Tertiary Phosphine and Arsine Complexes of Tungsten(IV)

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Improved methods for the preparation of complexes $[WCl_4L_2]$ and the preparation of new complexes $[WOCl_2L_3]$ (L = tertiary phosphine or tertiary arsine) are described. The structures are assigned on the basis of i.r. and ^1H and ^{31}P n.m.r. spectroscopy. The magnetic and n.m.r. properties are discussed.

In recent years, many tertiary phosphine and arsine complexes of halides of the heavier transition elements of Groups VII and VIII have been described, but the tertiary phosphine complexes of the earlier transition metals are more difficult to manipulate and the chemistry of their lower oxidation states, except in carbonyl complexes, is particularly obscure. Here we describe some experiments to elucidate the chemistry of the tertiary phosphine complexes of tungsten(IV).

The paramagnetic complexes *trans*-$[WCl_4(PMe_2Ph)_2]$ and *trans*-$[WCl_4(PEt_2Ph)_2]$ [1] have been described and their ^1H n.m.r. spectra and magnetic properties were discussed. The compounds were synthesised by a cumbersome three-stage process, although yields at each stage can be high. The diene may be, for example,

$$[W(CO)_6] \longrightarrow [W(CO)_4(\text{diene})] \longrightarrow [W(CO)_4L_2] \longrightarrow [WCl_4L_2]$$

norbornadiene or 1,5-cyclo-octadiene, and L is a tertiary phosphine. A rather insoluble material, $[WCl_4(Ph_2PCH_2CH_2PPh_2)]$,[2] has been prepared by fusion of potassium hexachlorotungstate(IV) with 1,2-bis(diphenylphosphino)ethane. If the reaction is carried out in acetonitrile $[\{WCl_3(Ph_2PCH_2CH_2PPh_2)\}_2]$, of unknown structure, is formed.[2] Salts of $[WCl_2(Ph_2PCH_2CH_2PPh_2)_2]^{2+}$ have also been prepared.[2]

Of complexes with other types of ligand, $[WCl_4(\text{pyridine})_2]$, $[WCl_4(\text{dipyridyl})]$, and $[WCl_4(RCN)_2]$ (R = Me, Et, or Pr^n) can all be prepared by the reaction of the ligand (sometimes with a reducing agent) with tungsten(VI) chloride in the appropriate solvent.[3-5] The alkyl cyanide complexes have been used to synthesise $[WCl_4(PPh_3)_2]$ [5] by ligand exchange. It therefore seemed worthwhile to attempt a direct synthesis of phosphine and arsine complexes $[WCl_4L_2]$ from tungsten(VI) chloride or an easily obtained derivative.

Complexes of the type $[WOCl_2(PR_3)_3]$ were previously unknown, but we have found a general method of synthesis. The molybdenum analogues have already been described.[6]

RESULTS AND DISCUSSION

Attempts to prepare compounds directly from tungsten(VI) chloride without reducing agents other than the phosphine were unsuccessful. Thus tungsten(VI) chloride and dimethylphenylphosphine in either cold or boiling tetrahydrofuran yielded an oil. A product was obtained from the chloride and tetrahydrofuran (thf) alone, apparently $[WOCl_2(thf)_3]$. Similarly, $[WCl_4(RCN)_2]$ with an excess of the phosphine yielded only oily materials. The reaction of $[NR_4][WCl_6]$ (R = Me or Et) [7] with tertiary phosphines in tetrahydrofuran gives a 5% yield of the orange $[WCl_4(PR_3)_2]$ ($PR_3 = PEt_2Ph$, $PPr^n{}_2Ph$, or $PBu^n{}_2Ph$). Dimethylphenylphosphine gives the red seven-co-ordinate complex $[WCl_4(PMe_2Ph)_3]$ [1] and triphenylphosphine yields an uncharacterised salt. Tri-n-butyl- and triethyl-phosphine gave only oils, but the main product in all these reactions was a white, uncharacterised salt, which is a 1 : 1 electrolyte. In the case of R = Et, the i.r. spectrum indicates that the salt contains $[NEt_4]^+$ and it is oxidised by dichlorine in dichloromethane to $[NEt_4][WCl_6]$.

Reactions involving tungsten(VI) chloride, the tertiary phosphine, and a variety of reducing agents were tried. Neither sodium naphthalene nor titanium(III) chloride gave isolable complexes, but a solution of tungsten(VI) chloride in dichloromethane or tetrahydrofuran with amalgamated zinc and two moles of the ligand gives roughly 40% yields of $[WCl_4L_2]$ ($L = PMe_2Ph$, $PMePh_2$, PEt_2Ph, $PEtPh_2$, $PPr^n{}_2Ph$, PPr^nPh_2, $PBu^n{}_2Ph$, PBu^nPh_2, $AsMe_2Ph$, $AsMePh_2$, PEt_3, or PPh_3) (Table 1). The reaction involving $Ph_2PCH_2CH_2PPh_2$ in solution in dichloromethane yields $[WCl_4(Ph_2PCH_2CH_2PPh_2)]\cdot 0{\cdot}5CH_2Cl_2$.

The tertiary phosphines PMe_2Ph, PEt_2Ph, and $PMePh_2$ react with $[NEt_4][WCl_6]$, $WOCl_4$, or WCl_6 in wet ethanol to give $[WOCl_2(PR_3)_3]$ in *ca.* 30% yield. These air-stable materials are purple and have a band in the i.r. spectrum in the range 940—960 cm^{-1}, assignable to $\nu(W{=}O)$. The complexes $[WO(NCO)_2(PMe_2Ph)_3]$ and $[WO(NCS)_2(PMe_2Ph)_3]$ were obtained by metathesis using sodium cyanate and potassium thiocyanate, respectively.

The orange complex *trans*-$[WCl_4(PMe_2Ph)_2]$ reacts reversibly with another mole of dimethylphenylphosphine to give red $[WCl_4(PMe_2Ph)_3]$.[1] We confirm this, and find that alkyl cyanides will also fill the seventh co-ordination position. Thus, a solution of $[WCl_4(PMe_2Ph)_2]$ in acetonitrile at reflux affords pale blue

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[1] J. R. Moss and B. L. Shaw, *J. Chem. Soc.* (*A*), 1970, 595.

[2] P. M. Boorman, N. N. Greenwood, and M. A. Hildon, *J. Chem. Soc.* (*A*), 1968, 2466.

[3] R. E. McCarley and T. M. Brown, *Inorg. Chem.*, 1964, **3**, 1232.

[4] J. L. Fergusson, *Halogen Chemistry*, vol. 3, ed. V. Gutmann, Academic Press, London, 1967, p. 200.

[5] E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J. Chem. Soc.*, 1964, 4531; E. A. Allen, K. Freeman, and G. W. A. Fowles, *J. Chem. Soc.*, 1965, 1636.

[6] A. V. Butcher and J. Chatt, *J. Chem. Soc.* (*A*), 1970, 2652.

[7] D. M. Adams, J. Chatt, and J. M. Davidson, *J. Chem. Soc.*, 1963, 2189.

$[WCl_4(MeCN)(PMe_2Ph)_2]$. These alkyl cyanide complexes show no band assignable to ν(C≡N) in their i.r. spectra. This band is also absent from the i.r. spectra of $[OsCl_3(MeCN)(PPh_3)_2]$ [8] and $[ReCl_3(MeCN)(PPh_3)_2]$.[9] The new complexes are detailed in Table 1.

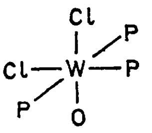
Configurations of the Complexes.—The complexes of the form $[WOX_2L_3]$ (X = anionic ligand, L = tertiary phosphine) are all diamagnetic. They generally decompose slowly in solution, but the ^1H n.m.r. spectrum of the methyl protons of $[WOCl_2(PMe_2Ph)_3]$ in deuteriochloroform shows two triplets centred at $\delta = -1{\cdot}95$ and $-1{\cdot}77$ and a doublet centred at $\delta = 1{\cdot}4$. The intensity ratios are 1 : 1 : 1. This spectrum may be rationalised in terms of a *meridional* arrangement of phosphine ligands with strong *trans*-P–P coupling and without a plane of symmetry through the P–W–P axis. Hence the chlorine atoms should be *cis* and stereochemistry as in (I).

TABLE 1

Some complexes of tungsten(IV)

Compound	Colour	M.p. (°C)	Analyses [a]						μ_{eff}/B.M.	ν(M–Cl)	ν(M=O)	δ(M=O)
			C	H	N	Cl	P	M [a]				
$[WCl_4(PMe_2Ph)_2]$ [b]	Orange	232—236(d.)	32·0(31·9)	3·6(3·7)	0·0(0·0)			602(640) [c]	2·18	318		
$[WCl_4(PMePh_2)_2]$	Orange-yellow	248—253(d.)	43·6(43·0)	3·9(3·6)		19·4(19·6)	8·5(8·5)	680(726) [c]	2·06	323		
$[WCl_4(PEt_2Ph)_2]$ [b]	Orange-yellow	152—157	37·1(36·5)	4·7(4·6)	0·0(0·0)				2·03	318, 292(sh)		
$[WCl_4(PEtPh_2)_2]$	Orange-yellow	245—248	44·6(44·6)						1·86	320, 326(sh)		
$[WCl_4(PPr^n{}_2Ph)_2]$	Orange	169—171	41·0(40·3)	5·5(5·3)	0·0(0·0)			767(713) [d]	2·08	326		
$[WCl_4(PPr^nPh_2)_2]$	Orange-yellow	238—240	45·7(45·9)	4·6(4·3)				792(782) [d]	1·83	323		
$[WCl_4(PBu^n{}_2Ph)_2]$	Orange	175—184	43·7(43·6)	5·9(6·0)	0·0(0·0)			770(750) [e]	2·02	320		
$[WCl_4(PBu^nPh_2)_2]$	Orange-yellow	200—203	47·1(47·4)	4·8(4·7)	0·0(0·0)			774(810) [d]	1·85	320(br)		
$[WCl_4(PPh_3)_2]$ [f]	Orange-yellow	292—300(d.)	50·4(50·9)	3·6(3·5)		16·7(16·7)	7·3(7·3)	860(850) [e]	1·90	320, 330(sh)		
$[WCl_4(PEt_3)_2]$	Orange	139—141(d.)	25·9(25·7)	5·5(5·4)		25·0(25·2)		638(562) [d]	2·09	310		
$[WCl_4(Ph_2PCH_2CH_2PPh_2]$ [g] $0{\cdot}5\ CH_2Cl_2$	Yellow-brown	324—325	40·6(40·7)	3·4(3·3)		22·7(22·9)	8·1(8·0)	Insoluble	1·33	320		
$[WCl_4(AsMe_2Ph)_2]$	Orange	189—194	28·1(27·0)	3·2(3·2)				*h*	1·88	316(sh), 324, 332(sh)		
$[WCl_4(AsMePh_2)_2]$	Yellow	202(d.)	38·3(38·3)	3·3(3·2)				*h*		328, 335(sh)		
$[WCl_4(MeCN)(PMe_2Ph)_2]$	Pale blue	140—155(d.)	33·6(33·5)	4·4(3·9)	2·2(2·2)	21·5(22·1)	9·5(9·6)	Insoluble	1·52			
$[WCl_4(EtCN)(PMe_2Ph)_2]$	Blue	137—151(d.)	34·5(34·7)	4·3(4·1)	2·2(2·1)			Insoluble	1·57			
$[WOCl_2(PMe_2Ph)_3]$	Purple	151—153	42·0(42·0)	4·9(4·8)	2·2(2·3) [i]	10·8(10·3)		685(643)	Diamagnetic	286	960	240
$[WOCl_2(PMePh_2)_3]$	Mauve	128—131	53·5(53·5)	4·6(4·5)		8·9(8·2)		*h*	Diamagnetic	284	950	250
$[WOCl_2(PEt_2Ph)_3]$	Purple	155—167(d.)	47·0(47·0)	6·0(5·9)	1·9(2·1) [i]	9·1(9·2)		*h*	Diamagnetic	283	943	249
$[WO(NCO)_2(PMe_2Ph)_3]$	Blue	122—129(d.)	45·1(44·6)	4·9(4·7)	3·9(4·0)			*h*	Diamagnetic		945, 939(sh)	
$[WO(NCS)_2(PMe_2Ph)_3]$	Blue	136—141	42·4(42·7)	4·4(4·5)	3·8(3·8)			*h*	Diamagnetic		952, 940(sh)	

[a] Required values in parentheses. [b] Prepared before, see ref. 1. [c] In benzene solution. [d] In 1,2-dichloroethane solution. [e] In chloroform solution. [f] Prepared before, see ref. 5. [g] Prepared before, see ref. 2. [h] Decomposes in solution. [i] Oxygen analysis.



(I)

This arrangement of the phosphine ligands in $[WOCl_2(PMe_2Ph)_3]$ is consistent with the ^{31}P n.m.r. spectrum in dichloromethane solution. The resonances are found as two singlets, of intensity ratios 2 : 1, at $\delta = 128{\cdot}3$ and $135{\cdot}8$ p.p.m. to high field of P_4O_6, respectively, corresponding to the two *trans*-phosphorus atoms and the single phosphorus *cis* to each of them in a *meridional* arrangement, but the *facial* conformation cannot be excluded. There is also an indication of tungsten–phosphorus coupling (^{183}W has a nuclear spin of $\frac{1}{2}$ and a natural abundance of 14%). $|^1J(W-P_{trans})|$ is 343 Hz and $|^1J(W-P_{cis})|$ is 442 Hz, which are consistent with the usual orders of W–P coupling constants for phosphorus *trans* to phosphorus and phosphorus *trans* to chlorine.[10]

The far-i.r. spectra tend to support configuration (I). An *X*-ray structure analysis of the blue isomer of *mer*-$[MoOCl_2(PMe_2Ph)_3]$ and of green *mer*-$[MoOCl_2(PEt_2Ph)_3]$ shows unequivocally that the halogen atoms are *cis* to each other.[11] Each of them has two very strong bands between 300 and 240 cm^{-1}, at 285 and 248 cm^{-1} for the former and at 292 and 244 cm^{-1} for the latter. Comparison with the analogous bromides shows that the higher frequency may be assigned to ν(Mo–Cl) but that the lower frequency is probably due to a metal–oxygen vibration.[6] Our new tungsten compounds likewise have two strong bands between 290 and 240 cm^{-1}, and therefore probably have the same structure. In theory, two metal–halogen stretching frequencies would be expected for *cis*-halogens, but the unreliability of far-i.r. data for determining stereochemistry has been well documented.[12]

The ^1H n.m.r. spectra of $[WO(NCO)_2(PMe_2Ph)_3]$ and $[WO(NCS)_2(PMe_2Ph)_3]$ both show two triplets and a doublet for the methyl protons, consistent with a configuration analogous to (I). The ^{31}P n.m.r. spectra show two singlets, intensity ratio 2 : 1, similar to the parent chloride. The Nujol-mull i.r. spectra show strong bands at 2235 and 2197 cm^{-1} (cyanate complex) and 2066 and 2032 cm^{-1} (thiocyanate complex). These are assigned to ν(NCO) and ν(CN) of thiocyanate respectively, and are at least consistent with *cis* cyanates and thiocyanates. Comparison of the spectra with the spectrum of $[WOCl_2(PMe_2Ph)_3]$ suggests that bands at 835 and 845 cm^{-1} may be associated with ν(CS). This is consistent

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[8] J. Chatt, J. R. Dilworth, and G. J. Leigh, unpublished observations.

[9] G. Rouschias and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 993.

[10] See J. F. Nixon and A. R. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 345.

[11] J. Chatt, Lj. Manojlovic Muir, and K. W. Muir, *Chem. Comm.*, 1971, 655.

[12] J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc.* (*A*), 1969, 1674.

with bonding W–NCS, because ν(CS) is generally found in the range 690—720 cm^{-1} when thiocyanate is *S*-bonded. The position of ν(CN) is not really diagnostic for N- or S-bonding. Bands at 622 and 614 cm^{-1} in the spectrum of the cyanate complex are assignable to δ(NCO) but these are not diagnostic frequencies for *N*- and *O*-bonding because there are no proven examples of *O*-bonding to provide basic data.

TABLE 2

The dependence of magnetic susceptibility (c.g.s.u.) of tungsten(IV) complexes upon temperature

T/K	$[WCl_4(PEtPh_2)_2]$ $1/\chi_M$	$[WCl_4(PBu^n_2Ph)_2]$ $1/\chi_M$
96		504
110	412	513
125		514
150	430	558
175		618
200	467	672
250	513	810
293		975
297	550	

^{1}H N.m.r. Spectra of Complexes $[WCl_4L_2]$.—The complexes $[WCl_4L_2]$ are all paramagnetic (d^2), their magnetic moments at 20° being between 1·8 and 2·2 B.M. The temperature variation of the magnetic susceptibility of *trans*-$[WCl_4(PMe_2Ph)_2]$ shows normal Curie–Weiss behaviour above 200 K, and no temperature-independent paramagnetism,[1] and both $[WCl_4(PEtPh_2)_2]$ and $[WCl_4(PBu^n_2Ph)_2]$ are similar (Table 2). The far-i.r. spectra of the complexes in Table 1 generally show one band assignable to ν(M–Cl), suggesting that all the complexes have a planar arrangement of chloride and *trans*-phosphorus. *X*-Ray analysis has confirmed that $[WCl_4(PMe_2Ph)_2]$ is *trans*.[13]

TABLE 3

The ^{1}H n.m.r. spectra (p.p.m.) [a] of *trans*-$[WCl_4L_2]$ in solution in $CDCl_3$ at 27 °C

L =	PEt_3	$AsMe_2Ph$	PMe_2Ph	$PMePh_2$	PEt_2Ph	$PEtPh_2$	PPr^n_2Ph	PPr^nPh_2	PBu^n_2Ph	PBu^nPh_2
CH_3	−6·61t	+24·20s	+26·50s	+26·40s	−5·42t	−5·26t	−1·32d?	−1·10t	−0·68t	−0·63q
γ-CH_2									−1·02m,br	−0·83q?
β-CH_2							−2·64,	−1·87m,br	−2·72d?	−1·65m,br
							ca. −1·4m,br			
α-CH_2	+24·30q				+23·75q?	+23·52d?	+23·50t	+23·85d?	+24·05t	+23·60t?
					+23·80q?		+21·75t		+22·80t	
o		−11·00d	−10·97d	−11·30d	−11·76d	−11·27d	−11·61d	−11·42d	−11·10d	−11·34d
m		−8·40t	−8·92t	−8·45t		−8·57t		−8·73t		−8·56t
					−8·61 [b]		−8·45 [b]		−8·85 [c]	
p		−8·80t	−8·30t	−8·15t		−7·81t		−8·00t		−7·83t

[a] + = High field, − = low field, of tetramethylsilane. [b] Asymmetric triplet. [c] Asymmetric doublet.

Despite the paramagnetism, all the complexes show sharp ^{1}H n.m.r. spectra (Table 3), and the spectra may be assigned by general comparison and by measurement of relative peak areas. Moss and Shaw, who first observed[1] sharp spectra in the tungsten(IV) complexes, compared this behaviour with that of d^4-complexes, based on rhenium(III) and osmium(IV).[12] These d^4-systems, however, exhibit temperature-independent paramagnetism, not Curie–Weiss behaviour, and there are several distinct differences between the respective ^{1}H n.m.r. spectra.

First, the signals for the d^4-systems are sharper (line-width *ca.* 1 Hz) than for the d^2-systems (line-width *ca.* 3 Hz). Second, the different line-widths allow better resolution of signals from apparently non-equivalent hydrogens of a common methylene group for the d^4-systems. The non-equivalence also occurs in the d^2-systems. Table 3 suggests that it is due to the geometrical inequivalence of two methylene protons on a common carbon atom of a tertiary phosphine when two alkyl groups (other than methyl) are present. The inequivalence occurs whether or not there is free rotation about the W–P bond. It does not occur with diarylalkylphosphines. Third, although the phenyl proton shifts are of the same order for both the d^2- and d^4-systems, the order of increasing downfield shift is generally *para* < *meta* < *ortho* for the former and $m < p < o$ for the latter. Fourth, in both systems, although in an alkyl chain attached to phosphorus there is a maximum downfield shift at the β-methylene protons, the β-methylene downfield shifts are generally greater for the d^4-systems (δ *ca.* −5 p.p.m. as compared to δ *ca.* −2 p.p.m. for the d^2), and the α-methylene shifts are very far upfield for the d^2-systems (δ *ca.* +25 p.p.m. as compared to δ *ca.* −4 p.p.m. for the d^4). The origin of this differing behaviour presumably lies in the different magnetic properties of the d^2- and d^4-systems.

The forms of the spectra (Table 3) are not easily explained on a first-order basis. A comparison of the spectra of $[WCl_4(PMe_2Ph)_2]$ and $[WCl_4(AsMe_2Ph)_2]$ shows clearly that there is no P–H coupling. The methyl groups generally give rise to triplets, presumably under the influence of the ω-methylene protons, but the other methylene protons give broad signals, which are obviously complex. The α-methylene signals are never simple and, although the triplets appear to be in the ratios 1 : 2 : 1, the quartets are not 1 : 3 : 3 : 1 and are possibly more complex. The absorptions due to the aryl protons fall into two classes. In the one, the spectra show a doublet (*ortho*) at lowest field and two triplets, that due to the *p*-protons generally being at

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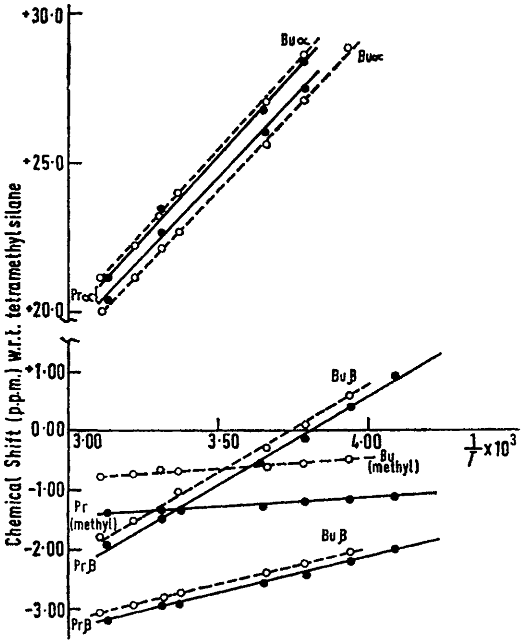
[13] L. Aslanov, R. Mason, A. G. Wheeler, and P. O. Whimp, *Chem. Comm.*, 1970, 30.

highest field. Decoupling experiments show that irradiation of the *p*- and *o*-protons causes a collapse of the *m*-signal to an approximate doublet. In the other class of compounds, which generally have only one phenyl group on the phosphine, *m*- and *p*-protons give rise to an asymmetric doublet. The d^4-systems occasionally exhibit this phenomenon,[12] although there is no apparent correlation with structure.



Temperature dependence of the chemical shifts in deuteriochloroform solution of alkyl protons in *trans*-$[WCl_4(PPr^n{}_2Ph)_2]$ (full line) and *trans*-$[WCl_4(PBu^n{}_2Ph)_2]$ (broken line)

We have studied the effect of temperature on the ^1H n.m.r. spectra of these complexes. Theory suggests that the chemical shift changes inversely with temperature.[14] It is found that the chemical shifts of the α, β, and γ protons vary linearly with $1/T$ (see Figure). However, the situation is not simple, because the proportionality constants are different for each set of protons. Thus at +52°, α, β, γ, and methyl protons in the butyl chain of $[WCl_4(PBu^n{}_2Ph)_2]$ are clearly resolved with the β protons giving rise to two groups of signals. As the temperature falls each set of signals moves upfield, the α moving fastest (see Figure). At 20°, one of the β absorptions overlaps with the γ. At 0° it has moved through the γ and is highfield of the methyl, and by this temperature γ and methyl protons also overlap. Apparently the rate of change with temperature increases with the magnitude of the chemical shift of the proton absorption away from its position in a diamagnetic situation. The anisotropic nature of the magnetic field of the tungsten causes the differences in the absorptions of the various alkyl protons, and the effect seems to fall off with increasing distance from the magnetic nucleus, perhaps according to $1/r^3$, as demanded by theory.[14]

Temperature studies have clarified the absorption pattern of the aryl protons. Thus at +52° the *o*-protons of $[WCl_4(PBu^n{}_2Ph)_2]$ give rise to a doublet, and the *m*- and *p*-protons to an asymmetric doublet with the more intense absorption to higher field. The rate of change of shift with temperature is much smaller than for the alkyl protons. At 0°, the *o*-protons still give rise to a doublet, but the *meta–para* doublet now has its more intense absorption to lower field. At −30°, the *o*-doublet remains, but the *m*- and *p*-absorptions are now distinct triplets, with the *meta* to higher field. The complex $[WCl_4(PPr^n{}_2Ph)_2]$ exhibits similar phenomena. Table 3 shows that generally the *m*-protons are at a lower field than the *para*. This suggests that in all cases at an appropriate high and low temperature, both *m*- and *p*-protons can give rise to triplets, with the *p*-protons to higher field at the higher temperature. Intermediate temperatures should give rise to complex unresolved spectra. The direction of change of chemical shift with decreasing temperature for *m*- and *p*-protons is apparently downfield.

The ^1H n.m.r. spectrum of $[WCl_4(PMe_2Ph)_3]$ is also temperature dependent. At 45° in chloroform solution it has the following form: +25·9, sharp singlet, intensity 3 (assigned to methyl); +12·2, singlet, intensity 3 (methyl); −7·9, triplet, intensity 1 (impurity?); −8·5, multiplet, intensity 3 (*m* and *p*); −10·6, doublet, intensity 1 (*o*); and −19·2, broad singlet, intensity 1 (*o*). This spectrum can be interpreted as arising from a pair of stereoisomers because of the two methyl and two *o*-proton resonances. Alternatively, it could be due to a configurational inequivalence within a single structure, as noted above for the methylene protons in $[WCl_4(PR_2Ph)_2]$ (R = alkyl, not methyl). This is, however, difficult to envisage.

At 27°, the chemical shifts are different and relative intensities are non-integral although the total number of protons has not changed: +27·8, sharp singlet, intensity 2·2; +13·0, broad singlet, intensity 3·8; −7·9, triplet, intensity 1; −8·5, asymmetric triplet, intensity 3·1; −10·5, doublet, intensity 0·8; −20·1, doublet, intensity 1·2. Thus the methyl resonances and *o*-proton resonances are no longer split into equal contributions. This suggests strongly the presence of isomeric forms. Addition of dimethylphenylphosphine did not alter the spectra, so that dissociation is not occurring.

It is hoped that further experiments will clarify the nature of the magnetic interactions in these molecules.

EXPERIMENTAL

Reactions were carried out in an atmosphere of dry dinitrogen or dry argon, using a Schlenk tube technique and anhydrous solvents. Carbon, hydrogen, and nitrogen analyses were carried out by Mr. A. G. Olney of the Chemical Laboratory, University of Sussex, and halogen, oxygen, and phosphorus analyses by Bernhardt Microanalytical

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[14] D. R. Eaton and W. D. Phillips, *Adv. Magn. Resonance*, 1965, **1**, 103.

Laboratories, Mulheim, West Germany. Far-i.r. spectra of dispersions in Polythene discs were recorded using an R.I.I.C. FS 620 interferometer, and ^{1}H n.m.r. spectra were measured on Varian Associates A 60 and HA 100 and Jeol PS 100 spectrometers in deuteriochloroform solution using tetramethylsilane as internal standard. ^{31}P N.m.r. spectra were measured in dichloromethane solution (P_4O_6 external standard) using a Perkin-Elmer R 10 spectrometer. Molecular weights were determined using a Perkin-Elmer-Hitachi vapour-pressure osmometer at 43° (for benzene solutions) and 37° (for chloroform solutions). M.p.s were determined in evacuated, sealed tubes. Magnetic moments were determined by the Faraday technique.

The compounds $[WCl_4L_2]$ (L = tertiary phosphine or tertiary arsine) were all prepared by the same route. The arsine complexes are slightly more soluble than the phosphine, and their solutions are more sensitive to dioxygen.

trans-*Tetrachlorobis(ethyldiphenylphosphine)tungsten*(IV).—A mixture of tungsten hexachloride (2·0 g), amalgamated zinc (5·0 g), and dichloromethane (50 ml) was stirred for 3 min. Ethyldiphenylphosphine (2·5 g, 2·3 mol) was added and the mixture stirred for a further 3 min. The solution was then filtered and solvent removed from the filtrate at 15 mmHg until the volume was 25 ml. After a further 2 h at 0° the *product* had crystallised and was filtered off, washed with acetone (5 ml) and then ether, and finally dried *in vacuo*. Yield 1·3 g, 35%.

The following compounds were prepared analogously.—*trans*-Tetrachlorobis(dimethylphenylphosphine)tungsten(IV) [1] [tungsten(VI) chloride (11·0 g), amalgamated zinc (11·0 g), dichloromethane (90 ml), and dimethylphenylphosphine (7·1 g); yield, 3·9 g, 23%]. trans-*Tetrachlorobis(methyldiphenylphosphine)tungsten*(IV) (2·0 g; 5·0 g; 30 ml; 2·5 g; 0·9 g, 25%). *trans*-Tetrachlorobis(diethylphenylphosphine)tungsten(IV) [1] (11·8 g; 20·0 g; 100 ml; 9·9 g; 4·2 g, 22%). trans-*Tetrachlorobis(triethylphosphine)tungsten*(IV) (2·0 g; 5·0 g; 40 ml; 2·0 g; 0·7 g, 25%). trans-*Tetrachlorobis(di-n-propylphenylphosphine)tungsten*(IV) (2·0 g; 5·0 g; 50 ml; 3·0 g; 1·5 g, 42%). trans-*Tetrachlorobis(n-propyldiphenylphosphine)tungsten*(IV) (2·0 g; 5·0 g; 30 ml; 2·5 g; 1·6 g, 40%). trans-*Tetrachlorobis(di-n-butylphenylphosphine)tungsten*(IV) (2·5 g; 5·0 g; 100 ml; 2·8 g; 1·6 g, 38%). trans-*Tetrachlorobis(n-butyldiphenylphosphine)tungsten*(IV) (2·0 g; 5·0 g; 50 ml; 3·5 g; 1·0 g, 25%). *trans*-Tetrachlorobis(triphenylphosphine)tungsten(IV) [5] (2·5 g; 5·0 g; 100 ml; 5·0 g; 2·1 g, 40%). *Tetrachloro(1,2-bisdiphenylphosphinoethane)tungsten*(IV) (1·9 g; 5·0 g; 100 ml; 5·0 g; 1·2 g, 36%). This compound crystallises with 0·5 mole dichloromethane and is very sensitive to dioxygen, even in the solid state. trans-*Tetrachlorobis(dimethylphenylarsine)tungsten*(IV) (2·0 g; 5·0 g; 30 ml; 2·5 g; 1·2 g, 34%). trans-*Tetrachlorobis(methyldiphenylarsine)tungsten*(IV) (2·0 g; 5·0 g; 50 ml; 3·2 g; 2·1 g, 51%).

Tetrachloro(acetonitrile)bis(dimethylphenylphosphine)tungsten(IV).—Tetraethylammonium hexachlorotungstate(V) (0·7 g) was dissolved in acetonitrile (20 ml) to give a yellow solution. Dimethylphenylphosphine (1·7 g, 6·5 mol) was then added, producing a white precipitate which redissolved as the solution was warmed to reflux temperature. After 1 h, the solution had turned green and a blue *solid* was precipitated on cooling. This was filtered off and recrystallised from dichloromethane. Yield 0·51 g, 62%. The solid is air-stable and has a magnetic moment of 1·52 B.M. It is a non-conductor in nitrobenzene solution but was too insoluble for molecular-weight determinations. This compound can also be obtained from $[WCl_4(MeCN)_2]$ and dimethylphenylphosphine in acetonitrile solution and from *trans*-$[WCl_4(PMe_2Ph)_2]$ in acetonitrile.

Tetrachloro(propionitrile)bis(dimethylphenylphosphine)tungsten(IV).—Tetraethylammonium hexachlorotungstate(V) (0·85 g) was dissolved in propionitrile (25 ml) and dimethylphenylphosphine (1·2 g, 4 mol) added. The reaction mixture was heated under reflux for 1 h and the yellow-brown solution evaporated at room temperature and 15 mmHg pressure to yield a brown oil. This was dissolved in dichloromethane (15 ml), and pentane (15 ml) added. During 12 h at −20°, a blue *solid* crystallised, yield 0·51 g, 60%. This air-stable solid has a magnetic moment of 1·57 B.M. It was too insoluble for molecular-weight determinations.

Tetrachlorotris(dimethylphenylphosphine)tungsten(IV) can be prepared as reported [1] from *trans*-$[WCl_4(PMe_2Ph)_2]$ and dimethylphenylphosphine in 80% yield. A 6% yield was obtained from tetraethylammonium hexachlorotungstate(V) and dimethylphenylphosphine in dichloromethane solution.

Oxodichlorotris(dimethylphenylphosphine)tungsten(IV).—Tungsten(VI) chloride (1·7 g) was dissolved in ethanol (70 ml, dry, out-gassed). When effervescence ceased, dimethylphenylphosphine (2·5 g, 7·7 mol) was added and the mixture heated under reflux for 5 min until the solution became blue. The solution was filtered and the filtrate held at −20° for 15 h. The violet, crystalline *product* was filtered off, washed with cold ethanol, and dried at 80° and 10^{-3} mmHg. Yield, 0·80 g, 25%; m.p. 151—153°. This product was also obtained from tungsten oxide tetrachloride with dimethylphenylphosphine in ethanol solution, and from tetraethylammonium hexachlorotungstate(V) and dimethylphenylphosphine, also in ethanol solution, but these are not recommended methods.

Tertiary phosphines other than dimethylphenylphosphine are not strong enough reducing agents under these conditions to produce tungsten(IV). Therefore, for other oxodichloro-derivatives, zinc was used as an additional reducing agent.

Oxodichlorotris(diethylphenylphosphine)tungsten(IV).—Tungsten(VI) chloride (1·4 g) was treated with dry ethanol (70 ml) and, when effervescence ceased, diethylphenylphosphine (2·2 g, 3·3 mol) added. This produced a white precipitate. The mixture was brought to reflux temperature, and then zinc (*ca.* 5 g) added. After 1·5 h at reflux, the solution was dark green. The solution was cooled, filtered, evaporated to half volume at 15 mmHg and the *blue, crystalline product* (0·4 g, 14%) allowed to crystallise during 14 h at −20°. The product was recrystallised from dry, cold dichloromethane–methanol.

Oxodichlorotris(methyldiphenylphosphine)tungsten(IV).—This compound was prepared analogously from tungsten(VI) chloride (1·5 g), ethanol (70 ml), methyldiphenylphosphine (4·5 g, 6·0 mol), and zinc (*ca.* 5 g). After 5 h at reflux the solution was light mauve. It was not evaporated down. Yield 1·4 g, 42%.

Oxobis(cyanato)tris(dimethylphenylphosphine)tungsten(IV).—Oxodichlorotris(dimethylphenylphosphine)tungsten(IV) (1·0 g) was heated under reflux in methanol (40 ml) with sodium cyanate (2·0 g) for 5 min. The mixture was cooled and filtered, the product extracted from the filter with dichloromethane (5 ml), methanol (25 ml) was added to the extract, and the solution left to crystallise. Yield, 0·6 g, 59%.

Oxodi(thiocyanato)tris(dimethylphenylphosphine)tungsten-(IV) was prepared in 53% yield using the same method and quantities as above, but with potassium thiocyanate (2·0 g) in place of the sodium cyanate.

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