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Chemistry of Molybdenum and Tungsten. 10.¹ Oxotungsten(V) and Oxotungsten(IV) Complexes of Diphosphine and Diarsine Ligands

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The reaction of oxotrichlorobis(tetrahydrofuran)tungsten(V) [$\text{WOCl}_3(\text{THF})_2$] with bidentate ligands [L-L = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dpe), $o\text{-C}_6\text{H}_4(\text{PPh}_2)_2$ (pp), $\text{cis-Ph}_2\text{PCH}=\text{CHPPh}_2$ (VPP), $\text{cis-Ph}_2\text{AsCH}=\text{CHAsPh}_2$ (VAA), $\text{Me}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PMe}_2$ (dmp), $\text{Me}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2$ (dmpa), $\text{Me}_2\text{AsCH}_2\text{CH}_2\text{CH}_2\text{AsMe}_2$ (dma), $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$ (mpp), $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$ (das), $o\text{-C}_6\text{H}_4(\text{AsMe}_2)(\text{SbMe}_2)$ (stars)] has led to the isolation of [$\text{WOCl}_3(\text{L-L})$] complexes. The phenyl-substituted arsines [L-L = $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ (dae), $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$ (ape), and $o\text{-C}_6\text{H}_4(\text{AsPh}_2)_2$ (aa)] react with [$\text{WOCl}_3(\text{THF})_2$] to produce blue, diamagnetic powders " $\text{W}_2\text{O}_4\text{Cl}_4(\text{L-L})$ " which contain both terminal $\text{W}=\text{O}$ and bridging $\text{W}-\text{O}-\text{W}$ moieties. The possible nature of these products is discussed. Reactions of [$\text{WOCl}_3(\text{THF})_2$] with PPh_3 and $\text{PMePh}_2(\text{L})$ yield [WOCl_3L_2], while $\text{P}(\text{C}_6\text{H}_{11})_3$ produces $\{\text{WOCl}_3[\text{P}(\text{C}_6\text{H}_{11})_3]\text{THF}\}$. Bis(diphenylphosphino)methane (dpm) and [$\text{MOCl}_3(\text{THF})_2$] (M = Mo, W) produce the novel [$\text{MOCl}_2(\text{dpm})_2$]⁺[MOCl_4]⁻, containing five-coordinate trigonal-bipyramidal cations and monodentate dpm. The complexes have been characterized by the use of IR, electronic absorption and EPR spectroscopy. The EPR spectra suggest that the [$\text{WOCl}_3(\text{L-L})$] species have a *fac* structure and that the [WOCl_3L_2] are the *mer* isomers. Refluxing the [$\text{WOCl}_3(\text{L-L})$] (L-L = dpe, pp, VPP) with excess L-L and NaBPh_4 in ethanol resulted in reduction to [$\text{WOCl}(\text{L-L})_2$]BPh₄, which have trans structures on the basis of their IR and ³¹P NMR spectra.

The preparation and properties of a range of oxomolybdenum(V) complexes of mono-³ and bidentate^{1,4-7} group 5B donor ligands have been reported. In previous parts of this series, we have described systematic studies on alkyl-¹ and aryl-substituted⁴ bidentate complexes [$\text{MoOCl}_3(\text{L-L})$] and their reduction to oxomolybdenum(IV) [$\text{MoOCl}(\text{L-L})_2$]⁷. In marked contrast no oxotungsten(V) complexes of group 5B donor ligands have been reported; indeed few complexes of the types [WOCl_3L_2] or [$\text{WOCl}_3(\text{L-L})$] are known at all — examples are L-L = bipyridyl, $\text{Et}_4\text{P}_2\text{S}_2$; L = THF, MeCN, pyridine.⁸⁻¹¹ Butcher et al.¹² obtained [$\text{W}^{\text{IV}}\text{OCl}_2(\text{PR}_3)_3$] [$\text{R}_3 = \text{Me}_2\text{Ph}$, MePh₂, Et₂Ph] by reaction of WCl_6 , WOCl_4 , or [NEt_4] $[\text{WCl}_6]$ with the phosphines in wet ethanol. Here we report on a systematic study of the reaction of [$\text{WOCl}_3(\text{THF})_2$] with a range of monodentate (L) and bidentate (L-L) group 5B donor ligands, which have resulted in [WOCl_3L_2] and [$\text{WOCl}_3(\text{L-L})$] complexes, and the reduction of several of the latter to [$\text{WOCl}(\text{L-L})_2$]BPh₄.

Experimental Section

Tetrahydrofuran, *n*-pentane, toluene, and cyclohexane were dried by distillation from sodium benzophenone ketyl, dichloromethane was dried over molecular sieves, and absolute ethanol was dried by distillation from magnesium ethoxide. All preparations were conducted under a dry nitrogen atmosphere using standard Schlenk tube and drybox techniques. Physical measurements were made as described previously.⁴ EPR spectra were obtained on a Varian E9 EPR spectrometer using the dual cavity mode and were run in the X-band

(~9.3 GHz) in dichloromethane solution at various temperatures +35 to -160 °C. The ligands were prepared by literature methods^{1,4} except for *o*-phenylenebis(dimethylphosphine), the preparation of which will be described elsewhere.

Oxotrichlorobis(tetrahydrofuran)tungsten(V), [$\text{WOCl}_3(\text{THF})_2$]. Tungsten hexachloride (RIC, Kirby and Co., Liverpool) (25 g) was treated with cyclohexane (100 cm³) and THF (50 cm³) and the mixture stirred. After 30–60 min an exothermic reaction developed and a turbid dark green solution formed. The mixture was stirred for a further 4 h and then filtered. The blue solid was rinsed with cyclohexane (~8 × 5 cm³) until the washings were no longer green and then with *n*-pentane (10 cm³) and dried in vacuo. The product was sealed in small ampoules (~1–1.5 g/ampoule) under nitrogen. The product will keep for about 4 weeks, but then decomposition sets in yielding a blue oil.

Oxotrichloro(*o*-phenylenebis(diphenylphosphine))tungsten(V), [$\text{WOCl}_3(\text{pp})$]. [$\text{WOCl}_3(\text{THF})_2$] (0.91 g, 2.0 mmol) was suspended in toluene (40 cm³), pp (0.9 g, 2.0 mmol) in dichloromethane (20 cm³) added, and the mixture stirred for 18 h. *n*-Pentane (30 cm³) was added and the mixture stirred for a further 1 h. The greenish solid was filtered off, rinsed with 1:1 toluene:CH₂Cl₂ (10 cm³) and *n*-pentane (2 × 10 cm³), and dried in vacuo (yield 80%).

The same general method was used to prepare the other complexes, with the exceptions noted below.

Oxotrichloro(*cis*-1,2-bis(diphenylarsino)ethylene)tungsten(V), [$\text{WOCl}_3(\text{VAA})$]. The ligand (0.95 g, 2.0 mmol) was dried at 60 °C (10⁻¹ Torr) for 1 h, dissolved in dichloromethane (20 cm³), and added to a suspension of [$\text{WOCl}_3(\text{THF})_2$] (0.91 g, 2.0 mmol) in toluene (40 cm³). After 24 h of stirring, *n*-pentane (20 cm³) was added, resulting in the precipitation of a sticky green solid. The solvent was decanted

off, and the sticky solid stirred vigorously with *n*-pentane (40 cm³) for 1 h, when a green microcrystalline product formed. This was worked up as described above (60%).

The [WOCl₂(dpm)₂][WOCl₄] and [MoOCl₂(dpm)₂][MoOCl₄] were prepared as described for [WOCl₃(VAA)] using a 1:1 ligand:metal ratio and [WOCl₃(THF)₂] and [MoOCl₃(THF)₂],¹³ respectively.

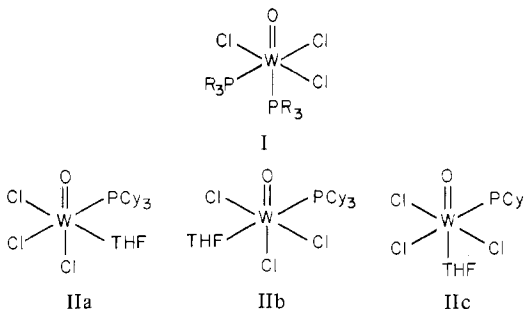
Oxochlorobis(1,2-bis(diphenylphosphino)ethane)tungsten(IV) Tetraphenylborate, [WOCl(dpe)₂]BPh₄. Freshly distilled ethanol (50 cm³) was added to [WOCl₃(dpe)] (0.35 g 0.5 mmol), and excess dpe (~0.6 g) sifted in. The mixture was refluxed for 6 h, during which time the color changed from green to deep purple. Sodium tetraphenylborate (1.0 g) dissolved in the minimum amount of ethanol was added, the solution allowed to cool, and the pink precipitate filtered off. Recrystallization from dichloromethane yielded a pink powder (~75%).

[WOCl(pp)₂]BPh₄ and [WOCl(VPP)₂]BPh₄ were made analogously.

Results and Discussion

The starting material for the syntheses of the oxotungsten(V) complexes was [WOCl₃(THF)₂], which was originally described by Fowles and Frost.⁸ Unlike the synthesis of the molybdenum analogue¹³ which is straightforward, the preparation of the tungsten complex is very sensitive to the reaction conditions and to the scale. A satisfactory preparation is described in the Experimental Section. Use of different reaction times, different solvents, or a smaller or larger scale often produced bluish solids which became oily even in sealed tubes after a few days, and yielded impure complexes on treatment with a variety of ligands. When made as described above, the [WOCl₃(THF)₂] is stable for several weeks in sealed ampoules but must be manipulated under rigorously dry conditions.

Complexes of Monodentate Ligands. The reaction of [WOCl₃(THF)₂] with a range of monodentate group 5B donor ligands, including PPh₃, AsPh₃, SbPh₃, Me₂PhP, MePh₂P, Et₂PhP, and PCy₃ (Cy = cyclohexyl, C₆H₁₁) was examined. Only PPh₃ and PMePh₂ yielded [WOCl₃L₂] complexes, PCy₃ afforded [WOCl₃(PCy₃)(THF)], but other phosphines produced oils which could not be solidified. Triphenylarsine and stibine yielded diamagnetic products with nonreproducible analyses, probably due to reduction. The very moisture sensitive [WOCl₃L₂] (L = PPh₃, PMePh₂) exhibited a single strong $\nu(\text{W}=\text{O})$ at 955 cm⁻¹ consistent with a terminal W=O bond^{10,14} and partially resolved $\nu(\text{WCl})$ at 350–290 cm⁻¹. The room temperature magnetic moments were ~1.7 μ_B close to the spin-only value for d¹ W(V).¹⁵ The EPR spectrum of [WOCl₃(PPh₃)₂] in CH₂Cl₂ at room temperature consisted of a doublet of doublets ($g_{\text{iso}} = 1.791$), this pattern being produced by coupling to two phosphorus atoms in different environments, indicative of a *mer* structure (I). The coupling



of the phosphorus cis to the W=O bond $A_{\text{iso}}(^{31}\text{P}) = 35$ G is larger than that trans to W=O, $A_{\text{iso}}(^{31}\text{P}) < 15$ G. The EPR spectrum of [WOCl₃(PMePh₂)₂] is similar (Figure 1—where it is shown as the double derivative). The oily product from the reaction of [WOCl₃(THF)₂] and Me₂PhP had a similar EPR spectrum but could not be solidified and was not further studied.

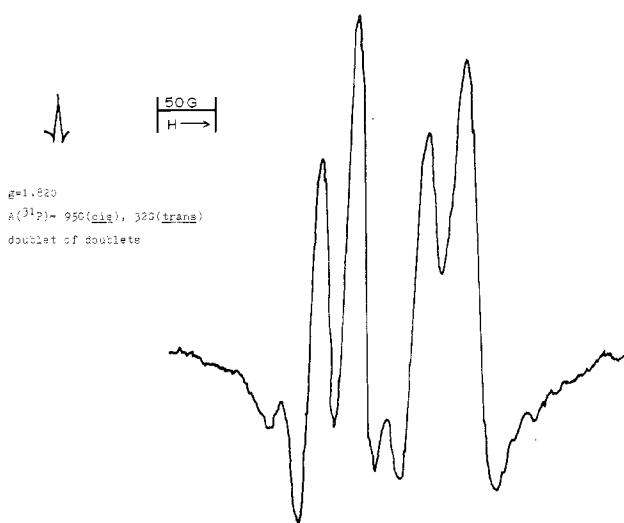


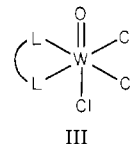
Figure 1. Double-derivative EPR spectrum of WOCl₃(PMePh₂)₂.

The bulky PCy₃ formed only [WOCl₃(THF)(PCy₃)], and even with excess PCy₃, we could not isolate a [WOCl₃(PCy₃)₂] complex. The former exhibited terminal $\nu(\text{W}=\text{O})$ at 970 cm⁻¹ and $\nu(\text{COC})$ of the THF at 1040, 860 cm⁻¹ confirming the THF is coordinated through the ether oxygen.¹⁶ The EPR spectrum exhibits a doublet $A_{\text{iso}}(^{31}\text{P}) = 55$ G, the large hyperfine coupling suggesting that the phosphine is *cis* to the W=O bond (IIa, IIb, or IIc).

The far-IR spectrum of [WOCl₃(THF)PCy₃] exhibits three poorly resolved $\nu(\text{WCl})$ at 345 (sh), 320, 295 (sh) cm⁻¹, compared with three bands in the range 345–310 cm⁻¹ for *mer*-[WOCl₃(PR₃)₂] which suggests that IIc is not present. The similarity of the spectrum to those of [WOCl₃(L-L)] (below) favors IIa, which would also account for the stoichiometry, since the very bulky PCy₃ (cone angle ~179°)¹⁷ prevents two of these ligands taking up a *cis* octahedral arrangement.

Complexes of Bidentate Ligands. The reactions of [WOCl₃(THF)₂] with 1,2-bis(diphenylphosphino)ethane (dpe), *cis*-1,2-bis(diphenylphosphino)ethylene (VPP), and *o*-phenylenebis(diphenylphosphine) (pp) produced [WOCl₃(L-L)] complexes as gray or green moisture-sensitive powders. In dry 10⁻³ M nitromethane they are nonelectrolytes, and they have magnetic moments ~1.5–1.7 μ_B . The dpe and VPP complexes exhibit a single strong $\nu(\text{W}=\text{O})$ at 950–960 cm⁻¹ consistent with a terminal W=O bond,¹⁴ while the [WOCl₃(pp)] exhibits two very closely spaced bands at 970 and 965 cm⁻¹. Since there was no evidence in the EPR spectrum for isomers of the latter, the splitting of the W=O vibration is probably due to solid-state effects. The far-IR spectra of the complexes show a pattern of three vibrations assignable to $\nu(\text{WCl})$ 330, 310, and 290 cm⁻¹, but due to the low symmetry of the complexes assignment of structures on this basis is unsafe.

The EPR spectrum of [WOCl₃(dpe)] (Figure 2) in dichloromethane at room temperature showed a 1:2:1 triplet due to coupling to two equivalent phosphorus atoms ($A_{\text{iso}}(^{31}\text{P}) = 20$ G) consistent with the *fac* structure (III). The [WO-



Cl₃(VPP)] complex showed no superhyperfine coupling at room temperature, but in frozen CH₂Cl₂ at -150 °C, the triplet pattern of a *fac* isomer is apparent. The reason that coupling

Table I

Compd	Color	Analytical data			ΔM , Ω^{-1} cm^{-2} M^{-1}	μ_{eff} , ^d μ_B	$\nu(\text{W}=\text{O})$, cm^{-1}	IR data		^{31}P NMR ($J(\text{W}-\text{P})$, Hz) ^f	$10^{-3}E_{\text{max}}$, ^g cm^{-1}	$10^{-2}E_{\text{max}}$ (ϵ_{max}), ^h cm^{-1}
		% C ^a	% H ^a	% Cl ^a				$\nu(\text{W}-\text{Cl})$, cm^{-1}				
[WOC ₃ (VPP)] ^{1/2} ·THF	Gray	44.8 (44.4)	3.7 (3.4)	14.1 (14.1)	4 ^b	1.65	950	330, 306, 285 sh		22.8, 18.1, 14.8	23.0 (830), 17.0 (350)	
[WOC ₃ (dpe)]	Gray	43.2 (44.3)	3.4 (3.4)	14.6 (15.1)		1.52	955	330, 300, 285 sh		22.7, 18.2, 14.4	23.0 (-), 18.1 (-)	
[WOC ₃ (pp)]	Yellow-green	47.7 (47.8)	3.3 (3.2)	13.8 (14.1)		1.70	970, 965	330, 310, 300 sh		25.0 sh, 22.7, 16.4 sh	22.6 (1050), 16.0 (130), 13.0 (-)	
[WOC ₃ (VAA)] ^{1/2} ·THF	Dark green	42.6 (42.6)	3.6 (3.5)	12.4 (12.3)		1.43	960	345, 320, 305 sh		21.7, 16.7, 13.0 sh	Decomposes	
[WOC ₃ (dmp)]	Green	19.3 (20.1)	4.4 (4.2)	20.5 (21.5)		1.22	960	350, 320, 295		23.0, 17.2, ~14.5 w	24.2 (-), 16.3 (-)	
[WOC ₃ (dma)]	Yellow-green	15.3 (15.1)	3.2 (3.3)	18.5 (19.0)		1.28	960	330, 305, 300		22.7, 16.1, ~14.7 w	23.0 (-), 17.0 (-) br	
[WOC ₃ (dmpa)]	Yellow-green	15.6 (16.3)	3.9 (3.5)	20.1 (20.7)		1.20	950	330, 310, 295 sh		23.0, 17.1, ~14.6 w	23.5 (-), 16.8 (-)	
[WOC ₃ (das)] ^{1/2} ·THF	Green	21.3 (21.6)	3.0 (3.0)	17.3 (17.4)	3.0 ^b	1.24	968	340 sh, 332, 312		23.8, 16.8, 14.8 w	24.8 (800), 16.5 (360)	
[WOC ₃ (stars)]	Blue	18.6 (18.8)	2.6 (2.5)	16.5 (16.6)	3.5 ^b	1.22	968	335, 315 br		23.6, 16.7, ~15.0 w	24.5 (950), 17.0 (300)	
[WOC ₃ (mpp)] ^{1/2} ·THF	Medium blue	28.6 (28.8)	3.3 (3.6)	19.5 (19.6)		1.20	960	340, 320, 306 sh		27.8, 22.2, 17.7, 15.2 sh		
[WO(dpm) ₂ Cl ₂][WOC ₃]	Dark blue	43.0 (43.3)	3.5 (3.2)	14.4 (15.4)	57 ^c	1.76 ^e	970, 975 sh	330 sh, 305, 290		21.8, 17.0 sh, 14.9, 11.4	16.9 (-), 14.7 (-)	
[MoO(dpm) ₂ Cl ₂][MoO-Cl ₄] ^{1/2} ·THF	Burgundy	50.5 (50.8)	4.0 (4.1)	15.5 (16.6)	55 ^c	1.61 ^e	955, 985	325 br, 310 sh, 290		23.0 sh, 20.0, 13.5 sh	20.0 (-), 13.5 (-)	
[WOC ₃ (dpe)] ₂ ·BPh ₃	Deep pink	66.5 (67.5)	5.1 (5.1)	3.0 (2.6)	71	Diamag	955	280	-27.9 (315)	20.6	20.8 (24)	
[WOC ₃ (VPP) ₂ ·BPh ₃	Pink	66.9 (67.7)	4.1 (4.7)	3.0 (2.6)	73	Diamag	950	278	-42.4 (310)	21.6	21.0 (17)	
[WOC ₃ (pp) ₂ ·BPh ₃	Pink	68.2 (69.7)	3.9 (4.7)	2.3 (2.4)	69	Diamag	950	280	-36.9 (315)	21.8 br	20.9 (28)	
[WOC ₃ (PPh ₃) ₂] ^{1/2} ·CH ₂ Cl ₂	Yellow-green	50.0 (51.0)	3.4 (3.1)	14.2 (14.5)		1.72	955	335 sh, 318, 312 sh		27.2 sh, 20.8, ~15.0	Decomposes	
[WOC ₃ (Meph ₂ P) ₂] ^{1/2} ·CH ₂ Cl ₂	Yellow-green	42.8 (43.3)	3.7 (3.6)	16.0 (17.0)		1.70	955	345, 335 sh, 320		21.7, ~15.0	22.0 (-), 16.0 (-)	
[WOC ₃ (PCy ₃)(THF)]	Blue	36.7 (36.2)	6.3 (5.4)	i		1.48	970	345 sh, 320, 295 sh		27.0 sh, 22.7, 16.9 sh, 14.0	Decomposes	

^a Found (calcd). ^b 10^{-3} M nitromethane. ^c 10^{-3} M *N,N*-dimethylformamide. Calculated on the formula given. 1:1 electrolytes have values of $60\text{--}90 \Omega^{-1} \text{cm}^2 \text{M}^{-1}$. ^d $\pm 0.05 \mu_B$. ^e $\mu_{\text{eff}}/\text{M atom}$. ^f Relative to external $85\% \text{H}_3\text{PO}_4$ ($J(\text{W}-\text{P})$). ^g Diffuse reflectance. ^h Dichloromethane solution. ⁱ % W = 27.0 (27.1).

Table II. EPR Data

Compd	Room temp (CH ₂ Cl ₂ soln)			-150 °C (CH ₂ Cl ₂ frozen glass)		
	g_{iso}	$A_{\text{iso}}(^{31}\text{P}$ or $^{75}\text{As})$, G		g_1	g_2	g_3
[WOC ₃ (VPP)] ^{1/2} ·THF	1.870			1.96	1.83	1.83
[WOC ₃ (dpe)]	1.860			1.93	1.84	1.84
[WOC ₃ (pp)]	1.860		~20 1:2:1 triplet	1.86	1.86	1.86
[WOC ₃ (VAA)] ^{1/2} ·THF	1.840		~17 1:2:3:4:3:2:1 septet	1.91	1.85	1.72
[WOC ₃ (dmp)]	1.877		22 1:2:1 triplet	1.95	1.85	1.85
[WOC ₃ (dma)]	1.860		20 1:2:3:4:3:2:1 septet	1.86	1.86	1.86
[WOC ₃ (dmpa)]	1.867		$A(^{31}\text{P}) \approx A(^{75}\text{As}) \approx 27$ 1:2:2:2:1 quintet	1.94	1.86	1.74
[WOC ₃ (das)] ^{1/2} ·THF	1.860			1.93	1.85	1.76
[WOC ₃ (stars)]	1.860			1.93	1.85	1.76
[WOC ₃ (mpp)] ^{1/2} ·THF	1.860			1.93	1.85	1.76
[WOC ₃ (PPh ₃) ₂] ^{1/2} ·CH ₂ Cl ₂	1.791		35, <15 (poorly resolved) doublet of doublets	1.85	1.75	1.72
[WOC ₃ (PMePh ₂) ₂] ^{1/2} ·CH ₂ Cl ₂	1.82		95, 32 doublet of doublets	1.91	1.81	1.74
[WOC ₃ (PCy ₃)(THF)]	1.86		25, <10 poorly resolved	1.76	1.72	1.69
[WOC ₃ (dpm) ₂][WOC ₃]	1.72		55 doublet	1.89	1.76	1.72
[WOC ₃ (dpm) ₂][WOC ₃]	1.805		~35 G doublet	1.79	1.73	1.69
[MoOCl ₂ (dpm) ₂][MoOCl ₄]	1.730		Singlet no hyperfine structure	~1.985	~1.940	~1.915
[MoOCl ₂ (dpm) ₂][MoOCl ₄]	1.950		~48 G doublet			
[MoOCl ₂ (dpm) ₂][MoOCl ₄]	1.949		Singlet no hyperfine structure			

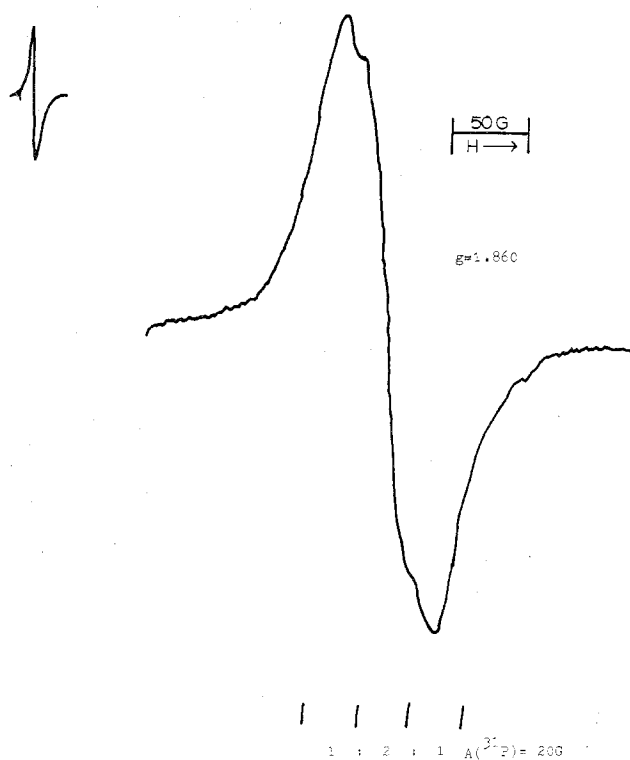


Figure 2. EPR spectrum of $\text{WCl}_3(\text{dpe})$ in CH_2Cl_2 at 25°C .

is not observed at room temperature is most probably due to the large line width of the signal (half-height ~ 60 G) while $A_{\text{iso}}(^{31}\text{P}) \approx 9\text{--}11$ G is not observed, until the lines sharpen on cooling. Even at -150°C $[\text{WCl}_3(\text{pp})]$ exhibits only a broad signal with no coupling evident. However, the very similar g_{iso} and comparable IR spectra suggest that the complex is isostructural with the dpe and VPP analogues. *cis*-1,2-Bis(diphenylarsino)ethylene (VAA) yields dark green, very moisture sensitive $[\text{WCl}_3(\text{VAA})]\cdot\text{THF}$. The IR spectra again shows terminal $\nu(\text{WO})$ 960 cm^{-1} and the weak $\nu(\text{COC})$ absorption of uncoordinated (lattice) THF at 1075 and 915 cm^{-1} .¹⁶ The complex is unstable in solution, but in rigorously dry CH_2Cl_2 , it exhibits an EPR spectrum which shows a septet (1:2:3:4:3:2:1) attributable to coupling to two equivalent arsenic atoms [$^{75}\text{As}(I = 3/2)$] and again indicates a *fac* isomer is present.

The reaction of 1,2-bis(diphenylarsino)ethane, *o*-phenylenebis(diphenylarsine), (*o*-diphenylphosphinophenyl)diphenylarsine, or 2-diphenylphosphinoethyldiphenylarsine with $[\text{WCl}_3(\text{THF})_2]$ yielded bluish, diamagnetic powders which failed to yield reproducible analysis, although the compositions from numerous preparations approximated to " $\text{W}_2\text{O}_4\text{Cl}_4(\text{L-L})$ ". The IR spectra all exhibited both terminal $\nu(\text{WO})$ at $\sim 970\text{ cm}^{-1}$ and bridging $\nu(\text{WOW})$ at $\sim 820\text{ cm}^{-1}$ and are probably polymeric oxotungsten(IV) species, produced by reduction of $[\text{WCl}_3(\text{THF})_2]$ by L-L. However, use of excess (L-L) under a variety of conditions failed to yield $[\text{WCl}(\text{L-L})_2]^+$; indeed treatment of the " $\text{W}_2\text{O}_4\text{Cl}_4(\text{L-L})$ " with NaBPh_4 in ethanol resulted in a product free of "L-L" and BPh_4^- , analyzing as $\text{Na}_2\text{W}_2\text{O}_4\text{Cl}_4\cdot 5\text{EtOH}$ suggesting that "L-L" may be present as a cation (L-LCl_2^{2+}) (cf. $[\text{Ph}_3\text{AsCl}][\text{MoOCl}_4]^{18}$). The nature of these products is being further studied. The different behavior of VAA and the other phenyldiarsines illustrates once more the great sensitivity of early transition-metal systems to small changes in ligand properties.

The alkyl-substituted bidentates *o*-phenylenebis(dimethylphosphine) (mpp), *o*-phenylenebis(dimethylarsine) (das), (*o*-dimethylarsinophenyl)dimethylstibine (stars), 1,3-

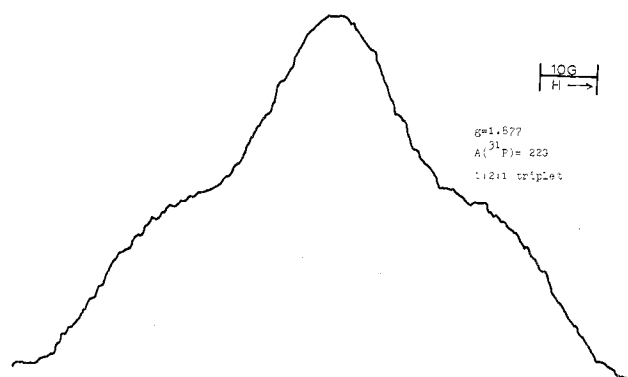


Figure 3. Double-derivative EPR spectrum of $\text{WCl}_3(\text{dmp})$ in CH_2Cl_2 at 25°C .

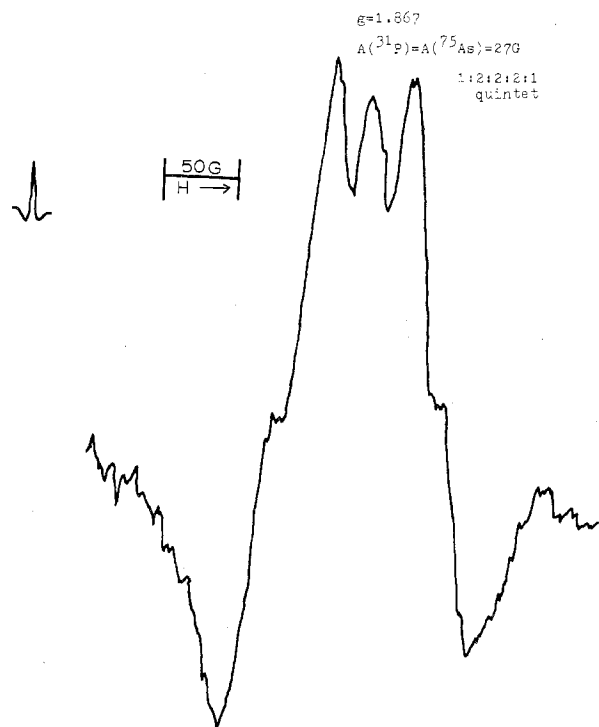


Figure 4. Double-derivative EPR spectrum of $\text{WCl}_3(\text{dmpa})$ in CH_2Cl_2 at 25°C .

bis(dimethylphosphino)propane (dmp), 1,3-bis(dimethylarsino)propane (dma), and (3-dimethylphosphinopropyl)dimethylarsine (dmpa) readily yielded $[\text{WCl}_3(\text{L-L})]$ complexes. These were poorly soluble in most organic solvents, were nonelectrolytes in nitromethane, and were rapidly decomposed by moist air. Their IR spectra are very similar to those of the phenyl analogues.

The EPR spectra of the complexes were again most useful in assigning structures. The $[\text{WCl}_3(\text{dmp})]$ (Figure 3, double derivative) exhibits a 1:2:1 triplet and $[\text{WCl}_3(\text{dma})]$ a 1:2:3:4:3:2:1 septet clearly indicating superhyperfine coupling to equivalent phosphorus [$^{31}\text{P}(I = 1/2)$] or arsenic [$^{75}\text{As}(I = 3/2)$] nuclei, respectively, and hence a *fac* structure. For $[\text{WCl}_3(\text{dmpa})]$ (Figure 4) the superhyperfine coupling appears as an apparent quintet 1:2:2:2:1, which is consistent with a *fac* structure with $A_{\text{iso}}(^{31}\text{P}) \approx A_{\text{iso}}(^{75}\text{As}) \approx 27$ G. The EPR spectra of the *o*-phenylene back-boned ligand complexes consisted of a broad signal with no hyperfine structure. However, in frozen solution (-160°C) they are very similar to that of $[\text{WCl}_3(\text{VAA})]$ and hence almost certainly have the same structure. Further support for the *fac* structure comes from the observation that the unsymmetrical ligand stars

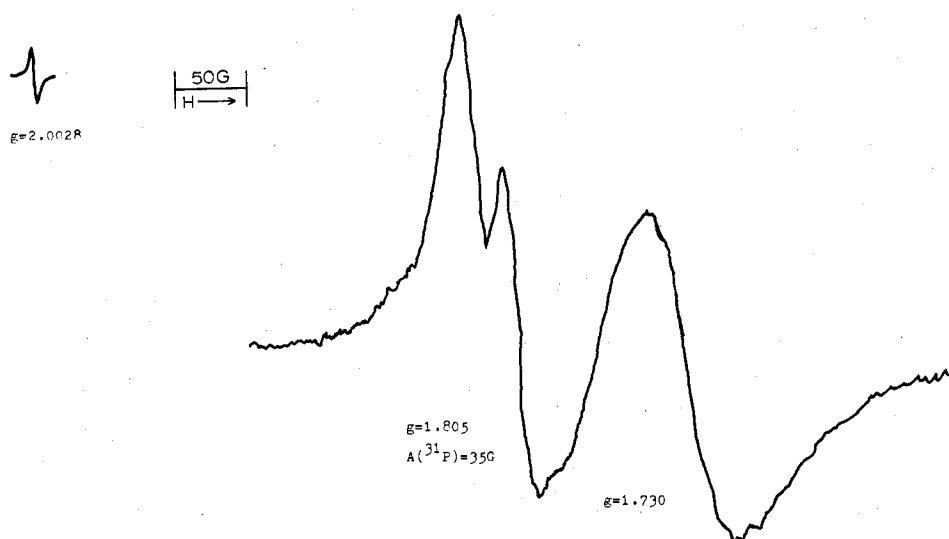
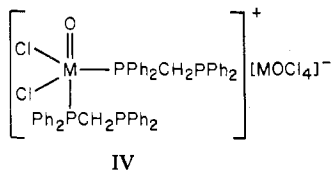


Figure 5. Double-derivative EPR spectrum of $[\text{WOCl}_2(\text{dpm})_2][\text{WOCl}_4]$ in CH_2Cl_2 at -20°C .

yielded only one isomer on the basis of the EPR spectral evidence. In a *mer* arrangement two isomers with Me_2As - and Me_2Sb - trans to the $\text{W}=\text{O}$ bond would be expected and should give different g_{iso} values.

All the $[\text{WOCl}_3(\text{L-L})]$ complexes are very moisture sensitive in solution, and only in a few cases were solubility and/or stability sufficient for extinction coefficients to be measured. The solution and solid reflectance spectra are essentially similar in profile consisting of an intense absorption at $(20\text{--}24) \times 10^3 \text{ cm}^{-1}$ with a shoulder or second band at $(\sim 16\text{--}18) \times 10^3 \text{ cm}^{-1}$ and a weak absorption at $(14\text{--}15) \times 10^3 \text{ cm}^{-1}$. The low symmetry of these complexes and the generally poorly resolved spectra make assignments uncertain, although the lowest energy bond is probably the ${}^2\text{E} \leftarrow {}^2\text{B}_2$ transition (O_h symmetry).

It was previously reported⁴ that an oxomolybdenum(V) complex of bis(diphenylphosphino)methane could not be isolated, but by using the modified method described in the Experimental Section, complexes of empirical formula $\text{MOCl}_3(\text{dpm})_2$ have been obtained for $\text{M} = \text{Mo}, \text{W}$. However, unlike the other complexes of this stoichiometry, both complexes are 1:1 electrolytes in 10^{-3} M *N,N*-dimethylformamide, and their EPR spectra show two metal environments to be present. The solution (CH_2Cl_2) EPR spectrum of $\text{MoOCl}_3(\text{dpm})$ run at several temperatures between $+35$ and -80°C showed a doublet $A(^{31}\text{P}) \sim 48 \text{ G}$ ($g_{\text{iso}} = 1.950$) upon which further fine structure is just evident but not clearly resolved, and a single peak $g_{\text{iso}} = 1.949$ with no fine structure. The latter signal corresponds well with the reported spectrum of MoOCl_4^- .^{4,19} This suggests that the complex should be formulated $[\text{MoOCl}_2(\text{dpm})_2][\text{MoOCl}_4]$. The structure of the cation clearly contains one phosphorus cis to the $\text{Mo}=\text{O}$ bond, accounting for the doublet observed, and a second phosphorus donor trans to the $\text{Mo}=\text{O}$ could account for the incompletely resolved fine structure [$A_{\text{iso}}(^{31}\text{P})$ cis $\text{MoO} \gg A_{\text{iso}}(^{31}\text{P})$ trans MoO]. (It is known,^{20,21} that a ligand trans to $\text{M}=\text{O}$ has a longer and weaker $\text{M}-\text{L}$ bond than a similar ligand in a cis position, which makes delocalization of the odd electron onto the trans L less favorable.) This tends to suggest structure IV.



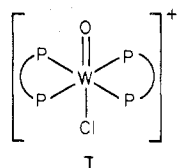
In support of this proposal, the IR spectrum exhibits two $\nu(\text{Mo}=\text{O})$ at 955 and 985 cm^{-1} assignable to the cation and anion,⁴ respectively. Previous studies upon the IR spectrum of coordinated $\text{dpm}^{22,23}$ have suggested that a band at $\sim 778 \text{ cm}^{-1}$ in the free ligand, usually assigned to a $-\text{CH}_2-$ deformation mode is unshifted if the dpm coordinates as a monodentate but shifts to higher frequency by $\sim 20 \text{ cm}^{-1}$ if the dpm chelates to the metal. In $[\text{MoOCl}_2(\text{dpm})_2]^+$ there is only a single absorption at 778 cm^{-1} consistent with both dpm ligands being monodentate. The " $\text{WOCl}_3(\text{dpm})$ " is similar, although the $\nu(\text{WO})$ partially overlap. The EPR spectrum (Figure 5) contains a doublet and a singlet due to the cation and anion, respectively. Unfortunately neither the IR nor EPR spectra of the WOCl_4^- ion²⁴ appear to have been reported, but extrapolation from the data on other WO^{3+} complexes²⁵ suggests that g_{iso} would lie in the range $1.71\text{--}1.77$ (cf. value of 1.73 for the singlet in this complex). The magnetic moment/metal atom of both complexes is consistent with one unpaired electron, but since the reported moments of MoOCl_4^- and especially²⁴ WOCl_4^- vary with the cation, the errors in calculating moments for the cations are likely to be large and were not attempted.

The formation of $[\text{MOCl}_2(\text{dpm})_2]^+$ rather than $[\text{MOCl}_3(\text{dpm})]$ is probably due to the decreased tendency of this ligand to chelate and form a strained four-membered ring, while its bulky nature as a monodentate presumably does not favor six-coordination. (Both the IR and EPR spectra rule out the possibility that the cations are six-coordinate with both chelating and monodentate dpm ligands present.) Attempts to replace the MOCl_4^- anions with tetraphenylborate were unsuccessful.

Oxotungsten(IV) Complexes. We have previously reported⁴ that $[\text{MoOCl}_3(\text{L-L})]$ complexes were reduced by boiling in ethanol with excess L-L, to $[\text{MoOCl}(\text{L-L})_2]^+$. Prolonged reflux (5–10 h) of the $[\text{WOCl}_3(\text{L-L})]$ with excess (L-L) (L-L = VPP, dpe, pp) in dry ethanol produced deep purple solutions, from which NaBPh_4 precipitated $[\text{WOCl}(\text{L-L})_2]\text{BPh}_4$. The reaction is much slower than with the corresponding molybdenum complexes. No reduction was apparent with $[\text{WOCl}_2(\text{dpm})_2]\text{WOCl}_4$ after 10 h, while $[\text{WOCl}_3(\text{VAA})]$ decomposed immediately in ethanol. Attempts to extend this reaction to the methyl-substituted ligands yielded blue tars and no products were isolated.

The pink $[\text{WOCl}(\text{L-L})_2]\text{BPh}_4$ (L-L = pp, dpe, VPP) are 1:1 electrolytes in 10^{-3} M nitromethane and are diamagnetic, as expected for W(IV) complexes containing a $\text{W}=\text{O}$ bond.^{5,12} All three complexes exhibit a single $\nu(\text{WO})$ at $\sim 950 \text{ cm}^{-1}$ and

a single $\nu(\text{WCl})$ at $\sim 280 \text{ cm}^{-1}$, both fairly insensitive to changes in L-L suggesting a trans structure. This was confirmed by the ^{31}P NMR spectra which showed only a single strong absorption, flanked by weak satellites due to $^{183}\text{W}-^{31}\text{P}$ coupling ($^{183}\text{W} = 14\%$ abundance). The magnitude of $J_{\text{W-P}} \sim 315 \text{ Hz}$ is comparable with other complexes containing trans phosphines¹² (V).



Comparison between the oxomolybdenum(V) and oxotungsten(V) complexes shows considerable similarities in properties, as would be expected, but also surprising differences. The latter complexes are considerably more difficult to obtain and less stable to moisture and generally less stable in solution. The different behavior of the weaker donor phenyl-substituted diarsines toward W(V) is also unexpected.

Acknowledgment. We are grateful to Ciba-Geigy Ltd. for obtaining the ^{31}P NMR spectra and wish to thank Dr. M. J. Parrott for assistance in obtaining the EPR spectra.

Registry No. $[\text{WOCl}_3(\text{VPP})]$, 63848-28-2; $[\text{WOCl}_3(\text{dpe})]$, 63848-27-1; $[\text{WOCl}_3(\text{pp})]$, 63848-26-0; $[\text{WOCl}_3(\text{VAA})]$, 63848-25-9; $[\text{WOCl}_3(\text{dmp})]$, 63848-24-8; $[\text{WOCl}_3(\text{dma})]$, 63848-23-7; $[\text{WOCl}_3(\text{dmpa})]$, 63848-22-6; $[\text{WOCl}_3(\text{das})]$, 63848-21-5; $[\text{WOCl}_3(\text{stars})]$, 63848-20-4; $[\text{WOCl}_3(\text{mpp})]$, 63848-19-1; $[\text{WO}(\text{dpm})_2\text{Cl}_2][\text{WOCl}_4]$, 63848-18-0; $[\text{MoO}(\text{dpm})_2\text{Cl}_2][\text{MoOCl}_4]$, 63848-16-8; $[\text{WOCl}(\text{dpe})_2]\text{BPh}_4$, 63848-14-6; $[\text{WOCl}(\text{VPP})_2]\text{BPh}_4$, 63833-70-5; $[\text{WOCl}(\text{pp})_2]\text{BPh}_4$, 63865-76-9; $[\text{WOCl}_3(\text{PPh}_3)_2]$, 63833-68-1; $[\text{WOCl}_3(\text{MePh}_2\text{P})_2]$, 63833-67-0; $[\text{WOCl}_3(\text{PCy}_3)(\text{THF})]$,

63833-66-9; $[\text{WOCl}_3(\text{THF})_2]$, 18131-65-2; $[\text{MoOCl}_3(\text{THF})_2]$, 20529-42-4; WCl_6 , 13283-01-7.

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^{31}P NMR Studies on Molybdic and Tungstic Heteropolyanions. Correlation between Structure and Chemical Shift

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^{31}P NMR has been carried out on 24 tungstic and molybdic heteropolyanions, the structures of which are derived from $(\text{PM}_{12}\text{O}_{40})^{3-}$ and $(\text{P}_2\text{M}_{18}\text{O}_{62})^{6-}$ by the removal or the partial substitution of metallic atoms. The chemical shift value is correlated with the PO_A bond strength, O_A being the oxygen atom of the central PO_4 tetrahedron. For those compounds containing several P atoms, the existence of one or several peaks allows one to suggest a structure. From considerations of δ values, the positions of holes or substituting elements are determined.

Introduction

The accurate determination of the structures of heteropolyanions by x-ray diffraction is generally difficult and has been undertaken for compounds containing one kind of heavy atom. Thus some physical techniques, namely IR and Raman spectroscopy, UV and visible spectroscopy, EPR, NMR, etc., have been lately used to explain the properties related to the Keggin structure.¹ For compounds with phosphorus as the central atom, ^{31}P NMR studies have been recently carried out.²⁻⁶ However, only a few compounds were concerned, and no satisfactory correlation between chemical shift and structure had been proposed until now. In the present work, which deals with 24 compounds, we intend to correlate more exactly chemical shift and structure and to shed more light on the

properties of the different series of heteropolyanions. The complexes are related to the $(\text{PM}_{12}\text{O}_{40})^{3-}$ series (noted as PM_{12}) and the $(\text{P}_2\text{M}_{18}\text{O}_{62})^{6-}$ series (noted as P_2M_{18}), $\text{M} = \text{W}$ or Mo .

The structure of PM_{12} consists of a central PO_4 tetrahedron sharing its oxygen atoms (called O_A) with four M_3O_{13} groups (noted as (M_3)). These M_3O_{13} groups, made of three edge-sharing octahedra, are linked together by corners. The α isomer has the well-known Keggin structure (T_d symmetry)^{1,7-9} shown in Figures 1a and 2a. The β isomer¹⁰ is derived from the α by rotating one (M_3) group by $\pi/3$ about a threefold axis (C_{3v} symmetry). "Unsaturated" compounds, i.e., compounds with a "defect-Keggin structure", are derived from $\alpha\text{-PM}_{12}$ by removing one MO_6 octahedron ($\alpha\text{-PM}_{11}$,