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Reactions of (η^3-Allyl)dicarbonyltungsten(II) Complexes Containing Group V Donor Ligands

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Reactions of $[WX(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2]$ *with the ditertiary arsines* $Ph_2AsCH_2CH_2AsPh_2$ *(dae) and* $Ph_2AsCH_2AsPh_2$ *(dam) yield complexes of stoichiometry* $[WX(\eta^3\text{-}C_3H_5)(CO)_2dae]$, *(X = Cl, Br or I) and* $[W_2X_2(\eta^3\text{-}C_3H_5)_2(CO)_4dam]$, *(X = Cl or Br). Whereas the former series of complexes contain chelating dae, the latter contain dam bridges which are readily cleaved by pyridine (py), the ditertiary phosphines* $Ph_2PCH_2PPh_2$ *(dpm) and* $Ph_2PCH_2CH_2PPh_2$ *(dpe), or chloride ions to give* $[WX(\eta^3\text{-}C_3H_5)(CO)_2L_2]$, *(*$L_2$ *= dpm, dpe or 2py) and* $[W_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]^-$ *respectively. Under forcing conditions the nitrile complexes react with ditertiary phosphines to give low yields of the tungsten(0) derivatives* cis-$[W(CO)_2(L_2)_2]$.

The solution ionization of $[WCl(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2]$ *to* $[W(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_3]^+[W_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]^-$ *and free nitrile is slight compared with the molybdenum analogue.*

Introduction

It was recently shown that the molybdenum complexes $[MoX(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2]$, (X = Cl, Br but not I), ionise in non-aqueous solvents [1, 2] according to:

$$3[MoX(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2] \rightleftharpoons [Mo(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_3]^+ + [Mo_2X_3(\eta^3\text{-}C_3H_5)_2(CO)_4]^- + 3MeCN \quad (1)$$

Removal of the free nitrile by washing with benzene resulted in the isolation of the ionic chlorocomplex, whose solid state structure was subsequently determined [3]. We were interested to see if the corresponding tungsten complexes behaved similarly, and whether their reactions with phosphorus and arsenic donor ligands were analogous to those of the related molybdenum complexes [4,5].

Experimental

Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin–Elmer 597 spectrophotometer using Nujol mulls and $CHCl_3$ solutions of the complexes. Far infrared studies were carried out on a Beckman FS 720 interferometer with samples dispersed in pressed polythene discs. ^{1}H NMR spectra were recorded on a JEOL PS 100 spectrometer equipped with a variable temperature controller and using tetramethylsilane as internal reference. Mass spectra were obtained on an AEI MS12 instrument using a direct insertion probe and an ionising energy of 70 eV.

Carbon and hydrogen analyses were determined by microanalytical techniques (Dr. Strauss, Oxford).

All preparations were carried out under dry nitrogen gas using solvents and reactants freed from moisture and oxygen by standard procedures.

Preparation of $[WX(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2]$*, (X = Cl, Br or I)*

These complexes were prepared by a similar route to that described by Hsieh and West [6], which involves preparation of $[W(CO)_3(MeCN)_3]$ and its subsequent reaction *in situ* with a slight excess of allyl halide.

A solution of $W(CO)_6$ (3.52 g, 10 mmol) in MeCN (50 cm^3) was maintained at its boiling point for 50 h. The reaction mixture was cooled to 60 °C and treated dropwise with an excess of allyl halide (2 cm^3). The solution was stirred at 60 °C until CO evolution had ceased. The product was formed as orange crystals on standing the partially evaporated solution at 0 °C.

Preparation of $[WX(\eta^3\text{-}C_3H_5)(CO)_2dae]$*, (X = Cl, Br or I)*

A solution of dae (0.49 g, 1 mmol) in acetone (10 cm^3) was added to $[WX(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2]$ (1 mmol) dissolved in acetone (15 cm^3). After stirring the reaction mixture at room temperature for 1 h, the precipitated orange crystalline solid was collected by filtration and washed with cold acetone.

Preparation of $[W_2X_2(\eta^3\text{-}C_3H_5)_2(CO)_4dam]\cdot$*toluene, (X = Cl or Br)*

The ditertiary arsine (0.47 g, 1.0 mmol) was dissolved in warm acetone (10 cm^3) and treated with $[WX(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2]$ (2 mmol). The reaction mixture was maintained at 40 °C for 0.5 h and the solvent subsequently removed *in vacuo* at room temperature. The residue was dissolved in boiling toluene (30 cm^3) and the solution filtered and stood at 10 °C for 12 h, yielding orange crystals of products (VII) or (VIII). Varying the ratio of reactants did not produce any other products, and no analogous dam-iodo complex could be prepared under any of these conditions.

Preparation of cis-$[W(CO)_2(dpe)_2]$

A solution of (I) (0.40 g, 1 mmol) dissolved in MeCN (30 cm^3) was treated with finely divided dpe (1.00 g, 2.50 mmol) resulting in a precipitate of $[WCl(\eta^3\text{-}C_3H_5)(CO)_2dpe]$. The mixture was heated under reflux for 50 h during which time the initial product gradually redissolved and was replaced by a yellow crystalline deposit. The solution was filtered whilst hot and the crude product recrystallised from $CHCl_3$–light petroleum (60–80 °C). Yield 40%; m.p. 315–320 °C (lit. 320–323); $\nu(CO)(CHCl_3)$ 1850; 1781 cm^{-1} (lit. 1847; 1782) [7].

Preparation of cis-$[W(CO)_2(dpm)_2]$

$[WCl(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2]$ (0.40 g, 1 mmol) in MeCN (30 cm^3) was treated with dpm (0.96 g, 2.5 mmol) and the solution heated under reflux for 24 h. Two products were formed under these conditions, and on keeping the filtrate at 0 °C overnight further quantities of these products were deposited. Both products had similar, very low, solubilities in common solvents, but the yellow crystals of *cis*-$[W(CO)_2(dpm)_2]$ were readily separated by hand from the fine brown powder. Yield 5%; m.p. 320–325 °C; $\nu(CO)(CHCl_3)$ 1840; 1780 cm^{-1} (lit. 1837; 1783) [8].

Attempts to improve the yield by varying the reaction time were not successful. After short reaction times neither product had formed in appreciable quantities, whereas extended reaction times resulted in an increase in the yield of the brown product at the expense of *cis*-$[W(CO)_2(dpm)_2]$.

Reactions of $[W_2Cl_2(\eta^3\text{-}C_3H_5)_2(CO)_4(dam)]$ *toluene with Other Ligands*

With the ditertiary phosphines dpm and dpe

A solution of phosphine (0.42 mmol) dissolved in MeCN (10 cm^3) was treated with (VII) (0.25 g, 0.21 mmol) and the mixture refluxed for 0.8 h. Orange crystals of the known complexes [4] $[WCl(\eta^3\text{-}C_3H_5)(CO)_2dpm]$ and $[WCl(\eta^3\text{-}C_3H_5)(CO)_2dpe]$ were deposited from the clear orange solution on cooling. Yields 80–85%.

With pyridine

Excess pyridine (1.3 cm^3, 16 mmol) was added to (VII) (0.25 g, 0.21 mmol) dissolved in $CHCl_3$ (6 cm^3). The reaction mixture was stirred at room temperature for 0.5 h and then treated with light petroleum (60 - 80 °C) to initiate the precipitation of complex (X) as a yellow powder.

With Ph_4AsCl

A solution of (VII) (0.25 g, 0.21 mmol) and $Ph_4AsCl\cdot H_2O$ (0.09 g, 0.21 mmol) in CH_2Cl_2 (10 cm^3) was stirred for 0.5 h. The dropwise addition of light petroleum (60–80 °C) precipitated complex (XI) in high yield.

Preparation of $[W(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_3]BF_4$

Complex (I) (0.40 g, 1.0 mmol) was dissolved in MeCN (7 cm^3) and treated with $AgBF_4$ (0.20 g, 1.0 mmol). After stirring for 0.3 h at room temperature, the mixture was filtered to remove AgCl and the filtrate evaporated to dryness *in vacuo*. The residue was redissolved in MeCN (7 cm^3), the solution filtered and the filtrate evaporated *in vacuo* to yield the pure product as a yellow powder.

Discussion

Solution Behaviour of $[WX(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2]$, *(X = Cl, Br or I)*

None of these compounds were very soluble in MeCN and consequently the ^1H NMR spectra obtained in this solvent were of poor quality. Nevertheless, there was no indication of more than a single allyl containing species for any of the three complexes (I–III) over the temperature range +70 to –40 °C, in contrast with the analogous molybdenum chloro- and bromo-complexes [1, 2]. Each set of resonances for the allyl moiety were typical of the A_2M_2X spin systems of symmetrical or fluxional η^3-allyl-metal complexes [9], although well-resolved spectra were only obtained for (I) and (II) above 28 °C or below 0 °C, between these temperatures the spectral bands were broad and poorly resolved in this solvent.

In CD_2Cl_2 ^1H N.M.R. studies showed that the chloro-complex (I) ionised in an analogous manner to the corresponding molybdenum complex [2] (eqn. 1), but to a much lesser extent (K, 6×10^{-2} mol^2 dm^{-2} compared with a value of 6×10^2 mol^2 dm^{-2} at 27 °C for the molybdenum analogue dissolved in $CDCl_3$ [2]), and signals due to the anionic, cationic and neutral species were readily identified

TABLE I. Analytical and Selected Infrared Data (cm^{-1}).

Complex		Yield %	Analyses found (calcd.) (%)			ν(C–O)^a	ν(M–X)	ν(C≡N)^a
			C	H	N			
$WCl(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2$	(I)	67	27.1	2.8	6.9	1935	288	2285(m)
			(27.1)	(2.8)	(7.0)	1837		
$WBr(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2$	(II)	72	24.4	2.6	6.3	1925	183	2280(m)
			(24.4)	(2.5)	(6.3)	1835		
$WI(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2$	(III)	45	22.3	2.2	5.9	1932	162	2275(m)
			(22.1)	(2.2)	(5.7)	1840		
$WCl(\eta^3\text{-}C_3H_5)(CO)_2$dae	(IV)	35	46.2	3.6		1930	245	
			(46.4)	(3.6)		1840		
$WBr(\eta^3\text{-}C_3H_5)(CO)_2$dae	(V)	39	43.7	3.4		1935	164	
			(44.0)	(3.5)		1844		
$WI(\eta^3\text{-}C_3H_5)(CO)_2$dae	(VI)	40	41.9	3.2		1937	132	
			(41.6)	(3.2)		1848		
$[W_2Cl_2(\eta^3\text{-}C_3H_5)_2(CO)_4$dam] toluene	(VII)	77	41.2	3.4		1935(sh); 1926	270	
			(42.1)	(3.4)		1863; 1840	228(m)	
$[W_2Br_2(\eta^3\text{-}C_3H_5)_2(CO)_4$dam] toluene	(VIII)	64	39.3	3.2		1935	179	
			(39.2)	(3.1)		1863; 1845	163(m)	
$[W(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_3]BF_4$	(IX)	65	26.8	2.9	8.6	1965(sh); 1945		2293(m)
			(26.9)	(2.9)	(8.6)	1851; 1830(sh)		
$WCl(\eta^3\text{-}C_3H_5)(CO)_2py_2$	(X)	93	37.4	3.1	5.9	1950(sh); 1945	257	
			(38.0)	(2.8)	(5.9)	1807	250(sh)	
$Ph_4As[W_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]$	(XI)	74	38.8	2.9		1923; 1905		
			(38.8)	(2.9)		1820; 1793		

^{a}Nujol mulls, all bands intense unless otherwise noted.

(Table II). At room temperature the coordinated MeCN groups of the cation gave rise to a single broad signal at 2.56 p.p.m., which was replaced at low temperatures by two bands of relative intensities 1:2 centred at 2.69 and 2.45 p.p.m. respectively. Since $[Mo(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_3]^+$ is known to have a pseudooctahedral structure in the solid state [3], it seems likely that $[W(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_3]^+$ adopts a similar structure at low temperatures in solution, but is dynamic at room temperature.

In more strongly coordinating and polar solvents such as acetone, anions, cations and neutral species co-exist on dissolution of complex (I). However, partial displacement of coordinated MeCN in both the cationic and neutral species by the solvent is also indicated by the appearance of new allyl and free MeCN signals in the N.M.R. spectra.

The bromo- and iodo-complexes (II and III) remained predominantly as neutral complexes on dissolution in both CD_2Cl_2 and $(CD_3)_2CO$, although there is some evidence of a very low concentration of cationic and anionic allyl species from the bromo-complex in the latter solvent. Weak signals indicative of new η^3-allyl species and free MeCN were also observed in CD_2Cl_2 for these two complexes, but the relative intensities of the signals were not reproducible, and in view of the air-sensitivity of solutions of these complexes may result from decomposition products.

For comparative purposes the tungsten anion $[W_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]^-$ and cation $[W(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_3]^+$ were synthesised separately and isolated as the Ph_4As^+ and BF_4^- salts respectively. Comparisons of the chemical shifts and coupling constants of the allyl protons of separate solutions of these salts (Table II) gave good agreement with the chemical shifts and coupling constants of the high and low-field sets of allyl protons in the spectra of $[WCl(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2]$ dissolved in CD_2Cl_2 (Table II). Furthermore mixing these two complexes in a 1:1 mol ratio in MeCN at 40 °C generated the spectrum of the neutral complex (I).

The chemical shifts of the ligated MeCN protons in both the neutral and cationic species were strongly solvent dependent. In CD_2Cl_2 the coordinated MeCN

TABLE II. ^1H NMR Data for MeCN Products and for $Ph_4As[W_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]$.

Complex	Solvent	Temperature (°C)	δ (p.p.m. rel. to $SiMe_4$, J/Hz)				Assignment[a]
			Allyl protons			MeCN	
			H_{anti}	H_{syn}	$H_{central}$		
(I)	CD_3CN	−35	1.32(d, 7.7)	3.00(d, 6.0)	3.10(m)	1.98(s)	N
	CD_2Cl_2	−20	1.19(d, 9.0)	3.27(d, 6.0)	3.02(m)		A
			1.48(d, 8.5)	~3.1(m)		2.46(s)	N
			1.70(d, 7.5)	3.30(d, 6.0)	3.20(m)	2.45(s)	C
						2.69(s)	
(II)	CD_3CN	−40	1.55(d, 8.0)	3.01(d, 6.4)	3.12(m)	1.98(s)	N
	CD_2Cl_2	−50	1.42(d, 7.9)	2.98(d, 6.5)	3.22(m)	2.36(s)	N
(III)	CD_3CN	−35	1.42(d, 7.7)	3.04(d, 6.0)	3.22(m)	1.98(s)	N
	CD_2Cl_2	−20	1.44(d, 7.6)	2.94(d, 6.0)	3.18(m)	2.33(s)	N
(IX)	CD_3CN	32	1.64(d, 8.0)	3.36(s)	3.12(m)	2.45(br s)	
	CD_2Cl_2	−20	1.64(d, 7.5)	3.26(s)	3.20(m)	2.41(s)[b]	
						2.65(s)	
(XI)	CD_3CN	30	1.10(d, 7.5)	3.04(s)	3.04(m)[c]		
	CD_2Cl_2	30	1.09(d, 9.0)	3.19(d, 6.5)	2.88(m)		

[a] N = neutral species, A = anion, C = cation. [b] At room temperature only one MeCN resonance was observed at 2.44 p.p.m. in this solvent. [c] Some solvolysis occurred in this solvent producing $[WCl(\eta^3\text{-}C_3H_5)(CO)_2(CD_3CN)_2]$.

TABLE III. ^1H NMR Data on Arsenic containing Complexes at 28 °C (δ in p.p.m. rel. to TMS, J in Hz).

Complex	$\eta^3\text{-}C_3H_5$			$-(CH_2)_n-$	Aromatic protons
	H_{anti}	H_{syn}	$H_{central}$		
IV	1.88(d, 8.2)	3.38(br s)	3.28(m)	2.48(m)[a]	7.48(m)
V	1.84(d, 8.3)	3.46(br s)	3.36(m)	2.56(m)[a]	7.48(m)
VI[b]	1.78(d, 8.5)	3.56(br s)	3.44(m)	2.55(m)[a]	7.50(m)
VII	1.84(d, 8.4)	3.46(m)		3.23(s)	7.27(m)
VIII	1.90(d, 8.3)	3.72(m)		3.58(s)	7.34(m)

[a] Centre of AA'BB' multiplet. [b] At −125 °C: H_{anti}, 1.44, 2.03; H_{syn}3.28, 3.64; $H_{central}$ 2.98 p.p.m.

signals of the neutral species occurred in the range 2.3–2.5 p.p.m. whereas in CD_3CN at room temperature these signals were in the free nitrile position of 1.98 p.p.m., irrespective of the halide present in the complex and were invariant over the temperature range +50 to −60 °C. Such behaviour is consistent with facile exchange between coordinated CH_3CN and the large excess of solvent CD_3CN. The methyl signal of fresh solutions of the cationic complex (IX) dissolved in CD_3CN at room temperature was observed as a broad singlet at 2.45 p.p.m., but on long standing or warming the solution above room temperature, this signal decayed and was replaced by a sharp singlet in the free MeCN position, indicating that MeCN exchange between the cation and solvent occurs, but less readily than in the neutral species.

Ditertiary Arsine Reactions

Analytical and spectroscopic data (Table I) show that the reactions of $[WX(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2]$ with dae and dam are analogous to those of molybdenum [5], affording $[WX(\eta^3\text{-}C_3H_5)(CO)_2dae]$ and $[W_2X_2(\eta^3\text{-}C_3H_5)_2(CO)_4dam]\cdot$solvent respectively.

Each of the dae complexes (IV–VI) exhibited dynamic N.M.R. spectra. At room temperature two sets of resonances of relative intensities 2:3 were observed for the *anti*, *syn* and central protons of the allyl ligand, with the *syn* protons resonating as a broad singlet instead of the usual doublet, due to

TABLE IV. Coupling Constants[a] (Hz) of the Methylene Region of $Ph_2AsCH_2CH_2AsPh_2$ in Complexes (IV–VI).

Complex	$N = (\gamma_1 - \gamma_3)$	$(M^2 + L^2)^{1/2} = (\gamma_9 - \gamma_{11})$	J_{AB}	$J_{AB'}$	$J_{AA'} = J_{BB'}$
IV	−4.3	−21.5	−12.9	8.6	5.9
V	−4.9	−21.3	−13.1	8.2	6.7
VI	−5.3	−20.8	−13.1	7.8	7.2

[a] $K = J_{AA'} + J_{BB'}$; $M = J_{AA'} - J_{BB'}$; $L = J_{AB} - J_{AB'}$; $N = J_{AB} + J_{AB'}$.

TABLE V. Tungsten-containing[a] Ions in the Mass Spectra of $[WX(\eta^3\text{-}C_3H_5)(CO)_2dae]$.

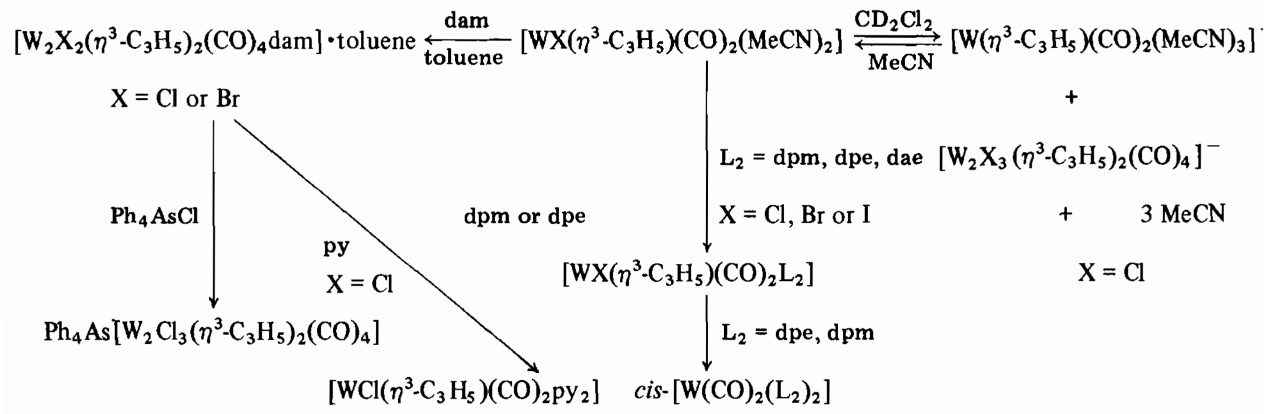
Ion	X = Cl		X = I	
	m/e	Rel. Int.	m/e	Rel. Int.
P^+	800	19	892	31
$(P - CO)^+$	772	61	864	76
$(P - 2CO)^+$	744	35	836	40
$WX(C_3H_3)dae^+$	742	54	834	66
$WXdae^+$	703	35	795	19
$WX(Ph_4As_2)^+$	675	12		
$WX(Ph_2AsC_2H_4AsPh)^+$	626	47		
$WX(Ph_3As_2)^+$	598	16	690	14
$W(dae)^+$			668	40
$W(Ph_4As_2)^+$			640	66
$WX(As_2C_{12}H_8)^+$	519	45	611	23
$WX(AsC_{12}H_8)^+$	444	100	536	54
$W(AsC_{12}H_7)^+$	408	74		
$WX(AsC_6H_4)^+$	368	58	460	56
$W(AsC_{12}H_8)^+$			409	100
unassigned	558		605, 575, 537	
metastables	772 → 744 744 → 703 675 → 598		864 → 836	

[a] Based on ^{182}W.

coincidence of the *syn* and central proton signals (Table III). The methylene protons of complexes (IV–VI) gave rise to AA′BB′ patterns, and since 20 of the expected 24 bands could be resolved, the spectra were analysed [10]. The resulting coupling constants are summarised in Table IV and are very similar to the data reported for $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2dae]$ [11]. At low temperatures all the spectral bands of complex (VI) broadened and lost fine structure. By −125 °C at least seven broad resonances were detected and could be assigned to overlapping ABCDX and ABCD spin patterns of an unsymmetrical allyl system and inequivalent methylene protons of dae respectively. This complex must therefore possess a low symmetry instantaneous structure as found for the molybdenum analogue [11]. The low temperature ^1H N.M.R. spectra of the corresponding chloro- and bromo-complexes (IV and V) also showed increased complexity, but even at −125 °C only very broad overlapping bands were observed.

The mass spectra of two of the dae complexes (IV and VI) have also been obtained and the strongest metal-containing ions observed listed in Table V. The bromo-complex (V) decomposed completely under the conditions used to obtain the mass spectra of the other two dae complexes, and even the iodo-complex (VI) showed a weak fragmentation

Reaction Scheme



pattern of $W(CO)_4$dae in its spectrum (not included in Table V), presumably from partial decomposition of the sample in the spectrometer. Both spectra also contained many ions associated with fragmentation of the arsenic ligand, but since these are well documented [12] they will not be considered further. The molecular ion is observed for both complexes, and step-wise elimination of carbonyl followed by loss of allyl is supported by the appropriate metastables for complex (IV).

$$[WX(C_3H_5)(CO)_2dae]^+ \xrightarrow{-CO} [WX(C_3H_5)(CO)dae]^+ \xrightarrow{-CO} [WX(C_3H_5)dae]^+ \xrightarrow{-C_3H_5} [WX(dae)]^+$$

Ligand fragmentation whilst still attached to the metal is also significant and involves both the arsine and allyl ligands. Loss of two hydrogens from the allyl group whilst bonded to the metal has now been observed in the mass spectra of several allyl complexes of the early transition metals, and has been ascribed to the formation of cyclopropenyl-metal species within the spectrometer [13, 14].

$Ph_2AsCH_2AsPh_2$ did not react with $[WX(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2]$ in an analogous manner to dae. Both products isolated (VII and VIII) were air-sensitive, had an allyl to dam ratio of 2:1 and crystallised with a solvent molecule which was not successfully removed. Crystallisation of the toluene adducts from acetone resulted in acetone solvates, and heating the solvates *in vacuo* led to decomposition. A binuclear molecular structure involving both halo- and dam bridges as proposed for the molybdenum analogues [5] seems likely, but attempts to determine molecular weights by mass spectrometry were unsuccessful, yielding a strong fragmentation pattern of the diarsine ligand only [12]. However, infrared data in the ν(C–O) and ν(M–X) regions provide some support for this formulation. The molecular symmetry of the binuclear complex can be no higher than C_{2v} and may be as low as C_1, consequently a minimum of three and a maximum of four ν(M–CO) and ν(M–X) stretches are predicted. Complexes (VII) and (VIII) show four and three carbonyl stretches respectively, while in the far-infrared region two halogen-sensitive bands were identified positively, in similar positions to those found for the isolectronic halo- and dam bridged complexes $[Re_2X_2(CO)_6dam]$ [15] and $[Mo_2X_2(\eta^3\text{-}C_3H_5)_2(CO)_4dam]$, (X = Cl or Br) [5].

Variable temperature ^1H NMR measurements indicated that both dam complexes were stereochemically non-rigid in solution. No new bands were observed over the entire temperature range +30 to −125 °C, but the sharply defined room temperature allyl signals became broad featureless bands by −40 °C, sharpened between −50 and −70 °C, and then broadened again at still lower temperatures, indicating that at least two dynamic processes occur in these molecules.

Reaction of the dam-bridged complexes with other neutral donors resulted in displacement of the arsine ligand and formation of the mononuclear products $[WX(\eta^3\text{-}C_3H_5)(CO)_2L_2]$, ($L_2$ = 2py, dpm or dpe), in high yields (Reaction Scheme). Reaction with Ph_4AsCl provided a high yield synthesis of the anionic complex $Ph_4As[W_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]$, which is not easily obtained by the route used to prepare the corresponding tetraalkyl-ammonium salts [16].

Ditertiary Phosphine Reactions

Reaction of (I) with dpe or dpm under forcing conditions produced low yields of *cis*-$[W(CO)_2(L_2)_2]$, (L_2 = dpe or dpm), via the intermediacy of the known complexes $[WCl(\eta^3\text{-}C_3H_5)(CO)_2L_2]$ [4]. Unlike the molybdenum analogues where yields of up to 70% were achieved [5], the tungsten *cis*-dicarbonyl products were obtained in comparatively low yields (⩽40%), and were contaminated with other carbonyl containing products of low solubility whose composition could not be established. Attempts so improve the yields of *cis*-[$W(CO_2)(L_2)_2$] by reacting [$W_2X_2(\eta^3$-$C_3H_5)_2(CO)_4$ dam] with dpm or dpe in acetonitrile were also unsuccessful because of the initial formation of [$WCl(\eta^3$-$C_3H_5)(CO)_2L_2$], which subsequently formed *cis*-[$W(CO)_2(L_2)_2$] slowly and in poor yields.

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