged piano stool" structures similar to those proposed [3] for complexes of the type $(\eta\text{-}C_5H_5)MoL(NO)I_2$. Depending on the arrangement of ligands in the basal plane of the square pyramid, two isomeric forms are possible for complexes II and IV and three for complex VII but we have no evidence as to the isomeric composition of the isolated species. The complexes all show two IR bands of medium intensity in the region 1620–1550 cm^{-1} (Table 1) which are tentatively assigned to the arene-ring coupled NN stretching frequency of the singly-bent arenediazo ligand.

In our earlier work [1] we found that reaction of $(\eta\text{-}C_5H_5)Mo(CO)_2(N_2C_6H_4CH_3\text{-}p)$ (VIII) with I_2, Br_2 or Cl_2 in CH_2Cl_2 at −78°C gave solutions in which the presence of the monocarbonyl species $(\eta\text{-}C_5H_5)Mo(CO)(N_2C_6H_4CH_3\text{-}p)X_2$ (IXa, X = I; IXb, X = Br; IXc, X = Cl) could be detected spectroscopically although only the iodo complex (IXa) could be isolated in the solid state. Decarbonylation of (IXb, IXc) took place on attempted isolation giving poorly characterised species which were presumed to have structures similar to the isolable dimeric iodo complex I. Complex VIII also reacted with SnI_4 to give an isolable monocarbonyl complex $(\eta\text{-}C_5H_5)Mo(CO)(N_2C_6H_4CH_3\text{-}p)(SnI_3)I$ (VI) which decarbonylated to give a poorly-characterised species of approximate composition $[(\eta\text{-}C_5H_5)Mo(N_2C_6H_4CH_3\text{-}p)(SnI_3)I]_2$ (X). Similar reactions with $SnBr_4$ and $SnCl_4$ yielded neither characterisable monocarbonyl complexes nor dimeric species. We have now found that reaction of the dicarbonylarenediazo complex VIII with I_2, Br_2, or Cl_2 at −78°C followed by treatment of the labile monocarbonyl complexes in situ with the neutral bidentate ligand 2,2′-bipyridyl yielded deep red solutions from which dark red ionic derivatives $[(\eta\text{-}C_5H_5)Mo(bipy)(N_2C_6H_4CH_3\text{-}p)X]X$ (XI) could be isolated. Complexes of the type XI could not be fully characterised by

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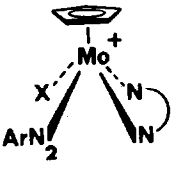
* In all the complexes described in this communication the arenediazo ligand is assumed to adopt the "singly-bent" coordination mode as is required if the metal atom is to attain an 18-electron configuration.

micoranalysis but were readily converted into the very stable hexafluorophosphate salts $[(\eta\text{-}C_5H_5)Mo(bipy)(N_2C_6H_4CH_3\text{-}p)X]PF_6$ (XIIa, X = I; XIIb, X = Br; XIIc, X = Cl). An analagous complex containing 1,10-phenanthroline (phen) $[(\eta\text{-}C_5H_5)Mo(phen)(N_2C_6H_4CH_3\text{-}p)I]PF_6$ (XIII) was prepared similarly.

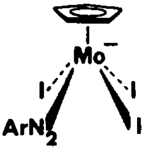
When a solution containing $(\eta\text{-}C_5H_5)Mo(CO)(N_2C_6H_4CH_3\text{-}p)(SnI_3)I$ (VI) or its decarbonylation product X was treated with 2,2′-bipyridyl the cationic iodo-complex XIIa could be isolated in good yield. Furthermore, the carbonyl-free solutions produced by the action of $SnBr_4$ and $SnCl_4$ upon the dicarbonyl VIII (see above) reacted with 2,2′-bipyridyl to yield the cationic bromo and chloro complexes (XIIb,XIIc). These results indicate that attack of 2,2′-bipyridyl on the triiodostannyl complex results in preferential displacement of SnI_3^- rather than I^- from the molybdenum coordination sphere. They also provide indirect evidence that the dimeric species $[(\eta\text{-}C_5H_5)Mo(N_2C_6H_4CH_3\text{-}p)(SnX_3)X]_2$ (XIV, X = Br; XV, X = Cl) are the ultimate products of the reaction of complex I with $SnBr_4$ and $SnCl_4$, respectively. The cationic species (XIIa,XIIb,XIIc) and XIII are assumed to adopt square-pyramidal geometries with the chelating character of the neutral ligand enforcing a mutually *cis*-orientation of halide and arenediazo ligands.



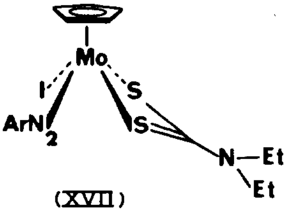
(XI)

= 2,2′-bipyridyl

The molybdenum(II) monocarbonyl complex $(\eta\text{-}C_5H_5)Mo(CO)(N_2C_6H_4CH_3\text{-}p)I_2$ (IXa) reacts with $[P(CH_3)(C_6H_5)_3]I$ to yield an olive-green anionic complex $[P(CH_3)(C_6H_5)_3][(\eta\text{-}C_5H_5(Mo(N_2C_6H_4CH_3\text{-}p)I_3]$ (XVI). It may be noted that while anionic nitrosyl complexes are common (the analagous nitrosyl anions $[(\eta\text{-}C_5H_5)Mo(NO)X_3]^-$ (X = Br, Cl) have been prepared by McCleverty [4]) we are aware of only one other reported example of an anionic arenediazo complex [6]. Reaction of diethyldithiocarbamate anion with the dimeric diiodo complex I produces the stable neutral purple η^2-dithiocarbamato complex $(\eta\text{-}C_5H_5)Mo(N_2C_6H_4CH_3\text{-}p)[\eta^2\text{-}S_2CN(C_2H_5)_3]I$ (XVII) in good yield. It is probable that both complex XVI and XVII have square-pyramidal structures and here again only one isomeric form is possible.



(XVI)



(XVII)

In an attempt to prepare an arenediazo analogue of the structurally novel nitrosyl complex $(C_5H_5)_3Mo(NO)$ [7] the dimeric diiodo complex I was treated with two equivalents of C_5H_5Tl. However, the only isolable product of this reaction was a low yield of the known [6] bis(arenediazo) complex $(\eta\text{-}C_5H_5)Mo(N_2C_6H_4CH_3\text{-}p)_2I$. We are continuing to study this reaction.

^{1}*H NMR spectra*

Our ability to record ^{1}H NMR spectra of several of the complexes described was inhibited by instability in solution. The spectra of the 2,2′-bipyridyl complexes (XIIa–XIIc) and of the 1,10-phenanthroline analogue XIII will be discussed first. The three complexes (XIIa–XIIc) all show singlets at ca. δ 2.35 and 6.32 ppm for the methyl group of the *p*-toluenediazo ligand and the $\eta\text{-}C_5H_5$ ligand, respectively. The aromatic protons of the *p*-toluenediazo ligand appear as an A_2B_2 doublet of doublets centred on ca. δ 7.1 ppm. The positions of these resonances are essentially independant of the nature of the halogen ligand. The resonances characteristic of the 2,2′-bipyridyl ligand fall into three well-defined groups: a quartet (two protons) centred on δ 7.9 ppm; an unsymmetrical complex of six lines (five protons) extending from ca. δ 8.3 to 9.1 ppm; and a doublet (one proton) at δ ca. 9.9 ppm. All these lines are somewhat broadened and show evidence of further splitting. These three groups of resonances exhibit a systematic dependence on the nature of the halogen ligand. The two high-field groups of lines are progressively deshielded by a total of ca. 0.14–0.15 ppm in the sequence I, Br, Cl, i.e. with increasing halogen electronegativity. The low-field single-proton resonance shows an opposite, and larger, shift, becoming progressively more shielded by a total of ca. 0.5 ppm as the electronegativity of the halogen ligand increases. While we have not attempted a detailed assignment of these resonances it seems probable that the unique low-field resonance at δ ca. 9.9 ppm may be ascribed to either the *ortho* (H(6)) or *para* (H(4)) hydrogen atoms of the chelating ligand pyridyl group which is *trans* to the halogen ligand (Fig. 1). The observed upfield shift of this resonance may then be due to conjugative π-donation from lone-pair orbitals on the halogen ligand, via the metal atom, into the vacant π^* orbitals of the chelate ligand. The efficiency of this effect would be anticipated to increase with increasing compactness of the halide non-bonding orbitals, i.e. in the sequence observed. The possibility of a direct through-space interaction between halide ligand and the adjacent *ortho* (H(6′)) proton cannot be completely ruled out however. The down-field shift of the remaining

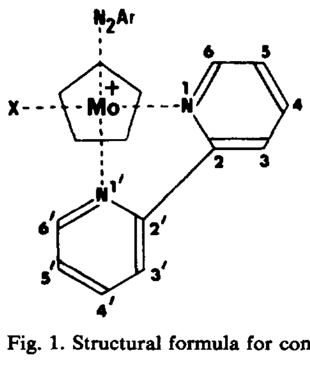


Fig. 1. Structural formula for complexes XIIa–XIIc showing the atom numbering scheme.

2,2'-bipyridyl resonances correlates with increasing halide electronegativity and may be ascribed to inductive electron-withdrawal from the ligand as a whole. (The ^{1}H NMR spectrum of a related complex, $[(\eta\text{-}C_5H_5)Mo(bipy)(NO)Br]^+$, has been reported by McCleverty [4]. However, only the average position of the resonances of the 2,2'-bipyridyl ligand are given so that it is not clear whether the overall resonance pattern is the same as that observed here.) The 1,10-phenanthroline complex $[(\eta\text{-}C_5H_5)Mo(phen)(N_2C_6H_4CH_3\text{-}p)I]PF_6$ (XIII) exhibits a qualitatively similar spectrum to that of its 2,2'-bipyridyl analogues (XIIa–XIIc). The protons of the chelating ligand appear as two complex multiplets centered on 8.1 and 9.1 ppm (seven protons) together with a broad doublet (one proton) at δ 10.42 ppm. An attempt to identify the unique low-field proton by comparison with the spectrum of the 2,9-dimethylphenanthroline analogue was thwarted by the failure of the latter to form a stable complex with $[(\eta\text{-}C_5H_5)Mo(N_2C_6H_4CH_3\text{-}p)I]_2$ (I).

Attempts to record the ^{1}H NMR spectrum of the iodo-bridged complex $[(\eta\text{-}C_5H_5)Mo(N_2C_6H_4CH_3\text{-}p)I]_2$ (I) in $(CD_3)_2SO$ (dmso-d_6) yielded evidence that the behaviour of I in solution is far from simple. A freshly-prepared solution of I in dmso is deep purple. Apart from a singlet at δ 2.38 ppm (*p*-tolyl methyl group) and a broad multiplet at ca. δ 7.14 ppm (aryl protons), four cyclopentadienyl resonances were observed at δ 6.01, 6.19, 6.31 and 6.42 ppm, the high-field pair of resonances being about twice the intensity of the low-field pair. Over a period of hours the low-field pair of resonances increased in intensity at the expense of the high-field pair. On longer standing the peak at δ 6.31 ppm began to decrease and that at 6.42 ppm to increase in intensity until after ca. 15 h the latter resonance alone was observed and the aryl protons of the *p*-toluenediazo ligand now appeared as a sharp singlet at δ 7.28 ppm. A single unambiguous interpretation of these results is not possible at our present state of knowledge. However, if we assume that cleavage of the halogen bridges in dimeric I is likely to be rapid in a strong donor solvent such as dmso, then the first species to be formed in solution would be the neutral solvate $(\eta\text{-}C_5H_5)Mo(dmso)(N_2C_6H_4CH_3\text{-}p)I_2$ (XVIII) for which two isomeric forms are possible (A and B, Fig. 2). Further solvolysis of XVIII [3] would generate the ionic complex $[(\eta\text{-}C_5H_5)Mo(dmso)_2(N_2C_6H_4CH_3\text{-}p)I]I$ (XIX) which can also exist in two isomeric forms (C and D, Fig. 2). A plausible interpretation of the data would then assign the resonances at δ 6.01 and 6.19 ppm to the two isomers of XVIII and their gradual disappearance to their conversion into both isomers of the cationic XIX (resonances at δ 6.31 and 6.42 ppm). The final disappearance of the resonance at δ 6.31 ppm and increase in intensity of that at δ 6.42 ppm would then be accounted for by gradual conversion of the isomeric mixture of XIX into whichever form is the thermodynamically more stable of the pair.

The ^{1}H NMR spectrum of the neutral η^2-dithiocarbamato complex $(\eta\text{-}C_5H_5)Mo(N_2C_6H_4CH_3\text{-}p)[\eta^2\text{-}S_2C(C_2H_5)_2]I$ (XVII) in $CDCl_3$ was well resolved and in accord with the proposed structure. The resonances of the dithiocarbamato-ethyl groups consisted of a six-line multiplet (two overlapping triplets at δ 1.26 and 1.33 ppm) together with a five-line multiplet (two overlapping quartets at δ 3.73 and 3.87 ppm. The inequivalence of the ethyl groups arises from partial π-bond character (and hence restricted rotation) in the C–N bond of the dithiocarbamato ligand and the assymmetry at the molybdenum atom. Variable-temperature ^{1}H NMR studies in chlorobenzene revealed that the methyl group resonances coalasced to a sharp triplet at 90°C while the methylene quartets had undergone considerable broadening at this

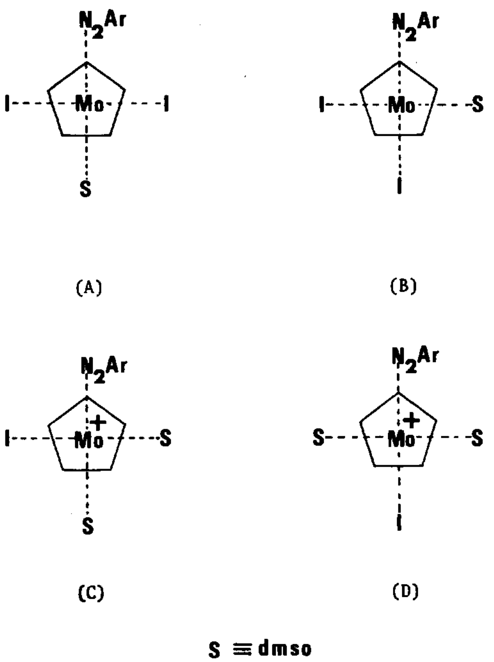


Fig. 2. Isomeric forms of complexes XVIII (A and B) and XIX (C and D).

TABLE 1

INFRARED AND MICROANALYTICAL DATA

Complex	$\nu(NN)$[a] (cm^{-1})	Analysis (Found (Calcd.) (%))		
		C	H	N
II	1620,1565	45.04 (45.25)	3.45 (3.42)	3.39 (3.52)
IV	1614,1558	53.85 (53.55)	4.34 (3.93)	2.60 (2.99)
VII	1618,1563	31.30 (30.83)	2.60 (2.33)	2.08 (2.40)
XIIa	1625,1578	37.34 (37.31)	2.68 (2.85)	7.96 (7.91)
XIIb	1630,1585	39.46 (39.96)	3.03 (3.05)	8.23 (8.47)
XIIc	1631,1588	42.44 (42.84)	3.21 (3.27)	8.62 (9.08)
XIII	1626,1570	39.46 (39.96)	3.03 (3.05)	8.23 (8.47)
XVI	1612,1545	39.80 (39.68)	3.14 (3.22)	2.89 (2.98)
XVII	1610,1535	37.24 (36.77)	4.18 (3.99)	7.58 (7.57)

[a] CH_2Cl_2 solution. Assignment tentative in the absence of ^{15}N labelling.

temperature but had not fully merged. At 100°C the methylene resonances coalesced to a broad featureless singlet (line-width ca. 3 ppm at half-height). At temperatures above 100°C decomposition took place. The spectroscopic changes up to 100°C were fully reversible.

Experimental

Published procedures were employed to prepare the complexes I, VI, IX, [1], III and VIII [8]. Other reagents and solvents were commercial samples and were used as received. IR spectra were recorded on a Perkin–Elmer 257 spectrophotometer and ^{1}H NMR spectra were obtained using a Perkin–Elmer Hitachi R20-A spectrometer operating at 60 MHz and ambient temperature. Microanalyses were determined by the staff of the Microanalytical Laboratory of University College Cork. IR and microanalytical data are summarised in Table 1.

η-Cyclopentadienyl(p-toluenediazo)(triphenylphosphine)diiodomolybdenum(II)

Iodine (0.22 g, 0.87 mmol) in 50 ml of CH_2Cl_2 was added dropwise to a stirred solution of $(\eta\text{-}C_5H_5)Mo(CO)(PPh_3)(N_2C_6H_4CH_3\text{-p})$ (III), (0.5 g, 0.87 mmol) in 20 ml of CH_2Cl_2 at 0°C. After 45 min the solvent was removed in vacuo and the brown residue was recrystallised from CH_2Cl_2/hexane. Yield 0.45 g, 65%.

η-Cyclopentadienyl(p-toluenediazo)bis(triphenylphosphine)iodomolybdenum hexafluorophosphate (IV)

Triphenylphosphine (0.76 g, 2.92 mmol) was added to a stirred solution of $[(\eta\text{-}C_5H_5)Mo(N_2C_6H_4CH_3\text{-}p)I_2]_2$ (II) (0.78 g, 0.73 mmol) in 70 ml CH_2Cl_2 at room temperature. After 30 min the solvent was removed in vacuo. The residue was dissolved in a little CH_2Cl_2 and added to 40 ml of methanol containing excess NH_4PF_6. The volume of this solution was reduced to ca. 20 ml. in vacuo and water was added to precipitate the product which was collected by filtration, dried in vacuo and recrystallised from CH_2Cl_2/ether. Yield 0.42 g, 53%.

η-Cyclopentadienyl(p-toluenediazo)(triphenylphosphine)(triiodostannyl)iodomolybdenum (VII)

Complex VII was best prepared (ca. 60% yield) by addition of SnI_4 to $(\eta\text{-}C_5H_5)Mo(CO)(PPh_3)(N_2C_6H_4CH_3\text{-}p)$ (III) as described above for the diiodo analogue II.

η-Cyclopentadienyl(p-toluenediazo)(2,2′-bipyridyl)iodomolybdenum hexafluorophosphate, (XIIa), and related compounds

2,2′-Bipyridyl (0.23 g, 1.47 mmol) was added to a stirred solution of $[(\eta\text{-}C_5H_5)Mo(N_2C_6H_4CH_3\text{-}p)I_2]_2$ (I) (0.78 g, 0.73 mmol) or $(\eta\text{-}C_5H_5)Mo(CO)(N_2C_6H_4CH_3\text{-}p)(SnI_3)I$ (VI) (1.37 g, 1.47 mmol) in 70 ml CH_2Cl_2 at room temperature. After 30 min the solution was filtered, reduced in volume in vacuo and added to a solution of ca. 2 g NH_4PF_6 in 40 ml methanol. The combined solutions were then reduced to ca. 20 ml in vacuo and poured into water to precipitate the red product which was recrystallised from CH_2Cl_2/ether. Yield ca. 65%. The related complexes XIIb and XIIc were prepared in a similar fashion either from the monocarbonyldihalo complexes IXb and IXc prepared in situ or from the carbonyl-free solutions produced by the action of $SnBr_4$ or $SnCl_4$ on complex VIII [1]. The *o*-phenanthroline complex XIII was prepared as for XIIa.

Methyl(triphenyl)phosphonium η-cyclopentadienyl(p-toluenediazo)triiodomolybdate (XVI)

Solid $[CH_3(C_6H_5)_3P]I$ (0.3 g, 0.74 mmol) was added to a stirred solution of $(\eta\text{-}C_5H_5)Mo(CO)(N_2C_6H_4CH_3\text{-}p)I_2$ (IXa) (0.41 g, 0.73 mmol) in 60 ml CH_2Cl_2. After 25 min the solvent was reduced to small volume in vacuo and the olive-green product was precipitated by addition of ether and recrystallised from CH_2Cl_2/ether. Yield 0.55 g, 80%.

η-Cyclopentadienyl(p-toluenediazo)(η²-diethyldithiocarbamato)iodomolybdenum (XVII)

A solution of $(C_2H_5)_2NCS_2Na \cdot 3H_2O$ (0.16 g, 0.73 mmol) in 20 ml of ethanol was added dropwise to a stirred solution of $(\eta\text{-}C_5H_5)Mo(CO)(N_2C_6H_4CH_3\text{-}p)I_2$ (IXa) (0.41 g, 0.73 mmol) in 60 ml CH_2Cl_2 and the solution allowed to stir for 1 h, during which time the original green colour became deep purple. The solvent was removed in vacuo and the solid residue was chromatographed on neutral alumina, eluting with CH_2Cl_2. The purple band yielded a purple microcrystalline solid which was recrystallised from CH_2Cl_2/hexane to yield the product XVII (0.3 g, 75%).

¹H NMR spectra

(I). (Dmso-d_6, Me_4Si). Freshly-prepared solution: δ 2.38 (singlet, 3H) $p\text{-}CH_3C_6H_4N_2$; 6.01, 6.19, 6.31 and 6.42 (singlets, 5H total) $\eta\text{-}C_5H_5$; 7.14 (multiplet, 4H) $p\text{-}CH_3C_6H_4N_2$. Aged solution (see text): δ 2.35 (singlet, 3H) $p\text{-}CH_3C_6H_4N_2$; 6.42 (singlet, 5H) $\eta\text{-}C_5H_5$; 7.28 (singlet 4H) $p\text{-}CH_3C_6H_4N_2$ ppm.

XIIa. (Acetone-d_6, Me_4Si). δ 2.32 (singlet, 3H), $p\text{-}CH_3C_6H_4N_2$; 6.33 (singlet, 5H), $\eta\text{-}C_5H_5$; 6.99, 7.25 (doublet of doublets, *J* 9.0 Hz, 4H), $p\text{-}CH_3C_6H_4N_2$; 7.72, 7.97 (quartet, $J \approx 6.0$ Hz, 2H); 8.26–9.0 (six line multiplet, 5H); 10.14 (doublet, *J* 6.0 Hz, 1H), $C_{10}H_8N_2$, ppm.

XIIb. (Acetone-d_6, Me_4Si, splitting pattern, relative intensities and assignments as for XIIa). δ 2.36; 6.31; 7.13; 7.29; 7.87; 8.06; 8.31–9.16; 9.97 ppm.

XIIc. (Dmso-d_6, Me_4Si, splitting pattern, relative intensities and assignments as for XII a). δ 2.38; 6.32; 6.98; 7.33; 7.88; 8.12; 8.31–9.22; 9.64 ppm.

XIII. (Dmso-d_6, Me_4Si). δ 2.31 (singlet, 3H) $p\text{-}CH_3C_6H_4N_2$; 5.28 (singlet, 5H) $\eta\text{-}C_5H_5$; 6.85; 7.16 (doublet of doublets, *J* 9.0 Hz, 4H) $p\text{-}CH_3C_6H_4N_2$; 8.10, 9.10 (multiplets, 3H, 4H), 10.42 (doublet, *J* 5.4 Hz) $C_{12}H_8N_2$, ppm.

XVI. ($CHCl_3$-*d*, Me_4Si). δ 2.24 (singlet, 3H) $p\text{-}CH_3C_6H_4N_2$; 2.99 (doublet, J(PH) 12.9 Hz, 3H), $[CH_3(C_6H_5)_3P]^+$; 5.92 (singlet, 5H), $\eta\text{-}C_5H_5$; 6.7–8.05 (multiplet, 19H), $[CH_3(C_6H_5)_3P]^+$ and $p\text{-}CH_3C_6H_4N_2$ ppm.

XVII ($CHCl_3$-*d*, Me_4Si) room temperature: δ 1.26, 1.33 (two overlapping triplets, *J* 6.75 Hz, 6H) $\eta^2\text{-}S_2CN(CH_2CH_3)_2$; 2.39 (singlet, 3H) $p\text{-}CH_3C_6H_4N_2$; 3.73, 3.87 (two overlapping quartets, *J* 6.75 Hz, 4H) $\eta^2\text{-}S_2CN(CH_2CH_3)_2$; 5.89 (singlet, 5H) $\eta\text{-}C_5H_5$; 7.19 (singlet, 4H) $p\text{-}CH_3C_6H_4N_2$, ppm.

(C_6H_5Cl, Me_4Si) 100°C: δ 1.02 (triplet, *J* 6.75 Hz, 6H) $\eta^2\text{-}S_2CN(CH_2CH_3)_2$; 2.18 (singlet, 3H) $p\text{-}CH_3C_6H_4N_2$; 3.54 (broad singlet, 4H) $\eta^2\text{-}S_2CN(CH_2CH_3)_2$ ppm.

Acknowledgement

We are grateful to the Department of Education of the Irish Republic for a Post-graduate Maintenance Award to D.C.

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