Reactivity of Group 6 Cationic Complexes. Part 5.[1] Photochemical Water Reduction by a Chromium(II) Metallorganic System and *X*-Ray Crystal and Molecular Structure of *cis*- and *trans*-$[Cr(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}_2]^+$ *

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Laser irradiation at 488 nm of a methanol solution of $[Mo(CO)_3(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]BF_4$ (**1**) gives $[Mo(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}(MeOH)]BF_4$ (**2**), as a mixture of *cis* and *trans* isomers. Irradiation at 458 nm of methylene chloride or methanol solutions of the corresponding chromium derivative $[Cr(CO)_3(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]BF_4$ (**4**) gives a mixture of *cis* and *trans*-$[Cr(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}_2]BF_4$ (**5**), together with unidentified products. The solid-state structures of both *cis*-and *trans*-(**5**) were determined by single-crystal *X*-ray diffraction. The structural models were refined to *R* = 0.078, (*R'* = 0.080) for 770 independent reflections [*cis*-(**5**)] and to *R* = 0.046 (*R'* = 0.049) for 2 439 independent reflections [*trans*-(**5**)]. Crystal data: *cis*-(**5**), orthorhombic, space group *Pbca*, *a* = 17.738(5), *b* = 26.370(6), *c* = 11.344(7) Å; *trans*-(**5**), monoclinic, space group *I2/a*, *a* = 16.167(5), *b* = 19.814(6), *c* = 16.106(2) Å, β = 90.20(2)°. Complex (**5**) photochemically reduces water, being transformed into the chromium(III) cluster $[Cr_4(\mu\text{-}OH)_6(\eta\text{-}C_5Me_5)_4][BF_4]_2$ (**6**). Quantum-yield data are reported for this process.

Since the problem of solar-energy utilization was stated considerable efforts have been made to find appropriate systems for solar-energy storage in the form of hydrogen produced through water reduction.[2–4]

The main way of hydrogen photoproduction from water involves sensitized redox reactions.[2–5] Alternative methods employ metal hydrides,[6] simple metal ions in acidic media,[7] or complex metal ions;[8] even in the latter case, hydrogen production is believed to occur through metal hydride intermediates.[8] Photochemical hydrogen production in these systems cannot always be considered a real energy storing process: some of the metal ions employed are thermodynamically capable of reducing water in dilute acids also in the dark.[2,9]

As part of our study of the reactivity of cationic Group 6 carbonyl derivatives,[1] we report here some photosubstitution reactions of the four-legged piano-stool complexes $[M(CO)_n(\eta\text{-}C_5Me_5)\{P(OMe)_3\}_{4-n}]BF_4$ (M = Mo, *n* = 3; M = Cr, *n* = 2 or 3), the photoreduction of water by $[Cr(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}_2]BF_4$, and the *X*-ray crystal structures of *cis*- and *trans*-$[Cr(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}_2]BF_4$.

Results and Discussion

Laser irradiation (488 nm) of a methanol solution of $[Mo(CO)_3(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]BF_4$, (**1**), causes slow evolution of CO, the colour of the solution turning from yellow to deep red with simultaneous growth of a new absorption at 466 nm in the electronic spectrum. The i.r. spectrum of the solution indicates the formation of a cationic dicarbonyl species [ν(CO) 1 980 and 1 905 cm^{-1}]. After work-up a red crystalline solid, identified from analytical and spectroscopic data as $[Mo(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}(MeOH)]BF_4$ (**2**), was isolated in 47% yield. The methanol molecule is co-ordinated to molybdenum as shown by the isolation of (**2**) as a mixture of *cis* and *trans* isomers (see Experimental section). Methanol can be slowly substituted at room temperature by CO, giving back (**1**) and by $P(OMe)_3$ giving a mixture of *cis*- and *trans*-$[Mo(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}_2]BF_4$ (**3**). Co-ordination of a solvent molecule to a 16-electron fragment, generated by thermal or photochemical ligand removal, is straightforward in cyclopentadienyl Group 6 carbonyls[10] as in other classes of metal complexes.[11]

When a methanol or methylene chloride solution of the chromium derivative $[Cr(CO)_3(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]BF_4$ (**4**) is irradiated (458 nm), $[Cr(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}_2]BF_4$ (**5**) is the only carbonyl derivative formed in the reaction (33% yield based on Cr). We have been unable to characterize other species present in the reaction mixture. As expected, (**5**) forms in high yield (75%) when CH_2Cl_2 solutions of (**4**) are irradiated in the presence of $P(OMe)_3$.

Fractional crystallization of complex (**5**) from acetone–Et_2O allowed separation of the *cis* and *trans* isomers.

Structural Characterization of cis- *and* trans-(**5**).—The molecular structures of both isomers are compared in Figure 1, and an ORTEP diagram of the *trans* isomer is given in Figure 2 together with the atomic labelling; relevant structural parameters for both species are listed in Table 1. The following discussion will be devoted to a comparison of the two solid-state structures. However, the poor quality of the data obtained for *cis*-(**5**) (see Experimental section) allows discussion of only the gross structural features of this isomer. Both isomers present the expected four-legged piano-stool geometry in which the Cr atom is seven-co-ordinated, the C_5Me_5 ligand being regarded as a formal tridentate six-electron donor group (as such acting as

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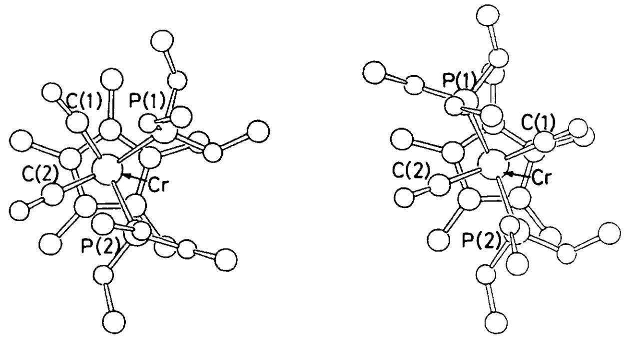
* *cis*- and *trans*-Dicarbonyl(η-pentamethylcyclopentadienyl)bis(trimethyl phosphite)chromium(II) tetrafluoroborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Relevant bond distances (Å) and angles (°) for *trans* and *cis*-(**5**)

	trans	*cis*		*trans*	*cis*
Cr–P(1)	2.292(2)	2.33(1)	P(1)–O(4)	1.59(1)	1.60(2)
Cr–P(2)	2.288(2)	2.31(1)	P(1)–O(5)	1.58(1)	1.56(2)
Cr–C(1)	1.85(1)	1.79(3)	O(3)–C(3)	1.44(1)	1.39(4)
Cr–C(2)	1.85(1)	1.83(3)	O(4)–C(4)	1.45(1)	1.45(4)
C(1)–O(1)	1.15(1)	1.21(4)	O(5)–C(5)	1.44(1)	1.46(3)
C(2)–O(2)	1.14(1)	1.15(4)	P(2)–O(6)	1.57(1)	1.58(2)
Cr–C(9)	2.21(1)	2.26(2)	P(2)–O(7)	1.57(1)	1.62(2)
Cr–C(10)	2.22(1)	2.21(2)	P(2)–O(8)	1.58(1)	1.58(2)
Cr–C(11)	2.22(1)	2.16(2)	O(6)–C(6)	1.46(1)	1.47(4)
Cr–C(12)	2.21(1)	2.19(2)	O(7)–C(7)	1.44(1)	1.36(4)
Cr–C(13)	2.20(1)	2.25(2)	O(8)–C(8)	1.47(1)	1.50(3)
P(1)–O(3)	1.58(1)	1.62(2)	C_{ring}–C_{methyl} (mean)	1.50(1)	1.50(1)
P(1)–Cr–P(2)	123.1(1)	81.9(3)	O(3)–P(1)–O(4)	105.1(2)	106(1)
C(1)–Cr–P(1)	76.4(2)	76(1)	O(4)–P(1)–O(5)	104.7(2)	110(1)
C(1)–Cr–P(2)	80.7(2)	125(1)	O(3)–P(1)–O(5)	99.3(3)	99(1)
C(2)–Cr–P(1)	75.4(2)	126(1)	O(6)–P(2)–O(7)	107.6(2)	106(1)
C(2)–Cr–P(2)	76.0(2)	80(1)	O(7)–P(2)–O(8)	99.2(2)	100(1)
C(2)–Cr–C(1)	124.1(3)	74(1)	O(6)–P(2)–O(8)	104.5(2)	106(1)
Cr–P–O (mean)	115(5)	114(4)	C_{ring}–C_{ring}–C_{methyl} (mean)	125(1)	126(3)
P–O–C (mean)	124(3)	124(4)			



(*a*) (*b*)

Figure 1. Comparison of the structures of *cis*- (*a*) and *trans*-(**5**) (*b*) showing the relevant atom labelling; H atoms of the Me groups are omitted for clarity

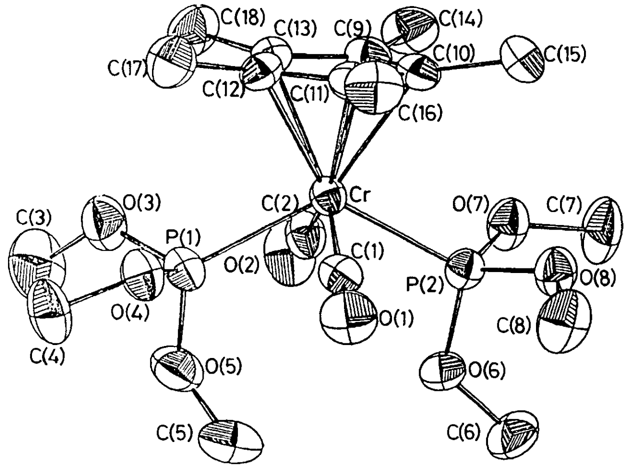


Figure 2. ORTEP drawing of *trans*-(**5**); H atoms of the Me groups are omitted for clarity

$C_5Me_5^-$). The four monodentate ligands are two CO groups and two $P(OMe)_3$ groups; their co-ordination defines the *cis* and *trans* isomerism at the metal centre. The Cr–P bond distances are comparable [mean 2.32(1) in *cis*-(**5**) and 2.290(2) Å in *trans*-(**5**)] while a larger difference is shown by the Cr–C distances [1.81(3) *versus* 1.85(1) Å in *cis*- and *trans*-(**5**), respectively], which can be attributed to the 'sliding effect'[12] due to different treatment of the atomic thermal motion (see Experimental section) and will not be discussed further.

An interesting comparison arises from the co-ordination angles around the Cr atoms (see Table 1) which clearly show that a somewhat more tense steric situation is realized in *cis*-(**5**) where the two bulky $P(OMe)_3$ groups are neighbours [*cis* P–Cr–P angle in *cis*-(**5**) 81.9(3)° *versus* an average of 77(2)° for *cis* angles in *trans*-(**5**)].

It is worth noting that the steric interaction between the two $P(OMe)_3$ groups is only partly accommodated by the opposite C–Cr–C angle [74(1)° in *cis*-(**5**)] being also alleviated by a slight flattening of the stool with respect to the *trans* isomer [*trans* angles average 123.6(7) and 125.5(7)° in *trans*- and *cis*-(**5**) respectively].

The C_5Me_5 ligands also adopt two slightly different rotameric configurations with respect to the piano-stool legs (see Figure 1), most certainly in order to optimize non-bonding interactions with the underlying ligands. In this respect it should be noted that the C_5 plane is almost parallel to the plane defined by the P and C(CO) atoms in *trans*-(**5**) (1° tilt) while is tilted *ca.* 10° in *cis*-(**5**).

Finally, the methyl groups in both *cis*- and *trans*-(**5**) appear to bend away from the Cr atom [mean elevation above the C_5 ring 0.2 Å in both *cis*- and *trans*-(**5**)]. The C(Me)–C(ring) as well as P–O and O–C distances agree with the values expected for this kind of interaction.

Water Photoreduction.—When the photolysis of complex (**4**) is performed in wet CH_2Cl_2 or MeOH a deep green-blue solution is observed instead of the yellow or pale green colour observed under strictly anhydrous conditions. The behaviour of (**5**) under the above conditions is exactly the same. On the contrary CH_2Cl_2 or MeOH solutions of (**5**) remain unchanged in the presence of an excess of water when kept in the dark. These observations prompted us to investigate the photoreaction of complex (**5**) in the presence of an excess of water: laser irradiation at 458 nm results both in a quick change of the colour from yellow to blue and in abundant gas evolution.

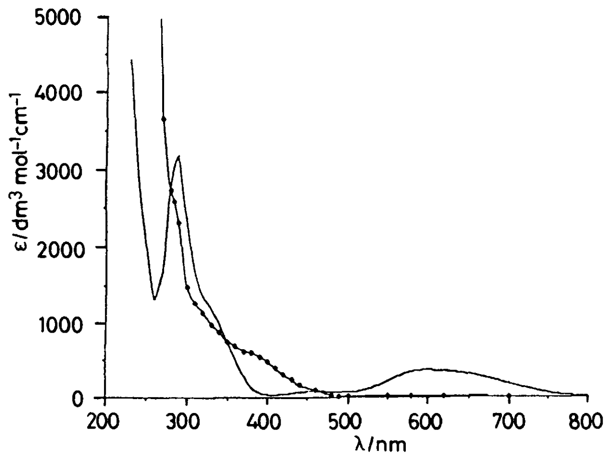


Figure 3. Electonic spectra of (——) $[Cr(CO)_2(\eta\text{-}C_5Me_5)\{P(OMe)_3\}_2]BF_4$ (**5**) and (-•-•-) $[Cr_4(\mu\text{-}OH)_6(\eta\text{-}C_5Me_5)_4][BF_4]_2$ (**6**). Solvent: CH_2Cl_2. In the case of complex (**6**) the absorption coefficients ε are referred to a single chromium

Table 2. Mean quantum yields for evolution of H_2

Run	α^*_i	$10^3\Phi_{Hi}$	$10^3\Phi_{Hi,i-1}$
1	0.36	1.4	1.4
2	0.52	3.3	6.9
3	0.72	4.2	7.1
4	0.86	4.5	7.4

α^*_i = Fraction of CO dissociated from complex (**4**) in run *i*; Φ_{H_i} = quantum yield of hydrogen evolved in run *i*; $\Phi_{Hi,i-1}$ = quantum yield of hydrogen evolved between conversion α^*_{i-1} and α^*_i. Solutions (0.083 mol dm^{-3}, 10 cm^3) of (**4**) were irradiated at 457.9 nm (0.170 W); the laser beam was enlarged with a lens to a diameter of 5 mm. Irradiation times ranged from 24 to 98 min.

Gas chromatographic analysis of the gas phase showed the presence of hydrogen and carbon monoxide.

Addition of Et_2O caused the precipitation of a blue crystalline solid which was identified by *X*-ray analysis as $[Cr_4(\mu\text{-}OH)_6(\eta\text{-}C_5Me_5)_4][BF_4]_2$ (**6**); the crystal structure of (**6**) had been previously reported by Rheingold and co-workers[13] and reference is made to that paper for details.

The above reported experimental data, *viz.* the reduction of water to hydrogen performed by Cr^{II} which is oxidized to Cr^{III}, are described by equation (1).

$$4\,(\mathbf{5}) + H_2O \xrightarrow{h\nu} [Cr_4(\mu\text{-}OH)_6(\eta\text{-}C_5Me_5)_4][BF_4]_2 + 2H_2 + 8CO + 8P(OMe)_3 + 2HBF_4 \quad (1)$$

The measured magnetic moment of complex (**6**) [3.59 B.M. (*ca.* 3.33×10^{-23} J T^{-1}) at 290 K] agrees well with most reported data[14] for polynuclear chromium(III) derivatives with bridging OH groups. The electronic spectrum (Figure 3) compares well with those reported for oligomers containing high-spin Cr^{3+} and bridging OH;[14,15] the absorption at 285 nm can hence be attributed to L–M charge transfer while the bands at 435 and 580 nm can be attributed to $^4A_{2g} \longrightarrow {}^4T_{1g}$ and $^4A_{2g} \longrightarrow {}^4T_{2g}$ transitions.[16] The ^1H n.m.r. spectrum in CD_2Cl_2 solution shows a broad absorption ($\nu_{\frac{1}{2}}$ = 300 Hz) at δ −64.5 attributable to the C_5Me_5 ligand bound to the paramagnetic metal centre.[10b,17]

The progress of the photoreaction was followed by recording electronic and i.r. spectra of the solution at different irradiation times. The progressive decrease in intensity of the CO absorptions of complex (**5**) in the i.r. spectrum and the growth in the u.v.–visible spectrum of an absorption at 580 nm, typical for a high-spin chromium(III) complex,[16] were observed; when the irradiation is interrupted, a slow decrease, broadening, and shift of the band at 580 nm (see Figure 3) is observed until the u.v. spectrum is superimposable upon that of an authentic sample of $[Cr_4(\mu\text{-}OH)_6(\eta\text{-}C_5Me_5)_4][BF_4]_2$.

These data and those reported in the literature for chromium(III) hydroxides of different nuclearity[14,15] suggest the formation of the tetranuclear cluster (**6**) in a relatively slow thermal reaction, which follows the photoreaction giving a chromium(III) hydroxo-complex of lower nuclearity.

More detailed information on the photoprocess can be obtained by analysis of the quantum yields for both hydrogen evolution and the photodecarbonylation of (**5**). A set of experiments was performed which used identical solutions of complex (**5**) from the same batch; each solution was irradiated, under identical experimental conditions, for different times and the samples were analysed by g.l.c. (gas phase), i.r. and u.v. spectrophotometry (solution). From the above measurements, the extent of CO loss from the original complex and the amount of H_2 in the gas phase were determined; the number of photons used to generate one hydrogen atom is reported in Table 2 as a function of the evolution of CO from the irradiated mixtures (the Appendix gives the details for the calculation of quantum yields).

It can be seen immediately that a sharp increase in the rate of evolution of H_2 (doubling of the quantum yield for hydrogen evolution) takes place when photodissociation of CO reaches around 50%. Calculation of the mean quantum yield for evolution of CO (method in Appendix) reveals it to be approximately constant in each experiment (0.086 ± 0.010); the amount of light (*F*) absorbed by the carbonylated species (**5**) is then calculated (Appendix).

A mean quantum yield for the evolution of H_2, Φ_H, in each experiment is computed as the ratio of the H_2 evolved in the reaction mixture (*Q*) to the above (*F*) number of photons. From the amount of H_2 evolved and from the energy absorbed within two consecutive experiments *i* and *i* + 1, we can deduce the value of $\Phi_{H(i,i+1)} = (Q_{i+1} - Q_i)/(F_{i+1} - F_i)$. For conversion degrees under 50%, Φ_H of the order of 0.002 is observed, while there is a five-fold increase when > 50% of CO has been evolved (see Table 2).

A detailed mechanistic study of these photoprocesses is not our purpose, but what these qualitative data suggest is that a series of kinetically distinct steps occurs. The photodecarbonylation of (**5**) and the formation of a metal aqua complex are probably the initial photoprocesses analogously to what has been reported for water photoreduction in the presence of $[Re_2(CO)_{10}]$[8l,m] affording the tetranuclear cluster $[Re_4(CO)_{12}(\mu\text{-}OH)_4]$.

Experimental

All reactions were carried out under a nitrogen atmosphere by using standard Schlenk techniques. All solvents were refluxed over a suitable drying agent and distilled and stored under nitrogen. The complexes $[Mo(CO)_3(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]BF_4$ (**1**) and $[Cr(CO)_3(\eta\text{-}C_5Me_5)\{P(OMe)_3\}]BF_4$ (**4**) were prepared as described previously.[18,19]

The solutions were usually irradiated by a Spectraphysics model 19 argon-ion laser source. An Helios Italquartz model UV 13 F medium-pressure mercury-vapour arc lamp was used for preparative purposes.

I.r. spectra were recorded on a Perkin-Elmer 283-B spectrophotometer, n.m.r. spectra on a Varian XL-100 spectrometer; chemical shifts are referred to $SiMe_4$.

G.c. analyses for H_2 and CO in the vapour phase were performed by using a Dani 3200 instrument equipped with a stainless-steel column packed with molecular sieves.

Table 3. Crystal data and intensity-collection parameters for *cis*- and *trans*-(**5**) *

	cis	*trans*
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	*I*2/*a*
a/Å	17.738(5)	16.167(5)
b/Å	26.370(6)	19.814(6)
c/Å	11.344(7)	16.106(2)
β/°		90.20(2)
U/Å^3	5 306.2	5 159.2
D_c/g cm^{-3}	1.45	1.49
μ(Mo-K_α)/cm^{-1}	5.5	5.7
Min. transmission factor	0.41	0.87
Crystal dimensions (mm)	0.25 × 0.3 × 0.2	0.15 × 0.35 × 0.25
θ Range/°	2.5—20	2.5—25
Octants of reciprocal space explored	h,k,l	$\pm h,k,l$
No. of measured reflections	1 484	3 680
No. observed [$I > 2\sigma(I)$]	770	2 439
Final R and R'	0.078, 0.080	0.046, 0.049
ω Scan width/°	$0.5 + 0.35 \tan\theta$	$0.6 + 0.35 \tan\theta$

* Details in common: formula $C_{18}H_{33}BCrF_4O_8P_2$; M_r 578.2; $Z = 8$; prescan speed, 5° min^{-1}; prescan acceptance, $\sigma(I)/I$ 0.5; maximum scan time 90 s; requested $\sigma(I)/I$ 0.02; scan mode ω—2θ.

Syntheses.—[Mo(CO)$_2$(η-C$_5$Me$_5$){P(OMe)$_3$}(MeOH)]BF$_4$ (**2**). A solution of complex (**1**) (0.696 g, 1.32 mmol) in methanol (50 cm^3) was irradiated with the laser source for 8.5 h (1 W, 488 nm). The photolysis was accompanied by a change in the colour of the solution from yellow to red together with a noticeable gas evolution (carbon monoxide by g.c. analysis). This gas was periodically removed. Evaporation of the resulting solution to small volume and addition of diethyl ether (20 cm^3) gave a red solid. The product, a mixture of *cis*- and *trans*-(**2**), was filtered off and vacuum dried. Yield *ca.* 47% (Found: C, 35.95; H, 5.20. $C_{16}H_{28}BF_4MoO_6P$ requires C, 36.25; H, 5.30%). I.r. (Nujol): 3 320br [ν(OH)]; 1 960s and 1 875s cm^{-1} [ν(CO)]. Both the *cis* and *trans* isomers, though not separated, were detected through ^{1}H n.m.r. spectroscopy (CDCl$_3$): isomer A, δ 3.80 [d, $J_{PH} = 12$, P(OMe)$_3$], 3.5 (d, $J_{ab} = 5$, C$H_3{}^a$OH^b), and 1.91 (s, C$_5$Me$_5$); isomer B, δ 3.79 [d, $J_{PH} = 12$, P(OMe)$_3$], 3.5 (d, $J_{ab} = 5$ Hz, C$H_3{}^a$OH^b), and 1.95 (s, C$_5$Me$_5$).

[Mo(CO)$_2$(η-C$_5$Me$_5$){P(OMe)$_3$}$_2$]BF$_4$ (**3**). A solution of complex (**1**) (0.690 g, 1.31 mmol) in methanol (50 cm^3) was irradiated with the laser source for 8.5 h (1 W, 488 nm) and the gas evolved was periodically removed. Five equivalents of P(OMe)$_3$ were then added to the resulting solution which was kept in the dark at room temperature 10 d. Over this period a change in colour from red to orange was observed. After evaporation to 10 cm^3, addition of diethyl ether (20 cm^3), and cooling at −78 °C, an orange microcrystalline solid precipitated. The solid, a mixture of *cis*- and *trans*-(**3**), was filtered off and vacuum dried. Yield *ca.* 35% (Found: C, 34.10; H, 5.70. $C_{18}H_{33}BF_4MoO_8P_2$ requires C, 34.75; H, 5.30%). I.r. (Nujol): ν(CO) 1 985s and 1 910vs cm^{-1}. The *cis* and *trans* isomers were detected by ^{1}H n.m.r. spectroscopy (CD$_3$OD): δ 3.86 [m, P(OMe)$_3$, signals of both isomers overlapping], 2.00 (s, C$_5$Me$_5$, isomer A), and 1.86 (s, C$_5$Me$_5$, isomer B).

[Cr(CO)$_2$(η-C$_5$Me$_5$){P(OMe)$_3$}$_2$]BF$_4$ (**5**). *Method* (*a*). Trimethylphosphite (2.47 mmol) was added to a solution of [Cr(CO)$_3$(η-C$_5$Me$_5$){P(OMe)$_3$}]BF$_4$ (**4**) (1.190 g, 2.47 mmol) in dichloromethane (50 cm^3). The solution was irradiated with the mercury-vapour arc lamp for 15 min. After evaporation to small volume (*ca.* 10 cm^3) and addition of diethyl ether (20 cm^3) a deep green solid precipitated; the suspension was cooled at −78 °C for a few hours and filtered. After vacuum drying the solid was recrystallized from a diethyl ether–acetone mixture giving yellow crystals of *cis*- and *trans*-(**5**), yield 1.075 g (75%). The *trans*/*cis* ratio in the isolated product was approximately 2:1 (Found: C, 37.0; H, 5.50. $C_{18}H_{33}BCrF_4O_8P_2$ requires C, 37.4; H, 5.7%). I.r. (Nujol): *cis*-(**5**), ν(CO) 1 910vs and 1 970s; *trans*-(**5**), ν(CO) 1 910s and 1 980vs cm^{-1}. ^{1}H N.m.r. (CDCl$_3$, 100 MHz): *cis*-(**5**), δ 3.85 [18 H, t, $^3J + {}^5J = 10.9$, P(OMe)$_3$] and 1.81 (15 H, s, C$_5$Me$_5$); *trans*-(**5**), δ 3.90 [18 H, t, $^3J + {}^5J = 10.9$ Hz, P(OMe)$_3$] and 1.80 (15 H, s, C$_5$Me$_5$).

Method (*b*). Complex (**4**) (0.60 g, 1.24 mmol) was dissolved in CH$_2$Cl$_2$ (40 cm^3). The solution was irradiated with the mercury-vapour arc lamp for 10 min. After evaporation to 20 cm^3 and addition of diethyl ether (20 cm^3), a small amount of dark solid precipitated which was filtered off. By addition of diethyl ether (20 cm^3) to the resulting solution and cooling at −78 °C for a few hours, 0.237 g (33% yield based on Cr) of a mixture of *cis*- and *trans*-(**5**) (*trans*/*cis* ratio 2:1) was obtained.

[Cr$_4$(μ-OH)$_6$(η-C$_5$Me$_5$)$_4$][BF$_4$]$_2$ (**6**). Water (0.05 cm^3) was added to a solution of complex (**5**) (0.298 g, 0.52 mmol) in methanol (30 cm^3). The mixture was irradiated with the laser source for 200 min (0.5 W, 457 nm) with periodical renewal of the nitrogen atmosphere. The initial yellow colour turned to deep blue and an abundant gas evolution (H$_2$ and CO, g.c. analysis) was observed. After evaporation to small volume and addition of diethyl ether (15 cm^3), blue crystals of (**6**) precipitated. The solid was filtered off and vacuum dried. Yield *ca.* 60% (Found: C, 46.3; H, 6.05. $C_{40}H_{66}B_2Cr_4F_8O_6$ requires C, 46.9; H, 6.45%). I.r. (Nujol): 530vs cm^{-1}. ^{1}H N.m.r. (CDCl$_3$; 100 MHz); δ −64.5 (br s, C$_5$Me$_5$).

X-*Ray Crystallography.*—Crystal data and details of measurements for *cis*- and *trans*-(**5**) are reported in Table 3. Diffraction intensities were collected at room temperature by the ω—2θ scan method on an Enraf-Nonius CAD-4 diffractometer with Mo-K_α radiation (λ = 0.710 69 Å) and reduced to F_o values. Due to poor diffraction and rapid decay under *X*-ray exposure of the crystals of *cis*-(**5**) only a very limited data set could be obtained. The structures were solved by direct methods and refined by full-matrix least-squares calculations. For all computations the SHELX 76[20] and 86[21] programs were used with the analytical scattering factors, corrected for real and imaginary parts of the anomalous dispersions, taken from ref. 22.

For *trans*-(**5**) all atoms, except H, were treated anisotropically, while anisotropy was confined to the Cr and P atoms in the case of *cis*-(**5**) because of the limited number of observations available. For both species the H atoms were added in calculated positions (C–H 1.08 Å) and refined 'riding' on their corresponding C atoms. A common isotropic thermal parameter was refined for the H atoms in both *cis*- and *trans*-(**5**) (0.12 and 0.054 Å^2, respectively). An absorption correction was applied by the Walker and Stuart method[23] after complete structural models were obtained and all atoms refined isotropically. Residual peaks in the final Fourier difference maps were about 0.5 e Å^{-3} for both species, in the proximity of the Cr atoms. As is often the case, orientational disorder of the BF$_4^-$ anions was found in crystals of *trans*-(**5**). There are two 'half' BF$_4^-$ units placed around crystallographic two-fold axes in the unit cell with the B atoms at 0.25, *y*, 0.0 and 0.75, *y*, 0.0 respectively. While the first BF$_4^-$ unit is well behaved, the second does not adopt an orientation compatible with the crystallographically imposed symmetry, showing four 50% positions for the F atoms, which were treated accordingly.

Final atomic co-ordinates for *cis*- and *trans*-(**5**) are listed in Tables 4 and 5.

Table 4. Fractional atomic co-ordinates of *cis*-(**5**)

Atom	*x*	*y*	*z*
Cr	0.359 8(2)	0.088 2(2)	0.209 0(4)
P(1)	0.299 7(4)	0.166 6(3)	0.222 8(8)
P(2)	0.420 0(5)	0.117 5(3)	0.376 2(9)
C(1)	0.261 5(18)	0.073 2(11)	0.199 7(29)
O(1)	0.198 8(13)	0.056 6(8)	0.185 5(19)
C(2)	0.344 9(18)	0.033 8(13)	0.307 1(34)
O(2)	0.338 1(12)	0.000 5(9)	0.371 0(21)
O(3)	0.256 7(13)	0.184 9(8)	0.103 7(19)
O(4)	0.237 0(11)	0.165 5(7)	0.324 6(16)
O(5)	0.353 5(11)	0.213 0(6)	0.240 8(17)
O(6)	0.469 0(11)	0.072 0(7)	0.425 6(18)
O(7)	0.370 7(13)	0.138 1(7)	0.487 1(19)
O(8)	0.476 5(11)	0.163 2(7)	0.360 8(18)
C(3)	0.178 5(17)	0.182 7(13)	0.094 3(34)
C(4)	0.211 7(22)	0.210 9(14)	0.384 7(36)
C(5)	0.343 2(17)	0.265 9(11)	0.205 3(32)
C(6)	0.522 9(24)	0.078 3(15)	0.523 5(34)
C(7)	0.320 8(22)	0.106 9(14)	0.542 2(34)
C(8)	0.481 5(18)	0.210 9(11)	0.432 6(27)
C(9)	0.474 0(9)	0.093 0(6)	0.120 5(18)
C(10)	0.451 7(9)	0.041 6(6)	0.133 7(18)
C(11)	0.383 7(9)	0.034 5(6)	0.069 5(18)
C(12)	0.364 1(9)	0.081 5(6)	0.016 7(18)
C(13)	0.419 9(9)	0.117 7(6)	0.048 2(18)
C(14)	0.548 8(11)	0.114 4(11)	0.157 0(28)
C(15)	0.489 2(16)	−0.003 4(8)	0.188 8(24)
C(16)	0.340 1(16)	−0.013 8(8)	0.051 2(30)
C(17)	0.304 7(16)	0.092 3(14)	−0.074 2(25)
C(18)	0.431 2(20)	0.169 3(8)	−0.004 5(28)
B	0.113 1(9)	0.334 9(7)	0.224 2(14)
F(1)	0.082 5(9)	0.379 9(7)	0.192 9(14)
F(2)	0.127 8(9)	0.307 5(7)	0.125 0(14)
F(3)	0.178 1(9)	0.343 1(7)	0.283 8(14)
F(4)	0.063 2(9)	0.309 0(7)	0.292 9(14)

Table 5. Fractional atomic co-ordinates of *trans*-(**5**)

Atom	*x*	*y*	*z*
Cr	0.043 59(5)	0.451 63(4)	0.236 05(5)
P(1)	0.095 12(10)	0.529 72(8)	0.327 59(10)
P(2)	0.014 01(9)	0.342 80(8)	0.272 89(10)
O(1)	0.216 8(3)	0.403 4(2)	0.265 7(3)
O(2)	−0.090 1(3)	0.468 6(2)	0.361 8(3)
O(3)	0.042 9(3)	0.596 8(2)	0.333 8(3)
O(4)	0.186 3(2)	0.553 6(2)	0.306 1(3)
O(5)	0.098 6(3)	0.510 2(2)	0.422 7(3)
O(6)	0.034 0(3)	0.332 4(2)	0.367 7(2)
O(7)	−0.080 7(2)	0.327 2(2)	0.259 6(3)
O(8)	0.051 9(2)	0.278 7(2)	0.228 9(3)
C(1)	0.149 8(4)	0.421 1(3)	0.257 7(4)
C(2)	−0.037 7(4)	0.460 4(3)	0.315 7(4)
C(3)	0.018 3(6)	0.633 4(5)	0.406 7(6)
C(4)	0.227 7(4)	0.606 4(4)	0.352 9(5)
C(5)	0.148 1(6)	0.455 0(4)	0.452 6(5)
C(6)	0.017 1(5)	0.270 0(3)	0.413 4(4)
C(7)	−0.121 1(4)	0.262 5(3)	0.252 7(6)
C(8)	0.139 6(4)	0.258 5(4)	0.234 3(6)
C(9)	−0.053 0(2)	0.459 6(2)	0.139 0(3)
C(10)	0.012 7(2)	0.419 7(2)	0.107 3(3)
C(11)	0.084 9(2)	0.460 4(2)	0.105 0(3)
C(12)	0.063 9(2)	0.525 5(2)	0.135 2(3)
C(13)	−0.021 3(2)	0.525 0(2)	0.156 2(3)
C(14)	−0.142 8(4)	0.440 4(4)	0.141 2(5)
C(15)	0.004 5(5)	0.352 4(3)	0.066 1(4)
C(16)	0.166 6(4)	0.441 0(4)	0.067 6(4)
C(17)	0.119 1(4)	0.586 6(3)	0.131 0(5)
C(18)	−0.072 9(4)	0.585 2(3)	0.180 9(5)
B(1)	0.2500	0.244 9(5)	0.0000
F(1)	0.2873	0.284 4(5)	0.0586
F(2)	0.1909	0.206 1(5)	0.0357
B(2)	0.750 00	0.263 48(34)	0.000 00
F(5)	0.808 14	0.220 84(34)	−0.032 49
F(6)	0.672 05	0.239 32(34)	−0.017 12
F(7)	0.758 37	0.326 61(34)	−0.036 99
F(8)	0.760 89	0.269 51(34)	0.083 67

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Appendix

Reliable quantum yield data for both the decarbonylation and hydrogen-evolution processes, at any degree of conversion of complex (**5**), would require knowledge of the light absorption features for each molecular species present in the reaction mixture. The real problem is the determination of the fraction of light effectively absorbed by (**5**). This difficulty was partially circumvented by irradiating (**5**) with the 457.8-nm blue emission of an argon-ion laser, *i.e.* at the wavelength corresponding to a quasi-isosbestic point in the visible absorption spectra of the irradiated solutions of (**5**).

A simplifed model is used here in which a molecular species A [(**5**) in our system] is photoconverted into a species B, B being the whole of the photoproducts. In the case of total absorption of monochromatic radiation of wavelength λ, species A absorbs the fraction $\varepsilon_A c_A/(\varepsilon_A c_A + \varepsilon_B c_B)$ of the light I_0 impinging on the sample, where ε_A and ε_B are the molar absorptions at λ of A and B respectively.

The rate of disappearance of A may then be written as in equation (A1). With $n_A = n_A{}^0\ (1 - \alpha)$, this can be transformed

$$\frac{dn_A}{dt} = -\ \Phi I_0 \cdot \frac{\varepsilon_A c_A}{\varepsilon_A c_A + \varepsilon_B c_B} \qquad \text{(A1)}$$

into a differential equation, in α, the extent of reaction. With a constant intensity of light, I_0, separation of variables, and integration of equation (A2) between 0 and t^* (the irradiation

$$\frac{d\alpha}{dt} = \frac{\Phi I_0}{n_A{}^0} \cdot \frac{(1-\alpha)\varepsilon_A}{\varepsilon_A + (\varepsilon_B - \varepsilon_A)\alpha} \qquad \text{(A2)}$$

time at which the conversion α^* is measured) the expression (A3) for Φ is finally obtained. The quantity of light absorbed by

$$\Phi = \left\{\alpha^*\left(1 - \frac{\varepsilon_B}{\varepsilon_A}\right) - \frac{\varepsilon_B}{\varepsilon_A}\ln(1 - \alpha^*)\right\}\frac{n_A{}^0}{I_0 t^*} \qquad \text{(A3)}$$

A, U_A, is now easily calculated from $U_A = \alpha^* n_A{}^0/\Phi$ which comes from the definition of Φ.

The above treatment can clearly be invalidated by energy-transfer processes.

As far as our system is concerned, preliminary runs showed the presence of three quasi-isosbestic points at 458, 375, and 283 nm (Figure 2). The samples were then irradiated at 457.9 nm and the above treatment was applied to the decarbonylation reaction [α^* was the ratio of the CO lost to that initially present in (**5**) and mean quantum-yield data are obtained for conversion α^*].

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