

521. Dinuclear Phosphorus and Arsenic Bridged Carbonyl Compounds. Part II.¹

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Complexes of formulæ $M_2(CO)_{10}(PMe_2)_2$ and $M_2(CO)_8(PMe_2)_2$, where $M = Cr, Mo, \text{ or } W$, are described, and spectroscopic evidence for their structure is discussed.

CHATT and THORNTON¹ have described two series of dinuclear chromium, molybdenum, and tungsten carbonyls having phosphorus bridging atoms. By their method of preparation not all members of both series were accessible. We now find that in an aromatic hydrocarbon solvent, reaction between $M(CO)_6$ ($M = Cr, Mo, \text{ or } W$) and tetramethyldiphosphine proceeds smoothly under autogenous pressure, and gives all three compounds



of formula $M_2(CO)_{10}(PMe_2)_2$ (I) at 190° and all three compounds of formula $M_2(CO)_8(PMe_2)_2$ (II) at 250°. Moreover the compounds (I) may well be intermediates in the formation of (II), as they are readily converted into (II) when heated at higher temperature.

The proton magnetic resonance spectra (Table I) of the six products are consistent with the structures suggested earlier.¹

TABLE I.

Chemical shifts (τ) and phosphorus-hydrogen coupling constants [$J(PH)$] for $CDCl_3$ solutions of dinuclear phosphorus-bridged carbonyl complexes.

Compound	τ	Multiplicity	$J(PH)$ (c./sec.)	Compound	τ	Multiplicity	$J(PH)$ (c./sec.)
(I; $M = Cr$)	8.28	Triplet	4.2	(II; $M = Cr$)	7.68	Doublet	10.6
(I; $M = Mo$)	8.31	Triplet	5.3	(II; $M = Mo$)	7.68	Doublet	9.4
(I; $M = W$)	8.15	Triplet*	4.3	(II; $M = W$)	7.56	Doublet	9.8

* Central peak poorly resolved.

Deuteriochloroform solutions of the complexes (I) give rise to the type of spectrum illustrated in the Figure,* in which the central band is a weak one with sharper peaks on either side of it. In contrast, the spectrum² of liquid tetramethyldiphosphine itself consists of a 1 : 2 : 1 triplet ($J = 7$ c./sec.), and we have found that a solution of tetramethyldiphosphine in chloroform gives a spectrum consisting of one singlet only ($\tau, 8.88$). Compounds (II) give rise to a sharp doublet; the splitting being *ca.* 10 c./sec. at both 60 and 100 Mc./sec.

The splitting pattern observed seems to be dependent on the environment of the dimethylphosphido-groups. The doublets obtained from compounds (II) can be attributed to spin-spin coupling of six identical hydrogen nuclei with their adjacent phosphorus nucleus, while the spectra obtained from the compounds (I) might arise from a delicate balance between proton-phosphorus coupling and a simple proton resonance. In this connexion it is of interest that very small side bands occur on the insides of the doublets

* Hayter, *Z. Naturforsch.*, 1963, **18b**, 581, and private communication, has obtained similar spectra from phosphido-bridged metal carbonyls.

¹ Part I, Chatt and Thornton, *J.*, 1964, 1005.

² Marshall, *J. Inorg. Nuclear Chem.*, 1960, **14**, 291.

TABLE 2.

Electronic spectra of hexane or cyclohexane solutions of dinuclear carbonyl complexes. Wavelengths of maximal absorption are given (together with the wavenumber) and molar extinction coefficients (ϵ_{max}). Infections are marked by asterisks.

Compound	Description	λ (m μ) ν (cm. ⁻¹) ϵ	360* 27,800 2,500	280* 35,700 7,000	230 43,500 36,000
(I; M = Cr)	Pale yellow needles				
(I; M = Mo)	Colourless flakes	λ (m μ) ν (cm. ⁻¹) ϵ	359 27,900 7,000	303 33,000 12,000	229* 43,700 56,000
(I; M = W)	Almost colourless prisms	λ (m μ) ν (cm. ⁻¹) ϵ	357 28,000 6,100	301* 33,200 9,900	229* 43,700 49,000
(II; M = Cr)	Red cubes	λ (m μ) ν (cm. ⁻¹) ϵ	369 27,100 7,000	311* 32,200 5,400	230* 43,500 35,000
(II; M = Mo)	Orange prisms	λ (m μ) ν (cm. ⁻¹) ϵ	352 28,400 6,400	310 32,300 26,000	230* 43,500 59,000
(II; M = W)	Orange prisms	λ (m μ) ν (cm. ⁻¹) ϵ	353 28,400 3,700	307 32,600 27,000	224 44,600 65,000

TABLE 3.

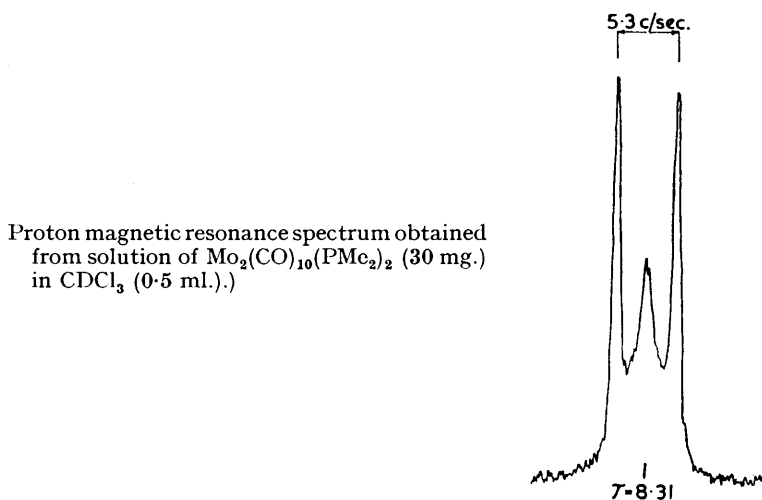
Preparation and properties of dinuclear bridged carbonyl complexes of type I [*e.g.*, μ -tetramethyldiphosphine-bis(pentacarbonylchromium)] and type II [*e.g.*, di- μ -dimethylphosphido-bis(tetracarbonylchromium)].

Compound	M(CO) ₅ used (g.)	Furnace temp. (time)	Yield (%)	M. p.	Analysis (%)		M (solv.)		Dipole moment (D) (solv.)	Infrared spectra* CO bands (cm. ⁻¹)
					Calc.	Found	Calc.	Found		
(I; M = Cr)	2.13	190—200 ^o (23 hr.)	47	129—132 ^o	C 33.2 H 2.4	33.5 2.5	506 530	530	4.6 (C ₆ H ₆)	2073w, sh, 2060m, 1987w, sh, 1951vs, b
(I; M = Mo)†	4.66	190 (24 hr.)	34	143—144	C 28.3 H 2.0	28.3 2.0	594 (CCl ₄)	599	4.8 (C ₆ H ₆)	2079w, sh, 2071m, 1990w, sh, 1957vs, b
(I; M = W)†	5.53	190 (24 hr.)	48	162—164	C 21.8 H 1.6	21.9 1.6	769 (CCl ₄)	722	4.6 (C ₆ H ₆)	2079w, sh, 2071m, 1990w, sh, 1949vs, b
(II; M = Cr)†	1.44	260 (24 hr.)	37	—	C 32.0 H 2.7	32.1 2.7	450 (C ₆ H ₆)	484	1.0 (μ -C ₇ H ₁₀)	2013ms, 1956vs, b
(II; M = Mo)	9.91	250 (24 hr.)	53	—	C 26.8 H 2.3	26.9 2.5	538 (C ₆ H ₆)	522	0.9 (μ -C ₇ H ₁₀)	2028ms, 1963vs, b
(II; M = W)	2.68	250 (25 hr.)	27	—	C 20.2 H 1.7	20.4 1.9	714 (C ₆ H ₆)	722	1.2 (μ -C ₇ H ₁₀)	2026ms, 1956vs, b

* Infrared spectra were determined on chloroform solutions of the complexes (0.3—0.6%). † Known compounds.

obtained from compounds (II), where $M = Mo$ and W . Alternatively, compounds (I) might exist as two forms in solutions with $^1H^{31}P$ coupling modified by exchange processes in one structure but not in the other; the structure of the form in which spin-spin coupling does not occur could be similar to that of the compound ¹ of formula $Fe_2(CO)_8(PMe_2)_2$, a solution of which gives a single, sharp singlet.³

Infrared spectra obtained from the six Group VI compounds show that the carbonyl groups are all terminal. Compounds (I) give four bands in the region of the spectrum ascribed to carbonyl stretching modes, but those of type (II) give only two, one of which is broad. These results are consistent with those reported in Part I.



Values obtained for molecular weights (determined ebullioscopically), and dipole moments of the complexes are consistent with the structures suggested previously.¹ The ultraviolet and visible spectra (Table 2) support the theory that compounds (I) all have a similar structure and those of type (II) another. In each case the molybdenum and tungsten compounds give very similar spectra but that obtained from the chromium compound has fewer bands.

EXPERIMENTAL

M. p.s are corrected and were determined on a Kofler hot-stage apparatus. Proton magnetic resonance spectra were determined by Drs. J. M. Pryce and J. K. Becconsall with Varian A60 and HR100 spectrometers, infrared spectra by Mr. L. H. Cross on a Grubb-Parsons GS2A spectrometer, and ultraviolet spectra by Mrs. R. M. Canadine on a Perkin-Elmer 137 instrument. Microanalyses were carried out by Messrs. W. Brown and A. Olney, the samples being burnt in the presence of potassium dichromate. Dipole moments were determined by Mrs. R. M. Canadine by Chatt and Thornton's method.¹

Preparation of Dinuclear Carbonyl Complexes.—The metal carbonyl (2 mol.) was placed in a Carius tube (diam. 15 mm.). Tetramethyldiphosphine ⁴ (1 mol.), in a sealed glass ampoule, was added to the tube followed by a small glass-encased solid steel cylinder. The tube was swept out with nitrogen, and oxygen-free benzene (5 ml.) added. The tube was cooled in liquid air, evacuated, and sealed. The mixture was allowed to attain room temperature, the ampoule broken by means of the steel cylinder, and the tube heated in a Carius furnace for *ca.* 24 hr. The products were purified by recrystallisation from chloroform, benzene, or light petroleum (b. p. 60–80°). Results of these preparations are summarised in Table 3.

Conversion of Compounds (I) into Compounds (II).—A solution of the compound I (*ca.* 0.1 g.) in oxygen-free benzene (5 ml.) was heated for 23 hr. at 250° in a sealed Carius tube. After

³ Thompson, unpublished work.

⁴ Christen, van der Linde, and Hooge, *Rec. Trav. chim.*, 1959, **78**, 161.

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removal of benzene it was found that, in all three experiments, the product had an identical infrared spectrum with that obtained from the corresponding compound (II).

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