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SYNTHESIS AND STRUCTURE OF PENTACARBONYL(MESITYLDIPHENYLMETHYLENEPHOSPHINE)-CHROMIUM(0)

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Summary

Mesityldiphenylmethylenephosphine (I), a stable all-carbon substituted phosphaalkene, reacts with $Cr(CO)_5 \cdot THF$ to furnish the title compound II, a relatively air-stable complex. Spectral data suggest a close structural similarity between the free and the complexed ligand and indicate I to be a ligand of moderate basicity towards chromium. X-ray crystal and molecular structure determination showed the phosphaalkene moiety to be nearly planar with a typically short P=C bond length of 1.679(4) Å and a C—P—C bond angle of 109.8(2)°. From a discussion of the bond lengths, it is tentatively concluded that in II, I is a π-acceptor of intermediate strength.

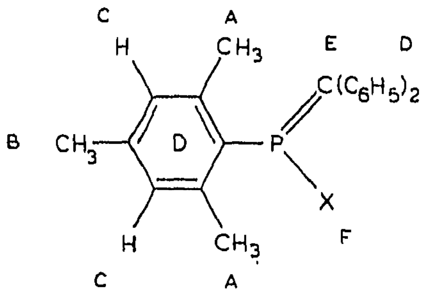
Introduction

The chemistry of trivalent phosphorus in the two-coordinate, $p\pi$-hybridized state is developing rapidly. For many years the compounds of this type which could be synthesized were generally unstable [1—4], unless the structural element, e.g. —P=C<, was incorporated into a charged and [5,6] or [7] delocalized system. Recently, the interest has increasingly turned to the study of stable compounds containing more or less localized double bonds of phosphorus to first row elements, in particular to nitrogen [8] and to carbon [9].

In most of the stable phosphaethenes, a heteroatom is directly attached to the P=C bond [9a,c,d]; these heteroatoms clearly have a strong influence on the stability of these compounds. Mesityldiphenylmethylenephosphine [9b] (I) is remarkable in being a phosphaethene with carbon substituents only. Its struc-

TABLE 1

SPECTRAL DATA OF I AND II



(I, X = : ;
II, X = $Cr(CO)_5$)

Compound	^1H NMR [a]				^{13}C NMR [a]					^{31}P NMR [b]	IR (ν(CO)) cm^{-1})	UV [c]
	A	B	C	D	A^d	B^d	D	E	F			
I	2.27 (s, 6 H)	2.19 (s, 3 H)	6.69 (s, 2 H)	7.60— 6.75 (m, 10 H)	22.06 [e] (d, ^3J(PC) = 8.8 Hz)	20.96 (s)	144.9— 125.5 (m)	193.37 (d, ^1J(PC) = 43.5 Hz)	—	233.06	—	254 (4.20) 268 (3.01) 324 (2.84)
II	2.52 (s, 6 H)	2.19 (s, 3 H)	6.78 (d, 2 H) ^4J(PH) = 2 Hz)	6.98 (m, 5 H); 7.41 (s, 5 H)	22.42 (d, ^3J(PC) = 5.9 Hz)	21.06 (s)	143.8— 127.9 (m)	190.94 (d, ^1J(PC) = 32.3 Hz)	221.4 [f] (d, ^2J(PC) = 3 Hz); 214.8 [g] (d, ^2J(PC) = 16 Hz)	237.3	1955, 1901 (C_6H_{12}) 2068, 1951 ($CHCl_3$)	253 (4.73) 402 (4.28)

[a] $CDCl_3$, δ from Me_4Si as internal standard. [b] $CDCl_3$, δ from 85% H_3PO_4 as external standard. [c] THF, λ in nm (log ε). [d] C^A and C^B had a signal intensity ratio of 2 : 1. [e] The previously assigned resonance at δ =22.67 [9b] was due to an impurity. [f] CO_{trans}. [g] CO_{cis}; the *trans/cis* assignment is based on the intensity ratio of the two signals being 1 : 4.

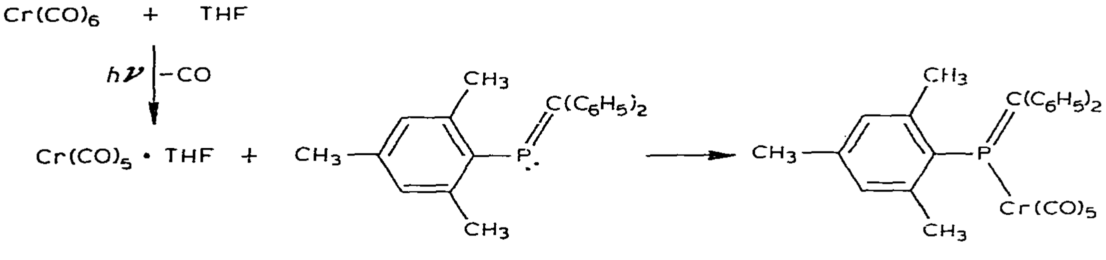
ture as an essentially localized phosphaethene has been derived from its spectral data and by comparison with less substituted analogs [9b]; nevertheless, it seemed desirable to confirm the structure assignment by an X-ray crystal structure determination.

As I is rather air-sensitive and difficult to handle, it was hoped that a more stable derivative could be obtained by the formation of a transition metal complex. Although only a limited number of crystal and molecular structures have been determined for transition metal complexes of phosphine ligands containing two-coordinate phosphorus [10,12], the available data justified the expectation that the structures of the free and the complexed ligand would be essentially similar. Furthermore, it was of interest to observe the properties of I as a transition metal ligand. While several transition metal complexes were investigated, as will be reported elsewhere, we describe here the preparation, characterization and molecular structure of pentacarbonyl(mesityldiphenylmethylenephosphine)chromium(0) (II).

Results

Synthesis of II

The synthesis of II was accomplished by the photochemical procedure reported by Strohmeier and Müller [13]. A solution of I in THF was added to that of $Cr(CO)_5 \cdot THF$, which had been obtained by irradiation of $Cr(CO)_6$ in THF. After 20 h at room temperature, the solution was evaporated. Recrystallization of the residue from n-pentane afforded yellow crystals of II, m.p. 170—171°C, in 89% yield.



(I) (II)

As expected, II is more stable than I. In the crystalline state it was unreactive towards water and oxygen; however, in solution (e.g. in THF) slow oxidation occurs, as evidenced by the ^1H NMR spectrum and by the appearance of a green color of Cr^{III} compounds. Nevertheless, recrystallization from n-pentane could be performed without special precautions. So far, we have not succeeded in liberating I from II by treatment with bases such as pyridine, DBU *, or triethylphosphine.

Spectral investigations

The spectral data of II are presented in Table 1, together with those of I for comparison. The similarity in the NMR resonances and coupling constants of all the three types of nuclei observed is striking and greater than expected. For

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* DBU = 1,5-diazabicyclo[5.4.0]undec-5-ene.

instance, larger downfield shifts of the ^{31}P NMR resonance were observed when 2,4,6-triphenylphosphorine [10], diaza- or triazaphospholes [12] were complexed to pentacarbonylchromium. Obviously, the factors which determine the ^{31}P chemical shift are not yet well understood [12,14,15]. However empirically the observed similarity in the spectra of I and II can be taken to indicate a close similarity in (electronic) structure between the free and the complexed ligand (vide infra).

The ^{13}C signals for the CO groups *trans* and *cis* to the phosphine ligand were assigned on the basis of their relative intensity (1 : 4); both the chemical shifts and the coupling constants to phosphorus have the expected values [12]. Because of the small range of the available data, reliable conclusions about the donor properties of I are difficult. The same situation arises with respect to the IR frequencies of the CO groups which, moreover, are strongly solvent dependent. However, if one compares the data of Table 1 with those in literature [10,12], I appears to be a slightly stronger donor towards $Cr(CO)_5$ than 2,4,6-triphenylphosphorin and a weaker donor than triphenylphosphine.

In the UV spectrum of II, the absorption of I at 324 nm, which is ascribed to a $n \rightarrow \pi^*$ transition, has disappeared, as is expected when the lone pair on phosphorus is involved in complexation. The observed absorption of II at 402 nm is probably due to a charge transfer band ($Cr \rightarrow CO$) of the metal carbonyl system [10]. The mass spectrum of II is remarkable for its relative simplicity. Although the usual fragmentation pattern is observed [10,12], none of the ion intensities exceeds 16% (I^+) except that of ICr^+ (100%).

Molecular and crystal structure of II

Crystals of II are triclinic with space group $P\bar{1}$ and 2 molecules in a unit cell of dimensions: $a = 10.040(1)$, $b = 11.644(1)$, $c = 11.889(1)$ Å, $\alpha = 107.23(1)$, $\beta = 104.83(1)$, $\gamma = 83.59(1)°$. 3342 reflexions with intensities above the 2σ level were measured on a NONIUS CAD4 diffractometer with graphite monochromatized Cu-K_α radiation. No absorption correction was applied.

Structure determination and refinement

Cr, P and the five CO groups were found from an $E^2 - 1$ Patterson synthesis. A ΔF-synthesis revealed the remaining C atoms and in a later stage the H atoms. Block-diagonal least-squares refinement, anisotropic for Cr, P, C and O and isotropic for H, converged to $R = 0.053$. A weighting scheme $w = 1/(5.4 + F_0 + 0.013F_0^2)$ was employed and an extinction correction was included. Anomalous dispersion of Cr and P was taken into account. The final coordinates are listed in Table 2. Tables of structure factors can be obtained from the authors on request.

The numbering of the atoms and the shape of the complex are indicated in Fig. 1. Bond distances and angles are listed in Table 3. The phosphaethene group as a whole is not exactly planar, but the part comprising P, C(6), C(7) and C(13), is planar within the limits of accuracy (see Table 4), as are the 3 benzene rings. The two phenyl groups C(7)—C(12) and C(13)—C(18) are rotated out of the plane of the phosphaethene group by 70 and 37°, respectively. The mesityl group is nearly perpendicular to the phosphaethene group (81°). These rotations are the result of the steric interaction between the rings

(Continued on p. 218)

TABLE 2

FINAL COORDINATES AND THEIR CALCULATED STANDARD DEVIATIONS (Cr, P $\times 10^5$, C, O $\times 10^4$, H $\times 10^3$)

	x	*y*	*z*
Cr	11740(6)	24775(6)	11349(5)
P	30504(9)	26098(8)	28243(8)
C(1)	−314(5)	2243(5)	−225(4)
C(2)	2008(5)	3411(5)	462(4)
C(3)	279(5)	3924(5)	1862(5)
C(4)	284(5)	1621(5)	1847(4)
C(5)	1990(5)	1042(4)	302(3)
C(6)	4724(4)	2834(3)	3002(3)
C(7)	5155(4)	3042(4)	1972(4)
C(8)	5604(5)	4167(4)	2074(4)
C(9)	6056(6)	4380(6)	1165(6)
C(10)	6082(6)	3476(6)	132(6)
C(11)	5660(6)	2351(6)	3(5)
C(12)	5192(5)	2126(4)	929(4)
C(13)	5861(4)	2834(4)	4085(4)
C(14)	5719(5)	3315(5)	5271(4)
C(15)	6821(6)	3296(5)	6250(4)
C(16)	8081(6)	2799(5)	6052(5)
C(17)	8249(5)	2336(5)	4901(5)
C(18)	7160(4)	2356(4)	3923(4)
C(19)	2815(4)	2194(3)	4121(3)
C(20)	3103(4)	1102(4)	4175(4)
C(21)	2866(5)	694(4)	5149(4)
C(22)	2342(6)	1520(4)	6056(4)
C(23)	2045(5)	2684(4)	5967(4)
C(24)	2256(4)	3040(3)	5018(3)
C(25)	3660(5)	50(4)	3213(5)
C(26)	2121(8)	1156(7)	7103(6)
C(27)	1879(5)	4314(4)	4962(3)
O(1)	−1192(4)	2092(5)	−1066(3)
O(2)	2399(4)	4003(5)	17(5)
O(3)	−310(5)	4796(4)	2228(4)
O(4)	−256(5)	1118(5)	2284(4)
O(5)	2474(5)	169(4)	−219(4)
H(8)	579(6)	469(5)	280(5)
H(9)	634(6)	525(5)	123(6)
H(10)	631(6)	366(5)	−47(5)
H(11)	564(6)	173(5)	−60(5)
H(12)	487(5)	141(4)	86(4)
H(14)	485(4)	365(4)	538(4)
H(15)	658(5)	354(4)	703(5)
H(16)	879(6)	269(5)	680(5)
H(17)	914(5)	204(5)	472(5)
H(18)	722(5)	209(4)	311(4)
H(21)	314(5)	−7(5)	521(4)
H(23)	167(5)	323(4)	657(4)
H(251)	309(6)	4(5)	243(5)
H(252)	453(6)	28(5)	321(4)
H(253)	386(6)	−70(5)	347(5)
H(261)	131(7)	79(6)	678(6)
H(262)	287(8)	72(6)	748(6)
H(263)	176(7)	173(6)	761(7)
H(271)	245(7)	473(6)	461(6)
H(272)	108(7)	434(5)	435(6)
H(273)	172(6)	480(5)	570(5)

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°)

P—Cr	2.356(1)	CrPC(6)	130.8(2)	C(14)C(13)C(18)	117.3(4)
P—C(6)	1.679(4)	CrPC(19)	118.8(2)	C(13)C(14)C(15)	121.1(5)
P—C(19)	1.822(5)	C(6)PC(19)	109.8(2)	C(14)C(15)C(16)	119.8(5)
Cr—C91)	1.874(5)	PCrC(1)	175.5(2)	C(15)C(16)C(17)	120.1(5)
Cr—C(2)	1.893(7)	PCrC(2)	93.5(2)	C(16)C(17)C(18)	120.4(5)
Cr—C(3)	1.895(6)	PCrC(3)	94.6(2)	C(13)C(18)C(17)	121.2(5)
Cr—C(4)	1.896(7)	PCrC(4)	86.9(2)	PC(19)C(20)	119.4(3)
Cr—C(5)	1.891(4)	PCrC(5)	89.3(1)	PC(19)C(24)	120.3(3)
C(1)—O(1)	1.134(6)	C(1)CrC(2)	89.4(3)	C(20)C(19)C(23)	120.2(4)
C(2)—O(2)	1.137(10)	C(1)CrC(3)	88.9(2)	C(19)C(20)C(21)	118.5(4)
C(3)—O(3)	1.143(7)	C(1)CrC(4)	90.4(3)	C(19)C(20)C(25)	122.2(5)
C(4)—O(4)	1.141(9)	C(1)CrC(5)	87.3(2)	C(21)C(20)C(25)	119.3(5)
C(5)—O(5)	1.151(6)	C(2)CrC(3)	87.0(3)	C(20)C(21)C(22)	122.3(5)
C(6)—C(7)	1.489(7)	C(2)CrC(4)	176.8(2)	C(21)C(22)C(23)	117.9(5)
C(6)—C(13)	1.486(5)	C(2)CrC(5)	91.5(2)	C(21)C(22)C(26)	120.6(5)
C(7)—C(8)	1.394(7)	C(3)CrC(4)	89.8(3)	C(23)C(22)C(26)	121.4(5)
C(7)—C(12)	1.381(5)	C(3)CrC(5)	176.0(3)	C(22)C(23)C(24)	122.3(4)
C(8)—C(9)	1.368(10)	C(4)CrC(5)	91.7(3)	C(19)C(24)C(23)	118.8(4)
C(9)—C(10)	1.364(9)	CrC(1)O(1)	178.3(5)	C(19)C(24)C(27)	121.6(4)
C(10)—C(11)	1.375(10)	CrC(2)O(2)	174.2(4)	C(23)C(24)C(27)	119.5(4)
C(11)—C(12)	1.402(10)	CrC(3)O(3)	175.6(5)		
C(13)—C(14)	1.393(7)	CrC(4)O(4)	179.2(5)		
C(13)—C(18)	1.397(6)	CrC(5)O(5)	179.1(4)		
C(14)—C(15)	1.389(7)	PC(6)C(7)	118.0(3)		
C(15)—C(16)	1.378(8)	PC(6)C(13)	127.2(4)		
C(16)—C(17)	1.361(8)	C(7)C(6)C(13)	114.8(4)		
C(17)—C(18)	1.381(6)	C(6)C(7)C(8)	119.9(4)		
C(19)—C(20)	1.403(6)	C(6)C(7)C(12)	121.6(5)		
C(19)—C(24)	1.408(5)	C(8)C(7)C(12)	118.5(5)		
C(20)—C(21)	1.390(8)	C(7)C(8)C(9)	121.6(5)		
C(20)—C(25)	1.513(7)	C(8)C(9)C(10)	119.8(7)		
C(21)—C(22)	1.389(7)	C(9)C(10)C(11)	120.3(7)		
C(22)—C(23)	1.384(7)	C(10)C(11)C(12)	120.2(6)		
C(22)—C(26)	1.501(10)	C(7)C(12)C(11)	119.6(5)		
C(23)—C(24)—	1.382(8)	C(6)C(13)C(14)	123.6(4)		
C(24)—C(27)	1.506(6)	C(6)C(13)C(18)	119.1(4)		

and the carbonyl groups C(2)O(2) and C(4)O(4). Cr is octahedrally coordinated to the C atoms of the 5 carbonyl groups and to the P, the Cr—C(P) bonds making angles between 86.9 and 93.5°. The lengths of the 4 Cr—C bonds at

TABLE 4

PLANARITY OF THE PHOSPHAETHENE GROUP [a]

	A(Å)	B(Å)
P	0.081	—0.002
C(6)	0.021	0.005
C(7)	—0.045	—0.002
C(13)	0.007	—0.002
C(19)	—0.052	—0.201
Cr	—0.013	—0.114

[a] A = distances from the best plane through P, C(6), C(7), C(13), C(19), Cr. B = distances from the best plane through P, C(6), C(7) and C(13).

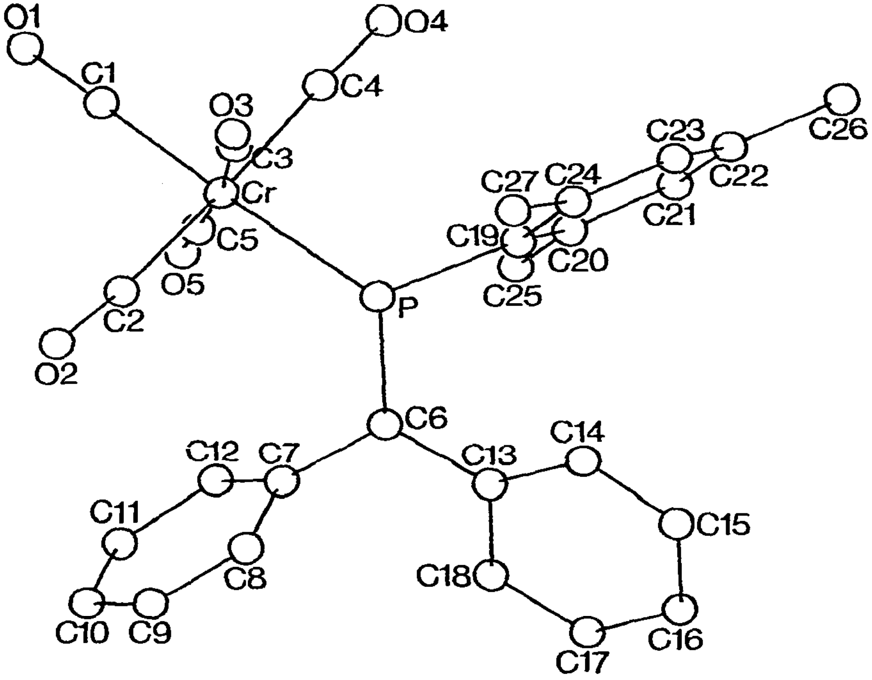


Fig. 1. Projection onto the plane of P, C(6), C(7), C(13), C(19) and Cr.

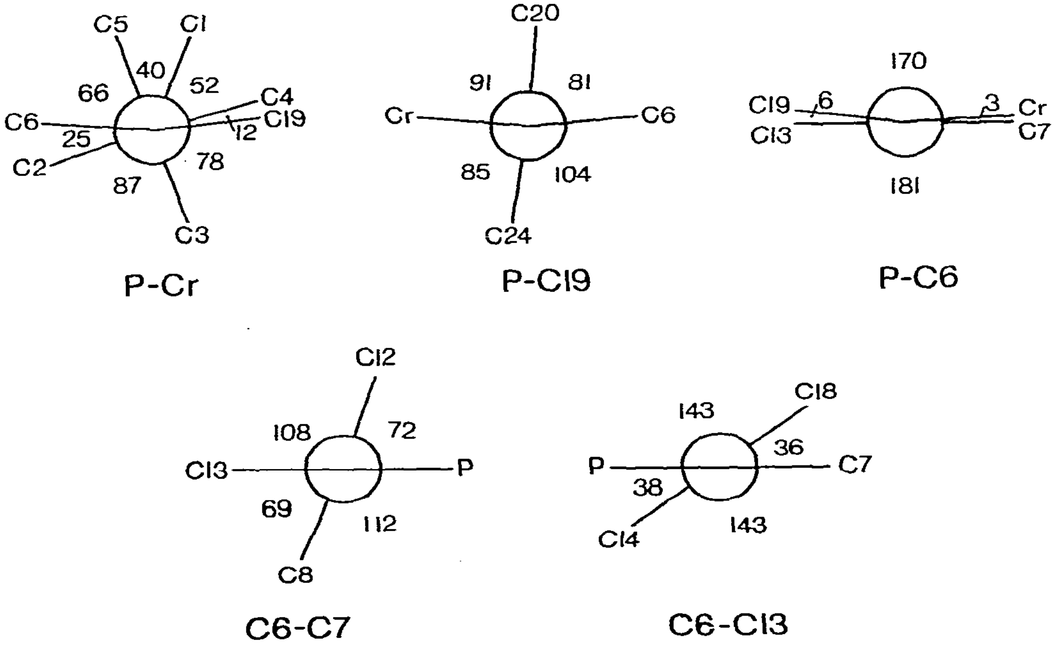
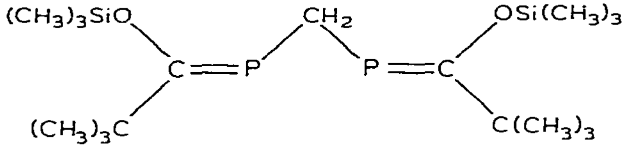


Fig. 2. Newman projections along the bonds of the phosphaethene group.

approximately right angles to Cr—P are equal within the limits of accuracy (av. 1.894(7) Å), the fifth is significantly shorter (1.874(5) Å). The deviations of the CO axes of the 5 carbonyl groups from the radial CrC directions are 1.7, 5.8, 4.3, 0.8 and 0.9° in order of numbering. The positions of the Cr octahedron and the benzene rings relative to phosphaethene groups are illustrated in the Newman projections of Fig. 2. The packing of molecules involves normal Van der Waals contacts.

Discussion

Of the greatest interest in connection with the problem of bonding in II (and thus indirectly in I, vide supra) are the near-planarity around the P=C bond and the P=C bond distance of 1.679 Å. This value is close to that reported for methylenephosphine (CH_2=PH; 1.670 Å [3a]) and, interestingly, to that of triphenylmethylenephosphorane ($(C_6H_5)_3P=CH_2$; 1.661 Å). It is significantly shorter than P=C bond lengths in delocalized systems, which generally are between 1.72 and 1.76 Å (cf. ref. 14 for a summary [6b,12]. A notable exception is III, in which the P=C bond (1.695 Å) is surprisingly short considering the presumably strong interaction with the oxygen atom [14].

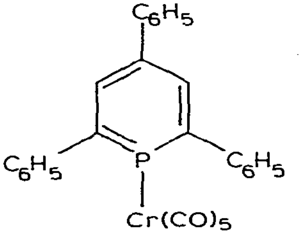


(III)

The bond angle at phosphorus (C(6)PC(19)) of 109.8° is the largest for any two-coordinate phosphorus compound investigated so far; CH_2=PH has an angle of 97.5° [3d], and other acyclic and cyclic compounds have angles of 92—103° [12,14]. Still, it is much smaller than the angle expected for sp^2-hybridization of 120°; *N*-mesitylbenzophenone-imine, having a C—N=C angle of 120.8° [16] illustrates that this angle can be realized in a closely related compound of a first row element. From the smaller bond angle, one may conclude that the lone pair of phosphorus has a degree of *s*-character higher than sp^2. Of interest is also the comparison of the bond angles around the sp^2-hybridized carbon atom in the two compounds. The angle PC(6)C(13), involving the phenyl group Z with respect to the mesityl group, is larger (127.2°) than the corresponding angle in the imine (124.9°), the difference being at the expense of the bond angle towards the two phenyl groups C(7)C(6)C(13) (114.8° for II, 117.4° for the imine). This cannot be due to steric factors, as the Z-phenyl group is clearly less hindered in II (cf. e.g. the dihedral angle between the planes of the Z-phenyl group and of the σ-skeleton of the X=C bond: 37° for II, 61.9° for the imine). For a conclusive interpretation of this phenomenon, however, structural data of I and of analogous compounds are needed.

The length of the P—C bond to the mesityl ring (1.822 Å) is approximately as expected for a phosphorus—carbon (sp^2) single bond; on comparison with triphenylphosphine (1.822 Å) [17] and its $Cr(CO)_5$ complex (1.828 Å) [18], the influence of the sp^2-type hybridization of the phosphorus atom in II is not apparent. The bond distances (and the bond angles) of the phosphaalkene carbon atom towards the phenyl rings are not significantly different from those of non-phosphorus-containing models [16,19], indicating the absence of unusual conjugative interaction between the P=C bond and the phenyl rings.

The metal—ligand bond length in II (2.356 Å) fits into the correlation between P—Cr bond length and CO stretching vibrations proposed by Plastas, Stewart, and Grim [18] (ν(CO) calculated: 1952 cm^{-1}; found 1951 cm^{-1}). However, this agreement might be fortuitous, as the closely related pentacarbonyl(2,4,6-triphenylphosphorin)chromium(0) (IV) does not follow this relation [10b].



(IV)

Considerable progress has been made in understanding the factors involved in bonding in $LM(CO)_5$ complexes [18,20], but the relative importance of the σ-donor and the π-acceptor properties of a phosphine ligand is still a controversial issue [21,22]. As both the hybridization of phosphorus and the type of atoms bonded to it are of importance [12], we confine the discussion to a comparison of II and IV (Table 5).

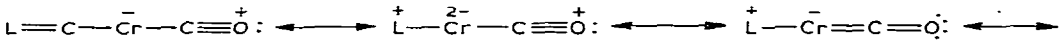
The P—Cr bond length is shorter in II than in IV, implying a slightly stronger bond in II. This is accompanied by the well-known *trans*-effect, i.e. in II the $Cr—C_{trans}$ bond is longer and the $C—O_{trans}$ bond shorter than in IV. It is difficult to reconcile these observations with σ-donation alone; the lone pair of phosphorus in II apparently has more *p*-character than that in IV (compare the CPC-angles!), which in itself should result in a longer P—C bond in II. On the other hand, the effects can be explained if the phosphorus ligand L in II is a stronger π-acceptor than in IV; in other words in II, resonance structure Va makes a relatively larger contribution than Vc, whereas the opposite is the case for IV.

TABLE 5

SELECTED DISTANCES (Å) IN II AND IV

Compound	P—Cr	$Cr—C_{trans}$	$Cr—C_{cis}$ [a]	$C—O_{trans}$	$C—O_{cis}$ [a]
II	2.356	1.874	1.894	1.134	1.143
IV [10b]	2.37	1.82	1.84	1.16	1.175

[a] Average value.



(Va) (Vb) (Vc)

With appropriate caution, ^{31}P NMR data may be adduced to support this view. If the chemical shifts reflect in part a larger positive charge on phosphorus in I ($\delta(P) = 233$ ppm) than in 2,4,6-triphenylphosphorin ($\delta(P) = 178.2$ ppm [7a]), a stronger π-acceptor capacity of L in II would indeed be expected. Also the stronger net flow of negative charge towards L in II could compensate for the usual downfield shift on complexation to $Cr(CO)_5$. However, our lack of a complete understanding of all the factors involved is illustrated by the unusually short $Cr—C_{cis}$ and long $C—O_{cis}$ bond distances in IV, which this simple reasoning does not account for.

Experimental

Melting points are uncorrected. IR spectra were recorded on a Beckman 580 B spectrophotometer. UV spectra were recorded on a Cary 118 spectrophotometer. Mass spectra were obtained with a Varian Mat CH5 spectrometer. NMR spectra were recorded with a Bruker WH-90 spectrometer. Elemental analyses were performed under supervision of Mr. W.J. Buis at the Microanalytical Department of the Institute for Organic Chemistry TNO, Zeist, The Netherlands.

Pentacarbonyl(mesityldiphenylmethylenephosphine)chromium(0) (II)

A solution of 220 mg (1 mmol) of $Cr(CO)_6$ in 75 ml of THF was irradiated under nitrogen for 2 h with a medium-pressure mercury lamp TQ 150 to give a solution of $Cr(CO)_5 \cdot THF$ (yellow). A solution of 355.5 mg (1.1 mmol) of I in 15 ml THF was then added; no color change was observed. The solution was stirred for 20 h at room temperature. After evaporation of the solvent, the residue was recrystallized from n-pentane to yield 450 mg (0.89 mmol, 89%) II; m.p. 170—171°C. Found: C, 63.61; H, 4.15. $C_{27}H_{21}CrO_5P$ (508.44) calcd.: C, 63.78; H, 4.16%. Mass spectrum, *m/e* (%): 508 (8) $[C_{27}H_{21}CrO_5P]^+$, 480 (4.5) $[M - CO]^+$, 452 (12) $[M - 2\ CO]^+$, 424 (3.5) $[M - 3\ CO]^+$, 396 (6) $[M - 4\ CO]^+$, 368 (100) $[M - 5\ CO]^+$, 316 (16) $[C_{22}H_{21}P]^+$, 301 (0.9) $[C_{21}H_{18}P]^+$, 167 (11) $[C_{13}H_{11}]^+$; $C_{27}H_{21}CrO_5P^+$, calcd. 508.0534, found 508.0530.

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