ELSEVIER

Journal of Organometallic Chemistry 548 (1997) 195–203

Journal of Organometallic Chemistry

Synthesis, characterisation and reactivity of group six alkylidynes bearing the tridentate phosphine $PPh(C_2H_4PPh_2)_2$-'triphos'. Crystal structure of *mer*-$[W(NCMe)(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)][BF_4]$

John C. Jeffery [1], Andrew S. Weller *,[2]

School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK

Received 30 April 1997; received in revised form 5 July 1997

Abstract

Reaction between $[WBr(\equiv CC_6H_4Me\text{-}4)(NC_5H_5Me\text{-}4)_2(CO)_2]$ and the tridentate, linear, phosphine $PPh(CH_2CH_2PPh_2)_2$ (triphos) in refluxing toluene affords *mer*-$[WBr(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)]$, **1**. Halide abstraction (with $TlBF_4$) in CH_2Cl_2 solvent results in carbonyl scavenging to afford the cationic dicarbonyl species *fac*-$[WBr(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)_2][BF_4]$, **2**, whereas removal of the halide in acetonitrile solvent affords the complex *mer*-$[W(NCMe)(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)][BF_4]$, **3**. Protonation of **1** (with $HBF_4 \cdot OEt_2$) results in the formation of the alkylidene complex *mer*-$[WBr\{=C(H)C_6H_4Me\text{-}4\}\{PPh(C_2H_4PPh_2)_2\}(CO)][BF_4]$, **4**. Methylation of **1** affords the methyl/alkylidyne complex *mer*-$[WCH_3(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)]$, **5**, which can be protonated to form $[WCH_3\{=C(H)C_6H_4Me\text{-}4\}\{PPh(C_2H_4PPh_2)_2\}(CO)][BF_4]$, **6**. The new complexes have been fully characterised by multinuclear NMR spectroscopy and, additionally, for **3** by a single crystal X-ray diffraction study. © 1997 Elsevier Science S.A.

1. Introduction

The chemistry of mononuclear alkylidyne complexes is well established, and is still attracting attention [1–6], with the chemistry of those complexes bearing monodentate phosphines being particularly well represented [7–9]. However, those complexed with bi-dentate chelating phosphines have attracted rather less attention [10–12] and there have been no reports of alkylidyne complexes ligated with poly-dentate phosphines ($n > 2$). In light of the advantages that complexes ligated with such phosphines have been shown to display over their mono-dentate and bi-dentate analogues [13,14], it is thus of interest to investigate the synthesis and reactivity of alkylidyne complexes bound with poly-dentate phosphorus ligands.

We report, here, the first example of such a species complexed with the potentially tridentate, linear phosphine bis(diphenylphosphinoethyl)phenylphosphine, triphos, and give details of a preliminary investigation of its reactivity, in halide abstraction, protonation and alkylation reactions .

2. Results and discussion

Heating to reflux a toluene solution of $[WBr(\equiv CC_6H_4Me\text{-}4)(NC_5H_5Me\text{-}4)_2(CO)_2]$ with one equivalent of $PPh(C_2H_4PPh_2)_2$ (triphos) for ca. 3 h affords the new bright yellow complex *mer*-$[WBr(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)]$, compound **1**, in moderate yield after low temperature column chromatography. The IR spectrum of **1** demonstrates that one carbonyl ligand has been lost in the reaction, only a single CO stretching band is observed at 1901 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum displays two tungsten bound phosphorus environments: a triplet resonance at δ 82.3 ppm and a doublet at δ 44.7 ppm, in

---

* Corresponding author.

[1] Also corresponding author.

[2] Present address: Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, U.S.A.

PII S0022-328X(97)00412-9

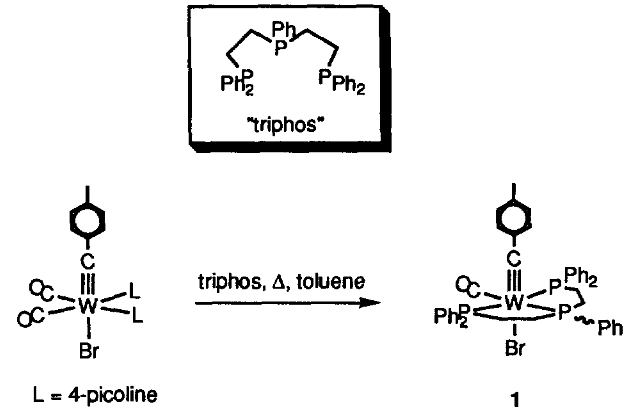
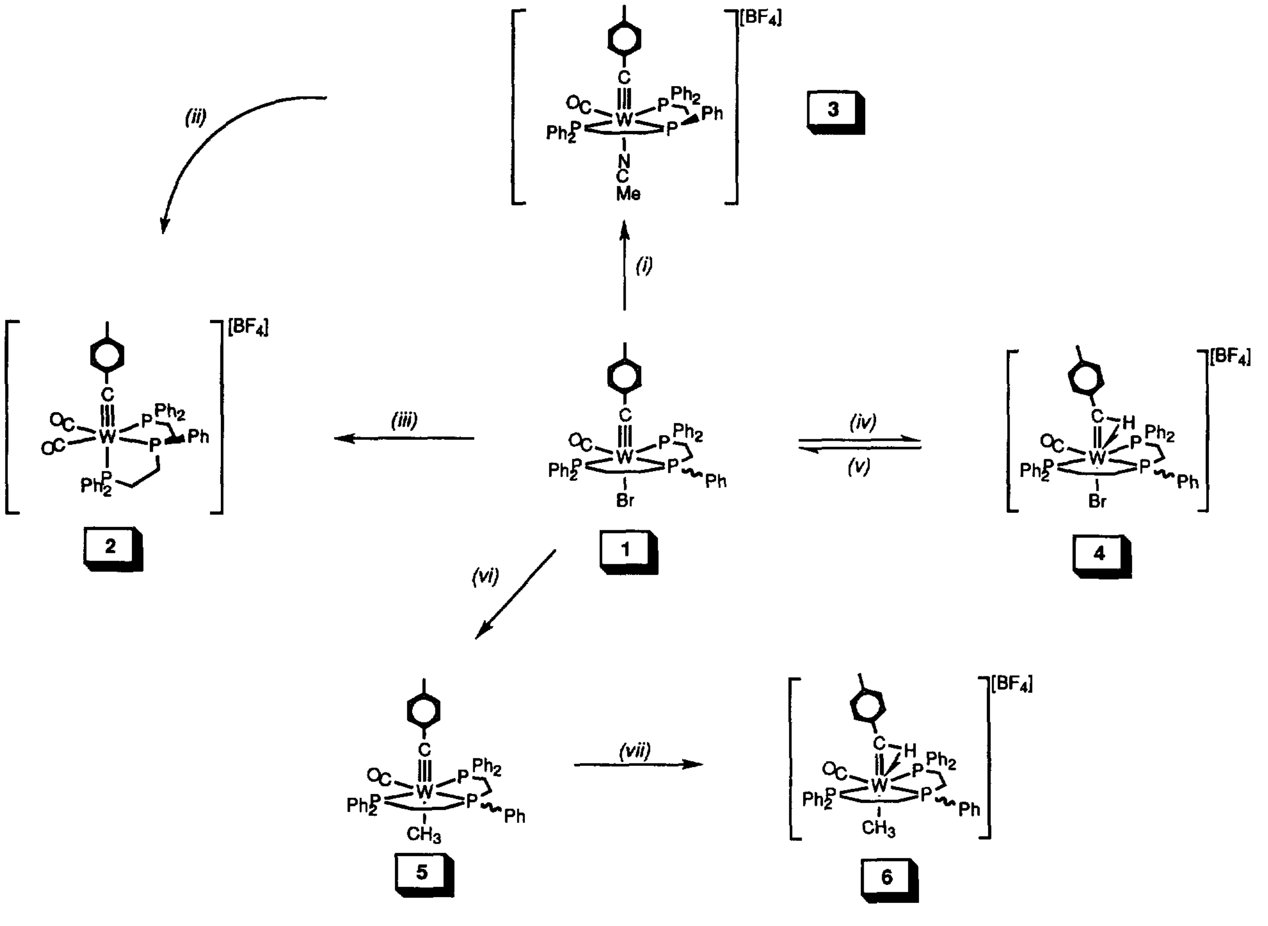


Fig. 1.

the ratio 1:2 respectively, displaying the expected *cis* $^{31}P-^{31}P$ coupling, as well as showing coupling to tungsten [J(WC) 200 and 291 Hz respectively]. That the molecule displays a mirror plane of symmetry in solution demonstrates that the tridentate phosphorus ligand is coordinated meridionally, the smaller $^{183}W-^{31}P$ coupling constant for the unique phosphorus atom implying that this atom is *trans* to either the high *trans* influence carbonyl or alkylidyne ligands. The gross stereochemistry of complex **1** was unequivocally established by examination of the $^{13}C\{^1H\}$ NMR spectrum. As well as resonances due to alkyl and aromatic carbons, a broad doublet is observed at δ 230.3 ppm [J(PC) 37 Hz] and assigned is to the single CO group, the large magnitude of this coupling showing that the unique phosphorus is *trans* to the carbonyl group. The *cis* coupling to the other two equivalent phosphorus atoms is evidently small. The alkylidyne carbon is observed at δ 268.8 ppm as a doublet of triplets [J(PC) 10 and 7 Hz], showing a *cis* coupling to the phosphorus atoms, confirming the structure of **1** as one in which the three phosphorus atoms and the CO lie in the same plane with the {≡CR} fragment and bromide ligand mutually *trans* to each other (Scheme 1).

Although we can be confident of the gross stereochemistry of compound **1**, the orientation of the phenyl group appended to the central phosphorus atom cannot be deduced from this NMR data alone. The phenyl



(i) MeCN, TlBF$_4$, Δ, *(ii)* CO, 1 atm *(iii)* CH$_2$Cl$_2$, TlBF$_4$, *(iv)* CH$_2$Cl$_2$, HBF$_4$.OEt$_2$, *(v)* thf, *(vi)* LiCuMe$_2$, *(vii)* CH$_2$Cl$_2$, HBF$_4$.OEt$_2$

Scheme 1.

group may be orientated towards the alkylidyne (the *syn* diastereoisomer), or towards the bromide (the *anti* diastereoisomer). The difference energetically between the two diastereoisomers would be expected to be small (although the barrier to inversion at phosphorus is high), but only one diastereoisomer is formed as the final product, as shown by NMR spectroscopy. Although this question could be resolved by a single crystal X-ray diffraction study, structural studies have so far been frustrated by a lack of suitable crystals. Moreover, ^{1}H NOE experiments, which have been successfully used in the resolution of the stereochemistry of the central phenyl ring in other metallo tridentate phosphine complexes [15,16], were ambiguous in this instance. However, if the reaction between [WBr($\equiv$CC$_6$H$_4$Me-4)(NC$_5$H$_5$Me-4)$_2$(CO)$_2$] and triphos is stopped after only 2 h heating two additional signals are observed in the ^{31}P{^{1}H} NMR spectrum (ca. 5%): a triplet at δ 55.9 ppm and a doublet at δ 31.8 ppm, in the ratio 1:2 respectively, with coupling constants similar to that of **1**. In the absence of other spectroscopic data, we tentatively assign this species as the alternative diastereoisomer of **1**. Attempts to isolate this minor component were not successful. Continued heating of this sample results in a complete conversion to pure **1**. It is interesting to note that the chemical shift for the central phosphorus atom of this alternative diastereoisomer occurs ca. δ 26 ppm to lower frequency than for that found in compound **1**, suggesting that the central phosphorus atom's chemical shift is somewhat sensitive to the orientation of the phenyl group, an observation that has been previously noted in other systems [16–18]. Clearly, one diastereoisomer is favoured over the other, but as the difference in energy between the two isomers would be expected to be small, then any steric or electronic effects determining the outcome must also be subtle. The mechanism of isomerisation could well be one which involves loss of the bromide, reorganisation of the ligand, and reco-ordination of the halide ion.

Putting the question of the stereochemistry of the central phenyl group to one side, complex **1** is the first example of a alkylidyne complex ligated with a tridentate phosphine. The potentially flexible coordination abilities of triphos (which has been shown to have no strong intrinsic preference for *fac* or *mer* geometries) are of interest, the ligand is able to reorganise as a consequence of the electronic and/or steric demands of the metal [19], and hence the reactivity of **1** was investigated.

Treatment of compound **1** with a slight excess of TlBF$_4$, resulted in the precipitation of insoluble TlBr and the formation of the new orange complex *fac*-[W($\equiv$CC$_6$H$_4$Me-4)({PPh(C$_2$H$_4$PPh$_2$)$_2$})(CO)$_2$][BF$_4$] **2**, in moderate yield (< 50% based on tungsten consumed). Complex **2** is formed via a carbonyl scavenging mechanism, accounting for the poor yield. Yields of complex **2** were increased significantly by bubbling CO through the reaction mixture. In accordance with the scavenging of a carbonyl ligand, the IR spectrum of **2** displays two strong CO stretching bands at 2005 cm^{-1} and 1941 cm^{-1}, indicating a *cis* orientation of CO groups. The change in geometry of the phosphine ligand from *mer* to *fac* is demonstrated by three inequivalent phosphorus environments being observed in the ^{31}P{^{1}H} NMR spectrum. The highest field resonance (at δ 19.9 ppm) displays a significantly smaller magnitude of ^{183}W–^{31}P coupling, and is therefore assigned to a phosphorus atom *trans* to the high *trans* influence alkylidyne ligand. In agreement with this assignment, the ^{13}C{^{1}H} NMR spectrum displays two doublets of virtual triplets (both showing two *cis* and one *trans* ^{31}P–^{13}C coupling respectively) at δ 217.9 ppm and δ 210.1 ppm assigned to the two inequivalent CO ligands, and a doublet of virtual triplets at δ 300.4 ppm (again showing one *trans* and two *cis* ^{31}P–^{13}C couplings) assigned to the alkylidyne moiety. Thus the removal of the halide results in an unstable, co-ordinatively unsaturated, 16-electron species, which scavenges CO from other molecules in solution. The change in co-ordination geometry of the triphos from *mer* to *fac* can be traced to the fact that CO will be unfavoured in residing *trans* to the alkylidyne ligand, due to the strong π acid character of both ligands.

Attempts to co-ordinate ligands other than CO, such as alkynes, alkenes or phosphines only resulted in the isolation of complex **2** or formation of intractable mixtures of products. However, heating to reflux for two hours an acetonitrile solution of compound **1** in the presence of TlBF$_4$, resulted in the near quantitative formation of the new red complex *mer*-[W(NCMe)($\equiv$CC$_6$H$_4$Me-4){PPh(C$_2$H$_4$PPh$_2$)$_2$}(CO)]-[BF$_4$] **3**. This new complex displays one strong CO stretching band at 1911 cm^{-1}, with a weak stretching band at 2284 cm^{-1}, assigned to the coordinated acetonitrile. In the ^{31}P{^{1}H} NMR spectrum a triplet at δ 80.9 ppm and a doublet at δ 47.7 ppm in the ratio 1:2 respectively are observed, demonstrating that the triphos ligand has retained a *mer* co-ordination geometry, whilst in the ^{1}H NMR spectrum the coordinated acetonitrile ligand is seen as an integral three singlet at δ 2.31 ppm. The ^{13}C{^{1}H} NMR spectrum confirmed the geometry of the ligand set. A doublet centred at δ 232.1 ppm is assigned to the single CO ligand, showing only the *trans* coupling to the unique phosphorus [*J*(PC) 32 Hz], whilst the alkylidyne carbon atom is observed as a broad signal at δ 289.4 ppm. The coordinated acetonitrile appears as two signals at δ 146.8 ppm and δ 5.0 ppm. Although NMR spectroscopy allowed the full characterisation of complex **3**, the stereochemistry of the central phenyl group was still ambiguous. A single crystal X-ray diffraction study on **3** resolved this question, the result of which is reported below.

Table 1
Selected bond lengths (Å) and angles (°) for complex **3**

W(1)–C(11)	1.816(9)	W(1)–C(10)	2.028(11)
W(1)–N(1)	2.291(7)	W(1)–P(1)	2.478(2)
W(1)–P(2)	2.481(2)	W(1)–P(3)	2.512(3)
C(10)–O(1)	1.137(2)	C(11)–C(31)	1.439(11)
N(1)–C(20)	1.112(11)		
C(31)–C(11)–W(1)	176.2(7)	N(1)–C(20)–C(21)	179.2(12)
P(1)–W(1)–P(2)	79.36(9)	P(1)–W(1)–P(3)	154.28(7)
P(2)–W(1)–P(3)	79.09(9)	C(11)–W(1)–P(3)	101.0(3)
C(11)–W(1)–P(2)	97.9(3)	C(11)–W(1)–N(1)	176.3(3)
C(11)–W(1)–P(1)	95.7(3)	C(11)–W(1)–C(10)	90.0(4)
C(10)–W(1)–N(1)	87.3(4)	C(10)–W(1)–P(1)	97.2(3)
N(1)–W(1)–P(1)	82.2(2)	C(10)–W(1)–P(2)	171.6(3)
N(1)–W(1)–P(2)	84.7(2)	C(10)–W(1)–P(3)	102.2(3)
O(1)–C(10)–W(1)	177.5(10)		

Compound **3** crystallises with no apparent close intermolecular contacts, and selected bond lengths and angles are given in Table 1. Fig. 2, meanwhile, shows a perspective view of compound **3**. The complex has an approximate, non-crystallographic, mirror plane of symmetry, passing through O(1), W(1), P(2) and C(11), the phosphine ligand being meridonally coordinated. The tungsten centre is essentially octahedral, slight distortions due to the fused chelate ring of the phosphine ligand. The acetonitrile ligand lies *trans* to the alkylidyne ligand, W(1)–N(1) 2.291(7) Å. This may be compared with the W–N bond distance in the related phosphine complex *fac*-[W(NCMe)(dppm)(CO)$_3$] at 2.190(5) Å (dppm = diphenylphosphinomethane), in which the acetonitrile is *trans* to a carbonyl group [20]. The longer W–N distance in **3** may be traced to the greater *trans* influence of $\equiv$CR over CO. The tungsten–alkylidyne distance [W(1)–C(11)] at 1.816(9) Å is in the range common for terminal alkylidyne ligands [7–9], with the alkylidyne ligand essentially linear, W(1)–C(11)–C(31) 176.2(7)°. The only other reported example of a crystallographically characterised tungsten–triphos complex is the simple tricarbonyl *fac*-[W{PPh(C$_2$H$_4$PPh$_2$)$_2$}(CO)$_3$] **A** [21]. The tungsten–phosphorus bond lengths are 2.478(2) Å and 2.481(2) Å for W–P(1) and W–P(2) respectively, whilst that for W–P(3) is slightly longer at 2.512(3) Å, which can be compared with those found in **A** at 2.474(2), 2.495(2) and 2.515(1) Å. As can be seen from the space filling diagram for complex **3** (Fig. 3), there is no significant interaction between the phenyl groups on the phosphine and the acetonitrile or the alkylidyne ligands, although it is evident that there is little room for incoming ligands, the 'rod-like' acetonitrile fitting snugly into the cavity afforded by the phenyl groups. The stereochemistry of the central phenyl group is clearly *syn*, pointing towards the alkylidyne ligand. Although we cannot be certain that this is the case for the precursor complex **1**, the similarity in ^{31}P{^{1}H} chemical shifts of the central phosphorus atom [δ 82.3 vs. δ 80.9 ppm] perhaps suggests that the stereochemistry is *syn* in complex **1** also. Complex **3** reacts virtually quantitatively over a period of six hours with CO to afford **2**, as shown by IR and ^{31}P{^{1}H} NMR spectroscopy. However, **3**, does not react with other ligands such as dimethylacetylene or diphenylacetylene, even under forcing reflux conditions.

Previous studies on the protonation of alkylidyne complexes ligated with phosphines have shown that either hydridic alkylidyne or alkylidene species may be formed [22,23], the result is often dependent on the type

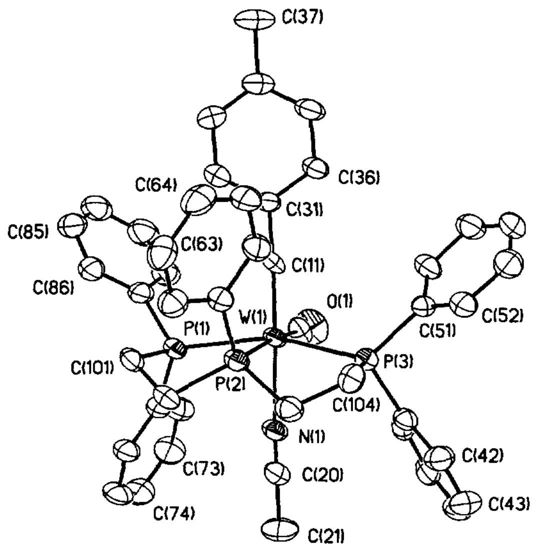


Fig. 2. Perspective view of compound 3. Thermal ellipsoids are drawn at the 30% probability level. Phenyl rings are numbered cyclically. Hydrogen atoms have been omitted for clarity.

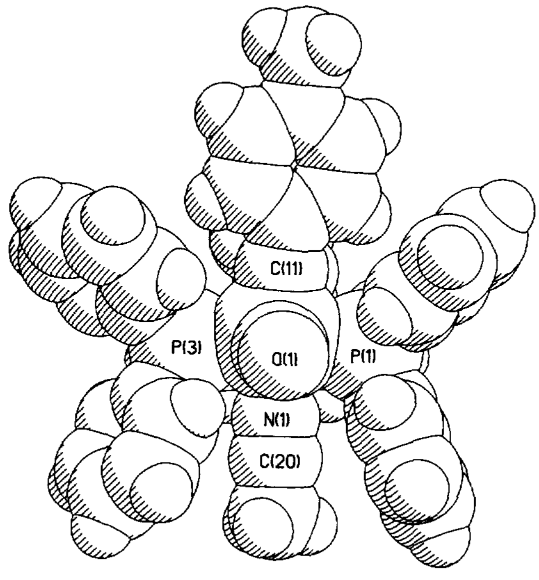


Fig. 3. Space filling diagram of compound 3.

phosphine present in the complex [24,25]. It was therefore of interest to investigate the protonation reactions of compound **1**, to see if the triphos ligand affected the outcome of protonation compared with mono-dentate and bi-dentate phosphines.

Treatment of a CH_2Cl_2 solution of compound **1** with HBF_4 at −78°C resulted in a change in colour of the solution from yellow to red on warming to room temperature, and the formation of the new alkylidene complex *mer*-$[WBr\{=C(H)C_6H_6Me\text{-}4\}\{PPh(C_2H_4PPh_2)_2\}(CO)][BF_4]$ **4** in good yield, which contains an agostic alkylidene ligand, relieving the formal unsaturation at the tungsten metal centre. The IR spectrum of complex **4** shows one strong CO stretching band at 1988 cm^{-1}, a shift of 87 cm^{-1} to higher frequency from that found in compound **1** consistent with the move from a neutral to cationic complex. The $^{31}P\{^1H\}$ NMR spectrum demonstrates that the phosphorus ligand is still meridonally coordinated, a triplet at δ 78.0 ppm and a doublet centred at δ 35.0 ppm are observed in the ratio 1:2 respectively. The ^1H NMR spectrum shows a high field, integral one, doublet of triplets at δ −4.71 ppm [J(PH) 6, 8 Hz respectively], also displaying a small coupling to tungsten [J(WH) 34 Hz]. Typically, formally 18-electron alkylidene species that have no agostic interactions display a diagnostic low field signal between δ 10 to 15 ppm for the methylidene proton, whilst those in which agostic interactions [26] are invoked generally have high field chemical shifts in the range δ 2 to −8 ppm. In the $^{13}C\{^1H\}$ NMR spectrum the single CO ligand is observed as a doublet at δ 212.2 ppm displaying only the *trans* coupling to the phosphorus ligand, whilst a doublet of triplets showing *cis* coupling to triphos is observed at δ 242.7 ppm, in the region associated with W=C double bonds [27]. The true nature, however, of the alkylidene ligand was confirmed by examination of the ^{13}C (gated NOE) spectrum. In this, the alkylidene signal is further split into a doublet of magnitude $J(HC) = 71$ Hz. This coupling constant is fully consistent with an agostic alkylidene. Agostic, alkylidene species have a coupling constant in the range 45 to 90 Hz, whilst in alkylidenes that do not invoke agostic interactions this is normally 110 to 130 Hz [24,25].

Thus, protonation of compound **1**, affords an alkylidene complex, in which the formal electronic unsaturation at the tungsten centre is relieved by an agostic interaction from the alkylidene bound proton. Complex **4** is readily deprotonated, even by mild bases, dissolution in thf causing yellow compound **1** to be re-generated in less than 1 minute. Treatment of compound **1** with other acids, such as HCl gas resulted in the formation of $[\mathbf{4}]^+$, with no further substitution at the metal centre by chloride, as has been reported for some related mono-dentate phosphine species [22].

Treatment of a thf solution of compound **1** with one equivalent of the methylating reagent $LiCuMe_2$ affords the new alkyl–alkylidyne complex *mer*-$[W(CH_3)(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)]$ **5** in moderate yield after low temperature column chromatography. The IR spectrum of compound **5** displays a single CO stretching band at 1908 cm^{-1}. The ^1H NMR spectrum is particularly diagnostic, a high field doublet of triplets [J(PH) 9 and 10 Hz] centred at δ −1.90 ppm, of integral three protons, demonstrates that the methyl group is *cis* to all three of the phosphorus atoms. This chemical shift for the tungsten bound methyl group is consistent with previously reported examples, such as $[W(CH_3)(\equiv CCH_3)(PMe_3)_4]$ at δ −1.58 ppm [28]. The $^{31}P\{^1H\}$ NMR spectrum confirms that the triphos retains a meridonal configuration, a broad signal at δ 77.1 ppm and a triplet at δ 42.9 ppm, displaying the expected magnitudes of ^{31}P and ^{183}W couplings. The $^{13}C\{^1H\}$ NMR spectrum confirms the stereochemistry of the complex, a broad signal at δ 265.2 ppm is assigned to the alkylidyne carbon, and the magnitude of the $^{183}W–^{13}C$ coupling of this signal is significantly smaller than in the precursor compound **1** [J(WC) 152 Hz in **5** vs. 203 Hz in **1**]. This is attributed to the high *trans* influence methyl ligand. A broad signal at δ 228.2 ppm is assigned to the single carbonyl group, the coupling to ^{31}P is unresolved. The methyl group is observed as a doublet of triplets centred at δ −8.2 ppm, further demonstrating the *cis* displacement of the alkyl ligand with respect to the phosphine ligand. The $^{183}W–^{13}C$ coupling constant is measured at 35 Hz. Although smaller that expected for a σ-bound carbon, with the methyl group *trans* to the alkylidyne ligand this coupling may well be expected to be small. Complex **5** is a further addition to the small group of low valent tungsten alkylidyne/alkyl complexes [28–31] previously reported. Complex **5** is stable a −20°C for a matter of weeks, but decomposes at room temperature under a nitrogen atmosphere. For this reason, satisfactory microanalysis was not obtained, however, the spectroscopic data leave us in no doubt of its formulation. Complex **5** reacts with CH_2Cl_2 over a period of three days to afford the chloro analogue of compound **1**, *mer*-$[WCl(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)]$, in essentially quantitative yield, in which the methyl group has been lost and replaced by chloride derived from the solvent. Micro-analysis, mass spectrometry and multinuclear NMR spectroscopy confirmed the identity of this new species.

Protonation of **5** at −78°C with $HBF_4 \cdot OEt_2$ afforded a red solution of the new complex *mer*-$[W(CH_3)\{=C(H)C_6H_4Me\text{-}4\}\{PPh(C_2H_4PPh_2)_2\}(CO)]$-$[BF_4]$ **6** in moderate yield. The IR spectrum of complex **6** displays one CO stretching band at 1991 cm^{-1} (comparable with complex **4** at 1988 cm^{-1}). The ^1H NMR spectrum confirms that the proton has attacked the alkylidyne carbon to give an agostic alkylidene, a high field doublet of triplets integrating to one proton centred at δ −4.49 ppm is observed (cf. complex **4** at δ −4.71 ppm) also showing $^{183}W-^{1}H$ coupling. That the methyl group has not been lost on protonation, is evidenced by an integral three doublet of triplets being seen at δ 2.74 ppm. This signal is shifted to higher frequency by ca. δ 4.6 ppm compared with **5**, an indication of the move from neutral to cationic species. The $^{31}P\{^{1}H\}$ spectrum, shows that the phosphorus ligand has not changed in gross geometry; a triplet at δ 78.7 ppm and a doublet at δ 42.9 ppm, in the ratio of 1:2, being observed.

Complex **6** decomposes in solution over a period of hours to unidentified products and thus satisfactory carbon-13 spectra were not obtained. However, by comparison with data from complex **4**, the formulation and stereochemistry of complex **6** may be confidently assigned.

3. Experimental

3.1. General

All manipulations were performed under an atmosphere of dry, deoxygenated, dinitrogen using standard Schlenck techniques. Solvents were distilled from the appropriate drying agents immediately prior to use: CH_2Cl_2 and MeCN:CaH_2; thf, diethyl ether, hexane, light petroleum (40°–60° fraction): Na/benzophenone. The complex $[WBr(\equiv CC_6H_4Me\text{-}4)(NC_5H_4Me\text{-}4)_2(CO)_2]$ was prepared by a slight modification of the method developed by McDermott et al. [32]. Bis(diphenylphosphinoethyl)phenylphosphine (triphos) and $HBF_4 \cdot OEt_2$ (85% solution) were used directly as supplied by Aldrich.

3.2. Spectroscopy

IR spectra were recorded as CH_2Cl_2 solutions on a Perkin-Elmer 1600 FTIR in 1 mm solution cells. NMR spectra were recorded on a Jeol GX 400 spectrometer in CD_2Cl_2 solutions at 297 K unless stated otherwise. Chemical shifts (δ) are quoted in ppm, coupling constants are quoted in Hz. Hydrogen-1 and carbon-13 spectra are quoted with reference to residual protio solvent in the sample. Phosphorus-31 spectra are with reference to H_3PO_4 (external).

3.3. *mer*-$[WBr(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)]$ **1**

$[WBr(\equiv CC_6H_4Me\text{-}4)(NC_5H_4Me\text{-}4)_2(CO)_2]$ (0.24 g, 0.39 mmol) and triphos (0.21 g, 0.39 mmol) were dissolved in toluene (20 cm^3) and heated to reflux for 3 h. The solvent was removed in vacuo, the residue dissolved in CH_2Cl_2 (5 cm^3) and columned on alumina (BA III, CH_2Cl_2, −20°C) eluting a single yellow band. This was recrystallised from CH_2Cl_2/hexane to afford *mer*-$[WBr(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)]$ 0.24 g, 65% yield. $C_{43}H_{40}BrOP_3W$ requires 55.6% C, 4.3% H. Found 55.9% C, 4.3% H. IR $\{\nu_{max}(CO)\}$: 1901(s) cm^{-1}. NMR: ^{1}H: 7.98–6.80 (m, 25H, Ph), 6.63 [d (AB), 2H, C_6H_4, J(HH) 7], 6.22 [d (AB), 2H, C_6H_4, J(HH) 7], 3.70–2.16 (m, 8H, CH_2), 2.11 (s, 3H, Me). $\mathbf{13}_{C}\{^{1}H\}$: 268.8 [dt, W≡C, J(PC)10, 7, J(WC) 203], 230.6 [d, CO, J(PC) 37, J(WC) 170], 148.3–127.5 (Ph and C_6H_4), 32.0 (m, CH_2), 26.3 (m, CH_2), 21.2 (s, Me). $^{31}P\{^{1}H\}$: 82.3 [t, 1P, J(PP) 10, J(WP) 200], 44.7 [d, 2P, J(PP) 10, J(WP) 291].

3.4. *fac*-$[W(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)_2][BF_4]$ **2**

In a typical experiment **1** (0.100 g, 0.11 mmol) was dissolved in CH_2Cl_2 (10 cm^3). $TlBF_4$ (0.034 g, 0.117 mmol) was added and the reaction stirred overnight. Filtration through celite and reprecipitation from CH_2Cl_2/hexane afforded impure *fac*-$[W(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)_2][BF_4]$ **2**. Analytically pure **2** may be obtained by reaction in the presence of CO, and recrystallisation of the product from CH_2Cl_2/Et_2O afforded orange *microcrystals* of **2**. 0.080 g, yield 76%. $C_{44}H_{40}BF_4O_2P_3W$ requires 54.8% C, 4.2% H. Found 55.4% C, 4.3% H. IR $\{\nu_{max}(CO)\}$: 2005 (vs.), 1941(s). NMR: ^{1}H: 7.86–6.76 (m, 25H, Ph), 6.91 [d (AB), 2H, C_6H_4, J(HH) 8], 6.76 [d (AB), 2H, C_6H_4, J(HH) 8], 3.68–2.12 (m, 8H, CH2), 2.22 (s, 3H, Me). $^{13}C\{^{1}H\}$ (Measured in CD_3CN) [3]: 300.4 [dt, W≡C, J(PC) 25, 15], 217.9 [dt, CO, J(PC) 25, 15], 210.1 [dt, CO, J(PC) 25, 15], 149.9–129.6 (Ph and C_6H_4), 30.5 (m, CH_2), 29.5 (m, CH_2), 29.2 (m, CH_2), 25.1 (m, CH_2), 22.0 (s, Me), $^{31}P\{^{1}H\}$: 68.1 [br, 1P, J(WP) 213], 41.5 [d, 1P, J(PP) 18, J(WP) 244], 19.9 [d, 1P, J(PP) 18, J(WP) 89]

3.5. *mer*-$[W(NCMe)(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)][BF_4]$ **3**

In a semi-jacketed, water cooled Schlenk tube, **1** (0.25 g, 0.27 mmole) and $TlBF_4$ (0.31 g, 1.08 mmole) were mixed. Acetonitrile (20 cm^3) was added and the reaction heated to reflux for 2 h. Removal of the solvent in vacuo and repeated washing of the resultant oil with diethyl ether afforded an orange *powder* of *mer*-$[W(NCMe)(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)][BF_4]$, 0.24 g, yield 95%. Analytically pure *microcrys-*

---

[3] Due to the low solubility of the complex, weak spectrum obtained and ^{183}W satellites not observed.

tals may be obtained by recrystallisation from CH_2Cl_2/Et_2O (co-crystallises with one mole of CH_2Cl_2) $C_{45}H_{43}BF_4ONP_3W.CH_2Cl_2$ requires 52.0% C, 4.3% H, 1.32% N. Found 51.8% C, 4.3% H, 1.80% N. IR $\{\nu_{max}(CO)\}$: 1911(s) cm^{-1}, 2284 (w) [$\nu(C\equiv N)$]. NMR: ^1H: 8.03 – 7.11 (m, 25H, Ph), 6.85 [d, (AB), 2H, C_6H_4, J(HH) 8], 6.66 [d, (AB), 2H, C_6H_4, J(HH) 8], 3.80 (m, 4H, CH_2), 3.05 (m, 4H, CH_2), 2.31 (s, 3H, MeCN), 2.21 (s, 3H, Me). $^{13}C\{^1H\}$ (CD_3CN): 285.5 [s, br, W≡C, J(WC) 224], 232.1 [d, CO, J(PC) 32, J(WC) 173], 146.8 (s, MeCN), 138.6–128.8 (Ph and C_6H_4), 32.5 (m, CH_2), 26.2 (m, CH_2), 21.4 (s, Me), 5.0 (s, *Me*CN). $^{31}P\{^1H\}$ (CD_3CN): 80.9 [d, 1P, J(PP) 4, J(WP) 204], 47.7 [d, 2P, J(PP) 4, J(WP) 289].

3.6. *mer*-[$WBr(=C(H)C_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)][BF_4]$ 4

1 (0.090 g, 0.097 mmol) was dissolved in CH_2Cl_2 and cooled to −78°C. $HBF_4 \cdot OEt_2$ (20 μl, 0.15 mmol) was added and the reaction warmed to room temperature. Removal of the solvent in vacuo and re-crystallisation from CH_2Cl_2/Et_2O afforded red *microcrystals* of *mer*-[$WBr(=CHC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)][BF_4]$ 0.096 g, yield 98%. $C_{43}H_{41}BBrF_4OP_3W$ requires 50.8% C 4.1% H. Found 51.2% C 4.6% H. IR $\{\nu_{max}(CO)\}$: 1988 cm^{-1}. NMR: ^1H: 7.80–7.09 (m, 25H, Ph), 6.86 [d, (AB), 2H, C_6H_4, J(HH) 9], 6.44 [d, (AB), 2H, C_6H_4, J(HH) 9], 3.63–2.85 (m, 8H, CH_2), 2.26 (s, 3H, Me), −4.71 [dt, 1H, W=C(H), J(PH) 6, 8, J(WH) 34]. $^{13}C\{^1H\}$: 242.7 [dt, br, W=C(H), J(PC) 5, 5, J(WC) 102], 212.1 [d, CO, J(PC) 44, J(WC) 162], 142.7–127.7 (Ph and C_6H_4), 33.2 (m, CH_2), 26.4 (m, CH_2), 21.9 (s, Me). ^{13}C (Gated NOE) (selected data): 242.7 [br, d, W=C(H), J(HC) 71], 212.1 [d, CO, JPC) 44]. $^{31}P\{^1H\}$: 78.0 [t, 1P, J(PP) 14, J(WP) 204], 35.9 [d, J(PP) 14, J(WP) 200].

3.7. *mer*-[$W(CH_3)(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)$] 5

$LiCuMe_2$ was prepared by adding 1.35 cm^3 of LiMe (1.4 M in hexanes) to finely divided CuI (18 g, 0.95 mmole) suspended in thf (10 cm^3), to afford a 0.095 M solution of $LiCuMe_2$. **1** (0.070 g, 0.076 mmole) was dissolved in thf (10 cm^3) and $LiCuMe_2$ (1.0 cm^3, 1.2 equivalents) added. The reaction was stirred for 4 h and the solvent removed in vacuo. The residue was dissolved in CH_2Cl_2 and columned on alumina (BA III, −20°C). Elution with CH_2Cl_2 afforded a yellow band (identified as complex **1**). Continued elution with CH_2Cl_2:thf (4:1) afforded a brown band, which was reprecipitated from CH_2Cl_2/light petroleum to afford a brown *powder* of *mer*-[$W(CH_3)(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)$] 0.032 g, yield 50%. Satisfactory microanalysis was not obtained, see text. IR $\{\nu_{max}(CO)\}$: 1908 cm^{-1}. NMR: ^1H: 7.94–7.02 (m, 25H, Ph), 6.98 [d, (AB), 2H, C_6H_4, J(HH) 7], 6.80 [d, (AB), 2H, C_6H_4, J(HH) 7], 3.44 (m, 2H, CH_2), 2.81 (m, 2H, CH_2), 2.47 (m, 2H, CH_2), 2.17 (s, 3H, Me), 2.02 (m, 2H, CH_2), −1.90 [dt, 3H, CH_3, J(PH) 9, 10]. $^{13}C\{^1H\}$: [br, W≡C, J(WC) 152], 228.2 [br, CO, J(WC) 180], 167.7 – 127.1 (Ph and C_6H_4), 32.8 (m, CH_2), 21.3 (s, Me-4), −8.2 [dt, CH_3, J(PC) 10, 7]. $^{31}P\{^1H\}$: 77.1 [br, J(WP) 190], 42.9 [d, J(PP) 8, I(WP) 263].

3.8. *mer*-[$W(CH_3)(=C(H)C_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)][BF_4]$ 6

Mer-[$W(CH_3)(\equiv CC_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)$], **5**, (0.10 g, 0.116 mmole) was dissolved in CH_2Cl_2 (5 cm^3) and cooled to −78°C. $HBF_4 \cdot OEt_2$ (15 μl, 0.12 mmole) was added and the reaction warmed slowly to room temperature. The solution was passed through a celite pad (plus CH_2Cl_2 washings), removal of the solvent in vacuo to minumum volume and addition of Et_2O resulted in the isolation of a red *powder* of *mer*-[$W(CH_3)(=C(H)C_6H_4Me\text{-}4)\{PPh(C_2H_4PPh_2)_2\}(CO)][BF_4]$ 0.069 g, yield 63%. $C_{44}H_{44}BF_4OP_3W$ requires 55.5% C, 4.7% H. Found

Table 2
Crystallographic for complex **3**

Formula	$C_{45}H_{43}BF_4NOP_3W$
M	977.37
System	Monoclinic
Space group	$P2_1/c$
a (Å)	12.831(9)
b (Å)	11.213(7)
c (Å)	29.95(2)
β (°)	94.16(5)
V (Å^3)	4297(5)
T (K)	293
Z	4
Crystal dimensions (mm)	0.4 × 0.6 × 0.8
D_{calc} (g cm^{-3})	1.511
μm(Mo–K_α) (mm^{-1})	28.5
F(000) (e)	1952
Scan method	Wyckoff ω scans
2θ range (°)	3–50
Number of unique data collected	7343
Number of data used in refinement $\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$	7342
$wR^2(RI > 2\sigma(I))$	0.174 (0.066)
S	0.999
Maximum residue (eÅ^{-3})	+1.950
Minimum residue (eÅ^{-3})	−3.710

$R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$.
$\omega R^2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.
$S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$ where n = number of data and p = number of variables.

54.3% C, 4.3% H. IR $\{\nu_{max}(CO)\}$: 1991 cm^{-1}. NMR: ^1H: 7.76–7.02 (m, 25H, Ph), 6.85 [d (AB), 2H, C_6H_4, J(HH) 8], 6.41 [d (AB), 2H, C_6H_4, J(HH) 8], 3.57 (m, 2H, CH_2), 3.00 (m, 2H, CH_2), 2.74 [dt, 3H, CH_3, J(PH) 9, 10], 2.27 (s, 3H, Me-4), −4.49 [dt, 1H, J(PH) 5, 9, J(WH) 35] (remaining CH_2 peaks obscured by W*Me* multiplet). $^{31}P\{^1H\}$: 78.7 [t, 1P, J(PP) 12, J(WP) 206], 42.9 [d, 2P, J(PP) 8, J(WP) 256]

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å \times 10^4$) for **3**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
W(1)	2646(1)	1390(1)	1100(1)	49(1)
P(2)	3049(2)	2964(2)	1669(1)	52(1)
P(3)	3814(2)	268(2)	1664(1)	52(1)
P(1)	1306(2)	2898(2)	865(1)	55(1)
C(10)	2118(8)	74(10)	678(4)	73(3)
O(1)	1820(8)	−634(9)	429(3)	109(3)
C(101)	1526(6)	4240(8)	1214(3)	64(2)
C(102)	1885(7)	3874(8)	1700(3)	60(2)
C(103)	3371(8)	2249(9)	2204(3)	67(2)
C(104)	4228(8)	1302(8)	2128(3)	66(2)
C(11)	3576(6)	1839(9)	703(3)	57(2)
N(1)	1395(5)	809(7)	1563(2)	59(2)
C(21)	−91(10)	−94(13)	1990(5)	106(4)
C(20)	755(7)	425(9)	1749(3)	69(2)
C(31)	4255(7)	2224(8)	369(3)	59(2)
C(32)	4021(8)	3201(11)	94(4)	75(3)
C(33)	4708(10)	3612(10)	−212(4)	81(3)
C(34)	5652(8)	3064(11)	−253(3)	74(3)
C(35)	5892(8)	2073(13)	14(4)	88(4)
C(36)	5220(8)	1667(12)	324(4)	85(4)
C(37)	6400(10)	3462(13)	−593(5)	105(5)
C(41)	3224(6)	−991(8)	1943(3)	57(2)
C(42)	3471(9)	−1318(9)	2392(4)	77(3)
C(43)	2970(10)	−2255(12)	2581(4)	92(3)
C(44)	2226(9)	−2898(10)	2327(5)	88(3)
C(45)	1990(8)	−2633(9)	1885(5)	82(3)
C(46)	2502(8)	−1691(9)	1692(4)	71(3)
C(51)	5056(6)	−362(7)	1522(3)	55(2)
C(52)	5901(7)	−454(10)	1836(4)	75(3)
C(53)	6822(8)	−949(13)	1731(5)	94(4)
C(54)	6924(8)	−1379(10)	1306(5)	84(3)
C(55)	6096(10)	−1274(10)	975(5)	85(3)
C(56)	5174(7)	−764(9)	1093(4)	68(2)
C(61)	4122(6)	4024(8)	1593(3)	56(2)
C(62)	4111(8)	5181(9)	1766(3)	70(2)
C(63)	4950(9)	5922(10)	1712(4)	80(3)
C(64)	5785(9)	5560(11)	1497(4)	85(3)
C(65)	5804(7)	4411(11)	1327(4)	81(3)
C(66)	4982(7)	3637(9)	1375(4)	67(2)
C(71)	−55(6)	2483(8)	951(3)	59(2)
C(72)	−499(9)	1539(11)	708(4)	85(3)
C(73)	−1510(9)	1181(12)	777(5)	95(4)
C(74)	−2062(8)	1778(15)	1088(5)	102(4)
C(75)	−1640(8)	2693(12)	1325(4)	84(3)
C(76)	−629(7)	3063(10)	1261(3)	71(2)
C(81)	1248(7)	3434(10)	288(3)	70(3)
C(82)	1216(9)	2613(12)	−52(3)	84(3)
C(83)	1202(11)	2985(17)	−494(4)	111(5)
C(84)	1278(11)	4203(18)	−595(5)	114(5)
C(85)	1331(10)	4988(14)	−259(5)	99(4)
C(86)	1286(8)	4643(11)	180(4)	84(3)
F(3)	9897(6)	5641(8)	1939(3)	115(2)
F(1)	8199(8)	5788(14)	1881(7)	247(8)
F(2)	9189(9)	7250(10)	1621(3)	149(3)
F(4)	9126(9)	6983(10)	2337(4)	153(4)
B(1)	9076(12)	6386(15)	1945(6)	92(5)

4. Crystallographic studies

Crystals of **3** were grown from a saturated CD_3CN solution. Selected crystals were mounted under solvent vapour in sealed Lindemann tubes. Data collection was carried out at room temperature on a Siemens R3 m V^{-1} diffractometer using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). Crystallographic computing was via the SHELXTL system [33] on a Silicon graphics IRIS workstation.

Table 2 lists details of unit cell data, intensity data collection and structure refinement. The unit cell parameters and orientation matrix for data collection were determined by the least-squares refinement of 25 centred reflections, with 2θ ranging from 15–30°. Data was collected by ω-scans. Standard reflections were re-measured every 100 data, and no crystal decay or electronic instability was found. Data were corrected for absorption by psi scans. The structure was solved by Patterson and difference Fourier methods and refined by full-matrix least-squares against F^2. All non-hydrogen atoms were allowed anisotropic thermal motion. Phenyl, methylene and methyl H atom positions were calculated and these atoms allowed to ride on their respective C atoms. Phenyl, methylene and methyl H atom displacement parameters were set at 1.2, 1.2 and 1.5 times U_{eq} for the bound atom respectively. The large residual electron density peaks (+1.95 and −3.67 $Å^{-3}$) where not removed successfully by absorption correction. The large positive peak located near to the hydrogens associated with C(37) was initially thought to be adventitious water from the deuterated solvent. However, refinement of this peak as an oxygen atom was not successful.

Co-ordinates of refined non-hydrogen atoms, together with equivalent isotropic thermal parameters for **3** appear in Table 3. Complete atomic co-ordinates, thermal parameters and bond lengths and angles (expect those involving H atoms) have been deposited with at the Cambridge Crystallographic Data Centre.

5. Conclusions

The first examples of alkylidyne complexes ligated with a poly-dentate phosphine have been synthesised. It has been shown that the ligand can adopt a co-ordination geometry (either *fac* or *mer*) to suit the electronic requirements of the complex. Protonation with HBF_4 affords an agostic alkylidene complex, while methylation results in a relatively rare example of an alkyl–alkylidyne species, protonation of which affords a methyl/alkylidene species.

Acknowledgements

We thank the SERC (EPSRC) and BP Chemicals for funding (CASE award to A.S.W.).

References

[1] A.F. Hill, J.M. Malget, J. Chem. Soc., Chem. Commun. (1996) 117.
[2] S. Ahn, A. Mayr, J. Am. Chem. Soc. 118 (1996) 7408.
[3] R.B. Bedford, A.F. Hill, A.J.P. White, D.J. Williams, Angew. Chem., Int. Ed. Engl. 35 (1996) 95.
[4] A.C. Filippou, D. Wossner, B. Lungwitz, G. Kociok-Kohn, Angew. Chem., Int. Ed. Engl. 35 (1996) 876.
[5] B.E. Woodworth, J.L. Templeton, J. Am. Chem. Soc. 118 (1996) 7418.
[6] L. Zang, M.P. Gamasa, J. Gimeno, R.J. Carbajo, F. Lopez-Ortiz, M. Lanfranchi, A. Tiripicchio, Organometallics 15 (1996) 4274.
[7] F.R. Kreissl in Carbyne Complexes, VCH Publishers, Weinheim, 1988.
[8] A. Mayr, H. Hoffmeister, Adv. Organomet. Chem. 32 (1991) 227.
[9] H.P. Kim, R.J. Angelici, Adv. Organomet. Chem. 27 (1987) 51.
[10] G.A. McDermott, A.M. Dorries, A. Mayr, Organometallics, 6 (1987) 925.
[11] K.R. Birdwhistell, T.L. Tonker, J.L. Templeton, J. Am. Chem. Soc. 107 (1985) 4474.
[12] G.A. Carriedo, G. Sanchez, V. Riera, C. Bois, Y. Jeanin, D. Miguel, J. Chem. Soc., Dalton Trans. (1990) 3355.
[13] C.A. McAuliffe, in: Comprehensive Co-ordination Chemistry, Pergamon, 1987, Chap. 2, 989 pp.
[14] H.A. Mayer, W.C. Kaska, Chem. Rev. 94 (1994) 1239.
[15] C. Young, S.M. Socol, P.J. Kountz, D.W. Meek, R. Glaser, Inorg. Chim. Acta., 114 (1986) 119.
[16] S.M. Socol, C. Young, D.W. Meek, R. Glaser, Can. J., Chem. 70 (1992) 2424.
[17] J.B. Letts, T.J. Mazanec, D.W. Meek, J. Am. Chem. Soc. 104 (1982) 3898.
[18] G. Jia, D.W. Meek, J.C. Gallucci, Inorg. Chem. 30 (1991) 403.
[19] D. Michos, X.-L. Luo, R.H. Crabtree, Inorg. Chem. 31 (1992) 4245.
[20] D.J. Darensbourg, D.J. Zalewski, C. Plepys, C. Campana, Inorg. Chem. 26 (1987) 3727.
[21] C.H. Ueng, L.-C. Leu, Acta Cryst. C47 (1991) 1591.
[22] A. Mayr, M.F. Asaro, M.A. Kjelsberg, K.S. Lee, D. Van Engen, Organometallics. 6 (1987) 432.
[23] A. Mayr, A.M. Dorries, A.L. Rheingold, S.J. Geib, Organometallics 9 (1990) 964.
[24] S.J. Holmes, D.N. Clark, H.W. Turner, R.R. Schrock, J. Am. Chem. Soc. 104 (1982) 6322.
[25] J.H. Wengrovius, R.R. Schrock, M.R. Churchill, H.J. Wassermann, J. Am. Chem. Soc. 104 (1982) 1739.
[26] M. Brookhart, M.L.H. Green, L.L. Wong, Prog. Inorg. Chem. 36 (1988) 1.
[27] B.E. Mann, B.F. Taylor, ^{13}C NMR Data for Organometallic Compounds, Academic Press, 1981.
[28] K.W. Chiu, R.A. Jones, G. Wilkinson, A.M.R. Galas, M.B. Hursthouse, K.M.A. Malik, J. Chem. Soc., Dalton Trans. (1981) 1205.
[29] P.R. Sharp, S.J. Holmes, R.R. Schrock, M.R. Churchill, H.J. Wassermann, J. Am. Chem. Soc. 103 (1981) 965.
[30] M.R. Churchill, H.J. Wassermann, Inorg. Chem. 20 (1981) 4119.
[31] J. Manna, S.J. Geib, M.D. Hopkins, Angew. Chem., Int. Ed. Engl. 32 (1993) 858.
[32] G.A. McDermott, A.M. Dorries, A. Mayr, Organometallics 6 (1987) 925.
[33] G.M. Sheldrick, SHELXTL Programs for use with a Siemens X-ray system, Revision 5.1, 1985, SHELXTL PLUS program system, Siemens, 1987.