Synthesis of $[M(CO)_4(Ph_2PCHRPPh_2)]$ (M = Cr, Mo, or W; R = COPh or COC_6H_4Me-*p*) and Photochemically Induced Reactions of the Complex $[W(CO)_4\{Ph_2PCH(COPh)PPh_2\}]$: Crystal Structures of the Complexes $[W(CO)_4\{Ph_2POC(Ph)=CHPPh_2\}]$ and $[W(CO)_4(PPh_2OH)(PPh_2CH_2COPh)]$†

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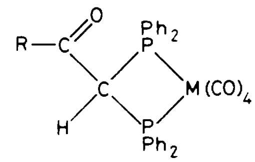
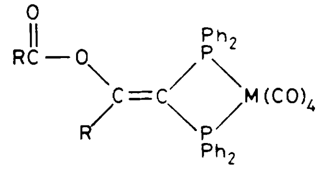
Compounds of type $[M(CO)_4(Ph_2PCH_2PPh_2)]$ (M = Cr, Mo, or W) are deprotonated by $LiBu^n$ and the resultant carbanions are acylated by RCOCl (R = Ph or C_6H_4Me-*p*) to give the complexes $[M(CO)_4\{Ph_2PCH(COR)PPh_2\}]$. These acylated complexes react with NaOMe, reversibly, to give enolate anions $[M(CO)_4\{Ph_2PC(=CO^-R)PPh_2\}]$ or with RCOCl/pyridine to give the complex $[M(CO)_4\{Ph_2P)_2C=CR(OCOR)\}]$. Irradiation of $[W(CO)_4\{Ph_2PCH(COPh)PPh_2\}]$ gives, initially, the six-membered-ring chelate complex $[W(CO)_4\{Ph_2POC(Ph)=CHPPh_2\}]$ (3a), which is in turn converted into $[W(CO)_4(PPh_2OH)(PPh_2CH_2COPh)]$ (4a) in the presence of light and traces of water. Crystals of both (3a) and (4a) are monoclinic, space group $P2_1/c$, with $Z = 4$. Those of (3a) have $a = 17.013(3)$, $b = 10.454(2)$, $c = 19.723(3)$ Å, and $\beta = 114.23(1)$°. Those of (4a) have $a = 18.629(3)$, $b = 9.931(1)$, $c = 18.182(4)$ Å, and $\beta = 94.58(1)$°. Final *R* factors were 0.030 for 3 634 and 0.068 for 4 027 observed reflections, respectively.

We have shown that the substituted Group 6A metal carbonyls of type $[M(CO)_4(Ph_2PCH_2PPh_2)]$ (M = Cr, Mo, or W) are deprotonated by a strong base and the resultant carbanion $[M(CO)_4(Ph_2PCH^-PPh_2)]$ can be alkylated *etc.*, to give $[M(CO)_4(Ph_2PCHRPPh_2)]$ (R = Me, Et, CH_2Ph, $CH_2CH=CH_2$, or $SiMe_3$).[1,2] In the present paper we show that treatment of the above carbanions with either benzoyl chloride or *p*-toluoyl chloride gives the corresponding acyl derivatives $[M(CO)_4\{Ph_2PCH(COR)PPh_2\}]$ as stable, crystalline complexes in good (48—92%) yields.



(1a) M = Cr, R = Ph
(1b) M = Cr, R = C_6H_4Me-*p*
(1c) M = Mo, R = Ph
(1d) M = W, R = Ph
(1e) M = W, R = C_6H_4Me-*p*



(2a) M = Cr, R = Ph
(2b) M = Cr, R = C_6H_4Me-*p*
(2c) M = Mo, R = Ph
(2d) M = W, R = Ph
(2e) M = W, R = C_6H_4Me-*p*

Results and Discussion

Preparative details for these acyl derivatives are in the Experimental section and characterizing analytical, molecular weight, i.r., and n.m.r. data are in Tables 1 and 2. We also found that these acyl derivatives (1a)—(1e) when treated with the acyl halide and pyridine gave the acyl derivatives of the enolates, (2a)—(2e) respectively (see Experimental section and Tables for further details). With three of these complexes, namely (2b), (2d), and (2e), the chemical shifts of the two P nuclei, although similar, were sufficiently different to give an AB pattern but with (2a) and (2c) they were not resolved. We also found that treatment of solutions of the *C*-benzoyl derivatives (1a), (1c), or (1d) with sodium methoxide immediately gave an AB pattern for the ^{31}P-{^1H} n.m.r. spectrum due to the formation of the corresponding enolate anions $[M(CO)_4\{Ph_2PC(=CO^-R)PPh_2\}]$, acidification giving back the benzoyl derivatives.

We noticed that solutions of (1d) were unstable to light, first changing to essentially one product which gave an AX ^{31}P-{^1H} n.m.r. pattern and then more slowly to other products. The progress of these transformations was readily followed by ^{31}P-{^1H} n.m.r. spectroscopy and on irradiation of a solution of (1d) in dry benzene using an n.m.r. tube positioned close to fluorescent light, the initial product of conversion was isolated in 62% yield (see Experimental section). Elemental analysis and molecular weight determination established it to be isomeric with the starting material and the ^{31}P-{^1H} n.m.r. spectrum (Table 2) showed that the chemical shifts of the two P nuclei were very different (by >140 p.p.m.). The structure of this isomerization product was established as the six-membered-ring chelate (3a) by *X*-ray crystallography (see below). We then found that further conversions of this isomerization product were dependent on the presence of water in the solvent and that with vigorously dried benzene as solvent and oven-baked apparatus (3a) was stable to light. Compound (3a) was also stable to wet (*i.e.* undried) benzene, in the absence of light. However, in wet benzene further irradiation caused slow conversion of (3a)

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† Tetracarbonyl(β-diphenylphosphino-α-diphenylphosphinoxystyrene-*PP′*)tungsten and tetracarbonyl(α-diphenylphosphinylacetophenone-*P*)(hydroxydiphenylphosphine-*P*)tungsten.

Supplementary data available (No. SUP 23874, 51 pp.): thermal parameters, structure factors, full bond length and angle data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Melting point, analytical,[a] molecular weight,[b] and i.r.[c] data

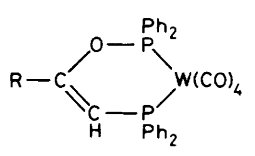
Complex	M.p. (°C)	Analysis (%) C	H	*M*	ν(C=O)	ν(C≡O)	ν(OH)
(1a)	216—219	66.35 (66.25)	4.0 (4.1)	667 (652)	1 665	2 015, 1 927, 1 908, 1 853	
(1b)	196—206	66.9 (66.65)	4.2 (4.25)	670 (666)	1 668	2 019, 1 918, 1 905, 1 860	
(1c)	178—182	61.95 (62.1)	3.7 (3.75)	712 (696)	1 665	2 030, 1 925, 1 920, 1 855	
(1d)	227—230	54.85 (55.1)	3.35 (3.35)	778 (784)	1 668	2 022, 1 918, 1 910, 1 850	
(1e)	200—205	55.85 (55.65)	3.6 (3.55)	784 (798)	1 669	2 022, 1 918, 1 904, 1 860	
(2a)	232—235	67.9 (68.2)	4.05 (4.0)	748 (756)	1 738	2 008, 1 912, 1 892, 1 873	
(2b)	236—239	68.9 (68.9)	4.4 (4.35)	755 (784)	1 745	2 010, 1 925, 1 879, 1 870	
(2c)	221—225	64.25 (64.5)	3.9 (3.8)	799 (800)	1 740	2 019, 1 924, 1 910, 1 885	
(2d)	248—250	57.8 (58.1)	3.25 (3.4)	861 (888)	1 740	2 018, 1 908, 1 896, 1 873	
(2e)	245—250	58.6 (58.9)	3.65 (3.75)	916 (873)	1 750	2 020, 1 920, 1 890, 1 888	
(3a)	190	55.1 (55.1)	3.55 (3.35)	785 (784)		2 023, 1 925, 1 912, 1 882	
(3b)	217—219	55.7 (55.65)	3.5 (3.55)	791 (798)		2 024, 1 923, 1 918, 1 887	
(4a)	199—201	54.0 (53.85)	3.7 (3.5)	791 (802)	1 645 [d]	2 020, 1 930, 1 900, 1 885 [e]	3 070 [e]
(4b)	167—169	54.5 (54.45)	3.7 (3.7)	804 (816)	1 645 [d]	2 026, 1 930, 1 920, 1 887	3 065

[a] Calculated values are in parentheses. [b] Molecular weights were determined osmometrically in chloroform at 30 °C; calculated values are in parentheses. [c] Spectra (cm^{-1}) recorded as Nujol mulls. [d] Recorded as KBr disc. [e] Recorded as a hexachlorobutadiene mull.

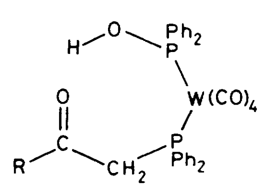
Table 2. Phosphorus-31 and hydrogen-1 n.m.r. parameters

Complex	δ(P) [a]	$^1J(^{183}W-P)$ [b]	$^2J(PP)$ [b]	δ(C*H*) [c]	$^2J(PCH)$ [d]	δ(C*H*$_3$) [c]
(1a)	43.9			7.0	15.7	
(1b)	43.6			7.0	16.2	2.4
(1c)	19.8			7.0	14.4	
(1d)	−7.0	215				
(1e)	−7.2	212				2.4
(2a)	51.2					
(2b)	51.5		28			2.3, 2.1
	51.4					
(2c)	26.5					
(2d)	4.9	211	70			
	4.4	210				
(2e)	5.2	211	73			2.3, 2.1
	4.6	209				
(3a)	139.5 [e]	273	34	6.0		
	−7.0	225				
(3b)	136.6 [e]	272	37	6.0		2.3
	−8.6	222				
(4a)	98.3 [e]	264	27	$\delta(OH) = 8.7$, $^2J(POH) = 4.0$		
	14.3	242		$\delta(CH_2) = 4.1$, $J(PCH_2) = 8.0, 0.5$		
(4b)	98.1 [e]	265	28	$\delta(OH) = 8.8$, $^2J(POH) = 4.0$		2.3
	13.6	240		$\delta(CH_2) = 4.1$, $J(PCH_2) = 8.0, 0$		

[a] δ Values (±0.5 p.p.m.) to high frequency of H_3PO_4. [b] *J* Values ±1 Hz. [c] δ Values (±0.01 p.p.m.) to high frequency of $SiMe_4$. [d] *J* Values ±0.1 Hz. [e] *O*-Bonded phosphorus.



(3a) R = Ph
(3b) R = C_6H_4Me-*p*



(4a) R = Ph
(4b) R = C_6H_4Me-*p*

into one main product ($^{31}P-\{^1H\}$ n.m.r. evidence). This was isolated (see Experimental section) in 20% yield with *ca.* 50% recovery of (3a). Elemental analysis and molecular weight determination indicated a molecular formula of $C_{36}H_{28}O_6P_2W$. A crystal structure determination established the structure to be the hydrolysis product (4a) (see below). The *p*-tolyl derivative (1e) underwent the same sequence of reactions to give (3b) and (4b). The characterization and spectroscopic data are given in Tables 1 and 2.

Crystal Structures of $[W(CO)_4\{Ph_2POC(Ph)=CHPPh_2\}]$ (3a) *and* $[W(CO)_4(PPh_2OH)(PPh_2CH_2COPh)]$ (4a).—An *X*-ray diffraction study on a crystal of the first compound isolated showed that a four- to six-membered chelate ring expansion had occurred, to give the molecular structure shown in Figure 1 [and as (3a)]. Bond lengths and selected angles are given in Table 3, in addition to endocyclic torsion angles around the chelate ring. The co-ordination around W is close to octahedral, allowing for the effect of *PP'*-chelation, and there are no remarkable bond lengths in the structure, nor any significant intermolecular contacts.

The structure of the photohydrolysis product, as determined by *X*-ray diffraction, is shown in Figure 2, with molecular parameters given in Table 3. The six-membered chelate ring of (3a) has been cleaved to give the photohydrolysis product (4a), confirming the presence of C=O and OH, as suggested by the i.r. and n.m.r. spectra respectively. Although ν(O−H)

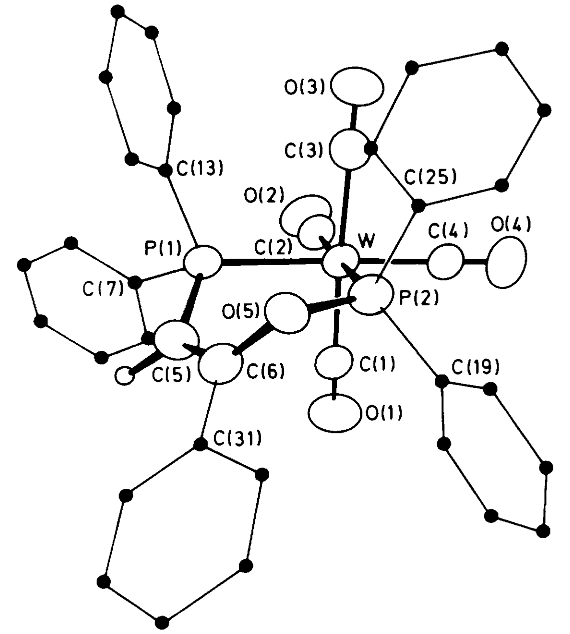


Figure 1. Molecular structure of $[W(CO)_4\{Ph_2POC(Ph)=CHPPh_2\}]$ (3a) showing the principal atomic numbering

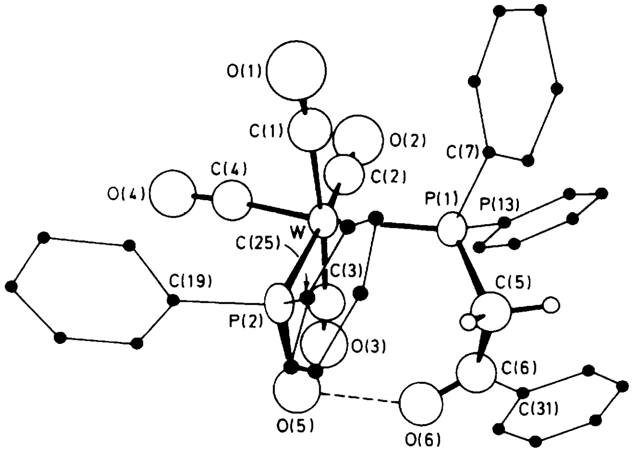
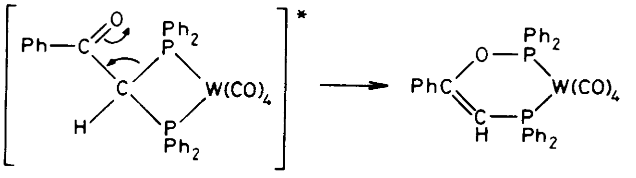


Figure 2. Molecular structure of $[W(CO)_4(PPh_2OH)(PPh_2CH_2COPh)]$ (4a) showing the principal atomic numbering. The dashed line indicates a hydrogen bond



(1d)*

(3a)

Scheme. It is suggested that the benzoyl derivative (1d) on absorption of light goes to an excited state (1d) * which then rearranges to (3a) by an electrocyclic mechanism. Further irradiation of (3a) converts it to an excited state which is then attacked by water to give the ring-opened product (4a)

Table 3. Molecular parameters

	Compound (3a)	Compound (4a)
(*i*) Bond lengths (Å)		
W–C(1)	2.040(7)	1.95(2)
W–C(2)	1.997(7)	1.86(2)
W–C(3)	2.043(7)	2.00(2)
W–C(4)	1.990(8)	1.87(2)
W–P(1)	2.508(2)	2.520(4)
W–P(2)	2.470(2)	2.496(4)
C(1)–O(1)	1.133(8)	1.16(2)
C(2)–O(2)	1.140(7)	1.34(2)
C(3)–O(3)	1.137(8)	1.18(2)
C(4)–O(4)	1.145(8)	1.23(2)
P(1)–C(5)	1.806(6)	1.87(2)
P(2)–O(5)	1.665(4)	1.64(1)
C(5)–C(6)	1.331(8)	1.47(2)
C(6)–O(5)	1.338(7)	—
C(6)–O(6)	—	1.22(2)
P(1)–C(7)	1.845(3)	1.838(8)
P(1)–C(13)	1.825(3)	1.849(8)
P(2)–C(19)	1.820(4)	1.812(8)
P(2)–C(25)	1.811(3)	1.838(8)
C(6)–C(31)	1.492(7)	1.52(2)
(*ii*) Selected bond angles (°)		
P(1)–W–P(2)	83.4(1)	96.1(1)
W–P(1)–C(5)	111.8(2)	119.1(5)
P(1)–C(5)–C(6)	125.2(5)	113(1)
C(5)–C(6)–O(5)	122.2(5)	—
C(6)–O(5)–P(2)	123.3(4)	—
C(5)–C(6)–O(6)	—	121(2)
O(5)–P(2)–W	117.7(2)	114.2(5)
C(5)–C(6)–C(31)	125.2(5)	122(1)
O(5)–C(6)–C(31)	112.6(5)	—
O(6)–C(6)–C(31)	—	117(2)
C(2)–W–P(2)	176.1(2)	171.7(5)
C(4)–W–P(1)	173.0(2)	170.8(5)
C(1)–W–C(3)	172.9(2)	173.9(7)
C–W–C (*cis*)	85.9(3)—92.2(3)	81.6(6)—92.6(8)
C–W–P (*cis*)	88.0(2)—97.6(2)	86.7(5)—93.9(4)
W–C–O	174.0(6)—179.6(4)	173(1)—177(2)
(*iii*) Selected torsion angles (°) *		
P(1)–C(5)–C(6)–O(5)	6.8	—
C(5)–C(6)–O(5)–P(2)	−61.1	—
C(6)–O(5)–P(2)–W	45.8	—
O(5)–P(2)–W–P(1)	4.8	−75.6
P(2)–W–P(1)–C(5)	−38.2	26.5
W–P(1)–C(5)–C(6)	45.8	62.4
P(1)–C(5)–C(6)–O(6)	—	−83.8
C(5)–C(6)–O(6) · · · O(5)	—	9.6
C(6)–O(6) · · · O(5)–P(2)	—	19.3
O(6) · · · O(5)–P(2)–W	—	44.9

* The sign convention is that of W. Klyne and V. Prelog, *Experientia*, 1960, **16**, 521.

in the i.r. spectrum was not identified unambiguously, a broad band at 3 070 cm^{-1} may be due to v(O–H) of a strong internal hydrogen bond. Indeed, although the H atom was not located in the *X*-ray study, the intramolecular oxygen–oxygen distance P–O · · · O=C [2.58(5) Å] is consistent with the presence of a strong chelating hydrogen bond. The angles associated with this interaction are P–O · · · O 112(3)° and O · · · O=C 136(3)°. The endocyclic torsion angles around this hydrogen-bonded ring are given in Table 3, and these show the increased puckering in (4a) compared with the ring in (3a), a feature which is not obvious from Figure 2. A related observation is that the acute P–W–P angle in the six-

Table 4. Fractional atomic co-ordinates, with e.s.d.s in parentheses

(*i*) Compound (3a)

Atom	*x*	*y*	*z*
W	0.223 18(2)	0.127 09(2)	0.073 96(1)
P(1)	0.3539(1)	0.0533(2)	0.0565(1)
P(2)	0.1769(1)	0.2046(2)	−0.0550(1)
C(1)	0.1658(3)	−0.0483(6)	0.0495(2)
O(1)	0.1333(3)	−0.1452(4)	0.0417(2)
C(2)	0.2674(3)	0.0723(6)	0.1802(3)
O(2)	0.2923(3)	0.0429(6)	0.2411(2)
C(3)	0.2766(3)	0.3031(6)	0.1093(3)
O(3)	0.3061(3)	0.4003(4)	0.1313(2)
C(4)	0.1146(4)	0.1949(6)	0.0755(3)
O(4)	0.0519(2)	0.2335(4)	0.0761(2)
C(5)	0.3265(3)	−0.0075(6)	−0.0362(2)
C(6)	0.2732(3)	0.0488(6)	−0.0987(2)
O(5)	0.2392(2)	0.1697(3)	−0.0992(2)
C(7)	0.4183(2)	−0.0832(2)	0.1102(2)
C(8)	0.5082(2)	−0.0818(2)	0.1420(2)
C(9)	0.5539(2)	−0.1919(2)	0.1758(2)
C(10)	0.5097(2)	−0.3032(2)	0.1778(2)
C(11)	0.4198(2)	−0.3045(2)	0.1459(2)
C(12)	0.3741(2)	−0.1945(2)	0.1121(2)
C(13)	0.4340(2)	0.1784(2)	0.0708(2)
C(14)	0.4556(2)	0.2243(2)	0.0143(2)
C(15)	0.5132(2)	0.3261(2)	0.0282(2)
C(16)	0.5492(2)	0.3819(2)	0.0986(2)
C(17)	0.5275(2)	0.3360(2)	0.1551(2)
C(18)	0.4699(2)	0.2342(2)	0.1413(2)
C(19)	0.0708(2)	0.1690(3)	−0.1272(2)
C(20)	0.0354(2)	0.2487(3)	−0.1891(2)
C(21)	−0.0424(2)	0.2161(3)	−0.2476(2)
C(22)	−0.0849(2)	0.1038(3)	−0.2441(2)
C(23)	−0.0495(2)	0.0241(3)	−0.1821(2)
C(24)	0.0283(2)	0.0567(3)	−0.1237(2)
C(25)	0.1829(2)	0.3772(2)	−0.0590(2)
C(26)	0.2515(2)	0.4392(2)	−0.0666(2)
C(27)	0.2567(2)	0.5724(2)	−0.0634(2)
C(28)	0.1935(2)	0.6436(2)	−0.0526(2)
C(29)	0.1249(2)	0.5816(2)	−0.0450(2)
C(30)	0.1197(2)	0.4484(2)	−0.0482(2)
C(31)	0.2467(2)	−0.0051(3)	−0.1749(2)
C(32)	0.1824(2)	0.0548(3)	−0.2356(2)
C(33)	0.1549(2)	0.0011(3)	−0.3063(2)
C(34)	0.1917(2)	−0.1125(3)	−0.3165(2)
C(35)	0.2560(2)	−0.1724(3)	−0.2558(2)
C(36)	0.2835(2)	−0.1187(3)	−0.1851(2)

(*ii*) Compound (4a)

Atom	*x*	*y*	*z*
W	0.252 01(3)	0.177 37(5)	0.123 65(3)
P(1)	0.2473(2)	—0.0749(3)	0.1095(2)
P(2)	0.2725(2)	0.1782(2)	0.2610(2)
C(1)	0.3550(9)	0.1821(13)	0.1101(9)
O(1)	0.4165(9)	0.1940(14)	0.1048(9)
C(2)	0.2270(9)	0.1960(16)	0.0233(9)
O(2)	0.2127(9)	0.2056(17)	−0.0498(9)
C(3)	0.1469(9)	0.1938(14)	0.1380(9)
O(3)	0.0856(8)	0.2104(14)	0.1466(8)
C(4)	0.2638(8)	0.3744(18)	0.1208(7)
O(4)	0.2652(6)	0.4880(14)	0.1229(6)
C(5)	0.2186(8)	−0.1799(13)	0.1873(8)
O(5)	0.2007(6)	0.1437(12)	0.3038(6)
C(6)	0.1441(8)	−0.1524(14)	0.2049(8)
O(6)	0.1305(6)	−0.0589(11)	0.2453(6)
C(7)	0.3363(3)	−0.1457(9)	0.0955(4)
C(8)	0.3693(3)	−0.0992(9)	0.0340(4)
C(9)	0.4387(3)	−0.1418(9)	0.0218(4)
C(10)	0.4752(3)	−0.2308(9)	0.0710(4)
C(11)	0.4422(3)	−0.2773(9)	0.1324(4)
C(12)	0.3728(3)	−0.2348(9)	0.1446(4)
C(13)	0.1908(4)	−0.1470(8)	0.0310(4)
C(14)	0.2092(4)	−0.2674(8)	−0.0023(4)
C(15)	0.1641(4)	−0.3214(8)	−0.0598(4)
C(16)	0.1006(4)	−0.2550(8)	−0.0840(4)
C(17)	0.0821(4)	−0.1346(8)	−0.0507(4)
C(18)	0.1273(4)	−0.0806(8)	0.0068(4)
C(19)	0.2963(6)	0.3452(7)	0.2949(6)
C(20)	0.3681(6)	0.3866(7)	0.3014(6)
C(21)	0.3854(6)	0.5190(7)	0.3215(6)
C(22)	0.3309(6)	0.6099(7)	0.3351(6)
C(23)	0.2591(6)	0.5684(7)	0.3287(6)
C(24)	0.2419(6)	0.4360(7)	0.3085(6)
C(25)	0.3414(4)	0.0746(8)	0.3121(4)
C(26)	0.3379(4)	0.0596(8)	0.3880(4)
C(27)	0.3889(4)	−0.0191(8)	0.4286(4)
C(28)	0.4433(4)	−0.0829(8)	0.3933(4)
C(29)	0.4468(4)	−0.0679(8)	0.3174(4)
C(30)	0.3958(4)	0.0109(8)	0.2768(4)
C(31)	0.0801(6)	−0.2311(11)	0.1702(6)
C(32)	0.0110(6)	−0.1776(11)	0.1716(6)
C(33)	−0.0479(6)	−0.2466(11)	0.1376(6)
C(34)	−0.0377(6)	−0.3691(11)	0.1024(6)
C(35)	0.314(6)	−0.4225(11)	0.1010(6)
C(36)	0.0903(6)	−0.3536(11)	0.1350(6)

membered ring of (3a) [83.4(1)°] has opened out to 96.1(1)° in (4a), which contains only monodentate ligands.

Within the limitations of this structural determination most bond lengths in (4a) are normal (Table 3), the tungsten–carbonyl group C(2)–O(2) deviating most from accepted values. Interestingly, there is a close contact between this O(2) atom in the reference molecule at *x*, *y*, *z* and the hydroxy-oxygen O(5) of the symmetry-related molecule at *x*, $\frac{1}{2} - y$, $\frac{1}{2} + z$. This O · · · O distance is 3.05 Å, which is within the range given by Speakman[3] for a 'long' O · · · O hydrogen bond (3.2—2.8 Å). However, molecular packing diagrams indicate that it would not be stereochemically reasonable for there to be a hydrogen atom more or less on the O(2) · · · O(5) line, and the hydrogen bond is most certainly intramolecular. There are no other significant intermolecular contacts. A preliminary account of these two crystal structures has been given.[4]

We do not know the mechanism by which these light-promoted reactions occur, but a possible route is shown and discussed in the Scheme.

Experimental

The general techniques used were the same as in other recent papers from this laboratory.[5]

[$Cr(CO)_4\{Ph_2PCH(COPh)PPh_2\}$] (1a).—A solution of LiBu^n (0.75 cm^3, 1.2 mmol) in diethyl ether was added to a solution of [$Cr(CO)_4(Ph_2PCH_2PPh_2)$] (0.468 g, 0.85 mmol) in benzene (*ca.* 10 cm^3). The resultant mixture was stirred at *ca.* 20 °C for 2 h, then cooled to 0 °C and PhCOCl (0.186 cm^3, 1.6 mmol) added. The mixture was then stirred at *ca.* 20 °C for 4 h after which the product was isolated from the organic layer. It formed yellow-orange plates from $CHCl_3$–MeOH. Yield 0.514 g, 0.78 mmol, 92%.

The following were prepared similarly in the yields shown: (1b), 77%; (1c), 48%; (1d), 80%; (1e), 66%.

[$Cr(CO)_4\{(Ph_2P)_2C=CPh(OCOPh)\}$] (2a).—A mixture of (1a) (0.504 g, 0.772 mmol) and pyridine (0.5 cm^3) in benzene

(10 cm^3) was treated with PhCOCl (0.098 cm^3, 0.85 mmol) and the resultant mixture refluxed gently for 10 min. The mixture was then cooled to *ca.* 20 °C, water (10 cm^3) added and the product isolated from the organic layer. It formed orange-red prisms from $CHCl_3$–MeOH. Yield 0.536 g, 92%.

The following were prepared similarly: (2b), 76%; (2c), 80%; (2d), 92%; (2e), 71%.

$[W(CO)_4\{Ph_2POC(Ph)=CHPPh_2\}]$ (3a).—A solution of (1d) (0.405 g, 0.516 mmol) in dry benzene (16 cm^3) was irradiated for 10 h in a 10-mm n.m.r. tube, positioned 2 cm from and parallel to a fluorescent tube (20 W, 56 cm long), using aluminium foil as reflector. The mixture was then passed through Florisil to remove brown material. The required product was then isolated and formed yellow prisms from CH_2Cl_2–MeOH. Yield 0.25 g, 0.316 mmol, 62%. The corresponding *p*-tolyl analogue (3b) was prepared similarly, in 58% yield.

$[W(CO)_4(PPh_2OH)(PPh_2CH_2COPh)]$ (4a).—A solution of (3a) (0.203 g, 0.258 mmol) in undried benzene (8 cm^3) was irradiated as above in a 10-mm n.m.r. tube for 5 d. The dark solution was then passed through Florisil to remove dark material and then chromatographed on silica gel (Fluka GF 254) as a thin layer, developing with benzene–light petroleum (b.p. 60—80 °C) (4 : 3 v/v). The required product was extracted using CH_2Cl_2 and formed yellow prisms from CH_2Cl_2–MeOH. Yield 0.045 g, 0.051 mmol, 20%. Unchanged starting material (3a) (0.098 g, 0.124 mmol, 48.5%) was recovered from the chromatogram.

The corresponding *p*-tolyl analogue (4b) was prepared similarly, in 21% yield.

Crystal Data.—For (3a). $C_{36}H_{26}O_5P_2W$, $M = 784.4$, monoclinic, $a = 17.013(3)$, $b = 10.454(2)$, $c = 19.723(3)$ Å, $\beta = 114.23(1)^\circ$, $U = 3\,199(1)$ Å^3, $Z = 4$, $D_c = 1.63$ g cm^{-3}, $F(000) = 1\,544$, space group $P2_1/c$, graphite-monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 38.3 cm^{-1}.

For (4a). $C_{36}H_{28}O_6P_2W$, $M = 802.4$, monoclinic, $a = 18.629(3)$, $b = 9.931(1)$, $c = 18.182(4)$ Å, $\beta = 94.58(1)^\circ$, $U = 3\,353(1)$ Å^3, $Z = 4$, $D_c = 1.59$ g cm^{-3}, $F(000) = 1\,584$, space group $P2_1/c$, graphite-monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 36.5 cm^{-1}.

Structure Determination.—Measurements were made, using a Syntex $P2_1$ diffractometer, on crystals of dimensions 0.23 × 0.33 × 0.50 mm (3a) and 0.22 × 0.28 × 0.63 mm (4a), both grown from dichloromethane–methanol. For each compound cell dimensions and their standard deviations were obtained by least-squares treatment of the setting angles for 15 reflections having $35 < 2\theta < 40^\circ$. Intensities of all independent reflections with $4 < 2\theta < 45^\circ$ were measured in the ω—2θ scan mode using scan speeds, according to a prescan intensity, between 2 and 29° min^{-1}, and with the scans running from 1° below $K_{\alpha1}$ to 1° above $K_{\alpha2}$. The structure analyses used those reflections having $I > 2\sigma(I)$, *viz.* 3 634 for (3a) and 4 027 for (4a); the numbers of ' unobserved ' reflections were 228 and 235, respectively. Corrections were applied for Lorentz, polarization, and transmission factors (A^*); the A^* values for the full data sets were 2.06—3.58 for (3a), 1.97—9.63 for (4a).

Solution by Patterson and difference syntheses was followed by full-matrix least-squares refinement using the SHELX program system.[6] For (3a) the carbonyl group atoms and W, P, O, and C atoms in the chelate ring were assigned anisotropic thermal parameters. For (4a) only W and P atoms were refined anisotropically; some twinning in the crystal of (4a) resulted in several dubious carbonyl bond distances and fairly large e.s.d.s throughout. In both structures all phenyl rings were refined as rigid groups with idealized D_{6h} geometry, the C atoms having individual isotropic thermal parameters and C–C distances of 1.395 Å. All H atoms were found in difference maps for (3a); only the methylene and a few phenyl H atoms were found for (4a). For both structures all H atoms [except for the $^-$OH proton in (4a)] were included in the calculation at idealized positions with C–H fixed at 1.08 Å; their isotropic temperature factors were treated as single parameters in each structure which refined to $U_{iso.} = 0.107(6)$ and 0.9(1) Å^2 for (3a) and (4a), respectively. The refinements converged at $R = 0.030$, $R' = (\Sigma w\Delta F^2/\Sigma wF_o^2)^{\frac{1}{2}} = 0.032$ for (3a) and $R = 0.068$, $R' = 0.078$ for (4a), employing the weighting scheme $w = 1/[\sigma^2(F_o) + gF_o^2]$. The final values of g [0.0 for (3a), 0.0004 for (4a)] were chosen to give the smallest systematic variation of $w\Delta^2$ with the magnitude of F_o. The final difference maps showed no significant residual electron density apart from two peaks of *ca.* 2.0 e Å^{-3} close to the W atom in (4a). Complex neutral-atom scattering factors were calculated from the analytical approximation and coefficients given in ref. 7. The final atomic co-ordinates for both structures are given in Table 4.

Acknowledgements

We thank the S.E.R.C., the University of Leeds, and the Iraqi Ministry of Higher Education and Scientific Research for support.

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Received 9*th August* 1983; *Paper* 3/1397