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Synthesis and molecular structure of the organometallic allylimido complex [*cis,trans*-$WCl_2(Ph_2PMe)_2(CO)(NCH_2CH{=}CH_2)$]

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Abstract

Addition of allyl isocyanate to [$WCl_2(Ph_2PMe)_4$] results in oxidative addition of the nitrogen-carbon bond to the metal centre to afford the allylimido complex [*cis,trans*-$WCl_2(Ph_2PMe)_2(CO)(NCH_2CH{=}CH_2)$], which has been crystallographically characterized. Reaction with t-butyllithium results in rapid deprotonation of one of the α-hydrogens of the allyl moiety, a process which is reversed upon addition of water.

Key words: Tungsten; Imide; Allyl; Carbonyl; Phosphine; Crystal structure

1. Introduction

Organometallic compounds containing the imido moiety are currently attracting considerable attention primarily because of their potential application as amination reagents in organic synthesis [1]. A number of routes to these species have been developed, through which it has proved possible to synthesise a range of complexes with various substituents at nitrogen [2]. Complexes containing allyl substituents are of particular interest owing to their suggested intermediacy in the heterogeneous "ammoxidation" of propylene, a process which accounts for virtually all the world production of acrylonitrile [3]. Surprisingly in view of this, only two accounts of allylimido complexes have appeared [4,5]. Thus, Maatta and co-workers have reported the synthesis of both [$WCl_4(thf)(NCH_2CH{=}CH_2)$] [4] and [$MoCl_3(PPh_3)_2(NCH_2CH{=}CH_2)$] [5]. The latter is the only crystallographically characterized member of this class of complex, but owing to an unresolved disorder in the allyl moiety the structure was of low accuracy [5]. Here we report the synthesis and structure of the first organometallic complex containing the allylimido ligand, namely [*cis,trans*-$WCl_2(Ph_2PMe)_2(CO)(NCH_2CH{=}CH_2)$] (1).

2. Experimental details

2.1. General comments

All reactions were carried out under N_2 in predried solvents. NMR spectra were recorded on a Varian VXR 400 spectrometer. IR spectra were recorded on a Nicolet 205 Fourier-Transform spectrometer. Elemental analysis was performed in the Chemistry Department of University College. Allyl isocyanate was purchased from Aldrich and used as supplied, and [$WCl_2(Ph_2PMe)_4$] was prepared by the published method [6].

2.2. Synthesis of [$WCl_2(Ph_2PMe)_2(CO)(NCH_2CH{=}CH_2)$](1)

Addition of allyl isocyanate (16 mg, 0.19 mmol) to a toluene solution (10 cm^3) of [$WCl_2(Ph_2PMe)_4$] (200 mg, 0.19 mmol) at room temperature resulted in a gradual colour change from orange to pink. After 14 h, removal of solvent and washing with hexane afforded an orange oil. Slow diffusion of methanol into a dichloromethane solution afforded 120 mg (85%) of pink crystalline [$WCl_2(Ph_2PMe)_2(CO)(NCH_2CH{=}CH_2)$](1) Anal. Found: C, 48.10; H, 4.24; P, 8.80; N, 1.92; Cl, 10.60. $W_1C_{30}H_{31}N_1O_1P_2Cl_2$ calcd: C, 48.78; H, 4.20; P, 8.40; N, 1.89; Cl, 9.62%. ^1H NMR ($CDCl_3$): δ 7.80-7.20 (m, 20H, Ph); 5.43 (ddt, $J = 12.7$, 9.9 Hz, 6.3, 1H, H_c); 4.83 (dd, $J = 9.9$, 1.2 Hz, 1H, H_B); 4.66

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(dd, $J = 12.7$, 1.2 Hz, 1H, H_A); 2.97 (q, $J = 6.3$ Hz, 2H, H_D), 2.28 (t, $J = 4.0$ Hz, 6H, Me). ^{31}P NMR ($CDCl_3$): δ 25.4 (s). IR (KBr): 1965vs, 1484w, 1434m, 1384w, 1265m, 1089m, 987w, 938w, 894vs, 748w, 734m, 693vs, 505s, 408m cm^{-1}.

2.3. *Synthesis of* $[NEt_4][WCl_2(Ph_2PMe)_2(CO)(NCHCH{=}CH_2)]$ *(2)*

Addition of ^tBuLi (0.30 mmol) to a THF solution (10 cm^3) of **1** (190 mg, 0.26 mmol) at −40°C resulted in an immediate colour change from pink to yellow. The mixture was allowed to warm to room temperature and NEt_4Cl (75 mg, 0.48 mmol) was added. Removal of solvent afforded an oily yellow solid, which was washed with hexane and extracted with dichloromethane. Addition of hexane to the extract afforded **2** as a yellow precipitate which was washed with hexane. ^1H NMR ($CDCl_3$): δ 8.20–7.10 (m, 20H, Ph); 5.44 (d, $J = 13.3$ Hz, 1H, H_A); 5.20 (dq, $J = 13.3$, 8.0 Hz, 1H, H_C); 4.96 (t, $J = 8.0$ Hz, 1H, H_B); 3.79 (t, $J = 8.0$ Hz, 1H, H_D); 3.17 (br, 8H, CH_2); 2.30 (t, $J = 4.0$ Hz, 6H, PMe); 1.20 (t, $J = 4.0$ Hz, 12H, Me). IR (KBr); 1963br cm^{-1}. Addition of an excess of methyl iodide to a THF solution of **2** did not result in any change. Addition of "wet" $CDCl_3$ to **2** resulted in the quantitative reformation of **1**, as shown by NMR spectroscopy. Addition of D_2O to a dry $CDCl_3$ solution of **2** resulted in the rapid formation of **1**, with 50% deuterium incorporation into the H_D position, as shown by careful integration of the ^1H NMR spectrum.

2.4. *X-Ray data collection and solution*

A pink single crystal of approximate size 0.48 × 0.30 × 0.30 mm^3 was mounted on a glass fibre. All geometric and intensity data were taken from this sample using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). Important crystallographic parameters are summarized in Table 1. The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 30 reflections taken from a rotation photograph and centred by the diffractometer. The ω–2θ technique was used to measure 6083 reflections (5841 unique) in the range $15° \le 2\theta \le 29°$. Three standard reflections were measured every 97 scans, and showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarization effects, and empirically for absorption. The 4107 unique data with $I \ge 3.0\sigma(I)$ were used to solve and refine the structure in the monoclinic space group $P2_1/n$.

The structure was solved by direct methods and developed by using alternating cycles of least-squares refinement and difference-Fourier synthesis. The non-hydrogen atoms were refined anisotropically while hydrogens were placed in idealized positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter ($U = 0.08$ Å^2). The final cycle of least-squares refinement included 334 parameters for 4107 variables and did not shift any parameter by more than 0.001 times its standard deviation. The final R values were 0.035 and 0.038, and the final difference-Fourier was featureless with no peaks greater than 1.25 e Å^{-3}. Structure solution used the SHELXTL PLUS program package on a microVax II computer. Atomic coordinates are listed in Table 2. A complete list of bond lengths and angles and tables of hydrogen atom coordinates and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

TABLE 1. Crystallographic data for [*cis,trans*-$WCl_2(PMePh_2)_2(CO)(NCH_2CH{=}CH_2)$](1)

Formula	$W_1C_{30}H_{31}N_1P_2Cl_2$
Space group	$P2_1/n$
a (Å)	11.4808(20)
b (Å)	15.0568(66)
c (Å)	18.0028(58)
β (°)	102.580(20)
V (Å^3)	3037.33
Z	4
$F(000)$	1456
d_{calc} (g/cm^{-3})	1.61
Crystal size (mm)	0.48 × 0.30 × 0.30
μ(Mo Kα) (cm^{-1})	41.88
Data collection instrument	Nicolet R3mV
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Orientation reflections; no.; range	30; $15 \le 2\theta \le 29$
Temperature (°C)	19
Data measured	6083
Unique data	5841
No. of unique with $I \ge 3.0\sigma(I)$	4107
No. of parameters	334
R [a]	0.035
R_w [b]	0.038
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.000975F^2$
Largest shift/e.s.d. final cycle	0.001
Largest peak (e/Å^{-3})	1.25

[a] $R = \Sigma[|F_o| - |F_c|]/\sigma|F_o|$. [b] $R_w = \Sigma w^{1/2}[|F_o| - |F_c|]/\Sigma w^{1/2}|F_o|$.

3. Results and discussion

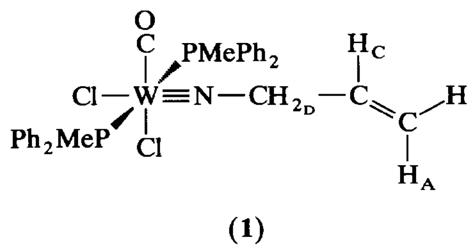
Addition of allyl isocyanate to a toluene solution of $[WCl_2(PPh_2Me)_4]$ resulted in the gradual colour change from orange to pink, and the allylimido complex [*cis,trans*-$WCl_2(Ph_2PMe)_2(CO)(NCH_2CH{=}CH_2)$] (**1**) was isolated in 85% yield. Identification was made on the basis of spectroscopic and analytical data. Thus in the IR spectrum, oxidative addition of the

TABLE 2. Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å×10³)

W(1)	501(1)	1876(1)	2370(1)	36(1)
P(1)	1413(2)	1756(1)	1225(1)	41(1)
P(2)	−710(2)	1674(1)	3382(1)	40(1)
Cl(1)	963(2)	273(1)	2580(1)	55(1)
Cl(2)	−1415(2)	1499(1)	1480(1)	54(1)
O(1)	−605(6)	3755(4)	1892(4)	78(3)
N(1)	1733(5)	2423(4)	2919(3)	50(2)
C(1)	−191(7)	3071(5)	2070(4)	51(3)
C(2)	2646(9)	3016(7)	3327(6)	84(4)
C(3)	2172(11)	3755(7)	3671(7)	103(5)
C(4)	2176(12)	3925(8)	4350(8)	110(6)
C(5)	764(7)	886(5)	570(4)	59(3)
C(6)	−1634(6)	677(5)	3239(4)	55(3)
C(10)	1312(6)	2749(5)	644(3)	46(2)
C(11)	716(8)	2798(7)	−97(5)	76(3)
C(12)	648(10)	3571(9)	−502(6)	99(5)
C(13)	1169(9)	4330(7)	−173(6)	85(4)
C(14)	1775(10)	4306(6)	560(7)	88(5)
C(15)	1861(8)	3525(5)	983(5)	64(3)
C(20)	3013(6)	1479(5)	1415(4)	49(2)
C(21)	3569(6)	1099(5)	2106(5)	60(3)
C(22)	4746(8)	824(6)	2207(5)	73(3)
C(23)	5361(8)	915(7)	1638(6)	80(4)
C(24)	4826(9)	1306(8)	983(6)	94(5)
C(25)	3649(8)	1592(7)	862(5)	73(3)
C(30)	136(6)	1549(5)	4360(4)	46(2)
C(31)	−468(8)	1445(7)	4943(5)	77(4)
C(32)	172(10)	1373(8)	5687(5)	93(5)
C(33)	1388(8)	1410(6)	5857(5)	71(3)
C(34)	1988(8)	1494(6)	5288(5)	71(3)
C(35)	1370(7)	1540(6)	4525(4)	57(3)
C(40)	−1746(6)	2586(4)	3432(4)	43(2)
C(41)	−1349(8)	3339(5)	3844(5)	62(3)
C(42)	−2141(10)	4034(6)	3851(6)	79(4)
C(43)	−3257(10)	4014(7)	3457(6)	81(4)
C(44)	−3659(9)	3287(8)	3027(6)	90(4)
C(45)	−2902(7)	2569(6)	3017(5)	71(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

nitrogen–carbon bond was confirmed by the appearance of an absorption at 1965 cm^{-1} assigned to the carbonyl group. In the ^1H NMR spectrum, the allylic protons appear at δ 5.43 (ddt, $J = 12.7, 9.9, 6.3$ Hz, 1H, H_C); 4.83 (dd, $J = 9.9$, 1.2 Hz, 1H, H_B); 4.66 (dd, $J = 12.7$, 1.2 Hz, 1H, H_A); 2.97 (q, $J = 6.3$ Hz, 2H, H_D), while the ^{31}P NMR spectrum consists of a singlet at 25.4 ppm (with tungsten satellites) assigned to equivalent phosphine environments.



(1)

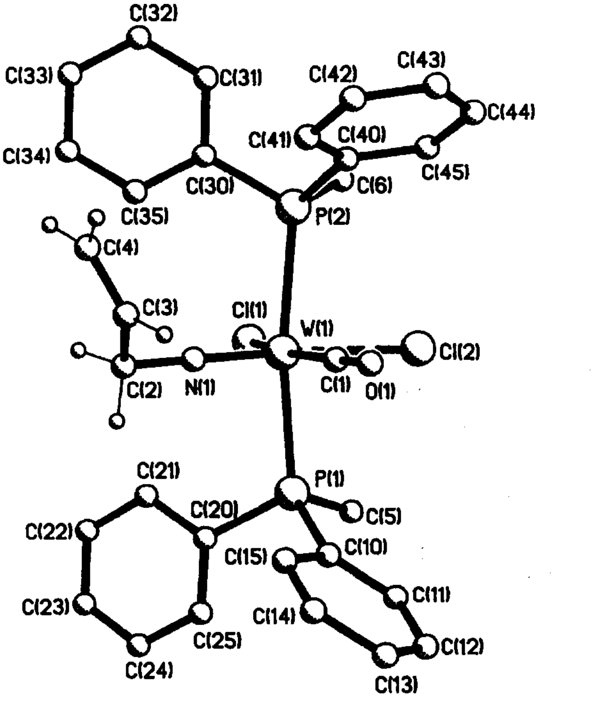


Fig. 1. Molecular structure of [*cis,trans*-$WCl_2(Ph_2PMe)_2(CO)$-$NCH_2CH{=}CH_2$)] (**1**).

In order to confirm the structure of **1** an X-ray crystallographic study was carried out and the results are shown in Fig. 1 and Table 3. The tungsten atom displays an approximately octahedral coordination geometry, with *trans* phosphine ligands and *cis* chlorides. One of the latter, Cl(1), lies *trans* to a π-acceptor carbonyl moiety, while the second, Cl(2), lies *trans* to the strong π-donor imido functionality, and within experimental error the tungsten–chlorine bond lengths are the same [W(1)–Cl(1) 2.483(2), W(1)–Cl(2) 2.488(2) Å]. The allylimido moiety lies *trans* to Cl(2), and is characterized by a short metal–nitrogen interaction [W(1)–N(1) 1.746(5) Å], and an almost linear W(1)–N(1)–C(2) linkage [angle 170.1(6)°]. The allyl group is as expected, with C(2) sp^3 hybridized, and C(3) and

TABLE 3. Selected bond lengths (Å) and angles (°) for [$WCl_2(PMePh_2)_2(CO)(NCH_2CH{=}CH_2)$](**1**)

W(1)–C(1)	1.994(8)	W(1)–N(1)–C(2)	170.1(6)
W(1)–Cl(1)	2.483(2)	N(1)–C(2)–C(3)	113.3(9)
W(1)–Cl(2)	2.488(2)	C(2)–C(3)–C(4)	131.4(11)
W(1)–N(1)	1.746(5)	Cl(1)–W(1)–N(1)	104.6(2)
W(1)–P(1)	2.514(2)	Cl(2)–W(1)–N(1)	165.0(2)
W(1)–P(2)	2.538(2)	Cl(1)–W(1)–C(1)	168.0(2)
N(1)–C(2)	1.449(11)	P(1)–W(1)–P(2)	166.1(1)
C(2)–C(3)	1.437(16)	P(1)–W(1)–N(1)	93.8(2)
C(3)–C(4)	1.247(20)	P(2)–W(1)–N(1)	98.8(2)

C(4) sp^2 hybridized. Consistent with this is the greater length of the long C(2)–C(3) α bond, 1.437(16) Å, compared with that of the C(3)–C(4) bond, 1.247(20) Å.

If the allylimido ligand is to be involved in the "ammoxidation" of propylene, then facile deprotonation of the allyl moiety at the α-position is a prerequisite. This has previously been considered by Maatta, and indeed facile deprotonation of the W^{VI} complex [WCl_4(thf)($NCH_2CH=CH_2$)] was found to afford the allylideneamido complex [$WCl_3(thf)_2(N=CHCH=CH_2)$] after loss of chloride [4]. At the tungsten(IV) centre, deprotonation of the allylimido was also found to be facile, although subsequent chloride loss was not observed.

Thus, addition of ${}^tBuLi$ to a THF solution of **1** resulted in an immediate colour change from pink to yellow, which after metathesis with NEt_4Cl afforded [NEt_4][$WCl_2(PMePh_2)_2(CO)(NCHCH=CH_2)$] (**2**) as a pale yellow solid. Owing to the extreme moisture sensitivity of **2**, we were unable to obtain satisfactory analytical data, but the spectroscopic data are in full accord with the proposed formulation. In the IR spectrum, the carbonyl now appears as a broad absorption at 1967 cm^{-1}, a shift of only 2 cm^{-1} with respect to **1**, indicating that in this instance, the allylideneamido formulation may be less important, the negative charge being localized on the α-carbon. This suggestion is also in agreement with the absence of an absorption in the 1600–1700 cm^{-1} region assignable to the C=N stretch of the allylideneamido ligand, and the observation that no dehydrohalogenation product is formed. This is perhaps not surprising since the dehydrohalogenation reaction would result in a two-electron reduction to produce a tungsten(II) centre, likely to be unfavourable in the presence of π-donor ligands. In the ^1H NMR spectrum the allenylidene protons are observed at δ 5.44 (d, $J = 13.3$ Hz, 1H, H_A); 5.20 (dq, $J = 13.3$, 8.0 Hz, 1H, H_C); 4.96 (t, $J = 8.0$ Hz, 1H, H_B); 3.79 (t, $J = 8.0$ Hz, 1H, H_D) ppm.

Complex **2** does not react with methyl iodide even at room temperature, but the presence of trace amounts of water results in the quantitative regeneration of **1**. This process was monitored by ^1H NMR spectroscopy in $CDCl_3$ in the presence of D_2O. The reduction in intensity by approximately half of the resonance attributed to the α-protons confirms that deprotonation/protonation occurs exclusively at this site.

Acknowledgements

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