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Phosphine complexes of tungsten(0) poly(alkyne); crystal structures of $W(PhC{\equiv}CPh)_3(PMe_3)$ and $W(TolC{\equiv}CTol)_2(\eta^4\text{-}C_4Tol_4)(PMe_3)$

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Abstract

Reactions of $W(PhC{\equiv}CPh)_3L$ (L = CO or NCMe) with PMe_3, PPh_2Me and PPh_3 produce $W(PhC{\equiv}CPh)_3(PMe_3)$, $W(PhC{\equiv}CPh)_3(PPh_2Me)$ and $W(PhC{\equiv}CPh)_3(PPh_3)$, respectively. Reaction of $W(PhC{\equiv}CPh)_3(NCMe)$ with 1,1′-bis(diphenylphosphino)ferrocene (dppf) forms $W(PhC{\equiv}CPh)_3(\eta^1\text{-dppf})$ and $[W(PhC{\equiv}CPh)_3]_2(\eta^1,\eta^1\text{-dppf})$. Treating $W(RC{\equiv}CR)_2(\eta^4\text{-}C_4R_4)(NCMe)$ (R = Ph and Tol) with PMe_3 affords $W(RC{\equiv}CR)_2(\eta^4\text{-}C_4R_4)(PMe_3)$. $W(PhC{\equiv}CPh)_3(PMe_3)$ crystallizes in the space group $P\bar{3}$ with $a = 14.000(4)$, $c = 11.183(3)$ Å, $V = 1898.3(7)$ Å^3, $Z = 2$ and $R_F = 0.032$. $W(TolC{\equiv}CTol)_2(\eta^4\text{-}C_4Tol_4)(PMe_3)$ crystallizes in the space group $P2_1/c$ with $a = 13.588(2)$, $b = 19.289(5)$, $c = 22.150(5)$ Å, $\beta = 90.57(2)°$, $V = 5805.(2)$ Å^3, $Z = 4$ and $R_F = 0.055$.

Keywords: Crystal structures; Tungsten complexes; Poly(alkyne) complexes; Phosphine complexes

1. Introduction

Tetrahedral tris(alkyne) complexes of the type $W(RC{\equiv}CR')_3(CO)$ have played an important role in developing the chemistry of unsaturated organic substrates coordinated onto metal centers, particularly in the ability of alkynes to act as four-electron donors [1–6]. The tris(alkyne) complexes of W(0) containing phosphine ligands are also known. For instance, reduction of $[WCl_4(PMe_3)_2]$ by sodium amalgam in the presence of $PhC{\equiv}CH$ produces $W(PhC{\equiv}CH)_3(PMe_3)$ [7] or direct substitution of the carbonyl group in $W(RC{\equiv}CR')_3(CO)$ with tertiary phosphines affords $W[PhC{\equiv}CC_6H_3(OMe)_2]_3(PPhMe_2)$ [8], $W(PhC{\equiv}CH)_3(PPh_3)$ and $W(PhC{\equiv}CPh)_3(PPhMe_2)$ [9]. The sterically congested $W(PhC{\equiv}CPh)_3(PPh_3)$ and $W(PhC{\equiv}CPh)_3(\eta^1\text{-dppm})$ complexes can be synthesized by treating $W(PhC{\equiv}CPh)_3(NCMe)$ with PPh_3 and dppm ligands, respectively [10]. Recently, we prepared [11,12] the bis(alkyne) complexes $W(PhC{\equiv}CPh)_2(\eta^4\text{-}C_4Ph_4)L$ (L = CO and NCMe) from $W(PhC{\equiv}CPh)_3L$ coupled with a diphenylacetylene. In this paper we report some new tungsten tris(alkyne) and bis(alkyne) phosphine complexes, as summarized in Scheme 1, in an attempt to evaluate the importance of steric factors within the two systems.

2. Experimental

2.1. General procedures

$W(PhC{\equiv}CPh)_3(CO)$ [1], $W(PhC{\equiv}CPh)_3(NCMe)$ [10], $W(PhC{\equiv}CPh)_2(\eta^4\text{-}C_4Ph_4)(NCMe)$ [11] and $W(TolC{\equiv}CTol)_3(CO)$ [13] were prepared from $W(CO)_6$ as described previously. Diphenylacetylene, ditolylacetylene, PMe_3 (1.0 M in toluene), 1,1′-bis(diphenylphosphino)ferrocene (dppf), PPh_2Me, PPh_3 and $W(CO)_6$ were purchased from Aldrich and used directly as received. Trimethylamine oxide was sublimed (10^{-2} torr, 90°C) from $Me_3NO \cdot 2H_2O$ (Aldrich) before use. Benzene and acetonitrile were distilled from sodium benzophenone ketyl and calcium hydride, respectively, immediately before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck, GF 254). ^1H, ^{31}P and ^{13}C NMR spectra were obtained on a Varian VXR-300 spectrometer at 300, 121.4 and 75.4 MHz, respectively. IR spectra were taken on a Hitachi-2001 spectrometer. Fast-atom bombardment (FAB) mass spectra were obtained on a VG-5022 mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Cheng-Kung University, Tainan.

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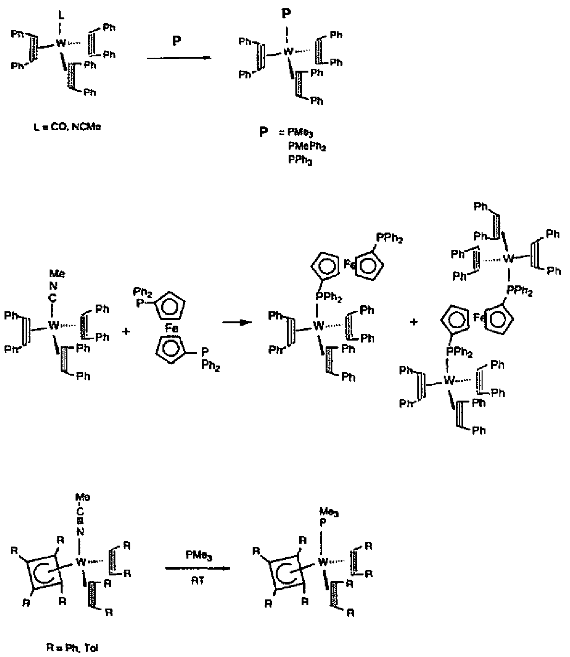

Scheme 1.

2.2. Preparation of W(PhC≡CPh)$_3$(PMe$_3$)

W(PhC≡CPh)$_3$(CO) (200 mg, 0.268 mmol) was dissolved in 5 ml of benzene in a 20 ml Schlenk flask, equipped with a magnetic stir bar and a rubber serum stopper, under an atmosphere of nitrogen. PMe$_3$ (400 μl, 0.4 mmol) was added slowly via a microsyringe. The mixture was stirred at ambient temperature for 24 h, and then the volatile materials removed under vacuum. The residue was dissolved in dichloromethane and applied on TLC plates, eluting with n-hexane/dichloromethane (3:1 vol./vol.). Crystallization of the material forming the colorless band afforded air-stable, white crystals of W(PhC≡CPh)$_3$(PMe$_3$) (158 mg, 0.2 mol, 74%). Mass spectroscopy (FAB): m/z 794 (M^+, ^{184}W), 718 (M^+ − PMe$_3$), 616 (M^+ − C$_2$Ph$_2$), 540 (M^+ − PMe$_3$ − C$_2$Ph$_2$). ^{1}H NMR (CDCl$_3$, 25°C): 7.47–6.76 (m, 30H, Ph), 1.43 (d, $^2J_{P\text{-}H}$ = 8 Hz, CH$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 25°C): 196.3 (d, $^2J_{P\text{-}C}$ = 5 Hz, C≡), 179.6 (d, $^2J_{P\text{-}C}$ = 18 Hz, C≡), 147.5 (s, *ipso*-C$_6$H$_5$), 141.8 (s, *ipso*-C$_6$H$_5$), 130.2, 127.8, 127.7, 127.4, 125.2, 125.0 (*o*, *m*, *p*-C$_6$H$_5$), 17.3 (d, $^1J_{P\text{-}C}$ = 26.2 Hz, Me) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, 25°C): −4.26, (s, with ^{183}W satellites, $^1J_{P\text{-}W}$ = 140 Hz) ppm. IR (KBr disc): ν(C≡C) 1662 cm^{-1}. *Anal.* Found: C, 67.87; H, 4.90. Calc. for C$_{45}$H$_{39}$PW: C, 68.02; H, 4.95%.

W(PhC≡CPh)$_3$(PMe$_3$) can also be prepared in 90% yield by treating W(PhC≡CPh)$_3$(NCMe) with PMe$_3$ in benzene solution at 25°C for 2 h.

2.3. Preparation of W(PhC≡CPh)$_3$(PPh$_2$Me)

The reaction of W(PhC≡CPh)$_3$(CO) (200 mg, 0.268 mmol) with PPh$_2$Me (63 mg, 0.322 mmol) was carried out and worked up in a fashion similar to that above, except that the reaction temperature was 70°C and the reaction time was extended to 6 h. W(PhC≡CPh)$_3$(PPh$_2$Me) (135 mg, 0.15 mmol, 55%) was isolated as air-stable, white crystals. Mass spectroscopy (FAB): m/z 918 (M^+, ^{184}W), 740 (M^+ − C$_2$Ph$_2$), 718 (M^+ − PPh$_2$Me). ^{1}H NMR (CDCl$_3$, 25°C): 7.37–6.48 (m, 40H, Ph), 2.21 (d, $^2J_{P\text{-}H}$ = 8 Hz, Me) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 25°C): 196.5 (br, C≡), 180.1 (br, −C≡), 146.0 (s, *ipso*-CC$_6$H$_5$), 142.0 (s, *ipso*-CC$_6$H$_5$), 136.0 (d, $^1J_{P\text{-}C}$ = 40 Hz, *ipso*-PC$_6$H$_5$), 133.2–124.7 (m, *o*, *p*-C$_6$H$_5$), 16.3 (d, $^1J_{P\text{-}C}$ = 26 Hz, Me) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, 25°C): 16.6 (s, with ^{183}W satellites, $^1J_{P\text{-}W}$ = 132 Hz) ppm. IR (KBr disc): ν(C≡C) 1652 cm^{-1}. *Anal.* Found: C, 71.77; H, 4.71. Calc. for C$_{55}$H$_{43}$PW: C, 71.90; H, 4.72%.

Comparatively, stirring a mixture of W(PhC≡CPh)$_3$(NCMe) and PPh$_2$Me in benzene solution at 25°C for 6 h produced W(PhC≡CPh)$_3$(PPh$_2$Me) in 91% yield.

2.4. Preparation of W(PhC≡CPh)$_3$(PPh$_3$)

W(PhC≡CPh)$_3$(CO) (60 mg, 0.08 mmol) and PPh$_3$ (40 mg, 0.15 mmol) were placed in an oven-dried, 25 ml Schlenk tube under nitrogen. The tube was set in an oil bath at 130°C for 24 h, and then cooled to room temperature. The reaction mixture was extracted with dichloromethane and subjected to TLC, eluting with n-hexane/dichloromethane (4:1 vol./vol.). Isolation of the material forming the yellow band afforded the known W(PhC≡CPh)$_3$(PPh$_3$) in 20% yield (16 mg).

W(PhC≡CPh)$_3$(PPh$_3$) was previously prepared [10] in 62% yield by reaction of W(PhC≡CPh)$_3$(NCMe) with PPh$_3$ in refluxing benzene solution. However, no reaction was observed by treating W(PhC≡CPh)$_3$(CO) with PPh$_3$ in refluxing toluene for 24 h.

2.5. Reaction of W(PhC≡CPh)$_3$(NCMe) with dppf

A toluene (5 ml) solution of W(PhC≡CPh)$_3$(NCMe) (50 mg, 0.066 mmol) and dppf (73 mg, 0.132 mmol) was placed in a 20 ml Schlenk flask, equipped with a magnetic stir bar and a reflux condenser. The solution was refluxed for 3 h. The solvent was removed under vacuum and the residue subjected to TLC, eluting with n-hexane/dichloromethane (5:1 vol./vol.). Dppf (43 mg) was recovered from the sixth band. Crystallization of the material forming the seventh, orange, band from dichloromethane–methanol produced air-stable, orange crystals of W(PhC≡CPh)$_3$(η^1-dppf) (46 mg, 0.036 mmol, 55%). Mass spectroscopy: m/z 1272 (M^+, ^{184}W). ^{1}H NMR (CDCl$_3$, 25°C): 7.62–6.10 (m, 50H, Ph), 3.91 (br, 2H), 3.80 (br, 2H), 3.76 (br, 2H), 3.63 (br, 2H, C$_5$H$_4$) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 20°C): −18.76 (s), 24.84 (s, $^1J_{W\text{-}P}$ = 128 Hz) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 20°C): 197.8, 181.3 (C≡), 144.6–124.5 (m, Ph), 81.3, 80.8, 74.6, 73.9, 72.6, 71.0 (Cp) ppm. Isolation of the material forming the ninth, orange band afforded [W(PhC≡CPh)$_3$]$_2$(η^1,η^1-dppf) (7 mg, 0.003 mmol, 5%). Mass spectroscopy: m/z 1991 (M^+, ^{184}W), 1272 ($M^+ - \mathrm{W(PhC{\equiv}CPh)_3}$). ^{1}H NMR ($CD_2Cl_2$, 25°C): 7.56–6.03 (m, 100H, Ph), 3.08 (br, 4H), 3.10 (br, 4H, Cp) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20°C): 25.04 (s, $^1J_{W-P} = 128$ Hz) ppm. The six further bands were not identified.

2.6. *Attempted reaction of* $W(PhC{\equiv}CPh)_2(\eta^4\text{-}C_4Ph_4)(CO)$ *with* PMe_3

$W(PhC{\equiv}CPh)_2(\eta^4\text{-}C_4Ph_4)(CO)$ (100 mg, 0.11 mmol), PMe_3 (1.0 M, 200 μl, 0.2 mmol) and toluene (3 ml) were sealed in a 5 ml Schlenk tube capped with a rubber serum stopper under nitrogen. The tube was placed in an oil bath at 80°C for 8 h, producing no reaction.

2.7. *Reaction of* $W(PhC{\equiv}CPh)_2(\eta^4\text{-}C_4Ph_4)(NCMe)$ *with* PMe_3

$W(PhC{\equiv}CPh)_2(\eta^4\text{-}C_4Ph_4)(NCMe)$ (150 mg, 0.16 mmol) and benzene (5 ml) were placed in an oven-dried, 25 ml Schlenk flask under nitrogen. A toluene solution of PMe_3 (1.0 M, 300 μl, 0.3 mmol) was added into the flask via a microsyringe. The mixture was allowed to stand at ambient temperature for 8 h, and then the volatile materials removed under vacuum. The residue was subjected to TLC, eluting with n-hexane/dichloromethane (3:1 vol./vol.). Crystallization of the material forming the orange band from n-hexane/dichloromethane gave air-stable, orange crystals of $W(PhC{\equiv}CPh)_2(\eta^4\text{-}C_4Ph_4)(PMe_3)$ (137 mg, 0.14 mmol, 88%). Mass spectroscopy (FAB): m/z 972 (M^+, ^{184}W), 896 ($M^+ - PMe_3$), 718 ($M^+ - PMe_3 - C_2Ph_2$). ^{1}H NMR ($CDCl_3$, 25°C): 7.25–6.83 (m, 40H, Ph), 1.03 (d, $^2J_{P-H} = 8.7$ Hz, 9H, Me) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −90°C): 186.1 (s, C≡), 166.8 (d, $^2J_{P-C} = 30$ Hz, C≡), 151.2, 146.2 (s, *ipso*-Ph), 136.6–124.4 (*o*, *m*, *p*-Ph), 85.4 (s, η^4-C_4), 18.0 (d, Me, $^1J_{P-C} = 46$ Hz) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25°C): −17.02 (s, with ^{183}W satellites, $^1J_{P-W} = 188.6$ Hz) ppm. IR (KBr disc): ν(C≡C) 1668 cm^{-1}. *Anal.* Found: C, 72.87; H, 5.04. Calc. for $C_{59}H_{49}PW$: C, 72.38; H, 5.00%.

2.8. *Preparation of* $W(TolC{\equiv}CTol)_3(NCMe)$

$W(TolC{\equiv}CTol)_3(CO)$ (200 mg, 0.238 mmol) and acetonitrile (40 ml) were placed in an oven-dried, 100 ml Schlenk flask equipped with a magnetic stir bar and a rubber serum stopper under a nitrogen atmosphere. A solution of Me_3NO (27 mg, 0.36 mmol) in acetonitrile (20 ml) was introduced into the flask via cannula over a period of 30 min. The mixture was stirred at room temperature for 6 h, and the solvent removed under vacuum. The residue was washed with fresh acetonitrile (3×5 ml) and then crystallized from dichloromethane/acetonitrile, affording air-stable, white crystals of $W(TolC{\equiv}CTol)_3(NCMe)$ in 72% yield (145 mg, 0.172 mmol). Mass spectroscopy (FAB): m/z 843 (M^+, ^{184}W), 802 ($M^+ - MeCN$). ^{1}H NMR ($CDCl_3$, 25°C): 7.37 (d, $J = 8$ Hz, Tol), 7.19 (d, $J = 8$ Hz, Tol), 7.12 (d, $J = 8$ Hz, Tol), 7.00 (d, $J = 8$ Hz, Tol), 2.47 (s, 3H, MeCN), 2.36 (s, 9H, Tol) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): 195.7 (s, C≡), 181.8 (s, C≡), 140.7, 138.3 (s, *ipso*-CTol), 136.6–128.0 (*o*, *m*, *p*-CTol), 21.3 (s, Me in Tol), 21.2 (s, Me in Tol), 4.52 (s, MeCN) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25°C): 16.6 (s, with ^{183}W satellites, $^1J_{P-W} = 132$ Hz) ppm. IR (KBr disc): ν(C≡C) 1662 cm^{-1}. *Anal.* Found: C, 71.03; H, 5.43; N, 1.60. Calc. for $C_{50}H_{45}NW$: C, 71.17; H, 5.38; N, 1.66%.

2.9. *Preparation of* $W(TolC{\equiv}CTol)_2(\eta^4\text{-}C_4Tol_4)(NCMe)$

A solution of $W(TolC{\equiv}CTol)_3(NCMe)$ (200 mg, 0.24 mmol) and ditolylacetylene (59 mg, 0.28 mmol) in benzene (10 ml) was heated to reflux under nitrogen for 5 min. The solvent was removed under vacuum, and the residue subjected to TLC, eluting with n-hexane/dichloromethane (3:1 vol./vol.). $W(TolC{\equiv}CTol)_2(\eta^4\text{-}C_4Tol_4)(NCMe)$ (195 mg, 0.19 mmol, 79%) was isolated from the major orange band. Mass spectrum (FAB): m/z 1049 (M^+, ^{184}W), 1008 ($M^+ - MeCN$). ^{1}H NMR ($CDCl_3$, 25°C): 7.10–6.69 (m, 32H, Tol), 2.32 (s, 6H, Tol), 2.27 (s, 6H, Tol), 2.21 (s, 12H, Tol), 2.04 (s, 3H, CH_3CN) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): 186.0 (s, C≡), 173.7 (s, C≡), 137.8–124.2 (m, Tol), 84.3 (s, η^4-C_4), 21.3, 21.2, 21.0 (s, Me in Tol), 4.63 (s, MeCN).

2.10. *Reaction of* $W(TolC{\equiv}CTol)_2(\eta^4\text{-}C_4Tol_4)(NCMe)$ *with* PMe_3

$W(TolC{\equiv}CTol)_2(\eta^4\text{-}C_4Tol_4)(NCMe)$ was treated with PMe_3 by the same method as described above, affording air-stable, orange crystals of $W(TolC{\equiv}CTol)_2(\eta^4\text{-}C_4Tol_4)(PMe_3)$ in 85% yield. Mass spectroscopy (FAB): m/z 1084 (M^+), 1008 ($M^+ - PMe_3$), 802 ($M^+ - PMe_3 - C_2Tol_2$), 596 ($M^+ - PMe_3 - 2C_2Tol_2$). ^{1}H NMR ($CDCl_3$, −50°C): 7.05 (d, $J = 8$ Hz, 4H), 7.00 (d, 8H), 6.75 (d, 8H), 6.70 (d, 4H), 6.66 (d, 4H), 6.58 (d, 4H, Tol), 2.31 (s, 6H), 2.23 (s, 12H), 2.21 (s, 6H, Me in Tol), 1.04 (d, $^2J_{P-H} = 8.7$ Hz, 9H, PMe_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): 134.5–127.7 (m, Tol), 84.3 (s, η^4-C_4), 21.1, 21.0 (s, Me in Tol), 17.9 (d, $^1J_{P-C} = 29$ Hz, PMe_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25°C): −16.32 (s, with ^{183}W satellites, $^1J_{P-W} = 190$ Hz) ppm. IR (KBr disc): ν(C≡C) 1671 cm^{-1}. *Anal.* Found: C, 73.98; H, 5.96. Calc. for $C_{67}H_{65}PW$: C, 73.76; H, 5.81%.

A crystal of $W(TolC{\equiv}CTol)_2(\eta^4\text{-}C_4Tol_4)(PMe_3)$ found suitable for X-ray analysis was grown from n-hexane/dichloromethane at room temperature.

2.11. *Structure determination for* $W(PhC{\equiv}CPh)_3(PMe_3)$

A crystal of $W(PhC{\equiv}CPh)_3(PPh_3)$ with approximate dimensions 0.13×0.50×0.50 mm was mounted in a thin-walled glass capillary and aligned on a Nonius CAD-4 diffractometer. Diffraction data were collected using the $\theta/2\theta$

Table 1
Crystal data and refinement details for W(TolC≡CTol)$_2$(η^4-C_4Tol_4)(PMe_3) and W(PhC≡CPh)$_3$(PMe_3)

	W(TolC≡CTol)$_2$(η^4-C_4Tol_4)(PMe_3)	W(PhC≡CPh)$_3$(PMe_3)
Chemical formula	$C_{67}H_{65}PW$	$C_{45}H_{39}PW$
Crystal solvent	CH_2Cl_2	H_2O
Crystal system	monoclinic	trigonal
Space group	$P2_1/c$	$P\bar{3}$
a (Å)	13.588(2)	14.000(4)
b (Å)	19.289(5)	
c (Å)	22.150(5)	11.183(4)
β (°)	90.57(2)	
V (Å^3)	5805(2)	1898.3(7)
Z	4	2
D_{calc} (g cm^{-3})	1.339	1.418
$F(000)$	2391.58	810
Radiation λ (Å)	0.70930	0.70930
T (K)	298	298
μ (cm^{-1})	21.9	31.756
Scan parameters	$0.65 + 0.35 \tan\theta$	$0.60 + 0.35 \tan\theta$
$2\theta_{max}$ (°)	49.8	55.0
No. unique data	10186	2920
No. data with $I > 2\sigma(I)$	4928	2408
R_F ^{a}	0.055	0.032
R_w ^{a}	0.051	0.038
Goodness of fit	1.24	1.00

^{a} $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \{\Sigma[w(|F_o| - |F_c|)^2]/\Sigma w|F_o|^2]\}^{1/2}$.

scan mode. Lattice parameters were determined from 25 randomly selected reflections with 2θ angle in the range 14.90–20.90°. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the heavy-atom method and refined by least-squares cycles; all non-hydrogen atoms were refined with anisotropic thermal parameters. The program used was the NRCSDP-VAX package. The data collection and refinement parameters are given in Table 1. Atomic positional parameters are collected in Table 2. Selected bond distances and bond angles are given in Table 3.

Table 2
Atomic coordinates of W(PhC≡CPh)$_3$(PMe_3)

Atom	x	y	z	B_{eq}
W	2/3	0.33333	0.04533(3)	3.20(1)
P	2/3	0.33333	−0.1786(2)	4.18(7)
C1	0.5110(4)	0.3139(4)	0.0270(4)	3.7(3)
C2	0.5353(4)	0.3229(4)	0.1405(4)	3.7(3)
C3	0.7801(6)	0.3291(6)	−0.2498(5)	5.8(4)
C11	0.4176(4)	0.2932(5)	−0.0496(4)	4.0(3)
C12	0.3292(5)	0.1864(5)	−0.0616(5)	5.1(3)
C13	0.2434(6)	0.1643(6)	−0.1389(6)	6.1(4)
C14	0.2446(6)	0.2475(8)	−0.2043(6)	6.7(5)
C15	0.3291(7)	0.3530(7)	−0.1907(6)	6.1(5)
C16	0.4152(5)	0.3770(5)	−0.1141(5)	4.8(3)
C21	0.4777(5)	0.3227(5)	0.2509(4)	4.3(3)
C22	0.3723(5)	0.3004(6)	0.2499(5)	5.5(4)
C23	0.3168(6)	0.2993(7)	0.3527(6)	6.2(4)
C24	0.3672(9)	0.323(1)	0.4555(7)	10.1(9)
C25	0.492(1)	0.387(1)	0.452(1)	5.4(9)
C26	0.545(1)	0.3822(9)	0.351(1)	3.9(6)
C25′	0.441(2)	0.288(3)	0.465(2)	13.(3)
C26′	0.502(2)	0.295(3)	0.363(2)	12.(2)
O	0	0	0.3726(9)	8.9(4)

2.12. Structure determination for W(TolC≡CTol)$_2$(η^4-C_4Tol_4)(PMe_3)

A crystal of W(TolC≡CTol)$_2$(η^4-C_4Tol_4)(PMe_3) with approximate dimensions 0.08×0.20×0.30 mm was mounted in a thin-walled glass capillary and aligned on a Nonius CAD-4 diffractometer. Diffraction data were collected using the $\theta/2\theta$ scan mode. Lattice parameters were determined from 25 randomly selected reflections with 2θ angle in the range 12.64–20.24°. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the heavy-atom method and refined by least-squares cycles; all non-hydrogen atoms were

Table 3
Selected bond distances and bond angles for W(PhC≡CPh)$_3$(PMe_3)

Bond distances (Å)			
W–P	2.504(2)	W–C1	2.067(5)
W–C2	2.066(5)	P–C3	1.803(6)
C1–C2	1.303(7)	C1–C11	1.467(7)
C2–C21	1.473(7)		
Bond angles (°)			
P–W–C1	84.3(1)	P–W–C2	121.0(2)
W–P–C3	116.2(3)	C3–P–C3	102.0(6)
W–C1–C2	71.6(3)	W–C2–C1	71.6(3)
C1–C2–C21	134.4(5)	C2–C1–C11	138.7(5)
C1–W–C2	36.8(2)	C1–W–C1	119.0(2)
C2–W–C2	95.9(3)		

Table 4
Selected atomic coordinates of W(TolC≡CTol)$_2$(η^4-C$_4$Tol$_4$)(PMe$_3$)

Atom	x	y	z	B_{eq}
W	0.35235(3)	0.25796(3)	0.27014(2)	2.46(2)
P	0.3526(2)	0.2749(2)	0.1575(1)	3.6(2)
C1	0.2543(9)	0.1671(6)	0.2631(5)	3.3(5)
C2	0.2712(8)	0.1752(5)	0.3269(5)	2.7(5)
C3	0.3703(8)	0.1504(6)	0.3227(5)	2.6(5)
C4	0.357(1)	0.1383(6)	0.2561(6)	4.3(7)
C5	0.2742(9)	0.3268(6)	0.3208(5)	3.4(6)
C6	0.2637(7)	0.3473(6)	0.2650(5)	3.0(5)
C7	0.4847(8)	0.2792(6)	0.3149(5)	3.1(5)
C8	0.4956(8)	0.2936(6)	0.2579(5)	3.1(5)
C11	0.1595(8)	0.1512(6)	0.2350(5)	3.1(5)
C21	0.2009(8)	0.1760(6)	0.3774(5)	3.2(6)
C31	0.4412(9)	0.1264(6)	0.3679(5)	3.1(6)
C41	0.4187(8)	0.1044(6)	0.2113(5)	3.2(5)
C51	0.2349(9)	0.3517(6)	0.3778(5)	3.6(6)
C61	0.2222(8)	0.4089(6)	0.2347(5)	3.3(6)
C71	0.5490(9)	0.2810(6)	0.3692(5)	3.6(5)
C81	0.5781(8)	0.3278(7)	0.2274(5)	3.4(6)
C91	0.2380(9)	0.2596(9)	0.1179(5)	5.1(7)
C92	0.4397(8)	0.2281(7)	0.1105(5)	5.1(7)
C93	0.382(1)	0.3616(7)	0.1317(5)	4.6(7)
C	0.814(2)	0.363(1)	0.325(1)	13.(2)
Cl1	0.8257(7)	0.4126(5)	0.3877(5)	20.1(7)
Cl2	0.9102(7)	0.3328(7)	0.3000(5)	28.(1)

refined with anisotropic thermal parameters. The program used was the NRCSDP-VAX package. The data collection and refinement parameters are given in Table 1. Selected atomic positional parameters are collected in Table 4. Selected bond distances and bond angles are given in Table 5.

3. Results and discussion

3.1. Preparation and characterization of *W(PhC≡CPh)$_3$(PMe$_3$)* and *W(PhC≡CPh)$_3$(PMePh$_2$)*

W(PhC≡CPh)$_3$(CO) undergoes a facile substitution reaction with PMe$_3$ at room temperature to give W(PhC≡CPh)$_3$(PMe$_3$). However, more vigorous conditions are required to effect the CO replacement as the number of phenyl substituents in the phosphine ligand increases, such as PMe$_2$Ph (THF reflux, 3.5 h) [9], PMePh$_2$ (benzene 70°C, 6 h) and PPh$_3$ (no reaction in refluxing toluene; low yield in molten PPh$_3$ at 120°C). This tendency is almost in agreement with the basicity decrease in the order PMe$_3$ > PMe$_2$Ph > PMePh$_2$ > PPh$_3$ [14], making PMe$_3$ the most reactive and PPh$_3$ the least reactive. However, it is more likely that steric interactions with the coordinated diphenylacetylene ligands hinder bulky phosphines adding to the central tungsten atom, leading to higher activation energy. On the other hand, replacing CO with a labile acetonitrile ligand alters the reactivity dramatically, such that W(PhC≡CPh)$_3$(NCMe) is able to react with large PPh$_3$, dppm and dppf molecules under moderate reaction conditions.

Table 5
Selected bond distances and bond angles for W(TolC≡CTol)$_2$(η^4-C$_4$Tol$_4$)(PMe$_3$)

Bond distances (Å)			
W–P	2.515(3)	W–C1	2.21(1)
W–C2	2.32(1)	W–C3	2.39(1)
W–C4	2.33(1)	W–C5	2.04(1)
W–C6	2.11(1)	W–C7	2.09(1)
W–C8	2.08(1)	P–C91	1.80(1)
P–C92	1.82(1)	P–C93	1.81(1)
C1–C2	1.44(2)	C1–C4	1.52(2)
C1–C11	1.46(2)	C2–C3	1.43(2)
C2–C21	1.48(2)	C3–C4	1.50(2)
C3–C31	1.46(2)	C4–C41	1.46(2)
C5–C6	1.31(2)	C5–C51	1.46(2)
C6–C61	1.47(2)	C7–C8	1.30(2)
C7–C71	1.48(2)	C8–C81	1.47(2)
Bond angles (°)			
W–P–C91	116.8(4)	W–P–C92	120.7(4)
W–P–C93	115.8(4)	C91–P–C92	101.7(6)
C91–P–C93	100.7(7)	C92–P–C93	97.6(6)
C2–C1–C4	90.1(9)	C2–C1–C11	125.(1)
C4–C1–C11	134.(1)	C1–C2–C3	92.3(9)
C1–C2–C21	130.(1)	C3–C2–C21	132.(1)
C2–C3–C4	90.9(9)	C2–C3–C31	133.(1)
C4–C3–C31	134.(1)	C1–C4–C3	86.7(9)
C1–C4–C41	140.(1)	C3–C3–C41	133.(1)
C1–W–C2	37.0(4)	C1–W–C4	38.9(5)
C2–W–C3	35.4(4)	C3–W–C4	37.1(4)
W–C5–C6	74.3(7)	C6–C5–C51	133.(1)
W–C6–C5	69.1(7)	C5–C6–C61	136.(1)
W–C7–C8	71.7(7)	C8–C7–C71	135.(1)
W–C8–C7	71.9(7)	C7–C8–C81	129.(1)

W(PhC≡CPh)$_3$(PMe$_3$) forms air-stable, white crystals. The ^{1}H NMR spectrum shows the phenyl proton resonances as a multiplet in the range 7.46–6.76 ppm, and the methyl proton resonance at 1.43 ppm as a doublet with $^2J_{P-H} = 8$ Hz. The ^{31}P{^{1}H} NMR spectrum gives a sharp singlet at −4.26 ppm accompanied by ^{183}W satellites with $^1J_{W-P} = 140$ Hz, indicating that PMe$_3$ is coordinated to the tungsten atom. The geometry of W(PhC≡CPh)$_3$(PMe$_3$) should lead to chemically inequivalent C≡C carbons and phenyl ring carbons. Thus, the ^{13}C{^{1}H} NMR spectrum exhibits two alkyne carbon resonances, both doublets, at 196.3 ($^2J_{P-C} = 5$ Hz) and 179.6 ($^2J_{P-C} = 18$ Hz) ppm, assigned to the distal and proximal ≡CPh groups, respectively. The phenyl carbons show eight resonance peaks ranging from 147.5 to 125.0 ppm, as expected. The methyl carbon resonance is observed at 17.3 ppm as a doublet with $^1J_{P-C} = 26$ Hz. The variable temperature ^{13}C{^{1}H} NMR spectra recorded in toluene-d$_8$ show the coalescence point for the two alkyne carbon resonances at ~110°C, and an approximate value of $\Delta G^{\neq} = 16.5$ kcal mol^{-1} for the alkyne rotation can be estimated. This value is in between those measured for W(PhC≡CPh)$_3$(CO) (17.0 kcal mol^{-1}) [15] and W(PhC≡CPh)$_3$(PMe$_2$Ph) (13.2 kcal mol^{-1}) [9]. Apparently, the increasing steric bulk from CO to PMe$_3$ and PMe$_2$Ph makes the alkyne ligands easier to rotate.

$W(PhC{\equiv}CPh)_3(PMePh_2)$ forms air-stable, white crystals. The FAB mass spectrum gives the molecular ion peaks with $m/z = 918$ for the ^{184}W isotope, and fragments from the loss of C_2Ph_2 and $PMePh_2$ species. The ^1H and $^{31}P\{^1H\}$ NMR spectra show the methyl proton resonance for the $PMePh_2$ group at 2.21 ppm as a doublet with $^2J_{P-H} = 8$ Hz, and the phosphorus resonance at 16.6 ppm with $^1J_{W-P} = 132$ Hz. The $^{13}C\{^1H\}$ NMR spectrum exhibits two broad alkyne carbon resonances at 196.5 and 180.1 ppm, assigned to the distal and proximal ≡CPh groups, respectively.

3.2. *Crystal structure of W(PhC≡CPh)₃(PMe₃)*

The labeling of atoms within the molecule is shown in Fig. 1. The geometry of the molecule has a three-fold axis of symmetry coincident with the W–P axis. The three P–Me groups are staggered with respect to the alkyne ligands as projected down the W–P vector. There is 50% disorder for the C25 and C26 atoms. The three acetylene groups are essentially eclipsed but inclined with respect to the W–P bond by a tilt angle of 13.2(3)°. This tilting angle is comparable with those measured for $W(PhC{\equiv}CPh)_3(CO)$ (13.4°) [16], $W(PhC{\equiv}CPh)_3(NH{=}CMe_2)$ (av. 13.1°) [17] and $[W(PhC{\equiv}CPh)_3(SnPh_3)]^-$ (av. 15.3°) [15] The acetylene C≡C distance is 1.303(7) Å, where the carbon atoms are bonded almost symmetrically to the tungsten atom with W–C bonds equal within the limits of experimental error (2.066 ± 0.006 Å). The phenyl groups are bent back from the C≡C axis with ∠C1–C2–C21 = 134.4(5)° and ∠C2–C1–C11 = 138.7(5)°. The geometry of the phenyl rings is modified in the expected manner.

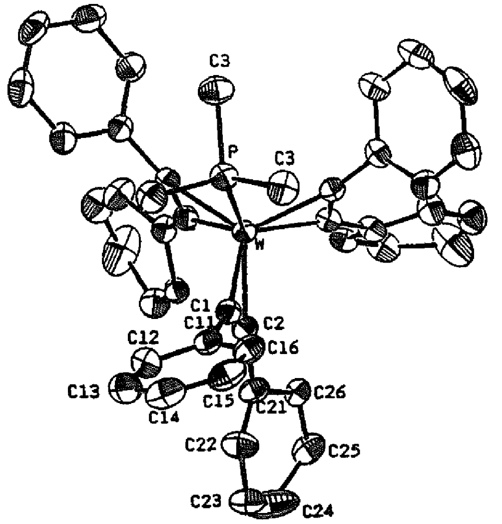

Fig. 1. Molecular structure of $W(PhC{\equiv}CPh)_3(PMe_3)$, showing the atomic labeling used in the text.

3.3. *Preparation and characterization of W(PhC≡CPh)₃(η¹-dppf) and [W(PhC≡CPh)₃]₂(η¹,η¹-dppf)*

$W(PhC{\equiv}CPh)_3(CO)$ and 1,1′-bis(diphenylphosphino)-ferrocene (dppf) give no reaction. Treatment of $W(PhC{\equiv}CPh)_3(NCMe)$ with dppf, however, affords $W(PhC{\equiv}CPh)_3(\eta^1\text{-dppf})$ as the major product together with a ditungsten complex $[W(PhC{\equiv}CPh)_3]_2(\eta^1,\eta^1\text{-dppf})$ in low yield.

$W(PhC{\equiv}CPh)_3(\eta^1\text{-dppf})$ forms air-stable, orange crystals. The $^{31}P\{^1H\}$ NMR spectrum shows two singlets at −18.76 and 24.84 ppm. The signal at −18.76 is close to the resonance for the free dppf molecule (−15.0 ppm) and is assigned to the uncoordinated phosphorus atom. In contrast, the signal at 24.84 ppm shows ^{183}W satellites with $^1J_{W-P} = 128$ Hz and can be assigned to the phosphorus coordinated to the tungsten atom. The ^1H NMR spectrum shows four broad signals at 3.91, 3.80, 3.76 and 3.63 ppm in equal intensities, assigned to the cyclopentadienyl ring protons in an AA′BB′ pattern. The $^{13}C\{^1H\}$ NMR spectrum shows two resonances at 197.8 and 181.3 ppm for the alkyne C≡C carbons, a multiplet in the range 144.6–124.5 ppm for the phenyl carbons, and Cp carbons ranging from 81.3 to 71.0 ppm.

$[W(PhC{\equiv}CPh)_3]_2(\eta^1,\eta^1\text{-dppf})$ forms a thermally sensitive, orange solid. Attempts to increase its yield by heating $W(PhC{\equiv}CPh)_3(\eta^1\text{-dppf})$ with $W(PhC{\equiv}CPh)_3(NCMe)$, or treating $W(PhC{\equiv}CPh)_3(NCMe)$ with a half equivalent of dppf ligand have been unsuccessful. The FAB mass spectrum gives the molecular ion peaks and the fragment from the loss of $W(PhC{\equiv}CPh)_3$ species. The spectroscopic data resemble those recorded for $W(PhC{\equiv}CPh)_3(\eta^1\text{-dppf})$, except that only one phosphorus resonance at 25.04 ppm with ^{183}W satellites, and two broad Cp proton resonances at 3.10 and 3.08 ppm are observed. This suggests an η^1,η^1-bridging mode for the dppf ligand. Apparently, an inverse center is imposed at the central iron atom, thus resulting in equivalent phosphorus atoms and Cp units.

3.4. *Preparation and characterization of W(PhC≡CPh)₂(η⁴-C₄Ph₄)(PMe₃) and W(TolC≡CTol)₂(η⁴-C₄Tol₄)(PMe₃)*

Reaction of $W(RC{\equiv}CR)_2(\eta^4\text{-}C_4R_4)(NCMe)$ (R = Ph and Tol) with PMe_3 at room temperature affords $W(RC{\equiv}CR)_2(\eta^4\text{-}C_4R_4)(PMe_3)$ in 85% yield. However, treating the related compound $W(PhC{\equiv}CPh)_2(\eta^4\text{-}C_4Ph_4)(CO)$ with PMe_3 gives no reaction even at 80°C in a sealed tube. We have no mechanistic information. It appears that steric congestion caused by the large cyclobutadiene group plays an important role here. Therefore, $W(PhC{\equiv}CPh)_2(\eta^4\text{-}C_4Ph_4)(CO)$ shows no reaction toward PMe_3, and the labilized complex $W(PhC{\equiv}CPh)_2(\eta^4\text{-}C_4Ph_4)(NCMe)$ can only react with PMe_3 but has no reactivity towards PPh_2Me, $PPh_2CH_2PPh_2$ and PPh_3.

Both W(PhC≡CPh)$_2$(η^4-C$_4$Ph$_4$)(PMe$_3$) and W(TolC≡CTol)$_2$(η^4-C$_4$Tol$_4$)(PMe$_3$) form air-stable, orange crystals and give satisfactory elemental analyses. The ^{1}H NMR spectrum of W(PhC≡CPh)$_2$(η^4-C$_4$Ph$_4$)(PMe$_3$) shows a multiplet between 7.25 and 6.83 ppm for the phenyl protons, and a doublet at 1.03 ppm ($^2J_{\text{P-H}} = 9$ Hz) for the PMe$_3$ protons. The ^{31}P{^{1}H} NMR spectrum gives a sharp singlet at -17.02 ppm accompanied by ^{183}W satellites with $^1J_{\text{W-P}} = 189$ Hz. The ^{13}C{^{1}H} NMR spectrum at 25°C exhibits the trimethylphosphine carbon resonance as a doublet at 18.0 ppm with $^1J_{\text{P-C}} = 46$ Hz and the cyclobutadiene carbon resonance as a singlet at 85.4 ppm, suggesting a facile ring rotation for the cyclobutadiene ligand. The alkyne C≡C carbon signals coalesce at room temperature, and at -90°C grow as a singlet at 186.1 ppm and a doublet at 166.8 ppm with $^1J_{\text{P-C}} = 46$ Hz, which can be assigned to the distal and proximal ≡CPh groups, respectively. Similar fast exchange behavior for the alkyne ligands was previously observed for W(PhC≡CPh)$_2$(η^4-C$_4$Ph$_4$)(NH=C(Ph)Me) and W(PhC≡CPh)$_2$(η^4-C$_4$Ph$_4$)(NH$_2$Et) [17]. In contrast, the slow exchange alkyne carbon resonances are recorded at room temperature for W(PhC≡CPh)$_2$(η^4-C$_4$Ph$_4$)(CO) and W(PhC≡CPh)$_2$(η^4-C$_4$Ph$_4$)(NCMe) [11]. One possible explanation is that the steric crowding caused by the phosphine group destablizes the ground state with the C≡C bond parallel to the W–P vector, leading to a lower energy barrier for alkyne rotation [9].

Variable temperature ^{1}H NMR spectra of W(TolC≡CTol)$_2$(η^4-C$_4$Tol$_4$)(PMe$_3$) were taken to further investigate the stereodynamics in solution. There is a sharp singlet at 2.18 ppm (12H) and two sets of doublets at 7.07 and 6.77 ppm (8H each), which remain unchanged from +50 to -50°C and can be assigned to the methyl and ring protons in the C$_4$Tol$_4$ group, respectively. The slow exchange spectrum for the ditolylacetylene ligands is recorded at -50°C, showing four doublet signals ranging from 7.11 to 6.57 ppm for the ring protons and two singlets at 2.32 and 2.21 ppm for the methyl protons. These signals collapse at 10°C, and at 50°C grow as two doublets and a sharp singlet. From the coalescence point at ~ -10°C, an approximate value of $\Delta G^{\neq} = 14.2$ kcal mol^{-1} for the alkyne rotation can be estimated. For comparison, we measured the alkyne rotational barrier for W(TolC≡CTol)$_2$(η^4-C$_4$Tol$_4$)(CO), obtaining 16.2 kcal mol^{-1}.

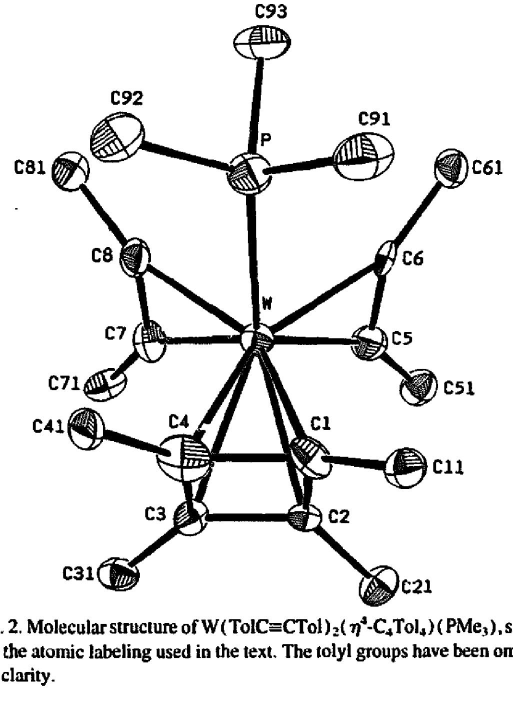

Fig. 2. Molecular structure of W(TolC≡CTol)$_2$(η^4-C$_4$Tol$_4$)(PMe$_3$), showing the atomic labeling used in the text. The tolyl groups have been omitted for clarity.

3.5. Crystal structure of W(TolC≡CTol)$_2$(η^4-C$_4$Tol$_4$)(PMe$_3$)

The molecular structure of W(TolC≡CTol)$_2$(η^4-C$_4$Tol$_4$)(PMe$_3$), illustrated in Fig. 2, consists of discrete molecules with each tungsten unit bonded to one trimethylphosphine, one tetratolylcyclobutadiene and two ditolylacetylenes. The overall geometry resembles that observed for W(PhC≡CPh)$_2$(η^4-C$_4$Ph$_4$)(CO) [11]. The cyclobutadiene ring (C1 to C4) is about planar with the maximum atomic displacement from the plane being 0.01(2) Å, which is bonded to the tungsten atom asymmetrically with W–C1 = 2.21(1) Å being significantly shorter than W–C2 = 2.32(1) Å, W–C4 = 2.33(1) Å and W–C3 = 2.39(1) Å. This probably gives a larger PMe$_3$ steric influence on the tolyl group connected to the C1 atom, where C11, C21, C31 and C41 are bent away from the cyclobutadiene plane by 34(2), 25(1), 16(1) and 9(2)°, respectively. The cyclobutadiene C–C bond distances are not equal, ranging from 1.43(2) (C2–C3) to 1.52(2) (C1–C4) Å, in contrast to those being equal in W(PhC≡CPh)$_2$(η^4-C$_4$Ph$_4$)(CO) (1.47±0.02 Å) [11] and W(η^4-C$_4$Ph$_4$)(C$_4$Ph$_4$H)(NHC(O)Me) (1.46±0.01 Å) [18].

The two ditolylacetylene ligands are essentially eclipsed with respect to the W–P vector as evidenced by the torsional angles P–W–C5–C6 = $-0.9(5)$° and P–W–C7–C8 = 3.0(5)°. However, the PMe$_3$ ligand is sterically forcing the alkyne ligands from being parallel, such that C5C6 is tilted from the W–P vector by 24.6° and C7C8 by 16.6°. This gives rise to a slight difference between the upper W–C6 distance (2.11(1) Å) and the lower W–C5 distance (2.04(1) Å), whereas the C7 and C8 atoms are equally bonded to the W atom, being 2.08±0.01 Å. The two alkyne C≡C lengths are about equal (1.31±0.02 Å), and the tolyl groups are bent back from the C≡C axis by angles averaging 132° (range 129–136°).

Acknowledgements

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References

[1] (a) D.P. Tate and J.M. Augl, *J. Am. Chem. Soc.*, *85* (1963) 2174; (b) D.P. Tate, J.M. Augl, W.M. Ritchey, B.L. Rose and J.G. Grasselli, *J. Am. Chem. Soc.*, *86* (1964) 3261.
[2] (a) R.B. King and A. Fronzaglia, *Inorg. Chem.*, *7* (1968) 1837; (b) R.B. King, *Inorg. Chem.*, *7* (1968) 1044.
[3] D.J. Wink and T. Creagan, *Organometallics*, *9* (1990) 328.
[4] S. Otsuka and A. Nakamura, *Adv. Organomet. Chem.*, *14* (1976) 245.
[5] J.L. Templeton, *Adv. Organomet. Chem.*, *29* (1989) 1, and Refs. therein.
[6] E. Sappa, A. Tiripicchio and P. Braunstein, *Chem. Rev.*, *83* (1983) 203.
[7] K.W. Chiu, D. Lyons, G. Wilkinson, M. Thornton-Pett and M.B. Hursthouse, *Polyhedron*, *2* (1983) 803.
[8] K.J. Odell, E.M. Hyde, B.L. Shaw and I. Shepherd, *J. Organomet. Chem.*, *168* (1979) 103.
[9] D.J. Wink and N.J. Cooper, *Organometallics*, *10* (1990) 494.
[10] W.-Y. Yeh, C.-S. Ting and C.-F. Chih, *J. Organomet. Chem.*, *427* (1991) 257.
[11] W.-Y. Yeh and L.-K. Liu, *J. Am. Chem. Soc.*, *114* (1992) 2267.
[12] W.-Y. Yeh, S.-M. Peng and G.-H. Lee, *J. Chem. Soc., Chem. Commun.*, (1993) 1056.
[13] J. Okuda and K.H. Zimmermann, *J. Organomet. Chem.*, *384* (1990) C21.
[14] W.A. Henderson, Jr. and C.A. Streuli, *J. Am. Chem. Soc.*, *82* (1960) 5791.
[15] J.M. Maher, J.R. Fox, B.M. Foxman and N.J. Cooper, *J. Am. Chem. Soc.*, *106* (1984) 2347.
[16] R.M. Laine, R.E. Moriarty and R. Bau, *J. Am. Chem. Soc.*, *94* (1972) 1402.
[17] W.-Y. Yeh, C.-S. Ting, S.-M. Peng and G.-H. Lee, *Organometallics*, *14* (1995) 1417.
[18] W.-Y. Yeh, S.-M. Peng and L.-K. Liu, *Inorg. Chem.*, *32* (1993) 2965.