

Use of the seven-coordinate complexes $[MXY(CO)_3(NCMe)_2]$ ($M = Mo$ or W ; $X, Y = \text{halide}$) and their derivatives in homogeneous catalysis

Mutlaq Al-Jahdali^a, Paul K. Baker^{a,*}, Aidan J. Lavery^b, Margaret M. Meehan^a,
David J. Muldoon^a

^a Department of Chemistry, University of Wales, Bangor, Gwynedd, LL57 2UW, Wales, UK

^b ZENeca Specialties, PO Box 42, Hexagon House, Blackley, Manchester, M9 3DA UK

Abstract

The seven-coordinate halocarbonyl complexes, $[MXY(CO)_3(NCMe)_2]$ ($M = Mo$ or W ; $X, Y = \text{halide}$) and their derivatives have been investigated in several types of homogeneous catalytic reactions. These include, the alkene metathesis polymerisation of norbornadiene using either, $[MX_2(CO)_3(NCMe)_2]$ ($M = Mo$ or W ; $X = Br$ or I), $[MI_2(CO)_3(L'-P, P')]$ ($M = Mo$ or W ; $L' = MeC(CH_2PPh_2)_3$) or $[MXY(CO)(L \text{ or } L'-P, P')(\eta^2-RC_2R')]$ ($X, Y = Cl, Br$ or I ; $L = PhP(CH_2CH_2PPh_2)_2$; $R, R' = Me, Ph$). The isolation and characterisation of a key intermediate, $[WI_2(CO)_2(\eta^4-nbd)]$ (**1**) ($nbd = \text{norbornadiene}$) is also described. The development of water soluble polymerisation catalysts using water-solubilising pyridine ligands, and the biphasic polymerisation of styrene using $[WI_2(CO)_3(NC_5H_4CO_2Na-4)_2]$, $ZrCl_4$, sodium lauryl sulphate and sodium hydrogen phosphate is also discussed. The room temperature polymerisation of phenylacetylene using $[WX_2(CO)_3(NCMe)_2]$ ($X = Cl, I$), $[WI_2(CO)_3(NCMe)L]$ ($L = PPh_3, AsPh_3$) or $[WBr_2(CO)(NCMe)(\eta^2-HC_2Ph)_2]$ (**4**) is also described, and a mechanism is proposed for these polymerisation reactions. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenum (II); Tungsten (II) complexes; Halocarbonyl; Polymerisation; Metathesis; Water soluble biphasic catalysts; Phenylacetylene polymerisation

1. Introduction

In 1986, we described the synthesis [1] and characterisation, including by X-ray crystallography ($M = Mo$, $X = I$ [2]; $M = W$, $X = I$ [3]) of the seven-coordinate complexes $[MX_2(CO)_3(NCMe)_2]$ ($M = Mo, W$; $X = Br, I$). These seven-coordinate molybdenum(II) and tungsten(II) complexes were prepared by oxidation

of the zero-valent complexes $fac-[M(CO)_3(NCMe)_3]$ (prepared in situ by refluxing $[M(CO)_6]$ in acetonitrile [4]) with X_2 at $0^\circ C$. In 1994 [5], we described an improved method of preparing the dibromo complexes, $[MBr_2(CO)_3(NCMe)_2]$ by carrying out the oxidation of $fac-[M(CO)_3(NCMe)_3]$ with bromine at $-78^\circ C$. We have also investigated the oxidation of $fac-[Mo(CO)_3(NCMe)_3]$ (prepared in situ [4]) with a variety of other oxidising agents, XY ($XY = ICl$, [6], IBr [7], $GeCl_4$ [8], $SnCl_4$ [9]) to afford the

* Corresponding author. Fax: +44-012-48-37-0528.

mixed-halogen seven-coordinate complexes, $[\text{MoXY}(\text{CO})_3(\text{NCMe})_2]$ ($\text{X} = \text{Cl}$, $\text{Y} = \text{I}$; $\text{X} = \text{Br}$, $\text{Y} = \text{I}$; $\text{X} = \text{Cl}$, $\text{Y} = \text{GeCl}_3$; $\text{X} = \text{Cl}$, $\text{Y} = \text{SnCl}_3$). Over the years, we have been studying the chemistry of these $[\text{MXY}(\text{CO})_3(\text{NCMe})_2]$ highly versatile seven-coordinate complexes, and we have prepared and characterised over 2000 derivatives from these complexes [10,11]. In this article, we describe some of the applications of the complexes $[\text{MXY}(\text{CO})_3(\text{NCMe})_2]$, and their derivatives in homogeneous catalysis.

2. Results and discussion

The purpose of this article is to show the versatility of the seven-coordinate complexes, $[\text{MXY}(\text{CO})_3(\text{NCMe})_2]$ and their derivatives in different types of catalytic reactions, which will be described in Sections 2.1–2.5.

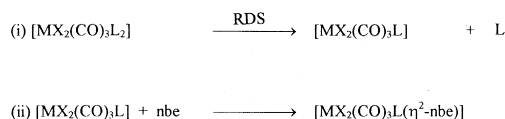
2.1. Metathesis polymerisation of norbornadiene using $[\text{MX}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}$, W ; $\text{X} = \text{Br}$, I)

In 1985, Bencze and Kraut-Vass [12] showed that the seven-coordinate dihalo-tricarbonyl complexes $[\text{MX}_2(\text{CO})_3\text{L}_2]$ ($\text{M} = \text{Mo}$, W ; $\text{X} = \text{Cl}$, Br ; $\text{L} = \text{PPh}_3$, AsPh_3) are single component catalysts for the ring-opening metathesis polymerisation of norbornene and norbornadiene. They found that the tungsten complexes were superior to their molybdenum analogues, and the AsPh_3 complexes were better catalysts than their PPh_3 analogues. The tungsten complexes, $[\text{WX}_2(\text{CO})_3(\text{AsPh}_3)_2]$ showed considerable activity in benzene at 353 K. The rate of polymerisation of $[\text{WCl}_2(\text{CO})_3(\text{AsPh}_3)_2]$ was $1.2 \pm 0.1 \times 10^4 \text{ mol dm}^{-3} \text{ s}^{-1}$ for norbornene concentrations of 0.25–3.0 mol dm^{-3} , and that the rate was found to be independent of monomer concentration. They also found that the activity was retained in the presence of air and moisture. They proved [12], that the rate-determining step in these reactions was loss of L, which was followed by alkene coordination (see Scheme

1). The norbornene intermediates, $[\text{MX}_2(\text{CO})_3\text{-L}(\eta^2\text{-nbe})]$ undergo a 2,3-hydrogen shift to give a metal-carbene initiator [13].

In view of these observations [12,13], we decided to study the catalytic activity of our $[\text{MX}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}$, W ; $\text{X} = \text{Br}$, I) complexes and their derivatives. The complex $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$ ($9.8421 \times 10^{-3} \text{ mol dm}^{-3}$) was suspended in toluene and a 200-fold excess of norbornadiene (nbd), (2.1 mol dm^{-3}) was added. The reaction was stirred at room temperature for 24 h and followed by gas chromatography. The solution was monitored at regular intervals to measure the concentration of nbd, which remained constant throughout the experiment, suggesting that none of the nbd had polymerised. The reaction was repeated at 35°C, 40°C and 50°C and similar results were obtained, i.e. no poly(norbornadiene) was formed. The metathesis polymerisation of nbd at room temperature was also attempted in thf, benzene and CHCl_3 , but again no catalytic activity was observed. The tungsten complexes $[\text{WI}_2(\text{CO})_3(\text{NCR})_2]$ ($\text{R} = \text{Bu}^t$, Ph) were also found to be inactive single component catalysts for the metathesis of nbd in both toluene and benzene at room temperature.

Bencze and Kraut-Vass [12] found that the use of a co-catalyst with $[\text{MX}_2(\text{CO})_3\text{L}_2]$ gave excellent catalytic activity. We studied the metathesis polymerisation of nbd with $[\text{MI}_2(\text{CO})_3(\text{NCR})_2]$ ($\text{M} = \text{Mo}$, $\text{R} = \text{Me}$; $\text{M} = \text{W}$, $\text{R} = \text{Me}$, Bu^t , Ph) in the presence of a co-catalyst, ZrCl_4 or “ AlCl_3 ”. A mixture of $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$, ZrCl_4 and nbd (molar ratio 1:3:200) (see experimental Section 4.2) were prepared. After stirring the mixture for 10 min, the viscous reaction mixture was poured into an excess of methanol to give a white polymer, poly(norbornadiene).



Scheme 1.

Similar reactions of the tungsten complexes, $[Wl_2(CO)_3(NCR)_2]$ ($R = Me, Bu^t, Ph$) also rapidly metathesised nbd at room temperature in toluene in the presence of $ZrCl_4$ (molar ratio 1:3:1000; $[Wl_2(CO)_3(NCR)_2]:ZrCl_4:nbd$). Very similar activity and results were obtained when using “ $AlCl_3$ ” as a co-catalyst. The polymers were characterised by 1H NMR ($CDCl_3, +25^\circ C$), and had two quintets at $\delta = 1.24$ and 2.41 ppm due to H_a and H_b (see Fig. 1.), a quartet at $\delta = 3.57$ ppm due to H_c , and a doublet and singlet at 5.23 ppm (H_d) and 5.56 ppm (H_e), respectively. The ^{13}C NMR spectra ($CDCl_3, +25^\circ C$) generally had resonances at $\delta = 29.86$ ppm and 30.77 ppm due to the cyclic carbons C_1 and C_2 atoms (see Fig. 2), and resonances at $\delta = 127.84$ and 128.31 ppm due to C_3 and C_4 , respectively. Due to the poor resolution of these spectra, it was difficult to assign whether the polymer is all *cis*-, all *trans*- or *cis/trans* in our studies.

Hughes [14], has shown that the catalytic activity of the molybdenum nitrosyl complexes, $[MoX_2(NO)_2L_2]$ was very dependent on the nature of X and L. It was found that the activity increased along the series, $AsPh_3 < 4-EtC_5H_4N < OPh_3$, and $I < Br < Cl$. From these observations [14], and those of Bencze and Kraut-Vass [12] and Bencze et al. [13], the lack of activity of $[MoI_2(CO)_3(NCMe)_2]$, as a single component nbd metathesis polymerisation catalyst, may be due to the halide. The analogous dibromo-complexes, $[MBr_2(CO)_3(NCMe)_2]$ ($M = Mo, W$) [5] were studied as single component catalysts for the ring-opening polymerisation of

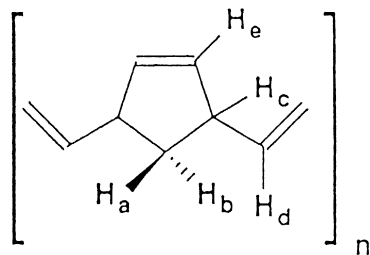


Fig. 1. The 1H NMR proton environments in poly(norbornadiene).

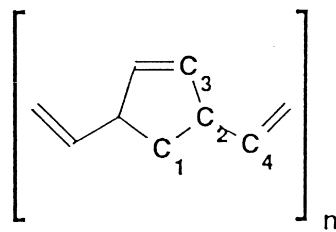


Fig. 2. The ^{13}C NMR environments for poly(norbornadiene).

nbd. To a toluene solution of $[MoBr_2(CO)_3(NCMe)_2]$, ($1.55 \times 10^{-2} \text{ mol dm}^{-3}$), was added a 200-fold excess of nbd, 3.09 mol dm^{-3} at room temperature. Within minutes, the solution had become too viscous to stir, and a high yield of poly(norbornadiene) was obtained, which was very difficult to separate from the molybdenum catalyst. 1H and ^{13}C NMR data confirmed the formation of poly(norbornadiene). Similar results were obtained for the metathesis polymerisation using the tungsten complex, $[WBr_2(CO)_3(NCMe)_2]$ [5], and the molybdenum complexes $[MoBr_2(CO)_3(NCMe)L]$ ($L = PPh_3, AsPh_3, SbPh_3$) [5].

We can conclude from these preliminary studies of the metathesis polymerisation of nbd using $[MX_2(CO)_3(NCMe)L]$, that the dibromo-complexes are room temperature single component polymerisation catalysts, whereas the diiodo-complexes must have a co-catalyst such as $ZrCl_4$ or “ $AlCl_3$ ” in order to initiate polymerisation.

2.2. Preparation and characterisation of the diene complexes $[Wl_2(CO)_2(\eta^4\text{-diene})]$ (diene = nbd, isoprene)

A number of diene dicarbonyl complexes of the type $[WBr_2(CO)_2(\eta^4\text{-nbd})]$ [15], $[WBr(SC_6F_5)(CO)_2(\eta^4\text{-nbd})]$ [16], $[MoX_2(CO)_2(\eta^4\text{-nbd})]$ ($X = Br, I$) [17], $[WBr(CO)_2(\text{terpyridine})(\eta^4\text{-nbd})]^+$ [18] and $[WCl(SnCl_3)(CO)_3(\eta^4\text{-nbd})]$ [19] have been described. In view of Bencze and Kraut-Vass's [12], observation that the rate determining step

in the metathesis polymerisation of nbd involved initial formation of an η^2 -alkene complex (see Scheme 1). It may be that after initial formation of our η^2 -nbd complexes, $[\text{MBr}_2(\text{CO})_3(\text{NCMe})(\eta^2\text{-nbd})]$ they could either undergo a 2,3-hydrogen shift or coordination of the other alkene unit on nbd to give $[\text{MBr}_2(\text{CO})_2(\eta^4\text{-nbd})]$ [15,17], which has been structurally characterised for $M = \text{W}$ [20].

In view of the lack of catalytic activity of $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ towards the polymerisation of nbd, we decided to try to prepare the new six-coordinate nbd complex, $[\text{WI}_2(\text{CO})_2(\eta^4\text{-nbd})]$. Refluxing the seven-coordinate complex $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ in hexane for 3 h with a slight excess of nbd eventually gave a dark green solid, which was recrystallised from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at -17°C to afford the new diiodo diene complex $[\text{WI}_2(\text{CO})_2(\eta^4\text{-nbd})]$ (**1**) in 17% yield. Complex (**1**) was characterised by elemental analysis (C, H and N), IR and ^1H NMR spectroscopy (see experimental Section 4.4). Since the IR (CHCl_3) spectrum has carbonyl bands at 2057 (w), 1989 (s) cm^{-1} , very similar to $[\text{WBr}_2(\text{CO})_2(\eta^4\text{-nbd})]$, which has been structurally characterised [20], it is likely (**1**) will have a similar structure (see Fig. 3). The strong asymmetric band at 1989 cm^{-1} is assigned to the *trans*-carbonyl ligands (see Fig. 3), whereas the weak band at 2057 cm^{-1} is due to the symmetric stretch activated by the distortion from octahedral geometry [20]. It should be noted that we have very recently [21] obtained the X-ray crystal structure of $[\text{WI}_2(\text{CO})_2(\eta^4\text{-$

nbd)], and it does have the geometry suggested above and shown in Fig. 3.

A similar reaction of equimolar amounts of $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ and isoprene in refluxing hexane for 5 h was not successful. However, refluxing $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ with a slight excess of isoprene in refluxing CHCl_3 for 24 h, gives the new black dicarbonyl product $[\text{WI}_2(\text{CO})_2(\eta^4\text{-isoprene})]$ (**2**), which has been fully characterised (see experimental Section 4.5). Since the IR spectral properties of (**2**) are similar to $[\text{WI}_2(\text{CO})_2(\eta^4\text{-nbd})]$, it will very likely have a similar structure as shown for the nbd complex in Fig. 3. The coordinated nbd (**1**) and isoprene (**2**), have their proton resonance's shifted slightly downfield as expected. Complex (**1**) is dark green and complex (**2**) is dark brown. Both complexes are relatively air-stable in the solid state, but air-sensitive in solution. Complex (**1**) was soluble in chlorinated solvents, but only slightly soluble in hydrocarbon solvents. Complex (**2**) was much less soluble in these solvents, but more soluble in methanol.

A summary of the reactions of nbd with $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ is given in Scheme 2.

2.3. Nbd metathesis polymerisation using, $[\text{MI}_2(\text{CO})_3(\text{L}-\text{P}, \text{P}')]$, $[\text{MXY}(\text{CO})(\text{L}-\text{P}, \text{P}')(\eta^2\text{-RC}_2\text{R}')]$, $[\text{MI}_2(\text{CO})_3(\text{L}-\text{P}, \text{P}')]$, $[\text{MXY}(\text{CO})(\text{L}-\text{P}, \text{P}')(\eta^2\text{-RC}_2\text{R}')]$ ($X = \text{Cl}, \text{Br}, \text{I}$; $L = \text{PPh}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$; $L' = \text{MeC}(\text{CH}_2\text{PPh}_2)_3$; $Y = \text{I}$; $R = R' = \text{Me}, \text{Ph}$; $R = \text{Me}, R' = \text{Ph}$)

Having described the catalytic activity of $[\text{WX}_2(\text{CO})_3(\text{NCMe})_2]$ ($M = \text{Mo}, \text{W}$; $X = \text{Br}, \text{I}$) for the polymerisation of nbd in Sections 2.1 and 2.2, herein we compare the activity of a series of complexes of the type $[\text{MI}_2(\text{CO})_3(\text{L}-\text{P}, \text{P}')]$ ($M = \text{Mo}$ or W), $[\text{MXY}(\text{CO})(\text{L}-\text{P}, \text{P}')(\eta^2\text{-RC}_2\text{R}')]$ and $[\text{MXY}(\text{CO})(\text{L}-\text{P}, \text{P}')(\eta^2\text{-RC}_2\text{R}')]$ $\{X = \text{Cl}, \text{Br}, \text{I}, Y = \text{I}; L = L = \text{PPh}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2; L' = \text{MeC}(\text{CH}_2\text{PPh}_2)_3; R = R' = \text{Me}, \text{Ph}; R = \text{Me}, R' = \text{Ph}\}$ towards the ring-opening polymerisation of nbd.

In 1988 [22], we described the synthesis and characterisation of a series of bis(alkyne) com-

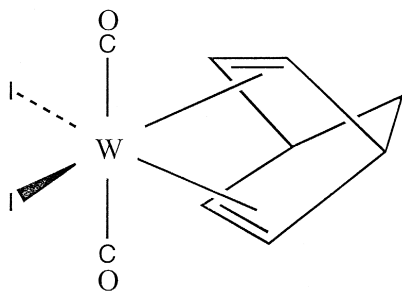
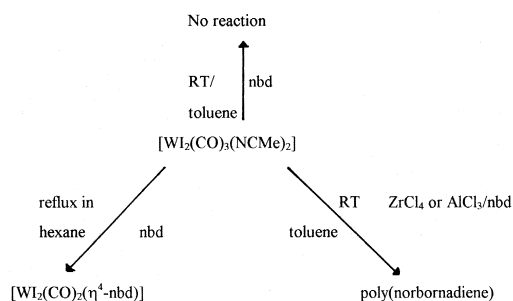


Fig. 3. Proposed structure of $[\text{WI}_2(\text{CO})_2(\eta^4\text{-nbd})]$ (**1**).



Scheme 2.

plexes $[W_{12}(CO)(NCMe)(\eta^2-RC_2R')_2]$, from the reaction of $[W_{12}(CO)_3(NCMe)_2]$ with excess RC_2R' . This was later extended to the molybdenum complexes, $[MoXY(CO)(NCMe)(\eta^2-RC_2R')_2]$ [23]. In 1996 [24], we described the synthesis and crystallographic characterisation ($R = R' = Me$; $R = Me, R' = Ph$) of the linear-triphos organometallic phosphines, $[W_{12}(CO)(L-P, P')(\eta^2-RC_2R')]$ $\{L = PPh(CH_2CH_2PPh_2)_2; R = R' = Me, Ph; R = Me, R' = Ph\}$. More recently [25], this was extended to the complexes $[MXY(CO)(L-P, P')(\eta^2-RC_2R)]$ ($M = Mo$ or W ; $X, Y = Cl, Br, I$; $R = Me, Ph$), which were crystallographically characterised for $M = W, X = Br$ or $I; R = Ph$. Very recently, we described the reactions of equimolar quantities of $[M_{12}(CO)_3(NCMe)_2]$ or $[MXY(CO)(NCMe)(\eta^2-RC_2R')_2]$ and $MeC(CH_2PPh_2)_3$ in CH_2Cl_2 at room temperature to give the organometallic phosphine ligands, $[M_{12}(CO)_3(L'-P, P')]$ [26] and $[MXY(CO)(L'-P, P')(\eta^2-RC_2R')]$ $\{X = Cl, Br, I, Y = I; L' = MeC(CH_2PPh_2)_3, R = R' = Me, Ph; R = Me, R' = Ph\}$ [27], respectively, in good yield. We have carried out a comparative study of the catalytic activity of a series of the above complexes towards the metathesis polymerisation of neat nbd. All experiments were carried out under exactly the same conditions (see experimental Section 4.6), and the results summarised in Table 1. It was found that the most active catalyst was for $M = W, X = Cl, Y = I, R = R' = Ph$. Again these results are in agreement with those observed by Hughes [14], and as de-

scribed in Sections 2.1 and 2.2, i.e. that the complexes with the more electronegative halide ligands are the most active towards the polymerisation of nbd. The polymers were characterised by 1H and ^{13}C NMR spectroscopy, but again the resolution was not good enough to be able to be sure of the *cis:trans* isomer ratios within the polymers.

2.4. Emulsion polymerisation of styrene using the completely water soluble catalyst, $[W_{12}(CO)_3(NC_5H_4CO_2Na-4)_2]$, $ZrCl_4$, sodium lauryl phosphate and sodium hydrogen phosphate

In 1958, Arhland et al. [28] described the first water-soluble phosphine, sodium 3-(diphenylphosphino)benzenesulfonate. Transition-metal complexes containing water-soluble phosphine ligands are very important in catalytic processes [29,30]. In 1995 [31], we described the synthesis of the first example of a completely water-soluble seven-coordinate complex, namely $[W_{12}(CO)_3(NC_5H_4CO_2Na-4)_2]$. This complex was prepared by reacting $[W_{12}(CO)_3(NCMe)_2]$ with two equivalents of $NC_5H_4CO_2H-4$ in MeOH at room temperature to yield, $[W_{12}(CO)_3(NC_5-$

Table 1
Preliminary study of the catalytic activity of novel molybdenum(II) and tungsten(II) monodentate phosphines

✓ = 50% conversion to polymer; ✓✓ = 100% conversion to polymer.

Where 0.007 mmol of complex was added to 2 cm³ of norbornadiene. L = PPh(CH₂CH₂PPh₂)₂; L' = MeC(CH₂PPh₂)₃.

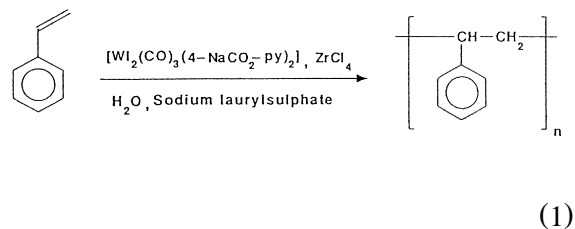
Complex	1 h/RT	40°C	24 h/RT
$[Mo_{12}(CO)_3(L-P, P')]$	X	X	X
$[W_{12}(CO)_3(L'-P, P')]$	X	✓	✓✓
$[Mo_{12}(CO)(L'-P, P')(\eta^2-MeC_2Me)]$	X	X	X
$[Mo_{12}(CO)(L-P, P')(\eta^2-MeC_2Me)]$	X	X	X
$[W_{12}(CO)(L-P, P')(\eta^2-MeC_2Me)]$	X	X	X
$[W_{12}(CO)(L'-P, P')(\eta^2-MeC_2Me)]$	X	✓	✓✓
$[W_{12}(CO)(L'-P, P')(\eta^2-HC_2Ph)]$	X	X	X
$[W_{12}(CO)(L'-P, P')(\eta^2-PhC_2Ph)]$	✓	✓	✓✓
$[WBrI(CO)(L'-P, P')(\eta^2-PhC_2Ph)]$	✓	✓	✓✓
$[WClI(CO)(L'-P, P')(\eta^2-PhC_2Ph)]$	✓✓	✓✓	✓✓

$\text{H}_4\text{CO}_2\text{H-4})_2]$, which when reacted with two equivalents of NaOH in EtOH gave the totally water-soluble complex, $[\text{WI}_2(\text{CO})_3(\text{NC}_5\text{H}_4\text{-CO}_2\text{Na-4})_2]$. We have extended the use of these cheap and easy to prepare water solubilising substituted pyridine ligands such as $\text{NC}_5\text{H}_4\text{-CO}_2\text{Na-4}$ and $\text{NC}_5\text{H}_4\text{SO}_3\text{Na-3}$ to other complexes such as the zero-valent complexes $[\text{M}(\text{CO})_n(\text{L})_{n-3}]$ ($\text{M} = \text{Cr, Mo, W}$; $\text{L} = \text{NC}_5\text{H}_4\text{CO}_2\text{Na-4, NC}_5\text{H}_4\text{SO}_3\text{Na-3, etc.}$) [32] and the π -allyl complexes $[\{\text{M}(\mu\text{-Br})(\text{CO})_2\text{-L}(\eta^3\text{-allyl})\}_2]$ and $[\text{MoX}(\text{CO})_2\text{L}_2(\eta^3\text{-allyl})]$ [33].

Emulsion polymerisation is an important technological process used to prepare acrylic polymers, poly(vinylchloride), poly(vinylacetate), and a number of copolymers. The technique involves the use of small particles of diameter 0.05–3 μm and a monomer-insoluble initiator. The system consists of a monomer, emulsifying agent, water and a water-soluble initiator. We have used this technique in the emulsion polymerisation of styrene using our $[\text{WI}_2(\text{CO})_3(\text{NC}_5\text{H}_4\text{CO}_2\text{Na-4})_2]/\text{ZrCl}_4$ co-catalyst system.

The emulsion polymerisation of styrene at 70°C was initiated by the free radical initiator potassium persulphate in an emulsion consisting of the surfactant sodium lauryl sulphate and sodium hydrogen phosphate in water. The addition of the reaction solution to an excess of methanol afforded polystyrene in high yield. In a similar reaction, the surfactant sodium lauryl phosphate, ($3.47 \times 10^{-2} \text{ mol dm}^{-3}$) and sodium hydrogen phosphate, ($7.04 \times 10^{-3} \text{ mol dm}^{-3}$) were dissolved in water and the solution was thoroughly degassed, before styrene was added. To the stirred emulsion was added the aqueous soluble catalyst $[\text{WI}_2(\text{CO})_3(\text{NC}_5\text{H}_4\text{CO}_2\text{Na-4})_2]$, ($3.08 \times 10^{-3} \text{ mol dm}^{-3}$), and the co-catalyst ZrCl_4 ($1.07 \times 10^{-2} \text{ mol dm}^{-3}$) were added. The solution was allowed to stir at 70°C for 5 h, before being poured into a large excess of methanol to yield a white polymeric product. The product was characterised by infrared and ^1H NMR spectroscopy. The infrared spectrum of the polymer as a KBr disc exhibited strong

C–H stretches at 2922 and 2848 cm^{-1} , suggesting that the monomer, which contains no aliphatic bonds had been successfully polymerised to give polystyrene (see Eq. (1)):



The room temperature ^1H NMR spectrum in CDCl_3 suggested that the monomer had been converted into polystyrene (see Fig. 4). The singlet at $\delta = 1.57 \text{ ppm}$ was assigned to the two protons H^b , and the singlet downfield at $\delta = 3.48 \text{ ppm}$ to the proton H^a attached to the carbon adjacent to the phenyl ring. The multiplet at $\delta = 7.06 \text{ ppm}$ was assigned to the aromatic protons H^c , confirming the synthesis of polystyrene. We are continuing to develop these water-soluble pyridine ligands, and their complexes in catalysis.

2.5. Polymerisation of phenylacetylene using $[\text{WX}_2(\text{CO})_3(\text{NCMe})\text{L}]$ ($\text{X} = \text{Cl, L} = \text{NCMe}$; $\text{X} = \text{I, L} = \text{NCMe, PPh}_3$ or AsPh_3 and $[\text{WBr}_2(\text{CO})(\text{NCMe})(\eta^2\text{-HC}_2\text{Ph})_2]$)

Over the years, Boroczak et al. [34], Szymanska-Buzar and Ziolkowski [35] and Szymanska-Buzar [36–38], have studied the catalytic

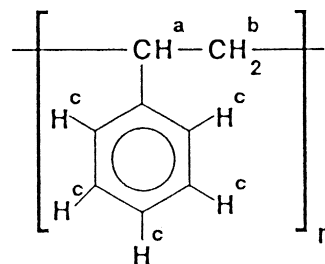


Fig. 4. The proton assignments of the ^1H NMR spectrum of polystyrene.

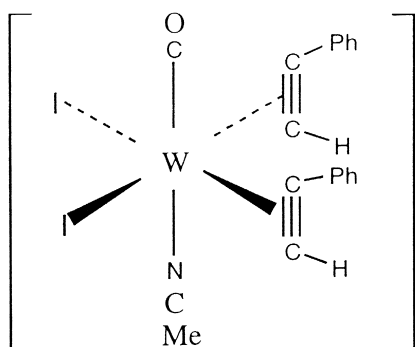


Fig. 5. Structure of $[WI_2(CO)(NCMe)(\eta^2-HC_2Ph)_2]$ [41].

activity of several tungsten(0)-Lewis acid systems, and they found the halocarbonyls obtained in the initial reaction are catalysts for the metathesis, isomerisation, and polymerisation of alkenes and alkynes. In 1997, Szymanska-Buzar [39] has shown that photochemical oxidation of $[W(CO)_6]$ with CCl_4 in cyclohexane/ CCl_4 (10:1) eventually gives $[\{W(\mu-Cl)Cl(CO)_4\}_2]$, which reacts with NCMe to give, $[WCl_2(CO)_3(NCMe)_2]$ (**3**). During the course of our work, we describe a simpler synthesis of (**3**) by reacting two equivalents of NaCl with $[WI_2(CO)_3(NCMe)_2]$, in acetone to give the halide exchanged product, (**3**) (see experimental Section 4.8). We could not isolate this complex in a pure state, as it is very unstable when subjected

to elemental analysis, however the complex is stable when stored and used in the solid state under a dinitrogen atmosphere.

As a background to this study, we have previously described [40], the trimerisation of MeC_2Ph using the molybdenum(II) bis(1-phenylpropyne) complex, $[MoI_2(CO)(NCMe)(\eta^2-MeC_2Ph)_2]$ in the presence of $P(O^iPr)_3$, which gave the crystallographically characterised 1,3,4-trimethyl-2,5,6-triphenylbenzene, [40]. We have also shown [41], that both the diiodide complexes, $[MI_2(CO)_3(NCMe)_2]$ ($M = Mo, W$) catalyse the polymerisation of phenylacetylene, and that these polymerisation reactions go via the bis(phenylacetylene) complex, $[WI_2(CO)(NCMe)(\eta^2-HC_2Ph)_2]$ [41], (see Fig. 5.), which has been crystallographically characterised.

In this paper, we describe preliminary studies of the catalytic polymerisation of HC_2Ph using $[WX_2(CO)_3(NCMe)_2]$ ($X = Cl, I$) and $[WI_2(CO)_3(NCMe)L]$ ($L = PPh_3, AsPh_3$) [42] and $[WBr_2(CO)(NCMe)(\eta^2-HC_2Ph)_2]$ (**4**) (which was prepared and characterised as described in Section 4.9) (see Table 2). The complexes $[WX_2(CO)_3(NCMe)_2]$ ($X = Cl$ or I) react with excess phenylacetylene to give orange to red poly(phenylacetylene) (ppa) in high yield. It is interesting that Szymanska-Buzar [39] observed that the amount of dimers of phenylacetylene

Table 2
Polymerisation of PA catalysed by tungsten(II) complexes

Complex	Conversion (%)		Yield (%)	dpbd		(pa) ₂		Other products (%)		
	1 h	24 h						1,2,3-TPB	1,2,4-TPB	1,3,5-TPB
$[WI_2(CO)_3(NCMe)_2]^a$	87	98	40	3	2	7	3	14	10	11
$[WI_2(CO)_3(NCMe)_2]^b$	80	96	10	–	–	–	6	–	–	–
$[WCl_2(CO)_3(NCMe)_2]^a$	33	95	36	5	10	–	9	15	–	–
$[WCl_2(CO)_3(NCMe)_2]^b$	23	71	43	–	–	–	–	13	–	–
$[WI_2(CO)_3(NCMe)(PPh_3)]^a$	17	98	27	2	0.2	5	5	7	1	–
$[WI_2(CO)_3(NCMe)(PPh_3)]^b$	27	97	5	–	–	–	4	–	5	7
$[WI_2(CO)_3(NCMe)(AsPh_3)]^a$	54	97	34	–	–	–	2	0.2	0.2	0.2
$[WI_2(CO)_3(NCMe)(AsPh_3)]^b$	91	96	6	5	5	–	28	20	19	10
$[WBr_2(CO)(NCMe)(\eta^2-HC_2Ph)_2]^a$	60	95	25	–	–	8	3	10	7	9
$[WBr_2(CO)(NCMe)(\eta^2-HC_2Ph)_2]^b$	48	94	3	–	–	–	66	–	5	0.1

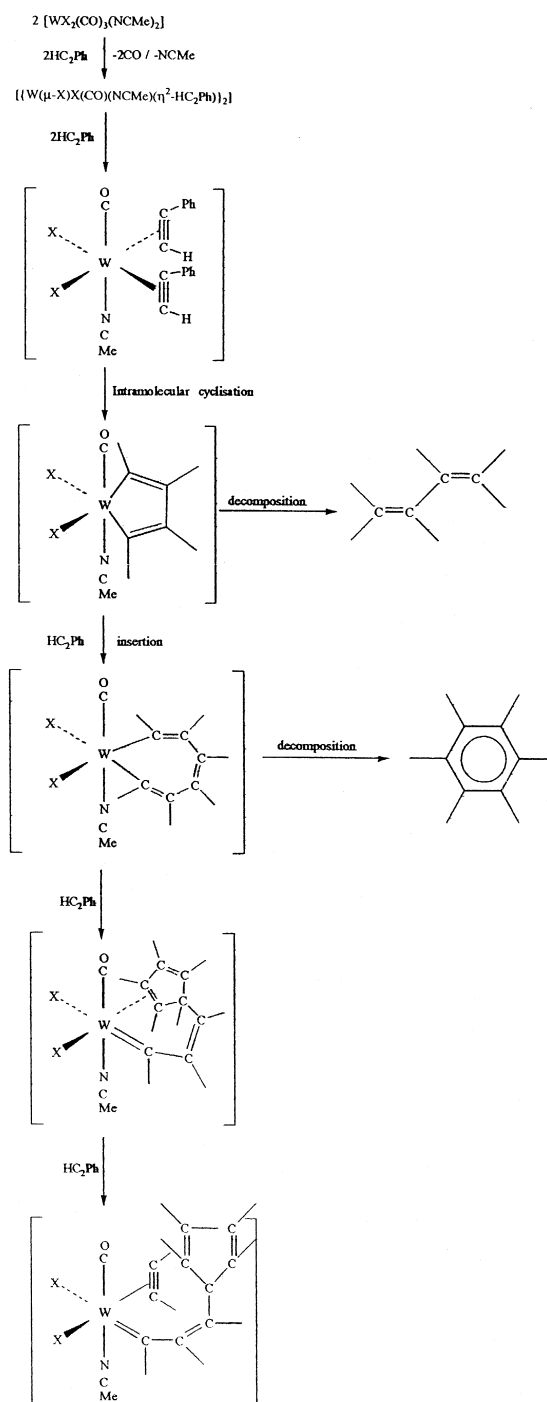
^a0.05 mmol of complex 2 cm³ of PA.

^b0.05 mmol of complex, 5 mmol of PA in 5 cm³ of toluene.

such as diphenylbutadiene(dpbd) and (pa)₂ {(pa)₂ = 1*H*-indene-1-phenylmethylene}-from MS results} are higher than when she used the tungsten dimers such as [$W(\mu\text{-Cl})Cl(CO)_4$]₂. We found significant amounts of these materials in our reactions.

The ppa observed in these reactions varies from orange to dark red. They are air stable and completely soluble in chlorinated solvents such as CH₂Cl₂, CHCl₃ and aromatic hydrocarbons. The structure of the ppas obtained were determined by consideration of the IR and ¹H NMR spectra of the polymers as described by Simionescu et al. [43]. The structure was shown to be the *cis*-isomer, as there is a strong band at 740 cm⁻¹ of high intensity, which can be ascribed to the *cis*-isomer. The resonances in the ¹H NMR spectra are also in accord with *cis*-isomer, by comparing with Simionescu et al., [43] data. Molecular weights of the polymers formed from these reactions are currently being measured.

The mechanism of the polymerisation reaction almost certainly involves initial coordination of the alkynes to [WX₂(CO)₃(NCMe)₂] in a two step process as shown in Scheme 3, to eventually give the complexes [WX₂(CO)(NCMe)(η²-HC₂Ph)₂] (X = Cl or I), which has been structurally characterised for X = I [41], (see Fig. 5). The synthesis and characterisation of the dibromo-complex (4) is given in the experimental Section 4.9, and from the spectroscopic data {IR = ν(CO) = 2092 cm⁻¹} and is very similar to the crystallographically characterised complex, [WI₂(CO)(NCMe)(η²-HC₂Ph)₂], is hence very likely to have a similar structure (see Fig. 5). As the alkynes are *cis*- and parallel to each other it is likely the two alkynes couple to give a metallocyclopentadiene intermediate. The metallocycles (Scheme 3) could insert an alkyne into a W–C bond to give a seven-membered ring, which could decompose, to give the trimers, 1,2,4- and 1,3,5-triphenylbenzenes. We have previously shown [40] that the complex [MoI₂(CO)(NCMe)(η²-MeC₂-Ph)₂] in the presence of P(OⁱPr)₃ catalytically



Scheme 3. The proposed mechanism for the polymerisation of phenylacetylene using [WX₂(CO)₃(NCMe)₂].

trimerises the alkyne to the crystallographically characterised arene, 1,3,4-trimethyl-2,5,6-tri-

phenylbenzene. Addition of a fourth phenylacetylene ligand could rearrange to an alkylidene as previously described by Yeh et al. [44]. They reacted the zero-valent complex, $[\text{W}(\text{CO})(\eta^2\text{-PhC}_2\text{Ph})_3]$ with excess PhC_2Ph . The diphenylbutadiene and triphenylbenzenes (1,2,4 and 1,3,5-tpb) detected by GS-MS in a residue obtained after separating the ppa with MeOH, also gives evidence for the formation of metallocyclopentadiene and metallocycloheptatrienes as intermediates (Table 2 and Scheme 3).

3. Conclusions

The seven-coordinate complexes $[\text{MXY}(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}, \text{W}$; $\text{X}, \text{Y} = \text{halide}$) and their wide range of derivatives undergo a variety of catalytic reactions with or without a co-catalyst including, metathesis polymerisation of norbornadiene, emulsion polymerisation of styrene and trimerisation and polymerisation of alkynes. Several of the catalytic intermediates, including **(1)** have been identified and fully characterised.

We are continuing to explore the catalytic activity of these versatile complexes and their derivatives, including attempts to develop multifunctional catalysts such as $[\text{RhCIL}''_3]$ ($\text{L}'' = [\text{MXY}(\text{CO})(\text{L}'\text{-P}, \text{P}')(\eta^2\text{-RC}_2\text{R}')])$ and $[\text{Co}_2(\text{CO})_7\text{L}'']$, which might be mixed hydrogenation (Rh) /metathesis (Mo or W) or hydroformylation (Co)/metathesis (Mo or W) catalysts, respectively.

4. Experimental

The synthesis, purification and other operations used in the catalytic work were carried out in an inert atmosphere using standard vacuum/Schlenk line techniques. The starting materials, $[\text{MX}_2(\text{CO})_3(\text{NCMe})_2]$ ($\text{M} = \text{Mo}, \text{W}$) [1], $[\text{MoBr}_2(\text{CO})_3(\text{NCMe})\text{L}]$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3$) [5], $[\text{WI}_2(\text{CO})(\text{L}\text{-P}, \text{P}')(\eta^2\text{-RC}_2\text{R}')]]$

[24], $[\text{MXY}(\text{CO})(\text{L}\text{-P}, \text{P}')(\eta^2\text{-RC}_2\text{R}')]]$ [25], $[\text{MX}_2(\text{CO})_3(\text{L}'\text{-P}, \text{P}')]$ ($\text{M} = \text{Mo}$ or W) [26], $[\text{MXY}(\text{CO})(\text{L}'\text{-P}, \text{P}')(\eta^2\text{-RC}_2\text{R}')]]$ [27] and $[\text{WI}_2(\text{CO})_3(\text{NC}_5\text{H}_4\text{CO}_2\text{Na-4})_2]$ [31] and $[\text{WI}_2(\text{CO})_3(\text{NCMe})\text{L}]$ ($\text{L} = \text{PPh}_3$ or AsPh_3) [42] were prepared using previously described procedures. All chemicals used were purchased from commercial sources. All solvents used were dried before use.

Elemental analyses (C, H and N) were determined on a Carlo Erba Analyser MOD 1108 (using helium as a gas carrier). IR spectra were carried out on a Perkin-Elmer 1600 FTIR spectrophotometer. ^1H and ^{13}C NMR spectra were obtained out on a Bruker AC 250 NMR spectrometer, and referenced to SiMe_4 .

The analysis of the products from the catalytic reactions were carried out on a Finnigan 4500 Automated GC-MS.

4.1. Attempted ring-opening metathesis of norbornadiene using $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$ in toluene

To a suspension of $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$ (0.15 g, 0.2908 mmol) in toluene (20 cm^3) was added norbornadiene (6.28 cm^3 , 5.36 g, 58.17 mmol). After stirring for 24 h, the solution was poured into methanol (200 cm^3). A polymeric product was not isolated.

Similar reactions of $[\text{WI}_2(\text{CO})_3(\text{NCR})_2]$ ($\text{R} = \text{Me}, \text{Bu}^t$ or Ph) with norbornadiene did not produce a polymer.

4.2. Ring-opening metathesis of norbornadiene using $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$ in the presence of ZrCl_4

To a stirred solution of norbornadiene (6.0 cm^3 , 5.12 g, 55.61 mmol) in toluene (20 cm^3) was added ZrCl_4 (0.19 g, 0.8342 mmol) and $[\text{MoI}_2(\text{CO})_3(\text{NCMe})_2]$ (0.14 g, 0.2781 mmol). After stirring for 10 min, the solution was poured into methanol (200 cm^3) to afford poly(norbornadiene). (Yield = 1.89 g, 37%).

4.3. Ring-opening metathesis of norbornadiene using $[\text{MoBr}_2(\text{CO})_3(\text{NCMe})_2]$

To $[\text{MoBr}_2(\text{CO})_3(\text{NCMe})_2]$ (0.12 g, 0.2845 mmol) dissolved in thf (20 cm³) with constant stirring, was added norbornadiene (6.14 cm³, 5.24 g, 56.90 mmol). After stirring for 15 min, the solution was poured into methanol (200 cm³) to afford poly(norbornadiene). (Yield = 1.41 g, 27%).

Similar reactions of $[\text{WBr}_2(\text{CO})_3(\text{NCMe})_2]$ and $[\text{WBr}_2(\text{CO})_3(\text{NCMe})(\text{EPh}_3)]$ (E = P, As or Ph) with norbornadiene in thf at room temperature, gave poly(norbornadiene).

4.4. Preparation and characterisation of (1)

To $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ (0.51 g, 0.8449 mmol) suspended in hexane (60 cm³) with constant stirring under a stream of dry nitrogen was added nbd (0.21 cm³, 1.95 mmol). After refluxing for 6 h, the solvent was removed in vacuo, and the resulting dark green product was resolated in CH_2Cl_2 (70 cm³) and filtered. The solvent was removed in vacuo and the green product was recrystallised from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at -17°C to give the analytically pure complex, (1). (Yield = 0.08 g, 17%).

Elemental analysis : $\text{C}_9\text{H}_8\text{O}_2\text{I}_2\text{W}$ requires C = 18.4, H = 1.4%; Found C = 18.3, H = 2.2%. IR (CHCl_3) $\nu(\text{CO}) = 2057$ (w), 1989 (s) cm^{-1} . ^1H NMR (CDCl_3 , + 25°C): $\delta = 4.52$ (m, 4H), 3.94 (m, 2H), 0.56 (t, 2H) ppm.

4.5. Preparation and characterisation of (2)

To $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ (0.5 g, 0.8283 mmol) dissolved in CHCl_3 (60 cm³) with constant stirring under a stream of dry nitrogen was added isoprene (iso) (0.17 cm³, 2.4849 mmol). After refluxing for 24 h, the solution was filtered and the solvent removed in vacuo. The resultant brown product was washed with hexane (15 cm³) CH_2Cl_2 (70 cm³) to afford the analytically pure complex (2). (Yield = 0.27 g, 57%).

Elemental analysis : $\text{C}_7\text{H}_8\text{O}_2\text{I}_2\text{W}$ requires C = 14.9, H = 1.5%; Found C = 14.4, H = 1.4%. IR (CHCl_3) $\nu(\text{CO}) = 2044$ cm^{-1} ; ^1H NMR (CDCl_3 , + 25°C): $\delta = 5.80$ (m, 1H, iso-H), 3.68 (q, $J = 7.86$ Hz, 4H, iso-H), 1.28 (t, $J = 8.57$, 3H, CH_3) ppm.

4.6. Catalytic studies using $[\text{MXY}(\text{CO})(\text{L}-\text{P}, \text{P}')](\eta^2-\text{RC}_2\text{R}')$ and related complexes

Norbornadiene (2 cm³, 1.86 g, 18.21 mmol) was added to $[\text{WBrI}(\text{CO})(\text{L}-\text{P}, \text{P}')](\eta^2-\text{PhC}_2\text{Ph})$ (0.008 g, 0.007 mmol) and the solution was stirred at room temperature for 1 h. The solution was poured into methanol to afford poly(norbornadiene). (Yield = 1.58 g, 85%).

Similar catalytic studies of the complexes, $[\text{MI}_2(\text{CO})_3(\text{L}-\text{P}, \text{P}')]$, $[\text{MXY}(\text{CO})(\text{L}-\text{P}, \text{P}')](\eta^2-\text{RC}_2\text{R}')$ and $[\text{MXY}(\text{CO})(\text{L}'-\text{P}, \text{P}')](\eta^2-\text{RC}_2\text{R}')$ were carried out in an exactly analogous manner and the results of these preliminary studies are given in Table 1.

4.7. Emulsion polymerisation of styrene using $[\text{WI}_2(\text{CO})_3(\text{NC}_5\text{H}_4\text{CO}_2\text{Na-4})_2]$ in the presence of ZrCl_4

To a stirred solution of $[\text{WI}_2(\text{CO})_3(\text{NC}_5\text{H}_4\text{CO}_2\text{Na-4})_2]$ (0.05 g, 0.0616 mmol) dissolved in H_2O (20 cm³) was added sodium lauryl sulphate (0.2 g, 0.6935 mmol) and sodium hydrogen phosphate (0.02 g, 0.1409 mmol). The co-catalyst ZrCl_4 (0.05 g, 0.2146 mmol) was added to the styrene (10 g, 10.21 cm³, 89.11 mmol), before being added to the aqueous solution. The solution was allowed to stir at 70°C for 5 h, and added to methanol (200 cm³) to produce polystyrene. (Yield = 6.5 g, 65 %).

4.8. Preparation and characterisation of (3)

To a stirred solution of $[\text{WI}_2(\text{CO})_3(\text{NCMe})_2]$ (2 g, 3.3 mmol) in acetone (25 cm³) was added two equivalents of NaCl (0.38 g, 6.6 mmol). After 24 h, the solution was filtered and the solvent removed in vacuo. The resultant dark

green oil was recrystallised from CH_2Cl_2 to afford (3). (Yield = 0.305 g, 22%).

IR (CHCl_3) $\nu(\text{N} \equiv \text{C}) = 2305$ (w), 2359 (w) cm^{-1} ; $\nu(\text{CO}) = 2080$ (s), 2009 (s) and 1949 (s) cm^{-1} . ^1H NMR (CDCl_3 , +25°C): $\delta = 2.40$, (s, 3H, *NCMe*) ppm; ^{13}C NMR (CDCl_3 , +25°C): $\delta = 4.20$ (s, *NCMe*), 124.13 (s, *N* \equiv *C*), 200.4 (s, *C* \equiv *O*) ppm.

4.9. Preparation and characterisation of (4)

To a stirred solution of $[\text{WBr}_2(\text{CO})_3(\text{NCMe})_2]$ (1 g, 1.86 mmol) in CH_2Cl_2 (30 cm^3) was added phenylacetylene (0.38 g, 0.40 ml, 3.72 mmol). After 24 h, the solution was filtered and the solvent removed in vacuo. The resultant dark brown solid was recrystallised from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ to afford (4) (Yield = 0.95 g, 85%).

Elemental analysis : $\text{C}_{54}\text{H}_{49}\text{BrIOP}_3\text{W}$ requires C = 37.0, H = 2.5, N = 2.3%; Found C = 37.0, H = 2.7, N = 2.3%. IR (CHCl_3) $\nu(\text{N} \equiv \text{C}) = 2343$ (w), 2321(w) cm^{-1} ; $\nu(\text{CO}) = 2092$ (s) cm^{-1} . ^1H NMR (CDCl_3 , +25°C): $\delta = 2.2$ (s, 3H, *NCMe*), 7.7–7.4 (m, 10 H, *Ph*), , 11.1 (s, 2H, *C}_2\text{H}*) ppm.

4.10. Polymerisation of HC_2Ph studies

Generally, the toluene solution of pa and the internal standard (xylene) was added to the catalyst, and the formation of pa was monitored by chromatography. The reactions were continued for 24 h and methanol was added to precipitate the polymer, which was collected, recrystallised from $\text{CH}_2\text{Cl}_2/\text{MeOH}$, dried in vacuo and analysed by IR and ^1H NMR spectroscopy.

The filtrate, which was obtained after precipitation of the various polymers, was evaporated to dryness, and the residue was dissolved in CH_2Cl_2 and then analysed by GC-MS. Analysis of the products showed that there were mainly diphenylbutadiene and triphenylbenzenes. The results of this work are given in Table 2.

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