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Reactions of monocyclopentadienylniobium(III) complexes with α-diketones. Crystal structure of the phosphonium salt [P{C(OH)MeC(O)Me}Me_2Ph]Cl

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Abstract

The reactions of $Nb(\eta^5\text{-}C_5H_5)Cl_2(CO)L_2$ (= PMe_3, PMe_2Ph) with α-diketones RCOCOR (R = Me, Ph) and 3,5-di-t-butyl-*o*-quinone have been studied. When L = PMe_2Ph and R = Ph the reaction in a molar ratio 1/1 gives $Nb(\eta^5\text{-}C_5H_5)Cl_2(O_2C_2Ph_2)(PMe_2Ph)_2$ (I) whereas the same reaction for R = Me gives the phosphonium salt [P{C(OH)MeC(O)Me}Me_2Ph]Cl (VII). When L = PMe_3 only the phosphonium salts [P{C(OH)RC(O)R}Me_3]Cl are obtained for R = Me (V) and Ph (VI), but the complex $Nb(\eta^5\text{-}C_5H_5)Cl_2(O_2C_2Ph_2)PMe_3$ (II) can be isolated by previous addition of MeI. Similar reactions with 3,5-di-t-butyl-*o*-quinone give $Nb(\eta^5\text{-}C_5H_5)Cl_2(o\text{-}O_2C_6H_2Bu^t)L$, L = PMe_3 (III), PMe_2Ph (IV). All the compounds have been characterized by IR, ^1H, ^{13}C, ^{31}P NMR spectroscopy and the crystal structure of VII has been determined by X-ray diffraction. VII crystallizes in the monoclinic space group $P2_1/c$ with a 7.440(2), b 10.377(3), c 17.644(4) Å, β 96.94(2)° and D_{cal} 1.039 g cm^{-3} for $Z = 4$. A final R value of 0.046 ($R_w = 0.049$) based on 2309 observed reflections was obtained. The geometry around the P atom is tetrahedral.

Introduction

Reactions of conjugated heterodienes $X{=}\overset{|}{C}{-}\overset{|}{C}{=}X$ (X = S, O, NH) with transition metals are well known models for electron transfer processes [1]. The use of quinones and α-diketones as reagents in oxidative addition processes to give many dienolate systems has been described [2,3]. We report here the reactions of benzil

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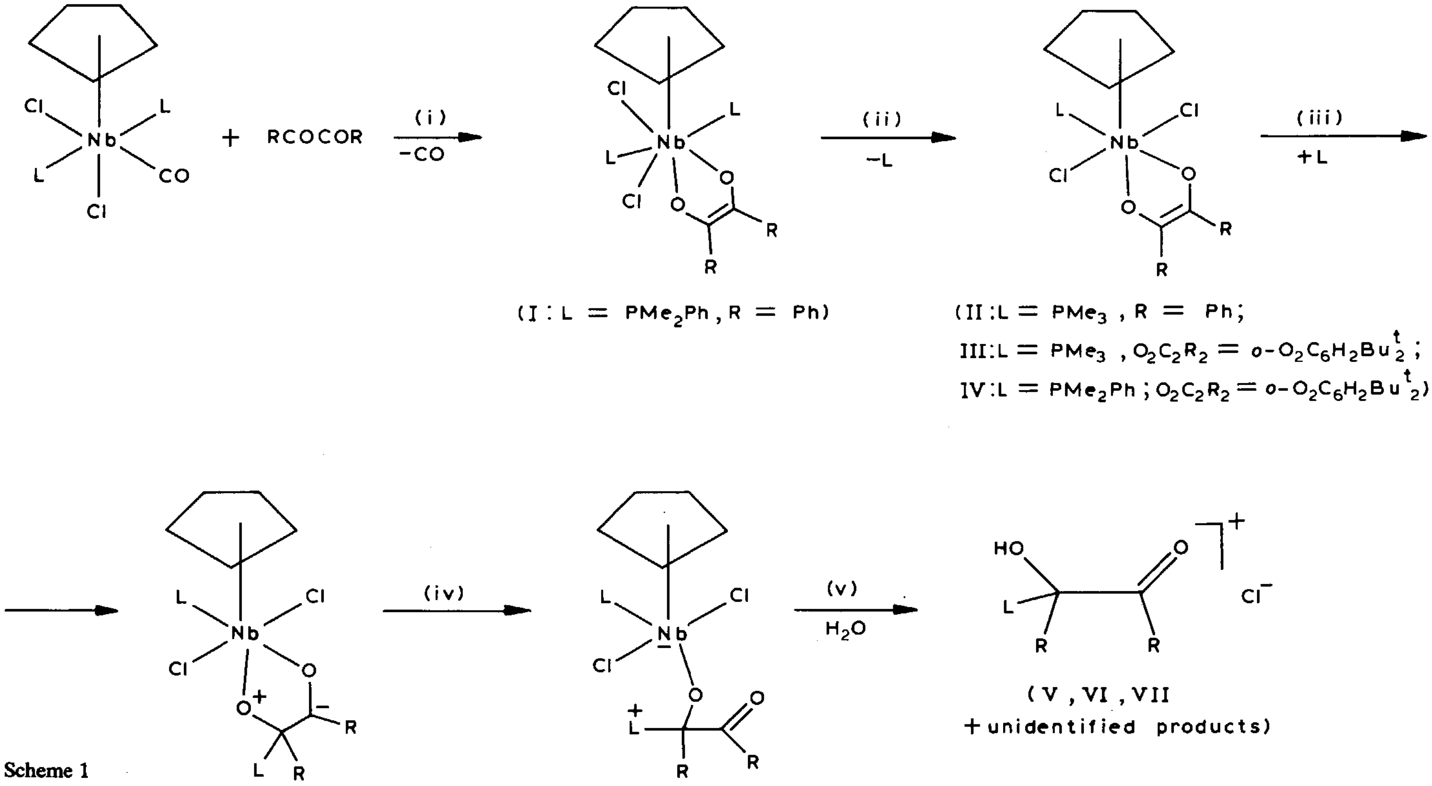


(I : L = PMe_2Ph, R = Ph)

(II : L = PMe_3, R = Ph;
III : L = PMe_3, $O_2C_2R_2$ = o-$O_2C_6H_2Bu^t_2$;
IV : L = PMe_2Ph; $O_2C_2R_2$ = o-$O_2C_6H_2Bu^t_2$)

(V, VI, VII
+ unidentified products)

Scheme 1

(PhCOCOPh), diacetyl, and the bulky 3,5-di-t-butyl-*o*-quinone with $Nb(\eta^5\text{-}C_5H_5)Cl_2(CO)L_2$, L = PMe_3 and PMe_3Ph, to give the dienolate derivatives $Nb(\eta^5\text{-}C_5H_5)Cl_2(O_2C_2R_2)L_x$, $x = 2$, R = Ph, L = PMe_2Ph; $x = 1$, R = Ph, L = PMe_3 and $O_2C_2R_2 = o\text{-}O_2C_6H_2Bu^t_2$, L = PMe_3 and PMe_2Ph, and the phosphonium salts $[P\{C(OH)RC(O)R\}R'_3]Cl$. The X-ray crystal structure of $[P\{C(OH)MeC(O)Me\}Me_2Ph]Cl$ has been determined.

Results and discussion

Synthetic studies

The reactions of monocyclopentadienylniobium(III) complexes $Nb(\eta^5\text{-}C_5H_5)Cl_2(CO)L_2$, L = PMe_3 and PMe_2Ph, with one equivalent of α-diketones RCOCOR, R = Ph, Me, lead to different results depending on L and R. The behaviour can be interpreted in terms of the following reaction sequence in Scheme 1.

When L = PMe_2Ph the reaction with benzil in a molar ratio 1/1 leads to the isolation of I, formed in step (i), which implies the replacement of the carbonyl group by the α-dicarbonylic compound to give the metalladienolate complex. This behaviour has been previously observed [2]. Such 18 electron niobium(V) species readily lose one phosphine ligand (step ii). This is what happens when the dienolate group is $C_6H_2Bu^t_2O_2$, and the resulting pseudo-octahedral complexes III–IV can be isolated as stable compounds. However diacetyl complexes are unstable in the presence of PMe_3 or PMe_2Ph, as is the PhCOCOPh complex in the presence of PMe_3. In these cases, the free ligands attack the metalladienolate ring to give (through iii–v) the corresponding phosphonium salts as the final products. When the nucleophilic character of the phosphine is low the dienolate complex I can be isolated. Reaction of α-diketones with phosphorus(III) compounds have been reported [4,5] to give substituted acetylenes through the intermediate formation of $[\overline{P\{OCRC(O)\}}R'_3]^+$ as a result of the oxophilic rather than the nucleophilic char-

Table 1

Monocyclopentadienyl dienolate complexes, $Nb(\eta^5\text{-}C_5H_5)Cl_2(O_2C_2R_2)L_x$ and phosphonium salts $[P\{C(OH)RC(O)R\}R'_3]Cl$

Compound	Analysis (Found (calc) (%))		Colour
	C	H	
$Nb(\eta^5\text{-}C_5H_5)Cl_2(O_2C_2Ph_2)(PMe_2Ph)_2$ (I)	58.4 (58.7)	5.4 (5.1)	Green
$Nb(\eta^5\text{-}C_5H_5)Cl_2(O_2C_2Ph_2)(PMe_3)$ (II)	51.1 (51.2)	4.6 (4.6)	Green
$Nb(\eta^5\text{-}C_5H_5)Cl_2(O_2C_6H_2Bu^t_2)(PMe_3)$ (III)	55.3 (55.2)	6.5 (6.1)	Green
$Nb(\eta^5\text{-}C_5H_5)Cl_2(O_2C_6Bu^t_2)(PMe_2Ph)$ (IV)	50.0 (50.3)	6.7 (6.4)	Green
$[P\{C(OH)MeC(O)Me\}Me_3]Cl$ (V)	55.2 (55.2)	6.6 (6.9)	White
$[P\{C(OH)PhC(O)Ph\}Me_3]Cl$ (VI)	63.2 (63.2)	6.3 (6.2)	White
$[P\{C(OH)MeC(O)Me\}Me_2Ph]Cl$ (VII)	42.4 (42.3)	8.8 (8.0)	White

acter of the phosphorus(III) compounds; we suggest that steric and electronic reasons are responsible for the ability of the phosphine to carry out nucleophilic attack on the metalladienolate ring with R = Me. With PMe_3 and benzil or diacetyl the phosphonium salts are obtained. The presence of MeI prevents the formation of the phosphonium salts as it decreases the concentration of the free phosphine through formation of LMe^+I^-. In this way compound II (step ii) can be isolated, and the dienolate compound formed in the reaction with diacetyl can be detected by IR and ^1H NMR spectroscopy.

Complexes I–IV are deep green crystalline solids; I and II are air stable for long periods, whereas III and IV must be stored under nitrogen. All the compounds are soluble in toluene, THF, chloroform and dichloromethane and insoluble in alkanes. Solutions of I and II slowly decompose with precipitation of unidentified white solids whereas those of III and IV are indefinitely stable under nitrogen but react with water to yield deep red solutions which have not been studied. The phosphonium salts V–VII are white hygroscopic crystalline solids soluble in chloroform and dichloromethane and insoluble in THF, toluene, and alkanes. All the reported compounds were characterized by analysis (see Table 1).

IR spectroscopy

Complexes I–IV show the absorptions expected for the η^5-cyclopentadienyl ligand [6] and a weak band at ca. 1500 cm^{-1} (Table 2) due to the coordinated α-diketone ligand, along with other absorptions of the phosphine ligands. The benzil ligand shows a strong band at 1760 cm^{-1} due primarily to the ν(C=O) stretching vibration. Upon complexation, the C–O double bond character decreases while the C–C single bond takes on double bond character. The band at ca. 1500 cm^{-1} in the complexes may therefore be predominantly ν(C=C), but with C=O mixing. The ν(C–O) stretching vibration for complexes I and II is observed at ca. 1080 cm^{-1} (see Table 2) in accord with reported data [7]. A band due to the ν(C–O) stretching vibration for complexes III and IV is observed at ca. 1300 cm^{-1} (see Table 2) [8]. For all these compounds the ν(Nb–O) stretching vibration may be observed between 550–650 cm^{-1}, but it cannot be easily assigned because it overlaps with strong bands from the phosphine ligands. The IR spectra of the phosphonium salts show characteristic absorptions due to the CO and OH groups (see Table 2).

Table 2

Selected IR absorptions of $Nb(\eta^5\text{-}C_5H_5)Cl_2(O_2C_2R_2)L_x$ complexes and $[P\{C(OH)RC(O)R\}R'_3]Cl$ phosphonium salts

Compound	ν(CO,C=C)	ν(C–O)	ν(Nb–Cl)	ν(CO)	ν(C–OH)
I	1525(w)	1070(s)	255(m)		
II	1530(w)	1080(vs)	245(m)		
III		1305(s)	245(m)		
IV		1300(s)	245(m)		
V				1710(s)	1150(s)
VI				1665(s)	1175(s)
VII				1710(s)	1150(s)

NMR spectroscopy

The ^1H NMR spectra of I–IV show the resonances due to the η^5-C_5H_5 protons and the phosphine ligands (see Table 3). A singlet is observed for the η^5-C_5H_5 protons, and the chemical shifts, between δ 6.02–6.63 ppm, are in agreement with those previously [9] observed for niobium(V) complexes. The methyl protons of the phosphine ligands in I–III appear as a doublet between δ 1.04–1.60 ppm, but as two doublets in IV, probably because the two methyl groups are not exactly equivalent.

Table 3

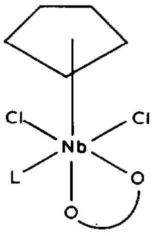
^1H, ^{13}C, ^{31}P NMR chemical shifts for Nb(η^5-C_5H_5)Cl_2($O_2C_2R_2$)L_x complexes and [P{C(OH)RC(O)R}R'_3]Cl phosphonium salts

Compound	^1H (internal standard TMS)			^{31}P	$^{13}C\{^1H\}$		
	δ(ppm) (int.) (mult)	J(P–H) (Hz)	Assignment	δ(ppm) (H_3PO_4)	δ(ppm)	J(P–C) (Hz)	Assignment
I	^{a} 6.53 (5) (mc)		η^5-C_5H_5		^{b} 118.2		η^5-C_5H_5
	1.60 (6) (d)	13.6	Me(PMe_2Ph)		16.4 (d)	60.2	Me(PMe_2Ph)
	7.01–7.77 (mc)		Ph(PMe_2Ph)		128–133		Ph(PMe_2Ph)
			Ph($O_2C_2Ph_2$)		128–133		Ph($O_2C_2Ph_2$)
					134.4, 135.0		C_2($C_2O_2Ph_2$)
II	^{a} 6.02 (5) (d)	1.7	η^5-C_5H_5		^{c} 121.0		η^5-C_5H_5
	1.04 (9) (d)	9.6	Me(PMe_3)		12.2 (d)	86.4	Me(PMe_3)
	6.17–7.67 (mc)		Ph($O_2C_2Ph_2$)		135.6, 134.0		C_2($O_2C_2Ph_2$)
III	^{a} 6.59 (5) (s)		η^5-C_5H_5				
	1.39 (9) (s)		^tBu				
	1.43 (9) (s)						
	1.10 (9) (d)	13.4	Me(PMe_3)				
	6.76 (1) (d)						
	6.91 (1) (d)	2.0	H($O_2C_6H_2{}^tBu_2$)				
IV	^{a} 6.63 (5) (s)		η^5-C_5H_5				
	1.37 (9) (s)						
	1.31 (9) (s)		^tBu				
	1.66 (3) (d)	11.7	Me(PMe_2Ph)				
	1.75 (3) (d)	13.7					
	6.83–7.05 (mc)		Ph(PMe_2Ph)				
			H($O_2C_6H_2Bu^t_2$)				
V	^{b} 2.08 (9) (d)	13.9	Me(PMe_3)	^{b} 10.1 (s)			
	1.74 (3) (d)	16.7	Me				
	2.49 (3) (s)		Me				
	8.48 (1) (s)		H(OH)				
VI	^{b} 1.95 (9) (d)	13.6	Me(PMe_3)	^{b} 22.5 (s)			
	7.00–7.90 (mc)		Ph				
	7.78 (1) (s)		H(OH)				
VII	^{b} 2.40(3)(d),						
	2.44(3)(d)	13.4	Me(PMe_2Ph)	^{b} 14.0 (s)			
	1.69 (3) (d)	18.4	Me				
	2.49 (3) (s)		Me				

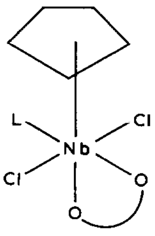
^{a} In C_6D_6. ^{b} In $CDCl_3$. ^{c} In THF.

The absence of virtual coupling [10] of the methyl protons in compound I suggests that the two phosphines are *cis* to one another, probably in a monoapical octahedral structure. A complex multiplet between δ 6.17–7.77 ppm is observed for the phenyl protons in complexes I and II and the two non equivalent Bu^t protons in complexes III and IV give two singlets shifted downfield with respect to those from the free *o*-quinone as a consequence of the aromatization of the ring.

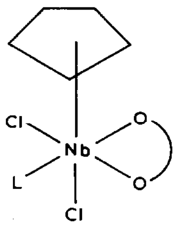
The $^{13}C\{^1H\}$ NMR spectra of I and II (see Table 3) show two resonances at ca. δ 175 ppm due to the two metalladienolate ring carbon atoms indicating that they are located in an asymmetric arrangement. The chemical shifts are consistent with those reported for $W_2(OR)_6(O_2C_2R'_2)_2$ [3]. These spectroscopic data suggest a pseudo-octahedral geometry for II–IV but do not permit a choice between the three possible different isomers A–C. The ^{31}P NMR spectra for V–VII (see Table 3) show one singlet shifted downfield with respect to that of the free ligand.



(A)

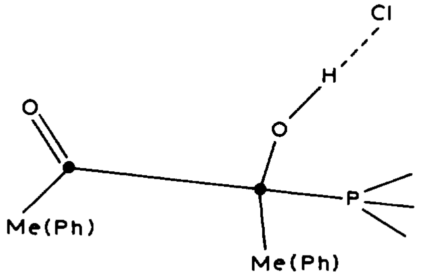


(B)



(C)

The ^1H NMR spectra of V and VI show one doublet between δ 1.95 and 2.44 ppm due to the methyl phosphine protons coupled with the phosphorus atom, whereas VII shows two doublets indicating that the two sets of methylphosphine protons are not equivalent; such non-equivalence is present in the crystal structure discussed below. The resonance of the methyl protons bonded to the chiral carbon atom appears as a doublet strongly coupled with the phosphorus atom, whereas the methyl protons bonded to the carbonyl group give a singlet shifted downfield. The singlet due to the OH proton is shifted downfield in accord with the interaction with the anion revealed by the crystal structure.



(V–VII)

Crystal structure of $[P\{C(OH)MeC(O)Me\}Me_2Ph]^+Cl^-$ *(VII)*

An ORTEP drawing of VII appears in Fig. 1, which also shows the numbering scheme. Atomic parameters for the non-hydrogen atoms are listed in Table 4. Important bond distances and angles are listed in Table 5. The symmetry of the

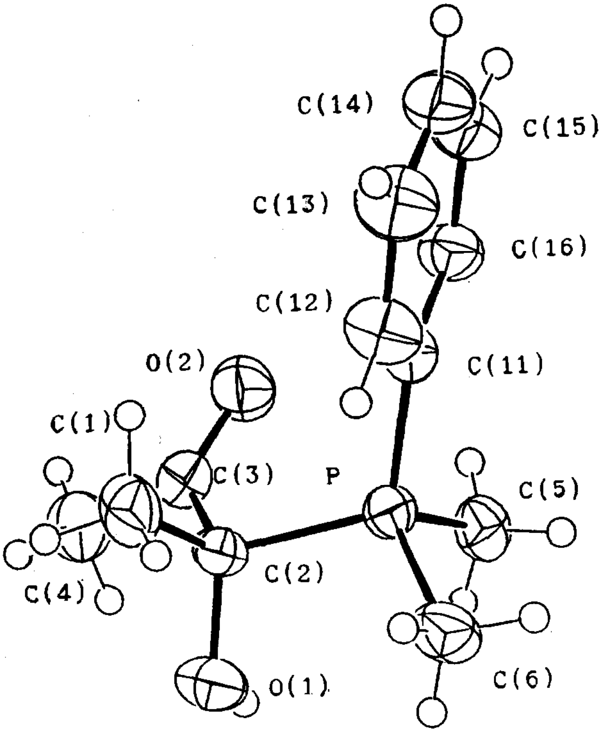


Fig. 1. Structure of $[P\{C(OH)MeC(O)Me\}Me_2Ph]^+ Cl^-$, with the atom numbering scheme.

lattice requires the presence of the two enantiomers; we present only the structure of the *s*-isomer in Fig. 1, which shows the geometry around the P atom to be tetrahedral (mean angles 109.4(1)°). Three of the P–C bond lengths those to C(11),

Table 4

Atomic and thermal parameters for $[P\{C(OH)MeC(O)Me\}Me_2Ph]^+ Cl^-$

Atom	x/a	y/b	z/c	U_{eq} [a]
P	0.72451(7)	0.22281(5)	0.13713(4)	348(2)
Cl	0.30036(10)	0.17282(7)	0.77129(5)	646(3)
O(1)	0.65882(26)	0.41170(19)	0.23144(11)	494(7)
O(2)	0.45931(26)	0.37077(19)	0.04508(12)	542(7)
C(1)	0.83201(41)	0.48105(28)	0.13551(22)	545(11)
C(2)	0.67468(31)	0.39652(21)	0.15412(14)	369(8)
C(3)	0.50463(33)	0.43462(23)	0.10110(16)	425(8)
C(4)	0.40362(58)	0.55048(34)	0.12204(24)	650(13)
C(11)	0.82396(30)	0.19557(20)	0.05068(15)	372(7)
C(12)	1.00693(34)	0.22159(30)	0.04866(18)	516(10)
C(13)	1.08315(39)	0.20345(32)	−0.01787(20)	603(11)
C(14)	0.98030(45)	0.15732(29)	−0.08176(21)	576(11)
C(15)	0.79969(43)	0.13074(29)	−0.08010(18)	558(11)
C(16)	0.72067(36)	0.15000(25)	−0.01438(16)	456(9)
C(5)	0.52630(35)	0.12747(26)	0.13950(10)	451(9)
C(6)	0.88175(43)	0.17301(31)	0.21610(20)	516(0)

[a] $U_{eq} = \frac{1}{3}\Sigma[u_{ij}a_i^\star a_j^\star a_i a_j \cos(a_i a_j)] \times 10^4$.

Table 5

Interatomic distances (Å) and angles (°) with e.s.d's

P-C(2)	1.872(2)	P-C(11)	1.796(3)
P-C(6)	1.784(3)	P-C(5)	1.780(3)
O(1)-C(2)	1.392(3)	O(1)-H(1)	0.852(38)
O(2)-C(3)	1.204(3)	C(1)-C(2)	1.530(4)
C(2)-C(3)	1.532(3)	C(3)-C(4)	1.488(5)
C(11)-C(12)	1.392(3)	C(11)-C(16)	1.385(3)
C(12)-C(13)	1.377(5)	C(13)-C(14)	1.370(5)
C(14)-C(15)	1.375(5)	C(15)-C(16)	1.377(4)
O(1)-Cl	2.971(2)		
C(6)-P-C(5)	106.7(1)	C(11)-P-C(5)	111.1(1)
C(11)-P-C(6)	108.6(1)	C(2)-P-C(5)	110.5(1)
C(2)-P-C(6)	106.1(1)	C(2)-P-C(11)	113.4(1)
O(1)-C(2)-C(1)	107.6(2)	C(2)-O(1)-H(1)	108.3(2.4)
P-C(2)-O(1)	107.9(2)	P-C(2)-C(1)	110.2(2)
O(1)-C(2)-C(3)	114.1(2)	C(1)-C(2)-C(3)	108.5(2)
O(2)-C(3)-C(2)	119.2(2)	P-C(2)-C(3)	108.4(2)
O(2)-C(3)-C(4)	123.3(3)	C(2)-C(3)-C(4)	117.5(2)
P-C(11)-C(12)	119.7(2)	P-C(11)-C(16)	120.9(2)
C(11)-C(12)-C(13)	120.0(2)	C(12)-C(11)-C(16)	119.4(2)
C(13)-C(14)-C(15)	120.2(3)	C(12)-C(13)-C(14)	120.2(3)
C(11)-C(16)-C(15)	119.8(3)	C(14)-C(15)-C(16)	120.4(3)

C(6) and C(5), are similar (mean 1.786(3) Å) to those observed in other phosphonium salts [11]. The fourth bond is larger than the other three (P(1)-C(2) 1.872(2) Å) and corresponds to a single $P-C_{sp^3}$ bond. Except for those of the phenyl ring, the C-C bond lengths correspond to single bonds; C(4)-C(3) is the shortest. The C(2)-O(1) bond length (1.392(3)) corresponds to a single bond to an sp^3 C atom and the C(3)-O(2) bond length (1.204(3)) to a double bond. The bond angles around the carbonyl group are close to 120°, corresponding to sp^2 hybridization of the C(3) atom. Except those of the phenyl group, the remaining bond angles are close to 109°, corresponding to sp^3 hybridization for the C(2), P and O(1) atoms. The atoms C(2), C(3), C(4) and O(2) atoms are located practically in a plane. The chloride anion is connected to O(1) with a hydrogen bond O(1)-H(1)-Cl (O(1) $\cdots$ Cl 2.971(2) Å) and an O(1)-H(1)-Cl angle of 172(3)°.

Experimental

All operations were carried out under vacuum or in an inert atmosphere with Schlenk type glassware. Solvents were dried and distilled under N_2 and degassed before use. $Nb(\eta^5\text{-}C_5H_5)Cl_2(CO)L_2$ were prepared as previously described [10]. Benzil and diacetyl were purchased from Aldrich. IR spectra were recorded with solutions or with Nujol mulls between CsI plates in the region 4000-200 cm^{-1} using a Perkin-Elmer 599 spectrophotometer. Carbon and hydrogen analyses were performed with a Perkin-Elmer 240B microanalyzer. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on Varian FT 80A and Bruker WP-60-CW instruments.

$Nb(\eta^5\text{-}C_5H_5)Cl_2(O_2C_2Ph_2)(PMe_2Ph)_2$ *(I)*

Benzil (0.118 g, 0.56 mmol) was added to $Nb(\eta^5\text{-}C_5H_5)Cl_2(CO)(PMe_2Ph)_2$ (0.300 g, 0.56 mmol) in toluene (30 ml). After 20 h stirring at room temperature a deep green solution and a precipitate were present. The solution was filtered and then evaporated under reduced pressure, and the residual green solid was washed with a mixture of toluene and hexane, dried under vacuum, and identified as complex I. Yield 83%.

$Nb(\eta^5\text{-}C_5H_5)Cl_2(O_2C_2Ph_2)(PMe_3)$ (II)

Benzil (0.153 g, 0.73 mmol) and MeI (0.110 g, 0.8 mmol) were added to $Nb(\eta^5\text{-}C_5H_5)Cl_2(CO)(PMe_3)_2$ (0.300 g, 0.73 mmol) in toluene (30 ml). The procedure used for I gave complex II. Yield 75%. The initial precipitate was identified as the phosphonium salt $[PMe_3Ph]I$.

$Nb(\eta^5\text{-}C_5H_5)Cl_2(O_2C_6H_2Bu^t_2)L$ (III, IV)

3,5-Di-t-butyl-*o*-quinone (0.154 g, 0.70 mmol) was added to $Nb(\eta^5\text{-}C_5H_5)Cl_2(CO)(PMe_2Ph)$ (0.286 g, 0.70 mmol) in toluene (30 ml). The procedure used for I gave a deep green solid but with a reaction time of 3 h and washing only with hexane gave the deep green complex IV. Yield 72%. Complex III was prepared similarly. Yield 75%.

$[P\{C(OH)RC(O)R\}R'_3]^+Cl^-$, (V), (VI), (VII)

Diacetyl (0.060 g, 0.70 mmol) was added to $Nb(\eta^5\text{-}C_5H_5)Cl_2(CO)(PMe_2Ph)_2$ (0.373 g, 0.70 mmol) in toluene (30 ml). After 48 h stirring at room temperature a white precipitate was present. The solid was filtered off and then extracted with dichloromethane/hexane (20/10 ml), and the extract was kept at $-20\,°C$ to give compound VII as a white crystalline solid. Yield 61%.

Compound V was prepared similarly. Yield 58%.

Compound VI was prepared from benzil at $-20\,°C$ by a similar procedure. Yield 45%.

Crystal structure of compound VII

Crystal data. $C_{12}H_{18}ClO_2P$, $M = 260.70$ monoclinic, space group $P2_1/c$, a 7.440(2), b 10.377(3), c 17.644(4) Å, β 96.94(2)°, V 1352.2(6) Å^3, D_x 1.039 g cm^{-3} for $Z = 4$, $\bar{F}(000) = 552$, Mo-K_α radiation ($\lambda = 0.7107$ Å), μ(Mo-K_α) 3.817 cm^{-1}.

Intensity, data collection and refinements

A white crystal of VII was mounted on a Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo-K_α radiation. Lattice parameters were determined by least-squares refinement of values for 25 reflections in the $2 < \theta < 28°$. Data collections were recorded by the $\omega/2\theta$ scan technique.

Two standard reflections ($12\bar{1}$,221) were measured after every 100 reflections and no significant changes in intensities were detected. A total of 3063 unique reflections were collected in the range h,0 10,k,0 14, l, 14 −14, but only 2309 with ($I > 3\sigma(I)$) were considered observed and used in further calculations. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structure was solved by the direct methods using MULTAN 80 [12] and DIRDIF 81 [13] programs. The structure was refined (on F) by full matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located from the Fourier difference synthesis, included in the calculation with temperature factors equivalent to those of the corresponding carbon atoms, and refined isotropically for two cycles. Final R values of 0.046 and $R_w = 0.049$ (weighting scheme, empirical fit as to give no trends in $\langle W\Delta^2 F\rangle$ vs. $\langle F_o\rangle$ and vs. $\langle \sin\theta/\lambda\rangle$, were obtained. Anomalous dispersion and atomic scattering factors were taken from International Tables for X-ray Crystallography [14]. Calculations performed with X-ray system 76 [15] and PARST [16] on VAX-11750 computer.

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