Synthesis and Complexation of α-Phosphine Enolates with Oxophilic and Carbophilic Metals

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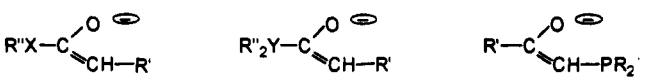
Deprotonation of acyldiphenylphosphines using Bu^nLi affords α-phosphino enolates. The lithium derivative, $[Ph_2P(CH_2)O\cdots Li(THF)_2]_2$ (**3**), was isolated and fully characterized. The reaction of the lithium α-phosphino enolates with cp_2ZrCl_2 led to the corresponding zirconium enolates $[cp_2Zr(Cl)O(CH_2)CPPh_2]$ (**4**), and $[cp_2Zr(Cl)O(CHMe)CPPh_2]$ (**5**). Complex **5** was isolated as pure *E* and *Z* isomers. The reaction of **4** and **5** with benzaldehyde and the stereochemistry of the resulting compounds are supported by ^1H NMR. The reaction of **4** with $[Cr(CO)_5\cdot THF]$ gave the bimetallic α-phosphino enolato complex $[cp_2Zr(Cl)OC(CH_2)P(Ph)_2\text{-}Cr(CO)_5]$ (**10**), in which the nucleophile "CH_2" unit is maintained free for further reactivity. The structures of **5** and **10** have been determined by an X-ray analysis. Crystallographic details: **5** is orthorhombic, space group $P2_12_12_1$, a = 14.009(3) Å, b = 15.890(4) Å, c = 10.101(4) Å, $\alpha = \beta = \gamma = 90°$, Z = 4, and R = 0.043; **10** is monoclinic, space group $P2_1/c$, a = 10.462(1) Å, b = 14.390(1) Å, c = 19.972(2) Å, $\alpha = \gamma = 90°$, β = 102.66(1)°, Z = 4, and R = 0.031.

Introduction

The ability of transition metals to drive the chemistry of the enolate functionality is, among other things, associated with the presence of a heteroatom (**A**–**D**). The role of the heteroatom is both to affect the electronic properties of the functionality and to provide an additional binding group for the metal.[1]



X = O, **A** X = S, **B** | Y = N, **C** Y = P, **D** | **E**

Our attention was recently drawn to the phosphorus analogue **D** of the well-known amido enolates **C**,[2] which have been widely used in organic synthesis. We should mention the existence of an important class of phosphino enolates, the β-phosphino enolates, **E**,[3,4] which can be regarded as positional isomers of **D** functioning essentially as bidentate ligands. In the case of α-phosphino enolates such a bonding mode can, however, be ruled out for geometric reasons. In terms of the electronic and geometric properties, the two classes of ligands are distinct. The α-phosphino enolates **D** represent an unprecedented class of enolates which have only briefly been communicated.[5]

In this paper, we report the details of the synthesis of complexes of type **D** along with their reactions with oxophilic and carbophilic metals. Such reactions lead to the isolation and structural characterization of O- and P-bonded metal derivatives. Furthermore, both heteroatoms have been complexed to two different metals. The precursor of the enolate form **D** is the corresponding α-keto phosphine, which has received relatively little attention despite its ready availability from the literature.[6] To our knowledge, only one application of the α-keto phosphines has been reported; that is the attempt to prepare the corresponding Schiff bases in the reaction with primary amines and to use them in metal complexation.[7]

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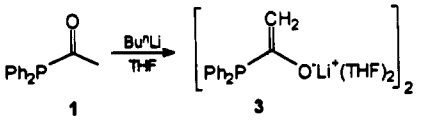
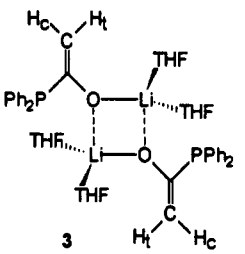
Results and Discussion

The synthesis of acetylphosphines is now a well established procedure. The deprotonation of Ph_2PCOMe is, however, a rather delicate reaction, the best results being obtained by carrying out the reaction at −100 °C with Bu^nLi:



1 3 (1)

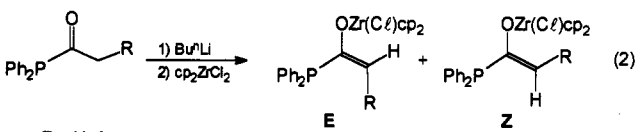
The lithium enolate (**3**) has been isolated in high yield as a white crystalline solid. Its dimeric nature is mainly inferred from the stoichiometry and the analogy with the lithium amido enolates[8] in addition to the spectroscopic characterization. In the ^1H NMR spectrum of **3**, the methylene protons appear as a singlet at 3.90 ppm (H *cis* to P, J_{HP} = 0 Hz) and as a doublet at 4.64 ppm (H *trans* to P, J_{HP} = 13.7 Hz).



3

The proton *cis* to the oxygen atoms appears at a lower field than the *trans* one, as has been observed in a number of titanium and zirconium enolates.[9] In the ^{13}C NMR spectrum, the methylene carbon is observed at 94.0 ppm with a chemical shift comparable with those of titanium acetophenone derived enolates.[9]

The transmetalation reaction of the lithium enolates with cp_2ZrCl_2 [cp = η^5-C_5H_5] affords the crystalline solids **4** and **5** in good yields.



(2)

R = H, **1** E R = H, **4** Z

R = Me, **2** R = Me, **5**

In the ^1H NMR spectrum of **4**, the methylene protons appear as a pair of doublets at 4.43 and 4.60 ppm, while the ^{13}C spectrum has a peak at 103.0 ppm for the methylene carbon. The proposed structures of **4**[5] and **5** have been supported by X-ray analyses (*vide infra*). In the case of **5**, the different solubilities of the *E* and *Z* isomers allowed their separation by fractional crystallization (the less soluble being the *E* isomer). The overall yield in terms of the isolated solid is 52%, while the yield for the *E* and *Z* isomers varies from 15 to 23 and 22 to 27%, respectively. The two isomers can be distinguished by analysis of their ^1H and ^{13}P NMR spectra. The ^1H NMR spectrum of the *E* isomer shows the enolic proton as a pair of quartets of 5.24 and 5.35 ppm (J_{HH}, 7.3 Hz; J_{HP}, 21.5 Hz), and the methyl protons as a doublet of doublets at 2.06 ppm (J_{HH}, 7.2 Hz; J_{HP}, 1.75 Hz), while in the ^{31}P NMR spectrum a singlet for the PPh_2 phosphorus is observed at −16.1 ppm. In contrast, the ^1H NMR spectrum for the *Z* isomer shows the enolic proton as a poorly resolved multiplet (very likely a doublet of quadruplets) centered at 4.72 ppm, due to the negligible J_{HP} coupling, and the methyl protons as a doublet at 1.68 ppm (J_{HH}, 6.7 Hz), while the PPh_2 phosphorus signal is observed at 1.05 ppm in the ^{31}P NMR spectrum.

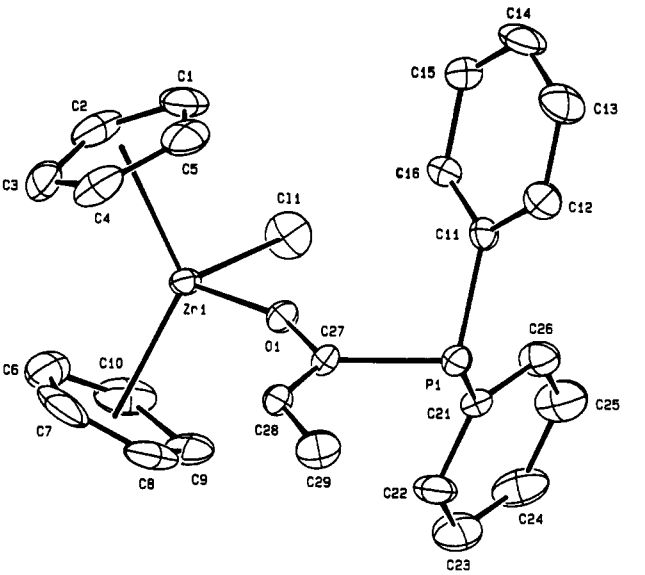
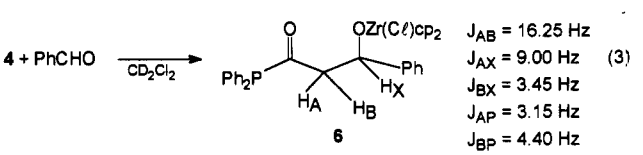


Figure 1. ORTEP view of complex **5** (isomer *E*, 30% probability ellipsoids).

A view of the structure of the *E* isomer of **5** is illustrated in Figure 1, and a list of selected parameters is given in Table 4. The picture shows that the chlorine Cl1 atom is *trans* to C27–C28 and *cis* to C27–P1. The phosphine enolato group (O1,C27,C28,P1,C29) is strictly planar and nearly coplanar with the equatorial plane (Zr1,O1,C11), the dihedral angle they form being 10.4(2)°. The phenyl planes C11···C16 and C21···C26 for dihedral angles of 101.1-(2) and 113.0(2)°, respectively, with the enolato plane (O1,-C27,C28,P1). The enolato fragment has a localized C27–C28 [1.311(12) Å] double bond, while the Zr–O interaction is particularly strong, as supported by the short Zr1–O1 distance [1.955(5) Å] and by the wide Zr1–O1–C27 angle [160.5(5)°].

The reactivity of the phosphino enolates **4** and **5** has been explored with benzaldehyde and acetophenone. The reactions have been monitored by ^1H NMR, as a result of some difficulties encountered in the isolation of the products as solids.



6 (3)

Reaction 3 is almost instantaneous and gave quantitatively **6**. The ^1H NMR spectrum shows five quartets for the ABXY (Y = P) system where AB is coupled with P. The four quartets for the H_A and H_B protons appear at 2.62, 2.70, 3.16, and 3.25 ppm, as well as a quartet at 5.71 ppm for the H_X proton. The related coupling constants are also listed in eq 3.

It is worth emphasizing the similarity between the aldol condensation products **6** and [cp_2(Cl)Zr—OCH-

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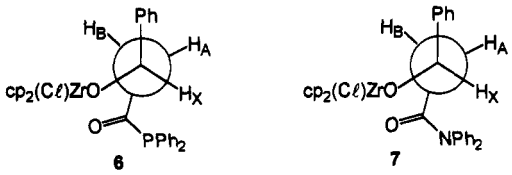
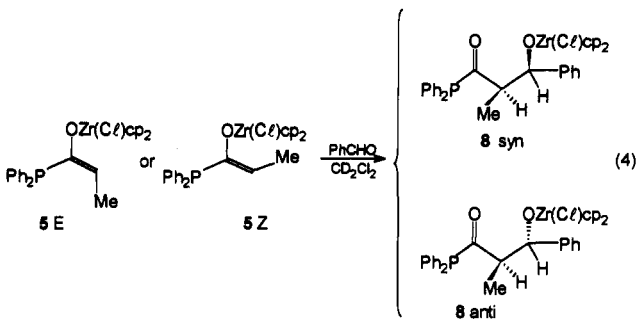
(Ph)—CH_2—(O)NPh_2] (7),[10] derived from respectively the reactions of benzaldehyde with **4** and with the amido enolate analogue [cp_2(Cl)Zr—O—C(NPh_2)=CH_2].[10] The corresponding Newman projections for **6** and **7** are



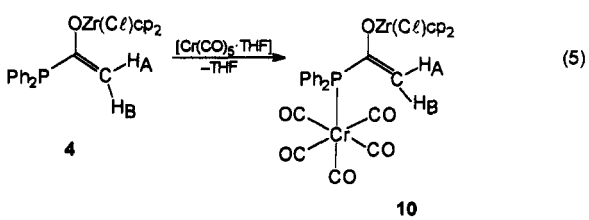
The chemical shifts are very close for both compounds: δ_A [2.66, **6**; 2.42, **7**]; δ_B [3.20, **6**; 2.93, **7**]; δ_X [5.71, **6**; 5.90, **7**]. In addition, we can observe the same geminal and vicinal coupling constants, since **A** and **B** are interchangeable in the figure: J_{AB} [16.25, **6**; 15.35, **7**]; J_{AX} [9.00, **6**; 3.50, **7**]; J_{BX} [3.45, **6**; 9.20, **7**]. The J_{AX} (ϕ = 50°) and J_{BX} (ϕ = 180°) values suggest the dihedral angles shown in the corresponding sets of parentheses.

The *E* and *Z* isomers of **5** react slower than **4** with benzaldehyde.



The isomer *E* reacts with good selectivity, yielding 90% of one of the diastereoisomers of **8**. The precise nature of the diastereoisomer is uncertain, but it would seem probable to be the *anti* one. The reaction of the *Z* isomer is less selective and produces the *syn*/*anti* mixture in an approximately 1:1 ratio (44% vs 56%). Chemical shifts and related coupling constants for the two diastereoisomers are reported in the experimental section, and they are very close to those we reported for the analogous compounds derived from the condensation of [cp_2(Cl)ZrO—C(NPh_2)=CH—CH_3] with benzaldehyde forming [cp_2(Cl)ZrO—CH(Ph)—C(Me)—C(O)—(NPh_2)], **9**.[10] Enolates **4** and **5** did not show any significant reactivity toward acetophenone.

The zirconium α-phosphino enolates **4** and **5** possess essentially two nucleophilic sites P and "CH_2" which may participate in reactions with both soft metals or electrophilic carbons. We demonstrated the former case in reaction 5, in which the phosphorus donor replaces the labile THF molecule in [$Cr(CO)_5$·THF].



(10) Veya, P.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. Manuscript in preparation.

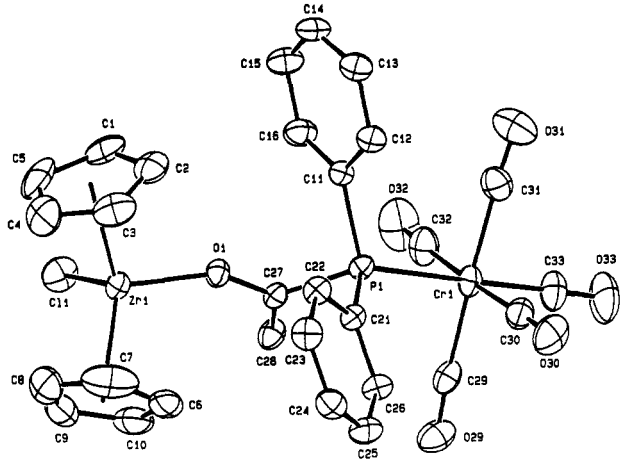


Figure 2. ORTEP view of complex **10** (30% probability ellipsoids).

An interesting comparison should be made between the spectroscopic and structural parameters of **4** and **10**. In particular, we can examine the effect that the introduction of the [$Cr(CO)_5$] group has on the steric and electronic requirements of the phosphino enolato fragment. The structure of **10** is shown in Figure 2, and a list of the structural parameters is given in Table 5. It consists of discrete complex molecules in which the coordination at the Zr atom is similar to that found in complex **5**. The Zr1–O1 bond distance [1.979(2) Å] is marginally but significantly longer than that found in complexes **4** [1.960(3) Å] and **5** [1.955(3) Å] and this is reflected in a narrowing of the Zr1–O1–C27 bond angle [152.1(2)° in complex **10** *vs* 160.5(5)° in complex **5** and 163.6(3)° in complex **4**]. The phosphine enolato group (O1,C27,C28,P1) is strictly planar and is folded with respect to the equatorial plane (Zr1,O1,Cl1), the dihedral angle they form being 40.2(1)°. Bond distances and angles within the enolator ligand are in good agreement with those observed in complex **5**, the double bond being localized between the C27 and C28 atoms [1.308(6) Å].

The introduction of the [$Cr(CO)_5$] fragment has a significant influence on the overall conformation of the molecule and the steric hindrance around the nucleophile. The C27–C28 bond is *trans* in **5** (as well as in complex **4**) to the chlorine atom, while it is *cis* in **10**, by comparison of the corresponding torsion angles [Cl1–Zr1···C27–C28 −170.7(6)° (**5**), −38.4(3)° (**10**), −165.8(3)° (**4**); Cl1–Zr1···C27–P1 3.9(5)° (**5**), 151.6(2)° (**10**), 8.5(2)° (**4**); Cl1–Zr1···O1–C27 −151.5(16)° (**5**), −67.4(5)° (**10**), −137.6(9)° (**4**)].

In both complexes **4** and **10** the enolato plane is accessible from both axial directions. The enolato plane forms a dihedral angle of 135.4(1)° with the Cr,C20,C31,C33 plane.

In the ^1H NMR spectrum of **10**, the methylene protons are deshielded with respect to those in **4**, showing two doublets of doublets at 4.59 and 4.76 ppm for H_A (J_{H_AP}, 33.8 Hz) and at 5.21 and 5.26 ppm for H_B (J_{H_BP}, 9.0 Hz). The higher deshielding of H_B (0.80 ppm) is attributed to the geometric proximity of H_B to the CO ligands, as can be understood by analysis of the solid state structure (Figure 2).

Experimental Section

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. Infrared spectra were recorded with a Perkin-Elmer

Table 1. Experimental Data for the X-ray Diffraction Studies on Crystalline Compounds 5 and 10

	5	10
chemical formula	$C_{25}H_{24}ClOPZr$	$C_{29}H_{22}ClCrO_6PZr$
a (Å)	14.009(3)	10.462(1)
b (Å)	15.890(4)	14.390(1)
c (Å)	10.101(4)	19.972(2)
α (deg)	90	90
β (deg)	90	102.66(1)
γ (deg)	90	90
V (Å^3)	2248.5(12)	2933.7(5)
Z	4	4
fw	498.1	676.1
space group	$P2_12_12_1$ (No. 19)	$P2_1/c$ (No. 14)
t (°C)	22	22
λ (Å)	0.710 69	0.710 69
ρ_{calc} (g cm^{-3})	1.471	1.531
μ (cm^{-1})	6.83	8.95
transm coeff	0.819–1.000	0.939–1.000
R^a	0.043 [0.044][b]	0.031
R_w[c]	0.048 [0.049]	0.034
R_G[d]	0.063 [0.064]	0.042

[a] $R = \sum||\Delta F|/\sum|F_o|$. [b] Values in square brackets refer to the "inverted" structure. [c] $R_w = [\sum w^{1/2}|\Delta F|/\sum w^{1/2}|F_o|]$. [d] $R_G = [\sum w|\Delta F|^2/\sum w|F_o|^2]^{1/2}$.

883 spectrophotometer, ^{1}H, ^{31}P, and ^{13}C NMR spectra were measured on a 200-AC Bruker instrument.

Preparation of 1.[6] Freshly distilled Ph_2PCl (25.45 g, 115 mmol) was added to an ether (250-mL) suspension of sodium sand (5.30 g, 230 mmol). The flask was equipped with a reflux condenser and immersed in a water bath to control the temperature of the very exothermic reaction. The solution was stirred overnight and turned dark yellow. It was then transferred to a dropping funnel and added dropwise over 4 h to an Et_2O (100-mL) solution of acetyl chloride (9.03 g, 115 mmol) at −50 °C. The solution turned light yellow and became viscous. NaCl was filtered off and washed under nitrogen with Et_2O (3 × 100 mL). The filtrate was evaporated to dryness and the residue distilled under reduced pressure (110–120 °C, 0.5 mmHg). The distillation must be carried out very quickly and under nitrogen, as the product is pyrophoric (70%). IR (Nujol): ν(C=O) 1672 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.24 (d, COMe, 3 H), 7.4–7.5 (m, Ph, 10 H). ^{13}C NMR (CD_2Cl_2): δ 33.4 (d, Me), 128.8–138.0 (m, Ph). ^{31}P NMR (CD_2Cl_2): δ 17.2 (s).

Preparation of 2.[6] The synthesis of **2** was performed as for **1**, using Ph_2PCl (22.00 g, 100 mmol), sodium sand (4.59 g, 200 mmol), and propionyl chloride (9.25 g, 100 mmol). Compound **2** was obtained after distillation under reduced pressure (120–135 °C, 0.5 mmHg) (70%). IR (Nujol): ν(C=O) 1665 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 0.86 (t, Me, 3 H, J = 7.3 Hz), 2.28 (2q, CH_2, 2 H, J = 7.3 Hz, J_{HP} = 2.90 Hz), 7.05 and 7.45 (m, Ph, 10 H). ^{31}P NMR (CD_2Cl_2): δ 13.2 (s).

Preparation of 3. Compound **1** (2.19 g, 9.6 mmol) was dissolved in THF (50 mL) which was added *via* syringe at −100 °C. To the solution obtained was added slowly and cautiously Bu^{n}Li (6 mL, 9.6 mmol). The color must remain light yellow. After a few minutes a white crystalline solid formed. Et_2O (30 mL) was added, and the solid was filtered out, dried, and collected (78%). At room temperature, the product turns slowly light yellow and loses its crystallization solvent. ^{1}H NMR (C_6D_6): δ 1.41 (s, THF, 4 H), 3.74 (s, THF, 4 H), 3.90 (s, =CH_2, 1H), 4.64 (d, =CH_2, 1 H, J_{HP} = 13.7 Hz), 7.05–7.20 (m, Ph, 6 H), 7.6–7.7 (m, Ph, 4 H). ^{13}C NMR (C_6D_6): δ 26.0 (s, THF), 68.7 (s, Ph), 94.0 (d, =CH_2), 127.9 and 140.5 (m, Ph), 169.9 (s, C—O). ^{31}P NMR (CD_2Cl_2): δ −5.1 (s).

Preparation of 4. Compound **1** (7.30 g, 32.0 mmol) was dissolved in THF (100 mL) which was added *via* syringe at −100 °C. To the solution obtained was added dropwise Bu^{n}Li (20 mL, 32.0 mmol). The solution was stirred for 1 h, then cp_2ZrCl_2 (9.35 g, 32.0 mmol) was added, and the color turned initially orange and then violet. The reaction was stirred overnight, allowing the temperature to rise gently to room temperature. The THF was evaporated to give a violet-red oil, which was left to stand overnight. It crystallized slowly and turned orange-red again. The partially crystallized oil was dissolved in ether (100 mL), and the solution was filtered. The white solid was purified by a 2-day extraction with fresh distilled Et_2O (100 mL) (62%). Anal. Calcd for $C_{24}H_{22}ClOPZr$: C, 59.55; H, 4.58. Found: C, 59.93; H, 4.55. ^{1}H NMR (CD_2Cl_2): δ 4.43 (d, =CH_2, 1 H, J_{HP} = 7.2 Hz), 4.60 (d, =CH_2, 1 H, J_{HP} = 26.5 Hz), 6.14 (s, cpZr, 10 H), 7.4–7.5 (m, Ph, 10 H). ^{1}H NMR (C_6D_6): δ 4.64 (d, =CH_2, 1 H, J_{HP} = 6.7 Hz), 4.78 (d, =CH_2, 1 H, J_{HP} = 25.6 Hz), 5.85 (s, cpZr, 10 H), 7.1 (m, Ph, 10 H). ^{13}C NMR (CD_2Cl_2): δ 103.0 (d, =CH_2), 114.9 (s, cpZr), 129.0–136.9 (m, Ph), 169.2 (s, C—O). ^{31}P NMR (CD_2Cl_2): δ −0.76 (s), −1.01 (s).

Table 2. Fractional Atomic Coordinates (×10^4) for Complex 5

atom	x/z	y/b	z/c
Zr1	298.1(5)	2529.1(5)	3556.1(6)
Cl1	1956(2)	2141(2)	4095(3)
P1	1403(2)	3248(1)	−588(2)
O1	477(4)	2842(4)	1701(5)
C1	246(5)	930(4)	3446(11)
C2	−182(5)	1160(4)	4668(11)
C3	−1036(5)	1606(4)	4385(11)
C4	−1137(5)	1651(4)	2988(11)
C5	−345(5)	1233(4)	2408(11)
C6	−380(8)	3301(5)	5504(8)
C7	−845(8)	3615(5)	4356(8)
C8	−160(8)	4060(5)	3592(8)
C9	728(8)	4021(5)	4267(8)
C10	592(8)	3552(5)	5448(8)
C11	1675(4)	2123(3)	−770(5)
C12	1691(4)	1825(3)	−2069(5)
C13	1819(4)	969(3)	−2313(5)
C14	1929(4)	410(3)	−1259(5)
C15	1913(4)	708(3)	40(5)
C16	1786(4)	1565(3)	284(5)
C21	2312(3)	3641(3)	554(6)
C22	2127(3)	4404(3)	1185(6)
C23	2836(3)	4791(3)	1939(6)
C24	3731(3)	4415(3)	2062(6)
C25	3917(3)	3651(3)	1431(6)
C26	3207(3)	3264(3)	677(6)
C27	347(6)	3225(5)	529(8)
C28	−469(6)	3567(5)	191(8)
C29	−693(8)	4002(6)	−1087(10)

Preparation of 5. Compound **2** (5.00 g, 20.64 mmol) was dissolved in THF (100 mL) which was added *via* syringe at −100 °C. To the solution obtained was added dropwise Bu^{n}Li (13.0 mL, 20.8 mmol). The solution was stirred for 1 h, then cp_2ZrCl_2 (5.87 g, 20.08 mmol) was added, and the color turned initially orange and then violet. The reaction was stirred overnight, allowing the temperature to rise gently to room temperature. The THF was evaporated, the residue was redissolved in CH_2Cl_2 (50 mL), and LiCl was filtered off. The solvent was evaporated to dryness yielding an oil, which was dissolved in Et_2O (50 mL). A white crystalline solid was collected (15%). Large crystals of the *E* isomer suitable for X-ray analysis were obtained by ether extraction. When *n*-hexane (50 mL) was added and the solution was cooled down to −25 °C for a few hours, the *Z* isomer was obtained (37%, overall yield *E* + *Z*, 52%). Anal. Calcd for $C_{25}H_{24}ClOPZr$: C, 60.28; H, 4.86. Found: C, 61.14; H, 5.04. *E* isomer: ^{1}H NMR (CD_2Cl_2) δ 2.06 (dd, Me, 3 H, J_{HH} = 7.2 Hz, J_{HP} = 1.75 Hz), 5.24 and 5.35 (2q, =CH, 1 H, J_{HH} = 7.3 Hz, J_{HP} = 21.5 Hz), 6.01 (s, cpZr, 10 H), 7.35–7.55 (m, Ph, 10 H); ^{31}P NMR (CD_2Cl_2) δ −16.1 (s). *Z* isomer: ^{1}H NMR (CD_2Cl_2) δ 1.68 (d, Me, 3 H, J_{HH} = 6.7 Hz, J_{HP} = 0 Hz), 4.72 (m, =CH, 1 H, J_{HH} = 6.8 Hz, J_{HP} = 0 Hz), 6.12 (s, cpZr, 10 H), 7.35–7.55 (m, Ph, 10 H); ^{31}P NMR (CD_2Cl_2) δ +1.05 (s).

Reaction of 4 with Benzaldehyde, Synthesis of 6. Compound **2** (0.048 g, 0.10 mmol), distilled benzaldehyde (10.0 μL, 0.10 mmol), and C_6D_6 were combined in a NMR tube. The ^{1}H NMR spectrum shows essentially an ABX system coupled with a phosphorus atom. A total of 20 peaks with five different coupling constants have been observed: J_{AB}, J_{AX}, J_{BX}, J_{AP}, and J_{BP}. ^{1}H NMR (C_6D_6): δ 2.66 (dq, CH_2(AB), 1 H), 3.20 (dq, CH_2-

Table 3. Fractional Atomic Coordinates (×10⁴) for Complex 10

atom	x/a	y/b	z/c
Zr1	304.1(3)	980.3(2)	2303.3(2)
Cr1	5605.4(6)	2964.6(4)	4399.8(3)
Cl1	-752.4(12)	2356.3(8)	1699.5(7)
P1	3834.1(9)	1940.6(6)	3941.9(5)
O1	1693(2)	1664(2)	2948(1)
C1	-1223(5)	1231(4)	3107(3)
C2	-314(5)	607(4)	3437(3)
C3	-438(6)	-200(3)	3047(3)
C4	-1480(6)	-73(5)	2478(3)
C5	-1966(5)	813(5)	2520(3)
C6	2213(5)	188(6)	1979(3)
C7	1158(9)	-452(4)	1875(4)
C8	203(6)	-103(4)	1327(3)
C9	644(6)	674(4)	1110(2)
C10	1859(6)	884(4)	1499(3)
C11	2611(4)	1884(3)	4465(2)
C12	2759(4)	1301(3)	5026(2)
C13	1825(5)	1304(4)	5426(2)
C14	779(5)	1896(4)	5274(3)
C15	642(5)	2494(4)	4731(3)
C16	1565(4)	2496(3)	4335(2)
C21	4220(4)	728(2)	3775(2)
C22	3437(4)	-16(3)	3862(2)
C23	3735(4)	-903(3)	3669(2)
C24	4797(4)	-1049(3)	3379(2)
C25	5563(4)	-314(3)	3284(2)
C26	5295(4)	575(3)	3488(2)
C27	2779(3)	2193(2)	3090(2)
C28	3067(4)	2820(3)	2672(2)
C29	6191(4)	2944(3)	3576(3)
O29	6594(3)	2944(2)	3088(2)
C30	6719(4)	1947(3)	4725(2)
O30	7424(3)	1353(3)	4915(2)
C31	5075(5)	3027(3)	5250(3)
O31	4794(5)	3113(3)	5759(2)
C32	4520(5)	3996(3)	4107(3)
O32	3902(4)	4645(3)	3954(2)
C33	6956(5)	3776(4)	4751(3)
O33	7792(4)	4301(3)	4950(2)

(AB), 1 H), 5.71 (q, CH(X), 1 H), 5.90 and 6.10 (2s, cpZr, 10 H), 6.95–7.20 (m, PPh, 1 H), 7.45–7.65 (m, Ph, 5 H). Geminal coupling constant: J_{AB} = 16.25 Hz. Vicinal coupling constant: J_{AX} = 9.00 Hz, J_{BX} = 3.45 Hz. J_{HP} coupling constant: J_{AP} = 3.15 Hz, J_{BP} = 4.40 Hz.

Reactions of *E* and *Z* Isomers of 5 with Benzaldehyde, Synthesis of 8. These reactions have been followed by ^{1}H NMR. The *E* isomer of 5 (45 mg, 0.091 mmol), distilled benzaldehyde (9.2 μL, 0.091 mmol), and CD_2Cl_2 were combined in an NMR tube. ^{1}H NMR (CD_2Cl_2), two isomers *syn/anti* = 10/90: δ (1) 0.55 (d, Me, 3 H, J = 7.0 Hz), 3.22 (p, COCH, 1 H), 5.19 (d, CHOZr, 1 H, J = 8.8 Hz), 6.02 and 6.12 (2s, cpZr, 10 H), 7.0–7.5 (m, Ph, 15 H); δ (2) 1.01 (d, Me, 3 H, J = 6.8 Hz), 3.09 (p, COCH, 1 H, J = 6.6 Hz), 5.50 (d, CHOZr, 1 H, J = 5.5 Hz), 6.20 and 6.30 (2s, cpZr, 10 H), 7.0–7.5 (m, Ph, 15 H). ^{31}P NMR (CD_2Cl_2): δ 18.9 (1) and 20.7 (2). The *Z* isomer of 5 (54 mg, 0.108 mmol), distilled benzaldehyde (15.0 μL, 0.148 mmol), and CD_2Cl_2 were combined in an NMR tube yielding two isomers *syn/anti* = 44/56 and identical chemical shifts.

Preparation of 10. A [Cr(CO)$_5$·THF] solution, prepared *in situ* from Cr(CO)$_6$ (0.77 g, 3.5 mmol) in THF (250 mL), was added dropwise at room temperature to a THF (50-mL) solution of 4 (1.58 g, 3.3 mmol). The dark yellow solution was stirred for 3–4 h, then the solvent was evaporated, and the oily residue was redissolved in Et_2O (50 mL). After a few hours of standing, white crystals were obtained (53%). IR (Nujol): ν(CrCO) 2063 (m), 1991 (w), 1945 (s), 1927 (s) cm^{-1}. Anal. Calcd for $C_{29}H_{22}ClCrO_6PZr$: C, 51.52; H, 3.28. Found: C, 51.73; H, 3.33. ^{1}H NMR (CD_2Cl_2): δ 4.67 (dd, =CH$_2$, 1 H, J_{HH} = 1.3 Hz, J_{AP} = 33.8 Hz), 5.23 (dd, =CH$_2$, 1 H, J_{BP} = 9.0 Hz), 5.64 (s, cpZr, 10 H), 7.0–7.2 (m, Ph, 6 H), 7.55–7.7 (m, Ph, 4 H). ^{13}C NMR (CD_2Cl_2): δ 105.5 (d, =CH$_2$), 114.6 (s, cpZr), 127.9–135.3 (m, Ph), 165.4 (s, =C—O), 217.6, 217.9, and 222.4 (3s, Cr—CO). ^{31}P NMR (CD_2Cl_2): δ -36.5 and -36.85 (2s).

Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 5

Zr1–Cp1[a]	2.222(7)	P1–C21	1.828(6)
Zr1–Cp2	2.212(8)	P1–C11	1.837(5)
Zr1–Cl1	2.464(3)	O1–C27	1.343(10)
Zr1–O1	1.955(5)	C27–C28	1.311(12)
P1–C27	1.861(9)	C28–C29	1.498(13)
Cp1–Zr1–Cp2	129.2(3)	C21–P1–C11	104.5(3)
O1–Zr1–Cp1	107.1(3)	C27–P1–C11	101.9(3)
O1–Zr1–Cp2	106.3(3)	C27–P1–C21	100.2(3)
Cl1–Zr1–Cp1	104.4(2)	P1–C27–O1	115.8(6)
Cl1–Zr1–Cp2	106.8(3)	O1–C27–C28	122.4(8)
Cl1–Zr1–O1	98.9(2)	P1–C27–C28	121.8(6)
Zr1–O1–C27	160.5(5)		

[a] Cp1 and Cp2 refer to the centroids of the cyclopentadienyl rings C1···C5 and C6···C10, respectively.

Table 5. Selected Bond Distances (Å) and Angles (deg) for Complex 10

Zr1–Cp1[a]	2.219(6)	P1–C11	1.823(5)
Zr1–Cp2	2.211(6)	P1–C21	1.838(3)
Zr1–Cl1	2.452(1)	P1–C27	1.850(4)
Zr1–O1	1.979(2)	O1–C27	1.345(4)
Cr1–C29	1.878(6)	C27–C28	1.308(6)
Cr1–C30	1.895(4)	C29–O29	1.144(7)
Cr1–C31	1.901(6)	C30–O30	1.138(6)
Cr1–C32	1.882(5)	C31–O31	1.125(8)
Cr1–C33	1.849(5)	C32–O32	1.139(6)
Cr1–P1	2.387(1)	C33–O33	1.158(7)
Cp1–Zr1–Cp2	130.2(2)	P1–Cr1–C31	91.0(2)
O1–Zr1–Cp2	108.4(2)	P1–Cr1–C30	91.2(1)
O1–Zr1–Cp1	106.2(2)	P1–Cr1–C29	91.7(2)
Cl1–Zr1–Cp2	105.9(2)	Zr1–O1–C27	152.1(2)
Cl1–Zr1–Cp1	104.9(2)	Cr1–P1–C27	119.2(1)
Cl1–Zr1–O1	96.1(1)	Cr1–P1–C21	118.2(1)
C32–Cr1–C33	88.8(2)	Cr1–P1–C11	113.1(1)
C31–Cr1–C33	88.8(2)	C21–P1–C27	97.5(2)
C31–Cr1–C32	88.1(2)	C11–P1–C27	100.6(2)
C30–Cr1–C33	89.8(2)	C11–P1–C21	105.7(2)
C30–Cr1–C32	178.0(2)	P1–C27–O1	112.9(2)
C30–Cr1–C31	90.5(2)	O1–C27–C28	123.9(3)
C29–Cr1–C33	88.5(2)	P1–C27–C28	123.2(3)
C29–Cr1–C32	91.8(2)	Cr1–C29–O29	177.3(4)
C29–Cr1–C31	177.3(2)	Cr1–C30–O30	177.6(4)
C29–Cr1–C30	89.7(2)	Cr1–C31–O31	176.0(4)
P1–Cr1–C33	178.9(2)	Cr1–C32–O32	176.7(5)
P1–Cr1–C32	90.2(2)	Cr1–C33–O33	177.6(5)

[a] Cp1 and Cp2 refer to the centroids of the cyclopentadienyl rings C1···C5 and C6···C10, respectively.

X-ray Crystallography. The crystals of 5 and 10 were mounted in glass capillaries and sealed under nitrogen. Crystal data and details associated with data collection are given in Table 1. The reduced cells quoted were obtained using TRACER.[11] Data were collected at room temperature (295 K) on a single-crystal four circle diffractometer (Rigaku AFC6S and Siemens AED for 5 and 10, respectively). For intensities and background individual reflection profiles were analyzed.[12] The structure amplitudes were obtained after the usual Lorentz and polarization corrections and the absolute scale was established by the Wilson method.[13] The crystal quality was tested by showing that crystal absorption effects could not be neglected for 5. Intensity data for 5 were corrected for absorption using a semiempirical method[14] based on a ψ scan. The function minimized during the full-

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matrix least-squares refinement was $\Sigma w|\Delta F|^2$. A weighting scheme $w = k/[\sigma^2(F_o) + g|F_o|^2]$, based on counting statistics, was applied.[15] Anomalous scattering corrections were included in all structure factor calculations.[16b] Scattering factors for neutral atoms were taken from ref 16a for non-hydrogen atoms and from ref 17 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary. All calculations were carried out on a IBM-AT personal computer equipped with an INMOS T800 Transputer using SHELX-76.[15]

Solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was first done isotropically and then anisotropically for all the non-H atoms. During the refinement the cyclopentadienyl and phenyl rings in **5** were constrained to be regular pentagons (C–C = 1.420 Å) and hexagons (C–C = 1.395 Å), respectively. The hydrogen atoms, put in geometrically calculated positions for **5** and located from a difference Fourier map for **10**, were introduced in calculations prior to the final cycles of refinement as fixed contributors (isotropic U's fixed at 0.08 Å^2). In **5** the crystal chirality was tested by inverting all the coordinates ($x, y, z \rightarrow -x, -y, -z$) and refining to convergence once again. The resulting R values ($R = 0.044$, $R_G = 0.064$ *vs* $R = 0.043$, $R_G = 0.063$) indicated the original choice should be the correct one.

The final difference map showed no unusual features, with no significant peak above the general background. Final atomic coordinates are listed in Tables 2 and 3 for non-H atoms and in Tables SII and SIII for hydrogens. Thermal parameters are given in Tables SIV and SV; selected bond distances and angles in Tables 4 and 5.[18]

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Supplementary Material Available: Tables of experimental details associated with data collection and structure refinement (Table SI), hydrogen atom coordinates (Tables SII and SIII), thermal parameters (Tables SIV and SV), and bond distances and angles (Tables SVI and SVII) for complexes **5** and **10** (9 pages). Ordering information is given on any current masthead page.

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