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Syntheses of $W(PhC{\equiv}CPh)_3(\eta^1\text{-}PPh_2CH_2PPh_2)$ and $W(PhC{\equiv}CPh)_3(PPh_3)$ from $W(PhC{\equiv}CPh)_3(NCCH_3)$

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Abstract

$W(Ph{\equiv}CPh)_3(NCCH_3)$ has been synthesized by treating $W(PhC{\equiv}CPh)_3(CO)$ with Me_3NO in acetonitrile solution. Reactions of $W(PhC{\equiv}CPh)_3(NCCH_3)$ with $(PPh_2)_2CH_2$ and PPh_3 afford $W(PhC{\equiv}CPh)_3(\eta^1\text{-}PPh_2CH_2PPh_2)$ and $W(PhC{\equiv}CPh)_3(PPh_3)$, respectively.

Introduction

Polyalkyne complexes of the type $W(RC{\equiv}CR')_3(CO)$ were first reported by Tate [1] in 1963 and have attracted much attention owing to their unique structure and mode of bonding, particularly in relation to the ability of alkyne ligands to act as two- and four-electron donors [2–11]. For comparison, it is of interest to prepare and study the analogous complexes, $W(RC{\equiv}CR')_3(L)$, with CO being replaced by other two-electron donor ligands. Previously, direct substitutions of the carbonyl ligand by tertiary phosphines to give $W(PhC{\equiv}CC_6H_3(OMe)_2)_3$. (PMe_2Ph) [12], $W(PhC{\equiv}CPh)_3(PMe_2Ph)$ and $W(PhC{\equiv}CH)_3(PPh_3)$ [13] have been reported. It has been argued that the steric effects induced by bulky alkynes and bulky phosphines might affect the substitution reaction, thereby explaining the failure of PPh_3 or $Ph_2PCH_2CH_2PPh_2$ to react with $W(PhC{\equiv}CPh)_3(CO)$ [14]. In contrast, the more compact bidentate phosphine $Me_2PCH_2CH_2PMe_2$ (dmpe) replaces the alkyne ligands in $W(PhC{\equiv}CPh)_3(CO)$ to form $W(CO)_2(dmpe)_2$ [14].

In attempts to effect substitution of CO in $W(RC{\equiv}CR')_3(CO)$ by bulky phosphine ligands, we decided first to replace CO with a labile ligand, such as THF or nitriles, and then to treat it with phosphines. Here we present results concerning the syntheses of $W(PhC{\equiv}CPh)_3(\eta^1\text{-}PPh_2CH_2PPh_2)$ and $W(PhC{\equiv}CPh)_3(PPh_3)$ from $W(PhC{\equiv}CPh)_3(NCCH_3)$ (Scheme 1).

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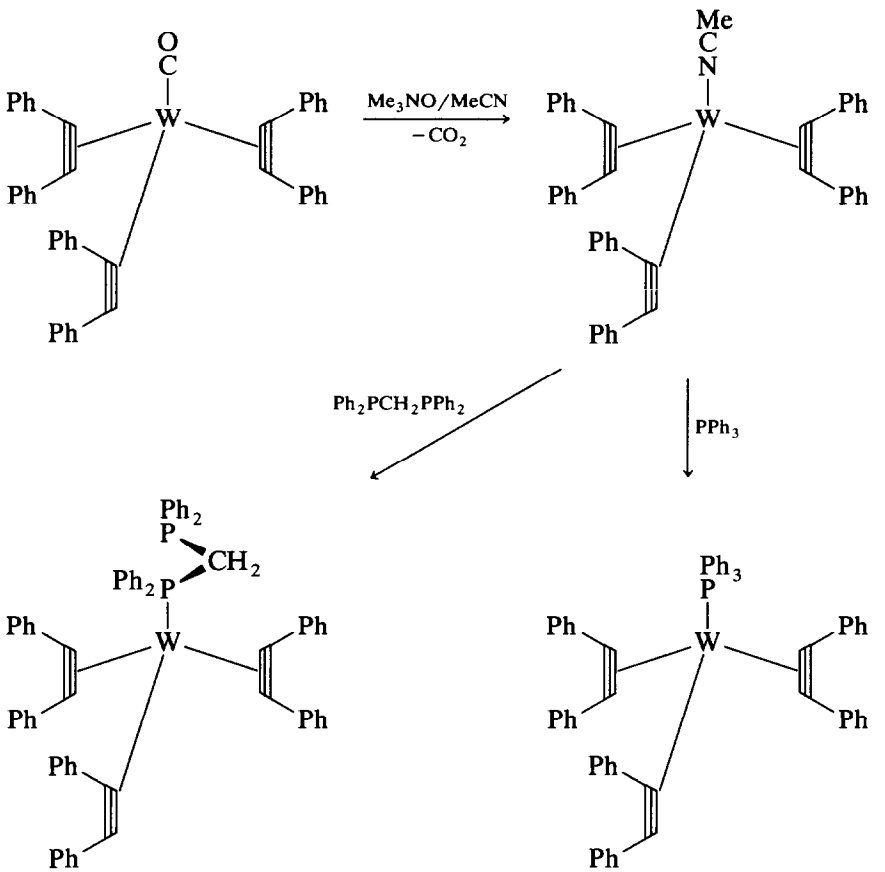

Scheme 1

Results and discussion

Preparation and characterization of $W(PhC{\equiv}CPh)_3(NCCH_3)$

Treatment of $W(PhC{\equiv}CPh)_2(CO)$ with Me_3NO in CH_3CN solution effects the displacement of CO ligand by the solvent molecule and generates $W(PhC{\equiv}CPh)_3(NCCH_3)$ in 80% yield. The compound is a white solid that is stable in air. However, it decomposes slowly in solution to give an uncharacterized greenish species when exposed to air. A related complex $W(CF_3C{\equiv}CCF_3)_3(NCCH_3)$, previously reported by King [5], was prepared quite differently, by heating $W(CO)_3(NCCH_3)_3$ and $CF_3C{\equiv}CCF_3$.

The FAB mass spectrum of $W(PhC{\equiv}CPh)_3(NCCH_3)$ gives molecular ion peaks with $m/e = 759$ for the ^{184}W isotope. The ^1H NMR spectrum shows a multiplet between δ 7.36 and 7.08 (30H) for the phenyl protons and a 3H singlet at δ 2.38 for the protons in the acetonitrile ligand. The room temperature ^{13}C NMR spectrum in $CDCl_3$ exhibits two alkyne carbon resonances at δ 196.4 and 182.4, assigned to the distal and proximal $\equiv$CPh groups respectively [13]. The phenyl

carbon resonances are between δ 143.2 and 127.0, and the $-C\equiv N$ carbon resonance is at δ 126.1. The IR spectrum shows a weak broad peak at 2310 cm^{-1} due to $\nu(C\equiv N)$ and a broad medium strength band at 1634 cm^{-1}, assigned as $\nu(C\equiv C)$. Since these values agree with literature data for analogous complexes [1–3,11,13], a structure resembling that established for $W(PhC\equiv CPh)_3(CO)$ [3] can be proposed for $W(PhC\equiv CPh)_3(NCCH_3)$.

Reactivity of $W(PhC\equiv CPh)_3(NCCH_3)$

Although solid $W(PhC\equiv CPh)_3(NCCH_3)$ is stable indefinitely, it shows a range of reactivities in solution. The CH_3CN ligand undergoes facile substitution reactions with phosphines, as shown below, whereas it remains intact when $W(PhC\equiv CPh)_3(NCCH_3)$ is treated with diphenylacetylene, affording a cyclobutadiene complex $W(\eta^4\text{-}C_4Ph_4)(PhC\equiv CPh)_2(NCCH_3)$ [15]. Thermolysis of $W(PhC\equiv CPh)_3(NCCH_3)$ in refluxing toluene results in slow decomposition, giving diphenylacetylene and a brownish material, but there is no evidence ditungsten poly(alkyne) complexes are formed. Hydrogenation of $W(PhC\equiv CPh)_3(NCCH_3)$ (1 atm H_2, 80°C in toluene solution) produces air-sensitive products, which are presently under investigation.

Preparation and characterization of $W(PhC\equiv CPh)_3(\eta^1\text{-}PPh_2CH_2PPh_2)$

Reaction of $W(PhC\equiv CPh)_3(NCCH_3)$ with $(Ph_2P)_2CH_2$ in refluxing toluene produces $W(PhC\equiv CPh)_3(\eta^1\text{-}PPh_2CH_2PPh_2)$ in 52% yield. This compound forms a white air-stable solid and has been characterized by microanalysis, ^1H, ^{13}C and ^{31}P NMR, IR and mass spectroscopies. Interestingly, this bidentate bisphosphine ligand is coordinated to the tungsten atom through only one end.

The room-temperature $^{31}P\{^1H\}$ NMR spectrum shows two doublet resonances at δ 27.48 and -23.77 with $^2J(P\text{–}P) = 13$ Hz. The signal at δ -23.77 is close to the resonance for free $(Ph_2P)_2CH_2$ molecule (δ -22.12) and is assigned to the uncoordinated phosphorus atom. In contrast the signal at δ 27.48 shows ^{183}W satellites with $^1J(W\text{–}P)$ of 125 Hz and can be assigned to the phosphorus coordinated to the tungsten atom. These values are comparable with those measured for $W(PhC\equiv CPh)_3(PMe_2Ph)$ (δ 4.28, $^1J(W\text{–}P) = 137$ Hz) [13], $W(PhC\equiv CH)_3(PPh_3)$ (δ 46.3, $^1J(W\text{–}P) = 127$ Hz) [12], $W(PhC\equiv CC_6H_3(OMe)_2)_3(PMe_2Ph)$ (δ 5.20, $^1J(W\text{–}P) = 134$ Hz) [12], and $W(PhC\equiv CH)_3(PMe_3)$ (δ 0.62, $^1J(W\text{–}P) = 140$ Hz) [16]. The ^1H NMR spectrum shows a multiplet between δ 7.21 and 6.02 (50H) for the phenyl protons and a 2H multiplet at δ 3.59, assigned to the methylene protons which are coupled to the two inequivalent phosphorus atoms. The $^{13}C\{^1H\}$ NMR spectrum demonstrates the two alkyne carbon resonances at δ 197.2 and 180.3, the phenyl carbon resonances between δ 146.3 and 125.0, and the methylene carbon resonance as a multiplet at δ 28.0. The IR spectrum in KBr disc includes a medium, broad band and 1650 cm^{-1}, assigned to $\nu(C\equiv C)$, consistent with the proposed formulation.

Attempts to grow single crystals of $W(PhC\equiv CPh)_3(\eta^1\text{-}PPh_2CH_2PPh_2)$ for X-ray diffraction study have been unsuccessful. However, based on the spectroscopic data, the structure is believed to the similar to that found for the anionic complex $[W(PhC\equiv CPh)_3(SnPh_3)]^-$ [8], with the three alkyne carbons forming a tapered trigonal-prismatic coordination sphere for the tungsten atom and the $PPh_2CH_2PPh_2$ ligand capping a trigonal face. The spatial orientation for the

$PPh_2CH_2PPh_2$ ligand should compromise with that of the diphenylacetylene ligands to minimize steric repulsion between the phenyl groups, although the exact position is not clear.

Reactivity of $W(PhC{\equiv}CPh)_3(\eta^1\text{-}PPh_2CH_2PPh_2)$

Since only one phosphorus atom in $PPh_2CH_2PPh_2$ is coordinated to the tungsten atom, we decided to prepare a ditungsten complex $(W(PhC{\equiv}CPh)_3)_2(\eta^2\text{-}(PPh_2)_2CH_2)$ by treating $W(PhC{\equiv}CPh)_3(\eta^1\text{-}PPh_2CH_2PPh_2)$ with $W(PhC{\equiv}CPh)_3(NCCH_3)$, but there was no reaction. Thermolysis of $W(PhC{\equiv}CPh)_3(\eta^1\text{-}PPh_2CH_2PPh_2)$ in refluxing benzene also results in no reaction. At higher temperature (110°C, refluxing toluene), considerable decomposition occurs, but no chelated compounds are observed. In contrast, Connor [14] has shown that $W(MeSC{\equiv}CSMe)_3(CO)$ reacts with $Me_2PCH_2CH_2PMe_2$ (dmpe) at ambient temperature to produce bidentate $W(MeSC{\equiv}CSMe)_2(dmpe)(CO)$ and $W(MeSC{\equiv}CSMe)_2(dmpe)$. Apparently, in $W(PhC{\equiv}CPh)_3(\eta^1\text{-}PPh_2CH_2PPh_2)$ the steric crowding arising from the phenyl groups in both the phosphine and the alkyne ligands would block the uncoordinated phosphorus atom and decrease its reactivity.

Preparation and characterization of $W(PhC{\equiv}CPh)_3(PPh_3)$

The reaction between $W(PhC{\equiv}CPh)_3(NCCH_3)$ and PPh_3 in toluene solution at reflux affords the air-stable, pale yellow complex $W(PhC{\equiv}CPh)_3(PPh_3)$ in 62% yield. The EI mass spectrum shows the molecular ion at $m/e = 980$ (^{184}W) and fragments resulting from successive loss of C_2Ph_2 and PPh_3 species. The ^1H NMR spectrum illustrates the phenyl proton resonances δ in the range 7.40–7.06 for the alkyne ligands and in the range 6.84–5.32 for the phosphine ligand. The $^{31}P\{^1H\}$ NMR spectrum presents a singlet at δ 36.03 accompanied by ^{183} W satellites with $^1J(W\text{–}P) = 128.3$ Hz. These values are compatible with those measured for $W(PhC{\equiv}CPh)_3(\eta^1\text{-}PPh_2CH_2PPh_2)$ mentioned above. The $^{13}C\{^1H\}$ NMR spectrum shows two alkyne carbon resonances, both doublets, at δ 198.7 ($^2J(P\text{–}C) = 3.3$ Hz) and δ 180.9 ($^2J(P\text{–}C) = 19$ Hz), assigned to the distal and proximal ≡CPh groups, respectively. The phenyl carbons show fifteen resonance peaks ranging from δ 145.8 to δ 124.9, although twelve signals would be expected for a molecule containing C_{3v} symmetry. This is because three sets of phenyl carbons in the PPh_3 group (*ipso*, *ortho* and *meta* carbons) are coupled to the phosphorus atom [17], thus giving three extra signals; however, we were unable to resolve them.

Experimental

General procedures

$W(PhC{\equiv}CPh)_3(CO)$ was prepared from $W(CO)_6$ as described in the literature [1]. Bis(diphenylphsophino)methane ($(PPh_2)_2CH_2$, Aldrich) and triphenylphosphine (PPh_3, Aldrich) were used as received. Acetonitrile was distilled from phosphorous pentoxide and toluene was distilled from sodium before use. Trimethylamine oxide was sublimed (10^{-2} Torr, 90°C) from $Me_3NO \cdot 2H_2O$ (Aldrich) before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Aldrich). ^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 Perkin–Elmer 1300 spectrometer. Elemental analyses were performed at the NSC Regional Instrumentation Center at National Cheng Kung University, Tainan. Mass spectra were obtained on a JOEL-HX110 mass spectrometer.

Preparation of $W(PhC{\equiv}CPh)_3(NCCH_3)$

$W(CO)(PhC{\equiv}CPh)_3$ (100 mg, 0.134 mmol) was placed in an oven-dried 100 ml Schlenk flask, equipped with a magnetic stir bar and a rubber serum stopper, under nitrogen atmosphere. A solution of Me_3NO (18 mg, 0.24 mmol, 1.8 equiv.) in a acetonitrile (20 ml) was introduced into the flask *via* a cannula through the serum stopper. The mixture was then placed under nitrogen and stirred at room temperature for 3 h, affording a white precipitate. The supernatant was removed by pipette and the product washed several times with fresh acetonitrile (3 × 3 ml). The air-stable, white solid, characterized as $W(PhC{\equiv}CPh)_3(NCCH_3)$, was dried under vacuum for 10 h and weighed 81 mg (0.106 mmol, 80%). Anal. Found: C, 69.49; H, 4.43; N, 1.84 $C_{44}H_{33}NW$ calc.: C, 69.57; H, 4.38; N, 1.84%. Mass spectrum (FAB): *m/e* 759 (M^+, ^{184}W). ^1H NMR (CD_2Cl_2, 25°C): δ 7.08–7.36 (m, 30 H, Ph), 2.38 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): δ 196.4, 182.4 (C≡C), 143.2, 141.1, 129.3, 128.0, 127.9, 127.0 (Ph), 126.1 (–C≡N). IR (KBr): 2310 (ν(C≡N)), 1634 (ν(C≡C)) cm^{-1}.

Preparation of $W(PhC{\equiv}CPh)_3(\eta^1\text{-}PPh_2CH_2PPh_2)$

$W(PhC{\equiv}CPh)_3(NCCH_3)$ (200 mg, 0.263 mmol), $(PPh_2)_2CH_2$ (202 mg, 0.53 mmol) and toluene (10 ml) were placed in a 50 ml round-bottomed flask, equipped with a reflux condenser and a magnetic stir bar. The colorless solution was refluxed under nitrogen for 3 h, by which time the color had become pale yellow. The mixture was allowed to cool to room temperature and the solvent removed under vacuum. The residue was subjected to TLC, eluting with n-hexane–dichloromethane (3:1 v/v). The excess $(PPh_2)_2CH_2$ was removed from the third colorless band. Isolation of the material forming the fourth colorless band produced a pale greenish-yellow solid, characterized as $W(PhC{\equiv}CPh)_3(\eta^1\text{-}PPh_2CH_2PPh_2)$ (150 mg, 0.136 mmol, 52%). Anal. Found: C, 72.58; H, 4.85 $C_{67}H_{52}P_2W$ calc.: C, 72.96; H, 4.75%. Mass spectrum (EI): *m/e* 1102 (M^+, ^{184}W). IR (KBr): 3040 (ν(C–H)), 1650 (ν(C≡C)) cm^{-1}. ^1H NMR ($CDCl_3$, 25°C): δ 7.21–6.02 (m, 50H, Ph), 3.59 (m, 2H, P–CH_2–P). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25°C): δ 27.48 (d, ^2J(P–P) = 13 Hz; with ^{183}W satellites, ^1J(W–P) = 125 Hz), –23.77 (d, ^2J(P–P) = 13 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): δ 197.2 (b, ≡C), 180.3 (b, ≡C), 146.3, 141.7, 138.8, 134.4, 132.5, 129.6, 128.3, 128.1, 127.9, 127.4, 127.3, 126.0, 125.0 (Ph), 28.0 (m, PCH_2P).

Preparation of $W(PhC{\equiv}CPh)_3(PPh_3)$

An oven-dried, 50 ml round-bottomed flask was equipped with a reflux condenser and a magnetic stir bar. $W(PhC{\equiv}CPh)_3(NCCH_3)$ (200 mg, 0.263 mmol), PPh_3 (90 mg, 0.343 mmol) and toluene (10 ml) were introduced into the flask. The mixture was refluxed under nitrogen for 3 h, cooled to room temperature, and the solvent removed under vacuum. The residue was subjected to TLC and eluted with n-hexane–dichloromethane (4:1 v/v). Crystallization of the material forming the yellow band from dichloromethane–methanol gave air-stable, pale-yellow crystals of $W(PhC{\equiv}CPh)_3(PPh_3)$ (160 mg, 0.163 mmol, 62%). Mass spectrum (EI): *m/e* 980

(M^+, ^{184}W), 802 ($M^+ - Ph_2C_2$), 718 ($M^+ - PPh_3$), 534 ($C_6Ph_6^+$), 446 ($WPPh_3^+$), 356 ($C_4Ph_4^+$), 184 (W^+). IR (KBr): 1643 cm^{-1} (m, br, ν(C≡C)). ^1H NMR (CD_2Cl_2, 25°C): δ 7.40–7.06 (m, 30H, Ph–C≡), 6.84–5.32 (m, 15H, Ph–P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25°C): δ 36.03 (s, with ^{183}W satellites, $^1J(W-P) = 128.2$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25°C): δ 198.7 (d, C≡C, $^2J(P-C) = 3.3$ Hz; $^1J(W-C) = 32$ Hz), 180.9 (m, C≡C, $^2J(P-C) = 19$ Hz; $^1J(W-C) = 45$ Hz), 145.8, 143.0, 135.4, 135.3, 134.7, 134.2, 130.3, 129.6, 128.5, 128.4, 128.1, 127.8, 127.6, 126.3, 124.9 (Ph).

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