((Diaryl- and Dialkylphosphino)alkyl)cyclopentadienyl Ligands and Their Use in the Preparation of Heterobinuclear Ti/Mo and Zr/Mo Complexes

Todd W. Graham, Angela Llamazares, Robert McDonald,† and Martin Cowie*

Department of Chemistry, University of Alberta, Edmonton, AB, Canada T6G 2G2

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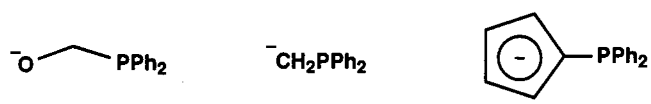
The syntheses of a series of bifunctional ligands, in which a cyclopentadienyl and a phosphine group are linked by either a CH_2 or a C_2H_4 fragment ($^-C_5H_4(CH_2)_nPR_2$; $n = 1, 2$; R = Me, Ph), are reported, as is that of the related ligand, $Li_2[Me_2C(C_5H_3CMe_2PPh_2)_2]$, in which both substituted cyclopentadienyl rings are linked by the CMe_2 group. The metallocene dichloride complexes Cp'_2MCl_2 (M = Ti, Zr; $Cp'_2 = 2C_5H_4(CH_2)_nPPh_2$ ($n = 1, 2$), $Me_2C((C_5H_3)C(Me)_2PPh_2)_2$) have also been prepared, and the X-ray structure of $(\eta^5\text{-}C_5H_4(CH_2)_2PPh_2)_2ZrCl_2$ (**7**) has been determined. This complex has the pendent phosphinoalkyl arms close to eclipsed on the two C_5H_4 groups and bisecting the $ZrCl_2$ angle, but bent in opposite directions away from the $ZrCl_2$ plane. Reaction of **7** and its Ti analogue with (COD)Mo(CO)$_4$ yields the heterobinuclear complexes $[(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PPh_2)_2MCl_2Mo(CO)_4]$ (M = Ti, Zr). Structure determinations of these bimetallic complexes show the expected cis arrangement of phosphine moieties at Mo, M−Mo separations of 6.895 Å (M = Ti) and 6.945 Å (M = Zr), and MCl_2 moieties aimed at right angles to the M−Mo vectors.

Introduction

The interest in early−late heterobimetallic (ELHB) complexes derives primarily from the goal of utilizing two metals, having widely divergent properties, to induce transformations that would not be possible through the use of either metal alone. When these early and late transition metals are in close proximity, their differing properties should result in a polar bifunctional environment that may be capable of displaying novel reactivity resulting from some form of cooperative interaction between the two metals.[1,2] Although a number of routes can be used for the preparation of ELHB complexes,[3−7] one commonly used method involves the use of a bifunctional ligand template that is capable of binding strongly to both metal types. This eliminates the need for metal−metal bonds to hold the metals close enough for a cooperative interaction and helps maintain the integrity of the complex during reactions of interest. A variety of bifunctional ligand types have been used, three of which are shown in structures **A**,[2a,4] **B**,[5] and **C**.[6] In each type shown, the phosphine functionality forms favorable interactions with the late metal, while the anionic functionality binds to the early metal.



A **B** **C**

The ubiquity of early-metal cyclopentadienyl and late-metal phosphine complexes prompted us to use a ligand similar to the type shown above in **C**. However, we felt that using the ligand in **C**, in which the PR_2 moiety is bound directly to the cyclopentadienyl ring,[6] would result in geometric constraints on the complex that might inhibit reactivity by holding the metals together in too rigid an environment. It seemed that the introduction of an alkyl spacer between the cyclopentadienyl and phosphino groups might alleviate these restrictions,

* To whom correspondence should be addressed.

† Faculty Service Officer, Structure Determination Laboratory.

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allowing greater conformational freedom of the two metal coordination spheres. Accordingly, we have decided to use (phosphinoalkyl)cyclopentadienyl ligands, containing a "C_1" or "C_2" spacer between the Cp and PR_2 functionalities as a template upon which to prepare our ELHB complexes. This approach has been used by a few others.[7]

Our strategy for the preparation of the ELHB complexes was to first synthesize early-metal metallocene-like species, in which the cyclopentadienyl rings are derivatized with a phosphinoalkyl moiety, and then to react these early-metal-containing monomers with late-metal sources. One aspect of interest was the elucidation of the effect of the different spacer lengths in the C_5H_4-$(CR_2)_nPR_2$ ligands ($n = 1$ or 2) on the structures of the ELHB products and a comparison of these data with the known ELHB complexes containing the bridging ligand shown in **C** above.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified argon with standard Schlenk techniques or in a nitrogen-filled Vacuum Atmospheres glovebox equipped with an HE−493 dri-train. Solvents were dried and distilled under nitrogen immediately before use. Sodium benzophenone was used as the drying agent for all solvents except CH_2Cl_2, which was distilled from P_2O_5. Group 4 metal salts and diphenylphosphine were purchased from Strem or Aldrich. Diphenylphosphine and $TiCl_4$ were used as received, and $ZrCl_4$ was sublimed immediately before use. Spiro[2.4]-hepta-4,6-diene,[8] fulvene,[9] and $[Mo(CO)_4(COD)]$[10] were prepared via literature methods. $KPPh_2$ was prepared by the reaction of $HPPh_2$ with excess KH in THF solution, and $LiPPh_2$ was prepared via the reaction of $HPPh_2$ with 1 equiv of *n*-BuLi (2.5 M in hexanes) in THF. Dimethylphosphine[11] was prepared via the reaction of tetramethyldiphosphine disulfide with $LiAlH_4$. The product was distilled from the reaction vessel directly into a flask containing ca. 1 molar equiv of *n*-BuLi in 50 mL of *n*-pentane that had been cooled to −80 °C, and the resulting $LiPMe_2$ was collected on a glass frit.

The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM-400 spectrometer operating at 400.1, 162.0, and 100.6 MHz for the respective nuclei. The internal deuterated solvent served as a lock for the spectrometer. Elemental analyses were performed by the microanalytical service within the department. NMR spectroscopic data for all compounds are given in Table 1, while infrared data for the appropriate compounds are reported together with the details of their preparation.

Preparation of Compounds. (a) $K[C_5H_4CH_2CH_2PPh_2]$ (1). A solution of 8.9 g (0.040 mol) of $KPPh_2$ in 220 mL of THF was added to 4.5 mL (0.044 mol) of spiro[2.4]hepta-4,6-diene in 450 mL of THF at −80 °C. The solution was warmed to room temperature and stirred for 3 h, during which time a white crystalline solid was produced. The solution was concentrated in vacuo to ca. two-thirds of the original volume, and the precipitate was collected on a glass frit. Yield: 9.0 g (72%) based on $KPPh_2$. The compound was obtained spectroscopically pure, but elemental analyses could not be obtained due to its highly air-sensitive nature.

(b) $Li[C_5H_4CH_2CH_2PMe_2]$ (2). A suspension of 1.694 g (0.025 mol) of $LiPMe_2$ in 10 mL of *n*-pentane was cooled to −80 °C, and then 40 mL of THF was added. This solution was added to 2.8 mL (0.027 mol) of spiro[2.4]hepta-4,6-diene in 20 mL of THF at −80 °C, and then the solution was warmed to room temperature. After stirring for 3 h, the solvent was removed in vacuo, and then the white solid was triturated in 50 mL of *n*-pentane, followed by collection on a glass frit and washing with 3 × 10 mL of *n*-pentane. The solid was dried in vacuo to give 2.792 g (70%) of a spectroscopically pure product. Elemental analyses were not obtained due to the highly air-sensitive nature of the compound.

(c) $K[C_5H_4CH_2PPh_2]$ (3). A 16.0 g (0.071 mol) sample of $KPPh_2$ in a mixture of 100 mL of THF and 300 mL of Et_2O was added to a solution of 4.45 g (0.057 mol) of fulvene in 300 mL of Et_2O at −80 °C, resulting in the immediate formation of an off-white precipitate. The mixture was warmed to room temperature with vigorous stirring, and then the solid was collected on a frit. Yield: 13.6 g, 63% based on $KPPh_2$. The compound was obtained spectroscopically pure, but elemental analyses were not obtained due to its highly air-sensitive nature.

(d) $[Me_2C((C_5H_3{=}C(CH_3)_2)_2]$ (4). This compound was prepared as previously reported,[12] with minor modifications. A 4.36 mL (0.052 mol) sample of pyrrolidine was added to 1.853 g (0.011 mol) of $(C_5H_5)_2CMe_2$ and 1.6 mL (0.022 mol) of acetone in 26 mL of a 10:1 mixture of $MeOH/Et_2O$ at 5 °C. The solution was stirred at room temperature for 16.5 h, and then 3.2 mL (0.0559 mol) of acetic acid was added at −10 °C. A 30 mL portion of water and 30 mL of Et_2O were added in air, and the organic layer was removed. The aqueous layer was washed with 3 × 20 mL of Et_2O, and then the organic portions were combined and washed with 3 × 20 mL of water and 1 × 20 mL of brine and then dried over Na_2SO_4 and molecular sieves. The solvent was removed under reduced pressure, and the crude yellow oil eluted through a 600 mL fritted glass filter containing an 8 cm thick plug of silica. The solvent was removed under reduced pressure yielding 2.243 g, 82% of a yellow oil.

(e) $Li_2[Me_2C(C_5H_3C(CH_3)_2PPh_2)_2]$ (5). A 2.20 g (8.72 mmol) sample of fulvene **4** in 50 mL of THF was added to a solution of $LiPPh_2$ (17.2 mmol) in 80 mL of THF at −80 °C over 5 min. The solution was warmed to room temperature and stirred for 16 h, and then the solvent was removed in vacuo. The orange foamy residue was triturated with 100 mL of *n*-pentane until a powdery off-white solid was obtained, which was collected on a glass frit and washed with 3 × 20 mL of *n*-pentane, followed by drying in vacuo. Yield: 7.69 g, 70% based on $LiPPh_2$. The compound was obtained spectroscopically pure, but elemental analyses could not be obtained due to the highly air-sensitive nature of the compound.

(f) $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2]$ (6). Method 1: A solution of 0.866 g (2.59 mmol) of $TiCl_4(THF)_2$ in 50 mL of THF was added dropwise to 2.246 g (7.10 mmol) of $K[C_5H_4CH_2CH_2PPh_2]$ (**1**) in 110 mL of THF over 2 h. After stirring overnight, a red solution had formed (if the solution was brown at this point, concentrated HCl could be added dropwise until a red solution formed), and the solvent was removed in vacuo. The residue was extracted with 3 × 20 mL of toluene, the extracts

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Table 1. NMR Spectroscopic Data for Compounds[a]

compound	NMR[b] $\delta(^{31}P\{^1H\})$ (ppm)	NMR[b] $\delta(^1H)$ (ppm)
$K[C_5H_4CH_2CH_2PPh_2]$ (**1**)[c]	−16.1(s)	2.82(dt, 2H, $^3J_{HH} = 7.0$ Hz, $J_{HP} = 11.1$ Hz, $C_5H_4CH_2CH_2PPh_2$) 2.29(t, 2H, $^3J_{HH} = 7.0$ Hz, $C_5H_4CH_2CH_2PPh_2$) 5.40(m, 2H, $C_5H_4CH_2CH_2PPh_2$) 5.43(m, 2H, $C_5H_4CH_2CH_2PPh_2$)
$Li[C_5H_4CH_2CH_2PMe_2]$ (**2**)[c]	−55.9(s)	1.61(dt, 2H, $^3J_{HH} = 7.8$ Hz, $J_{HP} = 1.2$ Hz, $C_5H_4CH_2CH_2PMe_2$) 2.61(dt, 2H, $^3J_{HH} = 7.8$ Hz, $J_{HP} = 10.3$ Hz, $C_5H_4CH_2CH_2PMe_2$) 5.48(m, 2H, $C_5H_4CH_2CH_2PMe_2$) 5.53(m, 2H, $C_5H_4CH_2CH_2PMe_2$)
$K[C_5H_4CH_2PPh_2]$ (**3**)[c]	−16.3(s)	3.41(s, br, 2H, $C_5H_4CH_2PPh_2$) 5.37(s, br, 4H, $C_5H_4CH_2PPh_2$)
$[Me_2C(C_5H_3{=}CMe_2)_2]$ (**4**)[d]		1.49(s, 6H, CMe_2) 2.16(s, 6H, $=CMe$) 2.17(s, 6H, $=CMe$) 6.22(m, 2H, C_5H_3) 6.42(m, 2H, C_5H_3) 6.49(m, 2H, C_5H_3)
$Li_2[Me_2C(C_5H_3CMe_2PPh_2)_2]$ (**5**)[c]	20.2(s)	1.30(d, 12H, $^3J_{HP} = 11.8$ Hz, CMe_2PPh_2) 1.61(s, 6H, $Me_2C(C_5H_3CMe_2PPh_2)_2$) 5.58(m, 2H, C_5H_3) 5.65(m, 2H, C_5H_3) 5.77(m, 2H, C_5H_3)
$[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2]$ (**6**)	−16.5(s)	2.36(t, 4H, $CH_2CH_2PPh_2$) 2.81(dt, 4H, $J_{HP} = 9.0$ Hz, $J_{HH} = 7.5$ Hz, $CH_2CH_2PPh_2$) 6.26(m, 4H, C_5H_4) 6.33(m, 4H, C_5H_4)
$[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2]$ (**7**)	−16.5(s)	2.33(t, 4H, $J_{HH} = 8.0$ Hz, $CH_2CH_2PPh_2$) 2.73(dt, 4H, $J_{HP} = 9.1$ Hz, $J_{HH} = 8.0$ Hz, $CH_2CH_2PPh_2$) 6.18(m, 4H, C_5H_4) 6.25(m, 4H, C_5H_4)
$[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2TiCl_2]$ (**8**)	−9.6(s)	3.51(s, br, 4H, CH_2PPh_2) 6.00(m, 4H, C_5H_4) 6.25(m, 4H, C_5H_4)
$[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2ZrCl_2]$ (**9**)	−9.7(s)	3.41(s, br, 4H, CH_2PPh_2) 5.94(m, 4H, C_5H_4) 6.17(m, 4H, C_5H_4)
rac-$[Me_2C(C_5H_3CMe_2PPh_2)_2ZrCl_2]$ (**10a**)	32.7(s)	1.48(d, 6H, $^3J_{HP} = 13.0$ Hz, CMe_2PPh_2) 1.58(s, 6H, $Me_2C(C_5H_3CMe_2PPh_2)_2$ 1.75(d, 6H, $^3J_{HP} = 16.2$ Hz, CMe_2PPh_2) 5.07(m, 2H, C_5H_3) 5.48(m, 2H, C_5H_3) 5.99(m, 2H, C_5H_3)
meso-$[Me_2C(C_5H_3CMe_2PPh_2)_2ZrCl_2]$ (**10b**)	33.2(s)	1.47(d, 6H, $^3J_{HP} = 14.9$ Hz, CMe_2PPh_2) 1.53(s, 3H, $Me_2C(C_5H_3CMe_2PPh_2)_2$ 1.73(s, 3H, $Me_2C(C_5H_3CMe_2PPh_2)_2$ 1.77(d, 6H, $^3J_{HP} = 17.6$ Hz, CMe_2PPh_2) 5.20(m, 2H, C_5H_3) 5.66(m, 4H, C_5H_3)
$[(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2Mo(CO)_4]$[d] (**11**)	26.6 (s, Mo-*P*)	6.24(br, 8H, C_5H_4) 2.45 (m, 4H, $CH_2CH_2PPh_2$) 2.55 (m, 4H, $CH_2CH_2PPh_2$)
$[(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2Mo(CO)_4]$[d] (**12**)	26.6 (s, Mo-*P*)	6.37 (m, 4H, C_5H_4) 6.31 (m, 4H, C_5H_4) 2.55 (m, 8H, $CH_2CH_2PPh_2$)

[a] Abbreviations used: for NMR (s) singlet, (d) doublet, (dt) doublet of triplets, (m) multiplet, (dd) doublet of doublets, (br) broad. [b] NMR spectra recorded in CD_2Cl_2 unless otherwise stated. [c] NMR spectra recorded in THF-d_8. [d] NMR spectra recorded in $CDCl_3$; phosphorus-bound phenyl groups omitted.

were filtered through Celite to remove KCl and polymeric materials, and then the solvent was removed in vacuo. The red residue was triturated with three 10 mL portions of Et_2O, yielding 520 mg of a red powder. Yield: 30%. Anal. Calcd for $C_{36}H_{32}P_2Cl_2Ti$: C, 67.77; H, 5.39. Found: C, 67.60; H, 5.38.

Method 2: A solution of 0.568 g (1.63 mmol) of $TiCl_3(THF)_3$ in 60 mL of THF was added to 1.100 g (3.47 mmol) of $K[C_5H_4CH_2CH_2PPh_2]$ (**1**) in 120 mL of THF at −80 °C over 30 min. The solution was warmed to room temperature and stirred for 19 h, during which time the color changed to dark green. The flask was opened to the air, and ca. 3.5 mL of concentrated HCl was added, resulting in a color change to red over 5 min. The solution was cooled to −40 °C, and then 2 mL of pyridine was added to the solution, which was then warmed to room temperature. After stirring for several minutes at room temperature, the solvent was removed in vacuo. The residue was extracted with 4 × 10 mL of toluene, then the extracts were filtered through Celite to remove KCl and polymeric materials, and the solvent was removed in vacuo. The red residue was triturated in Et_2O (4 × 15 mL), resulting in the formation of a red powder. Yield: 628 mg, 57%. The product was spectroscopically identical to that obtained by method 1.

(g) $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2]$ (7). A 815 mg (2.58 mmol) sample of $K[C_5H_4CH_2CH_2PPh_2]$ (**1**) in 20 mL of toluene was added to 300 mg (1.29 mmol) of $ZrCl_4$ in 20 mL of toluene at −80 °C. The solution was warmed slowly to room temperature and stirred for 18 h. The solvent was removed in vacuo, and then the residue was dissolved in 40 mL of CH_2Cl_2 and filtered through Celite. If the filtrate was yellow, then a small amount (ca. 100 mg) of activated carbon was added, followed by stirring for 5 min and filtration through Celite to give a colorless solution. Alternatively, the yellow impurity could be precipitated by the addition of *n*-pentane to a CH_2Cl_2 solution of the compound at 0 °C, followed by solvent removal via cannula. The solvent from the filtrate was removed in vacuo, and the colorless residue recrystallized by dissolving in 5 mL of CH_2Cl_2, cooling to −20 °C, and slowly adding 30 mL of *n*-pentane. The solvent was removed via cannula and the white microcrystalline solid washed with 3 × 10 mL of *n*-pentane and then dried in vacuo. Crystalline material could be obtained by adding *n*-pentane to a CH_2Cl_2 solution of the compound at 0 °C until the solution became slightly turbid, followed by cooling to −20 °C for 48 h. Yield: 415 mg, 45%. Anal. Calcd for $C_{38}H_{36}P_2Cl_2Zr$: C, 63.68; H, 5.06. Found: C, 63.45; H, 5.01.

(h) [(η^5-$C_5H_4CH_2PPh_2$)$_2$TiCl$_2$] (8). A 286 mg (0.823 mmol) sample of $TiCl_3(THF)_3$ in 30 mL of THF was added to 548 mg (1.81 mmol) of K[$C_5H_4CH_2PPh_2$] (**3**) in 60 mL of THF at −80 °C over 30 min. The solution was warmed to room temperature and stirred for 18 h. Concentrated HCl (25 drops) was added in air to the green solution, resulting in an immediate color change to red. After stirring for 2 min the solvent was removed in vacuo and the red residue extracted with 4 × 10 mL of toluene. The extracts were filtered through Celite, and the solvent was removed in vacuo. The red residue was triturated with *n*-pentane (3 × 10 mL) until a red powder was obtained, which was then dried in vacuo. Yield: 290 mg, 55%. Anal. Calcd for $C_{36}H_{32}P_2Cl_2Ti$: C, 67.00; H, 5.00. Found: C, 66.53; H, 5.23.

(i) [(η^5-$C_5H_4CH_2PPh_2$)$_2$ZrCl$_2$] (9). A suspension of 368 mg (1.22 mmol) of K[$C_5H_4CH_2PPh_2$] (**3**) in 15 mL of toluene was added to a suspension of 136 mg (0.583 mmol) of $ZrCl_4$ in 15 mL of toluene at −80 °C over 5 min. The suspension was warmed slowly to room temperature and stirred for a total of 18 h. The solvent was removed in vacuo and the residue dissolved in 20 mL of CH_2Cl_2, followed by filtration through Celite. The solvent was removed in vacuo and the yellow oily solid redissolved in 3 mL of CH_2Cl_2 and cooled to −10 °C. A 30 mL sample of *n*-pentane was added, resulting in the formation of an oily yellow solid and milky white suspension. The suspension was removed via cannula, the solvent volume was reduced to half in vacuo, and the mixture was cooled to −20 °C. A 10 mL sample of *n*-pentane was added, and the mixture was stirred at −20 °C for 30 min. The solvent was removed via cannula, and the white solid was washed with 2 × 10 mL of *n*-pentane and dried in vacuo. Yield: 107 mg of an analytically pure product. The oily solid was triturated in 3 × 10 mL of *n*-pentane and dried in vacuo to give 49 mg of a spectroscopically pure product. Total yield: 156 mg, 40%. Anal. Calcd for $C_{36}H_{32}P_2Cl_2Zr$: C, 62.78; H, 4.68. Found: C, 62.62; H, 4.66.

(j) [Me$_2$C(C$_5$H$_3$C(CH$_3$)$_2$PPh$_2$)$_2$ZrCl$_2$] (10). A 563 mg (0.884 mmol) sample of Li$_2$[Me$_2$C(C$_5$H$_3$C(CH$_3$)$_2$PPh$_2$)$_2$] (**5**) in 25 mL of toluene was added to 200 mg (0.858 mmol) of $ZrCl_4$ in 15 mL of toluene at −80 °C over 5 min. The solution was warmed slowly to room temperature and stirred for 16.5 h. The solvent was removed in vacuo, then 20 mL of CH_2Cl_2 was added, and the yellow solution was filtered through Celite. The solvent was removed in vacuo, and the residue was recrystallized by dissolving in 3 mL of CH_2Cl_2, cooling to − 15 °C, and then adding 20 mL of *n*-pentane, resulting in the formation of a yellow-brown solid. The solution was filtered through Celite at −15 °C, and then the solvent was removed in vacuo, yielding a bright yellow solid. Trituration of this solid with 3 × 10 mL of *n*-pentane gave a bright yellow powdery solid. Yield: 269 mg, 40%. Anal. Calcd for $C_{43}H_{44}P_2Cl_2Zr$: C, 65.80; H, 5.65. Found: C, 65.17, H, 5.65. Repeated attempts to obtain satisfactory carbon analyses were unsuccessful, presumably owing to the difficulties encountered in removing LiCl.

(k) [(μ-η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$PPh$_2$)$_2$TiCl$_2$Mo(CO)$_4$] (11). A 28.6 mg (0.091 mmol) sample of [(COD)Mo(CO)$_4$] in 10 mL of THF was added via cannula to 61 mg (0.091 mmol) of [(η^5-C$_5$H$_4$CH$_2$CH$_2$PPh$_2$)$_2$TiCl$_2$] (**6**) in 10 mL of THF. The red solution was stirred for 1 h, and then the solvent was removed in vacuo. The red residue was recrystallized by dissolving in 5 mL of CH_2Cl_2 and adding 20 mL of MeOH dropwise, followed by stirring for 1 h. The red microcrystalline solid that had formed was washed with 2 × 10 mL of MeOH and 1 × 10 mL of Et_2O and then dried in vacuo. Yield: 30 mg, 40% of an analytically pure product. Anal. Calcd for $C_{42}H_{36}P_2O_4Cl_2$-TiMo: C, 57.23; H, 4.12. Found: C, 57.11; H, 3.96. IR spectrum (Nujol): 2023 (med, sh), 1927 (s), 1896 (vs).

(l) [(μ-η^5:η^1-C$_5$H$_4$CH$_2$CH$_2$PPh$_2$)$_2$ZrCl$_2$Mo(CO)$_4$] (12). A 72 mg (0.227 mmol) sample of [(COD)Mo(CO)$_4$] in 30 mL of THF was added via cannula to 163 mg (0.227 mmol) of [(η^5-C$_5$H$_4$-CH$_2$CH$_2$PPh$_2$)$_2$ZrCl$_2$] (**7**) in 30 mL of THF. The yellow solution was stirred for 1.5 h, and then the solvent was removed in vacuo. The yellow residue was recrystallized by dissolving in CH_2Cl_2 and filtering if necessary, followed by the dropwise addition of MeOH until a white solid formed. The solid was washed with 2 × 10 mL of MeOH, then 1 × 10 mL Et_2O, followed by drying in vacuo. Yield: 173 mg, 84%. Anal. Calcd for $C_{42}H_{36}P_2O_4Cl_2ZrMo$: C, 54.55; H, 3.92. Found: C, 54.56; H, 3.88. IR spectrum (Nujol): 2022 (med, sh), 1928 (s), 1896 (vs).

X-ray Data Collection and Structure Solution. (a) Crystals of **7** were obtained by layering *n*-pentane onto a CH$_2$-Cl$_2$ solution of the compound. Data were collected to a maximum $2\theta = 50.0°$ on a Siemens P4/RA diffractometer using Mo Kα radiation at −60 °C. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 40 reflections with $25.4° < 2\theta < 28.0°$. The systematic absences indicated the space group to be *I*2/*a* (a nonstandard setting of *C*2/*c* [No. 15]). Three reflections were chosen as intensity standards and were remeasured after every 300 reflections, with no decay evident. The data were corrected for absorption through use of a semiempirical correction based on azimuthal (ψ) scans of several reflections. See Table 2 for a summary of crystal data and X-ray data collection information.

The structure was solved by direct methods (SHELXS-86[13]), and refinement was completed using the program SHELXL-93.[14] Hydrogen atoms were assigned positions based on the geometries of their attached carbon atoms and were given thermal parameters 20% greater than those of the attached carbons. The final model refined to values of $R_1(F) = 0.0279$ (for 2707 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.0676$ (for all 3053 independent data).

(b) Crystals of both **11** and **12** were obtained by slow diffusion of Et_2O into CH_2Cl_2 solutions of the compounds. Data were collected at −50 °C to a maximum $2\theta = 50.0°$ on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 24 reflections with $20.0° < 2\theta < 24.0°$. Both compounds crystallized in the space group $P\bar{1}$ (No. 2). Three reflections were chosen as intensity standards and were remeasured after every 7200 s of X-ray exposure time; in both cases no decay was observed. Absorption corrections were applied to the data for compound **12** using the method of Walker and Stuart,[15] whereas for **11** the crystal faces were indexed and measured, and a Gaussian integration was carried out. See Table 2 for a summary of crystal data and X-ray data collection information.

(13) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.
(14) Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination; University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections except for two having $F_o^2 < -3\sigma(F_o^2)$ for compound **11** and except for three having $F_o^2 < -3\sigma(F_o^2)$ for compound **12**. Weighted *R*-factors wR_2 and all goodnesses of fit *S* are based on F_o^2; conventional *R*-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1 and is not relevant to the choice of reflections for refinement. *R*-factors based on F_o^2 are statistically about twice as large as those based on F_o, and *R*-factors based on ALL data will be even larger.
(15) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158−166.

Table 2. Crystallographic Details for Compounds 7, 11, and 12

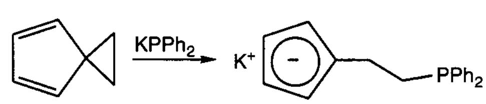
	7	**11**·0.5CH_2Cl_2	**12**·0.5CH_2Cl_2
A. Crystal Data			
formula	$C_{38}H_{36}Cl_2P_2Zr$	$C_{42.5}H_{37}Cl_3MoO_4P_2Ti$	$C_{42.5}H_{37}Cl_3MoO_4P_2Zr$
fw	716.73	923.85	967.17
cryst dimens (mm)	0.70 × 0.50 × 0.29	0.39 × 0.21 × 0.16	0.53 × 0.35 × 0.30
cryst system	monoclinic	triclinic	triclinic
space group	*I*2/*a* (a nonstandard setting of *C*2/*c* [No. 15])	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
unit cell params[a]			
a (Å)	26.974(3)	13.336(2)	13.4643(11)
b (Å)	6.4587(9)	13.547(3)	13.553(2)
c (Å)	20.671(2)	12.330(2)	12.4283(15)
α (deg)		104.46(2)	104.568(11)
β (deg)	105.598(8)	107.996(13)	108.050(8)
γ (deg)		77.340(14)	77.489(8)
V (Å^3)	3468.5(7)	2026.9(7)	2063.1(4)
Z	4	2	2
ρ_{calcd} (g cm^{-3})	1.373	1.514	1.557
abs coeff (mm^{-1})	0.589	0.825	0.869
B. Data Collection and Refinement Conditions			
diffractometer	Siemens P4/RA[c]	Enraf-Nonius CAD4[b]	Enraf-Nonius CAD4[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)	graphite-monochromated Mo Kα (0.71073)	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	−60	−50	−50
scan type	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$
data collection 2θ limit (deg)	50.0	50.0	50.0
total data collected	6236 ($-32 \le h \le 32$, $-7 \le k \le 7$, $-24 \le l \le 24$)[d]	7410 ($0 \le h \le 15$, $-15 \le k \le 16$, $-14 \le l \le 13$)	7517 ($-14 \le h \le 15$, $-15 \le k \le 16$, $0 \le l \le 14$)
indep reflns	3053	7073	7072
no. of observations (NO)	2707 ($F_o^2 \ge 2\sigma(F_o^2)$)	3404 ($F_o^2 \ge 2\sigma(F_o^2)$)	4563 ($F_o^2 \ge 2\sigma(F_o^2)$)
range of transmission factors	0.8765−0.8039	0.8878−0.8367	1.135−0.800
no. of data/restraints/params	3053 [$F_o^2 \ge -3\sigma(F_o^2)$]/0/195	7071 [$F_o^2 \ge -3\sigma(F_o^2)$]/3[e]/482	7069 [$F_o^2 \ge -3\sigma(F_o^2)$]/3[e]/482
goodness-of-fit (S)[f]	1.077 [$F_o^2 \ge -3\sigma(F_o^2)$]	1.007 [$F_o^2 \ge -3\sigma(F_o^2)$]	1.023 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[g]			
$R_1[F_o^2 > 2\sigma(F_o^2)]$	0.0279	0.0760	0.0703
$wR_2[F_o^2 \ge -3\sigma(F_o^2)]$	0.0676	0.2291	0.2274
largest diff peak and hole (e Å^{-3})	0.378 and −0.240	1.053 and −1.095	1.401 and −1.256

[a] Obtained from least-squares refinement of 40 reflections with 25.4° < 2θ < 28.0° for compound **7**, 24 reflections with 20.0° < 2θ < 23.9° for compound **11**, and 24 reflections with 19.8° < 2θ < 23.8° for compound **12**. [b] Programs for diffractometer operation and data collection were those supplied by Enraf-Nonius. [c] Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Siemens. [d] Data were collected from Friedel-opposite quadrants of reciprocal space with indices of the form ($+h - k \pm l$) and ($-h + k \pm l$). [e] An idealized geometry was imposed on the inversion-disordered CH_2Cl_2 solvent molecule by setting d(Cl(3)−C(99)) = d(Cl(3′)−C(99)) = 1.80(1) Å and d(Cl(3)···Cl(3′)) = 2.95(1) Å for compounds **11** and **12**. [f] $S = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_oP)^2 + a_1P]^{-1}$ where $a_o = 0.0342$, $a_1 = 1.9425$ for compound **7**, $a_o = 0.0988$, $a_1 = 0$ for compound **11** and $a_0 = 0.1170$ and $a_1 = 16.5289$ for compound **12**; $P = [\max(F_o^2, 0) + 2F_c^2]/3$). [g] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

Structure solution and refinement of **11** and **12** was as described for **7**. The final model for **11** refined to values of $R_1(F) = 0.0760$ (for 3404 data with $F_o^2 \ge 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.2291$ (for all 7073 independent data), while the final refinement indices for **12** were $R_1(F) = 0.0703$ (for 4563 observed data) and $wR_2(F^2) = 0.2274$ (for all 7072 independent data).

Results and Compound Characterization

Preparation of Cyclopentadienyl Phosphine Ligands. The first ligand synthesized, $^{-}C_5H_4(CH_2)_2PPh_2$, was prepared by a modification of an earlier method involving the reaction of lithium diphenylphosphide with spiro[2.4]hepta-4,6-diene, followed by hydrolysis and then purification via chromatography.[16] We have found that this ligand may be obtained more conveniently as a spectroscopically pure crystalline solid by using $KPPh_2$, instead of the lithium salt as shown in eq 1, and may be used directly without further purification. The compound K[$C_5H_4CH_2CH_2PPh_2$] (**1**) has a ^{31}P-



(1)

(1)

{^{1}H} NMR chemical shift of δ −16.1, and the ^{1}H NMR spectrum shows methylene signals at δ 2.29 as a triplet ($^3J_{HH}$ = 7.0 Hz) and δ 2.82 as a doublet of triplets (J_{HH} = 7.0 Hz, J_{HP} = 11.1 Hz). The cyclopentadienyl region of the ^{1}H NMR spectrum displays two AA′BB′ multiplets at δ 5.40 and 5.43, the pattern of which appears to be typical of these compounds. In a similar reaction (starting from $LiPMe_2$), the dimethylphosphino derivative Li[$C_5H_4CH_2CH_2PMe_2$] (**2**) is obtained, which displays a singlet in the ^{31}P{^{1}H} NMR spectrum at δ −55.9. The methylene and Cp′ resonances are as expected in the ^{1}H NMR spectrum.

The analogous "C_1" ligand, having a one-carbon spacer between the cyclopentadienyl and phosphine units, K[$C_5H_4CH_2PPh_2$] (**3**), is obtained by the addition of potassium diphenylphosphide to a solution of fulvene at low temperature, as shown in eq 2. The spectroscopy

(16) Kauffmann, T.; Bisling, M.; Teuben, J. H.; Konig, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 328.

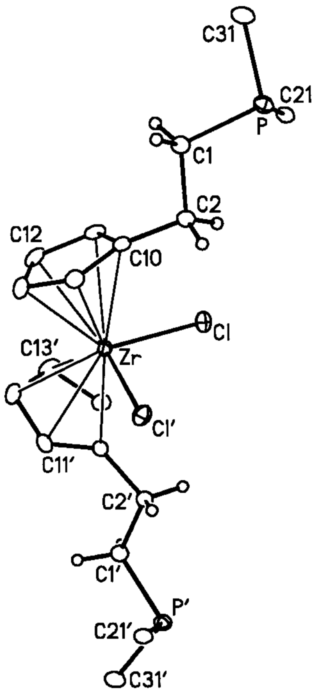
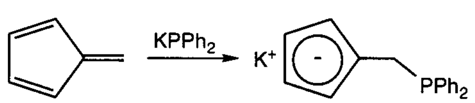


Figure 1. Perspective view of [(η^5-$C_5H_4C_2H_4PPh_2$)$_2$$ZrCl_2$] (**7**). Thermal ellipsoids are drawn at the 20% level except for methylene hydrogens, which are shown arbitrarily small. Only the ipso carbons of the phenyl rings are shown, and hydrogens on cyclopentadienyl rings are also not shown. These rings are numbered starting at the ipso carbon. Primed atoms are related to unprimed ones by a crystallographic 2-fold rotation axis ($^1/_4$, *y*, 0) passing through the Zr atom.

on this compound is similar to that of **1** except for the single ^{1}H resonance for the methylene group and a single resonance for the cyclopentadienyl hydrogens, which are apparently coincidentally degenerate.



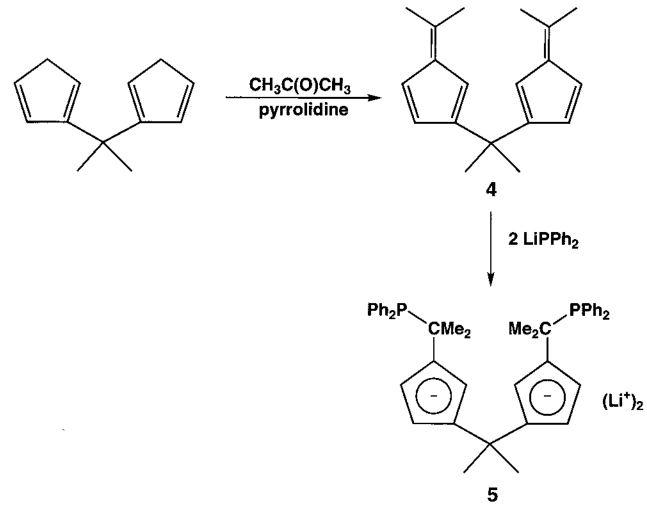
(2)

3

The related "C$_1$" ligand, Li_2[Me_2C(C_5H_3C(Me)$_2PPh_2$)$_2$] (**5**), in which each Cp ring is linked to the phosphine moiety by a C(CH_3)$_2$ spacer group, and in which the Cp rings are also connected to each other by a C(CH_3)$_2$ linker, is obtained by addition of lithium diphenylphosphide to the difulvene shown in Scheme 1. The presence of alkyl substituents on the spacer carbon between the Cp and PPh_2 groups results in a large change in the ^{31}P NMR chemical shift, when compared to K[$C_5H_4CH_2$-PPh_2] (**3**), with the resonance for the two equivalent phosphines appearing as a singlet at δ 20.2. The ^{1}H NMR spectrum shows a doublet for the methyls bound to the spacer carbon with phosphorus coupling of 11.8 Hz, and this coupling allows for the differentiation of this signal and that of the methyls bound to the linker carbon (linking the two Cp groups), which appears as a singlet. Three separate multiplets are observed for the cyclopentadienyl hydrogens.

Preparation of Metallocene Dichlorides. Our strategy for the preparation of ELHB complexes, or analogous compounds containing mid rather than late

Scheme 1



transition metals, was to first complex the cyclopentadienyl unit of the heterobifunctional ligands to an early metal, followed by reaction of these metallocene-like derivatives with late-metal sources. The compound [(η^5-$C_5H_4CH_2CH_2PPh_2$)$_2$$TiCl_2$] (**6**) was prepared initially by the reaction of K[$C_5H_4CH_2CH_2PPh_2$] (**1**) with $TiCl_4$-(THF)$_2$. This reaction proceeds with concomitant reduction of Ti(IV) to Ti(III), as evidenced by the formation of a dark green solution. It was found that pure **6** could be obtained, albeit in low yield, by air oxidation of these green solutions, followed by subsequent workup. Alternatively, **6** can be obtained in higher yield via the reaction of K[$C_5H_4CH_2CH_2PPh_2$] (**1**) with $TiCl_3$(THF)$_3$, followed by oxidation with HCl. Although an analytically pure product can be obtained via this method, signals in the ^{1}H and ^{31}P NMR spectra of the product are often broadened slightly, presumably due to the presence of small amounts of paramagnetic Ti(III)-containing impurities. The ^{31}P{^{1}H} NMR resonance for compound **6** is very similar to that of the free ligand, suggesting that the phosphorus is not coordinated to the titanium center, and the ^{1}H NMR spectrum also resembles that of the free ligand, apart from a shift of the Cp hydrogen signals to lower field. The zirconocene dichloride derivative, [(η^5-$C_5H_4CH_2CH_2PPh_2$)$_2$$ZrCl_2$] (**7**), is prepared via the reaction of K[$C_5H_4CH_2CH_2PPh_2$] (**1**) with either $ZrCl_4$ or $ZrCl_4$(THF)$_2$ and has remarkably similar spectroscopic properties to compound **6**, including an identical ^{31}P NMR chemical shift. Single crystals of **7**, suitable for X-ray analysis, were obtained by slowly cooling a CH_2Cl_2/*n*-pentane solution of the complex, and the resulting structure is shown to consist of a typical pseudotetrahedral ligand arrangement around zirconium (see Figure 1). A crystallographic 2-fold axis bisects the Cl−Zr−Cl′ angle. Selected bond lengths and angles are given in Table 3. The Zr−Cl bond length and Cl−Zr−Cl′ bond angle of 2.4448(6) Å and 99.69(3)°, respectively, are typical of zirconocene-type compounds.[17] Although one might have anticipated that the bulky substituents on the Cp′ ring would be staggered with respect to each other, thereby minimizing mutual repulsions, they are twisted only slightly from an eclipsed

(17) (a) Petersen, J. L.; Egan, J. W. *Inorg. Chem.* **1983**, *22*, 3571. (b) Green, J. C.; Green, M. L. H.; Prout, C. K. *J. Chem. Soc., Chem. Commun.* **1972**, 421, and references therein.

Table 3. Selected Bond Lengths and Angles for [(η^5-$C_5H_4CH_2CH_2PPh_2)_2ZrCl_2$] (7)

(a) Selected Interatomic Angles (Å)

atom 1	atom 2	distance	atom 1	atom 2	distance
Zr	Cl	2.4448(6)	P	C(31)	1.837(2)
Zr	C(10)	2.565(2)	C(1)	C(2)	1.539(3)
Zr	C(11)	2.509(2)	C(2)	C(10)	1.498(3)
Zr	C(12)	2.473(2)	C(10)	C(11)	1.424(3)
Zr	C(13)	2.462(2)	C(10)	C(14)	1.400(3)
Zr	C(14)	2.534(2)	C(11)	C(12)	1.398(3)
P	C(1)	1.850(2)	C(12)	C(13)	1.408(4)
P	C(21)	1.841(2)	C(13)	C(14)	1.410(3)

(b) Selected Interatomic Angles (deg)

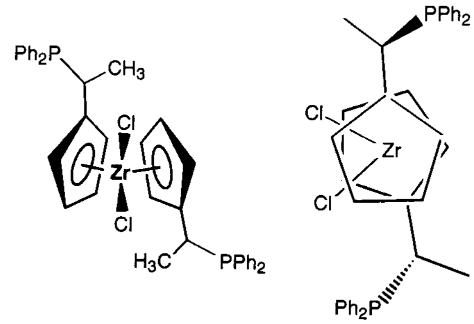
atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cl	Zr	Cl′[a]	99.69(3)	C(22)	C(21)	C(26)	118.7(2)
C(1)	P	C(21)	98.73(9)	C(21)	C(22)	C(23)	121.2(3)
C(1)	P	C(31)	102.25(10)	C(22)	C(23)	C(24)	119.8(3)
C(21)	P	C(31)	99.89(9)	C(23)	C(24)	C(25)	120.5(2)
P	C(1)	C(2)	111.54(15)	C(24)	C(25)	C(26)	119.9(3)
C(1)	C(2)	C(10)	110.2(2)	C(21)	C(26)	C(25)	119.9(2)
C(2)	C(10)	C(11)	125.4(2)	P	C(31)	C(32)	125.0(2)
C(2)	C(10)	C(14)	127.6(2)	P	C(31)	C(36)	116.8(2)
C(11)	C(10)	C(14)	106.7(2)	C(32)	C(31)	C(36)	118.1(2)
C(10)	C(11)	C(12)	108.8(2)	C(31)	C(32)	C(33)	120.9(3)
C(11)	C(12)	C(13)	107.7(2)	C(32)	C(33)	C(34)	120.6(3)
C(12)	C(13)	C(14)	107.8(2)	C(33)	C(34)	C(35)	119.3(3)
C(10)	C(14)	C(13)	108.9(2)	C(34)	C(35)	C(36)	120.8(3)
P	C(21)	C(22)	118.4(2)	C(31)	C(36)	C(35)	120.4(3)
P	C(21)	C(26)	122.9(2)				

[a] Primed atoms are related to unprimed ones via the 2-fold rotational axis ($^1/_4$, *y*, 0).

conformation, with a C(10)−Cp(c)−Cp(c)′−C(10′) torsion angle of 27.2° (Cp(c) = centroid of C_5 ring), in which the substituents essentially bisect the Cl−Zr−Cl′ angle, giving a C(2)−C(10)−Zr−X torsion angle of 12.9° (X = bisector of Cl−Zr−Cl′ angle). Despite the almost eclipsed alignment, the phosphinoalkyl arms are directed away from each other, with the alkyl substituents on each ring aimed in opposite directions away from the $ZrCl_2$ plane. In this orientation the bulky substituents minimize repulsions between each other. In addition, by occupying the carbons of the tilted monosubstituted Cp groups that are furthest from each other on opposite Cp rings, steric repulsions are further minimized. This orientation of the alkyl substituents is essentially that desired for using the $(Ph_2PC_2H_4C_5H_4)_2ZrCl_2$ moiety as a bidentate metalloligand on a late metal except that the phosphines are directed in essentially opposite directions (up and down in Figure 1). However, rotation about the C(10)−C(2) and C(10′)-C(2′) bonds, bringing the phosphine moieties closer, is all that is required to allow this unit to function as a chelating metalloligand.

The presence of a diphenylphosphinoethyl group bound to each cyclopentadienyl ring of **7** has resulted in a slight asymmetry in the Zr−C bond lengths, with these distances decreasing steadily from 2.565(2) Å at the substituted carbon to 2.468 Å (average) for C(12) and C(13). In addition, the asymmetry is also evident in the angles within the Cp′ groups (Cp′ = C_5H_4R), where that of the substituted carbon is 106.7(2)° and the average for the unsubstituted carbons is 108.3°. The Cp(c)−Zr−Cp(c)′ angle and the Cp(c)−Zr distances are remarkably similar to those found in Cp'_2ZrCl_2, with values of 130.9° and 2.205 (average) Å, respectively.

The structure of **7** can be compared with four closely related group 4 metallocenes.[7b,18−20] It differs substantially from the structures of *rac*-[$(C_5H_4CH(CH_3)PPh_2)_2ZrCl_2$], shown in **D**,[7b] and a related amine species *rac*-



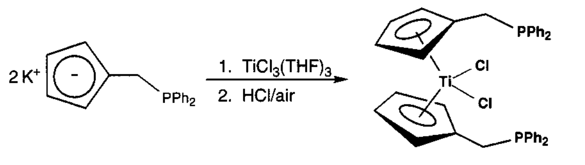
D

[$(C_5H_4CH(n\text{-}C_4H_9)NMe_2)_2ZrCl_2$],[18] mainly with respect to the orientation of the pendent groups to each other and to the chloro ligands. In compound **D**, these substituents are oriented with a C−Cp(c)−Cp(c)′−C′ dihedral angle of 178.6° (Cp(c) = centroid of C_5 ring, C and C′ are the spacer carbons), resulting in a staggered arrangement, and are also oriented at ca. 90° to the Cl−Zr−Cl bisector. In this case compound **D** can function as a chelating metalloligand by rotation of both Cp′ rings together by ca. 90°, to give an eclipsed arrangement. The related amine[18] has structural parameters closely resembling those of **D**. In [$(C_5H_4C(CH_3)_2PPh_2)_2Zr(CH_3)_2$][19] a slightly different geometry is observed. The phosphinoalkyl arms are eclipsed but are again directed approximately 90° to the bisector of the H_3C−Zr−CH_3 angle. This latter arrangement differs from **7** only by an approximate 90° rotation of the $Zr(CH_3)_2$ moiety. In these compounds[16,18,19] the pendent arms are oriented away from the ligands (Cl or CH_3) in the equatorial plane in order to minimize contacts between these

(18) Bertuleit, A.; Fritze, C.; Erker, G.; Fröhlich, R. *Organometallics* **1997**, *16*, 2891.
(19) Bosch, B. E.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1997**, 16, 5449.

ligands and the alkyl substituents on the spacer carbons. The [($C_5H_4CH_2CH_2N(^iPr)_2)_2TiCl_2$] complex,[20] on the other hand, having a C_2H_4 spacer between the C_5H_4 group and the amine functionality, has an arrangement of Cp′ groups much like that in **7**, in which the aminoalkyl arms are eclipsed and bisecting the $TiCl_2$ angle, but aimed away from the $TiCl_2$ plane. This arrangement is possible in which there are no substituents on the carbon linkers, since no unfavorable contacts involving the equatorial Cl ligands result. These differences in pendent arm orientation between these compounds may have important implications in the formation of ELHB complexes, with these observed orientations suggesting that oligomeric mixed-metal complexes may result by binding of the phosphine substituents to different late metals. A subsequent paper will describe a series of tetranuclear complexes formed in this way.[21]

The titanocene dichloride derivative with a diphenylphosphinomethyl unit bound to the cyclopentadienyl ring, [(η^5-$C_5H_4CH_2PPh_2)_2TiCl_2$] (**8**), was prepared similarly, by the reaction of K[$C_5H_4CH_2PPh_2$] (**3**) with $TiCl_3(THF)_3$, followed by oxidation with HCl, as shown in eq 3. ^{1}H NMR spectroscopy of this complex shows the

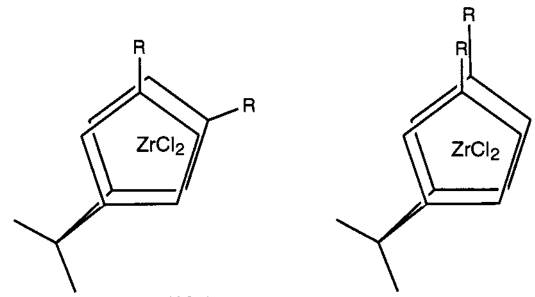


(3)

3 **8**

methylene singlet having no resolvable phosphorus coupling, as was observed for the free ligand, and the Cp′ resonances are again shifted slightly downfield compared to the free ligand. The $^{31}P\{^1H\}$ NMR spectrum of compound **8** shows a significant downfield shift, to δ −9.6, and contrasts with the observations in **6** and **7** of essentially no change in the ^{31}P NMR spectrum upon coordination of the Cp′ groups. In compound **8**, phosphine coordination to the early metal is not expected, as chelation should result in a significantly strained ring, although chelation of these ligand types has been observed in [(η^5:η^1-$C_5H_4CMe_2PPh_2)_2ZrMe$][$MeB(C_6F_5)_3$],[19] presumably to alleviate the electron deficiency at Zn that would otherwise result. The downfield ^{31}P shift in **8** is likely due to the smaller cyclopentadienyl−PPh_2 separation, which results in the phosphine unit being closer to the metal. The zirconium-containing derivative [(η^5-$C_5H_4CH_2PPh_2)_2ZrCl_2$] (**9**) was prepared via reaction of K[$C_5H_4CH_2PPh_2$] (**3**) with $ZrCl_4$ or $ZrCl_4(THF)_2$ and has spectroscopic features similar to compound **8**. The similarity of the ^{31}P NMR chemical shift provides further evidence that the phosphorus is not metal-bound, since one would expect a significant chemical-shift difference upon coordination to the two different metals.

Preparation of an *ansa*-metallocene dichloride was of interest in hopes that the presence of a one-carbon linker between the two cyclopentadienyl rings would decrease the rotational freedom of the cyclopentadienyl units, which may influence the tendency for binuclear complexes to form instead of oligomers. In addition, the linker should decrease the Cp(c)−M−Cp(c) angle, resulting in easier substrate access to the metal center.[22] Reaction of $Li_2[Me_2C(C_5H_3CMe_2PPh_2)_2]$ (**5**) with $ZrCl_4$ afforded a bright yellow product, the $^{31}P\{^1H\}$ NMR spectrum of which showed the presence of two compounds, *rac*- and *meso*-[$Me_2C(C_5H_3CMe_2PPh_2)_2ZrCl_2$] (**10a**, **10b**) in a 2.8:1 ratio.[23] These isomers have



rac (**10a**) meso (**10b**)

R = C(Me)$_2$PPh$_2$

differing solubility properties, allowing the rac isomer to be obtained spectroscopically pure, although the meso isomer was always found to be contaminated with the rac isomer. The $^{31}P\{^1H\}$ NMR spectrum of the rac isomer is similar to that of [(η^5-$C_5H_4CMe_2PPh_2)_2ZrCl_2$],[7b] with a ^{31}P NMR chemical shift of δ 32.7. ^{1}H NMR spectroscopy on this compound shows three cyclopentadienyl hydrogen resonances in the expected region, as well as doublets at δ 1.48 (J_{HP} = 13.0 Hz) and 1.75 (J_{HP} = 16.2 Hz) for the methyl groups adjacent to the PPh_2 groups, and a single resonance for the methyl groups on the CMe_2 moiety linking the two Cp′ groups. The spectral parameters for the meso isomer are very similar to those of **10a** (see Table 1) except that two of the C_5H_3 protons are accidentally equivalent, and two signals are observed for the methyl groups on the linker carbon. The key to determining whether the rac or meso isomer is obtained is the signal for the methyl hydrogens of the Me_2C group linking the two Cp′ groups. In the meso isomer, these methyl groups are in different chemical environments and are expected to have different chemical shifts, whereas in the rac isomer, which contains a C_2 rotation axis, the methyl groups are chemically equivalent. A pure sample of the rac isomer shows only the single resonance for the two methyls on the linker carbon.

Mixed-Metal Complexes of Mo. We began our studies of heterobimetallic complexes incorporating the bifunctional ligands described earlier with the synthesis of *cis*-[(μ-η^5:η^1-$C_5H_4CH_2CH_2PPh_2)_2MCl_2Mo(CO)_4$] (M = Ti (**11**), Zr (**12**)), in which the C_5H_4 and PPh_2 groups are linked by a C_2 spacer. It was of interest to compare the structures of **11** and **12** with the related compounds, [(μ-η^5:η^1-$C_5H_4PPh_2)_2ZrCl_2Mo(CO)_4$] (**E**)[6b] and [($\mu$-$\eta^5$;$\eta^1$-$C_5Me_4PPh_2)_2TiCl_2Mo(CO)_4$] (**F**),[6d] in which the PPh_2 groups are bound directly to the C_5H_4 or C_5Me_4 moieties,

(20) Jutzi, P.; Redeker, T.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 4153.
(21) Graham, T. W.; Llamazares, A.; McDonald, R.; Cowie, M. *Organometallics* **1999**, *18*, 3502.
(22) Smith, J. A.; Von Seyerl, J.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *173*, 175.
(23) Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965.

Table 4. Selected Bond Lengths and Angles for Compound 11

(a) Selected Interatomic Distances (Å)

atom 1	atom 2	distance	atom 1	atom 2	distance
Mo	P(1)	2.535(3)	P(2)	C(12)	1.826(10)
Mo	P(2)	2.535(3)	P(2)	C(41)	1.812(11)
Mo	C(1)	1.968(12)	P(2)	C(51)	1.831(11)
Mo	C(2)	2.067(13)	O(1)	C(1)	1.144(14)
Mo	C(3)	1.978(13)	O(2)	C(2)	1.132(13)
Mo	C(4)	1.965(11)	O(3)	C(3)	1.165(14)
Ti	Cl(1)	2.351(3)	O(4)	C(4)	1.176(13)
Ti	Cl(2)	2.325(4)	C(5)	C(6)	1.544(14)
Ti	C(7)	2.487(11)	C(6)	C(7)	1.50(2)
Ti	C(8)	2.422(12)	C(7)	C(8)	1.407(14)
Ti	C(9)	2.393(11)	C(7)	C(11)	1.43(2)
Ti	C(10)	2.333(12)	C(8)	C(9)	1.41(2)
Ti	C(11)	2.375(11)	C(9)	C(10)	1.35(2)
Ti	C(14)	2.431(11)	C(10)	C(11)	1.425(15)
Ti	C(15)	2.384(12)	C(12)	C(13)	1.498(14)
Ti	C(16)	2.344(12)	C(13)	C(14)	1.534(13)
Ti	C(17)	2.371(11)	C(14)	C(15)	1.388(15)
Ti	C(18)	2.437(12)	C(14)	C(18)	1.42(2)
P(1)	C(5)	1.816(11)	C(15)	C(16)	1.39(2)
P(1)	C(21)	1.835(12)	C(16)	C(17)	1.42(2)
P(1)	C(31)	1.850(11)	C(17)	C(18)	1.398(15)

(b) Selected Interatomic Angles (deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
P(1)	Mo	P(2)	100.64(10)	Mo	C(3)	O(3)	173.9(12)
P(1)	Mo	C(1)	90.0(4)	Mo	C(4)	O(4)	176.9(11)
P(1)	Mo	C(2)	90.9(3)	P(1)	C(5)	C(6)	120.5(8)
P(1)	Mo	C(3)	82.9(3)	C(5)	C(6)	C(7)	112.7(10)
P(1)	Mo	C(4)	173.5(4)	C(6)	C(7)	C(8)	128.0(11)
P(2)	Mo	C(1)	169.3(4)	C(6)	C(7)	C(11)	125.6(10)
P(2)	Mo	C(2)	89.2(3)	C(8)	C(7)	C(11)	106.4(10)
P(2)	Mo	C(3)	93.4(4)	C(7)	C(8)	C(9)	108.3(11)
P(2)	Mo	C(4)	85.4(4)	C(8)	C(9)	C(10)	109.3(10)
C(1)	Mo	C(2)	89.0(5)	C(9)	C(10)	C(11)	108.6(11)
C(1)	Mo	C(3)	89.4(6)	C(7)	C(11)	C(10)	107.2(10)
C(1)	Mo	C(4)	84.0(5)	P(2)	C(12)	C(13)	113.3(7)
C(2)	Mo	C(3)	173.6(5)	C(12)	C(13)	C(14)	115.8(9)
C(2)	Mo	C(4)	91.5(5)	C(13)	C(14)	C(15)	126.5(10)
C(3)	Mo	C(4)	94.4(5)	C(13)	C(14)	C(18)	125.5(10)
Cl(1)	Ti	Cl(2)	93.54(14)	C(15)	C(14)	C(18)	107.4(10)
Mo	P(1)	C(5)	112.7(4)	C(14)	C(15)	C(16)	110.2(11)
Mo	P(2)	C(12)	124.7(4)	C(15)	C(16)	C(17)	106.4(10)
Mo	C(1)	O(1)	173.3(11)	C(16)	C(17)	C(18)	108.9(10)
Mo	C(2)	O(2)	179.0(10)	C(14)	C(18)	C(17)	107.2(10)

to determine the effect on the geometry of having different length spacers between the C_5R_4 and PPh_2 moieties.

Compounds **11** and **12** were prepared via the reaction of [(η^5-$C_5H_4CH_2CH_2PPh_2$)$_2$$MCl_2$] (M = Ti (**6**), Zr (**7**)) with (COD)Mo(CO)$_4$, resulting in facile displacement of the labile diene group. The ^{31}P chemical shift upon coordination of the phosphino groups to the molybdenum center changes from δ −16.5 (for both **6** and **7**) to δ 26.6 and 26.5 (both singlets) for **11** and **12**, respectively. The Cp′ hydrogens in the ^{1}H NMR spectrum of compound **11** are apparently coincidentally degenerate and resonate at δ 6.24, whereas the two methylene resonances of the phosphine arms are complex multiplets at δ 2.55 and 2.45. The ^{1}H NMR spectrum of compound **12** is similar to that of **11** except that the Cp′ region now shows the expected AA′BB′ multiplets, centered at δ 6.34. The solution IR spectra of both compounds are virtually identical, with a carbonyl band pattern similar to that of (COD)Mo(CO)$_4$,[10] indicating that the phosphines, like the COD moiety, are bound to the molybdenum center in a cis arrangement. To confirm the structures of compounds **11** and **12** and to compare the differences due to the different group 4 metals, their structures were determined by single-crystal X-ray techniques. Both compounds are isostructural, with only subtle differences resulting from the two different metallic radii (Ti = 1.47 Å, Zr = 1.60 Å).[24] The general structural features of complexes **11** and **12** are quite similar, with pseudotetrahedral ligand arrangements around the group 4 metal and pseudooctahedral geometries about molybdenum, with the phosphines of the $C_5H_4CH_2CH_2PPh_2$ units bound cis to this metal. Figure 2 shows a perspective view of the Zr complex (**12**), while Figure 3 shows an alternate view of the same molecule looking down the Cp-Cp vector. The drawings for the Ti analogue (**11**) are not shown since they are essentially identical and the numbering scheme used is the same for both compounds. Selected bond lengths and angles for both compounds are given in Tables 4 and 5, respectively. The structural results confirm that the binuclear framework has been achieved in which the early and mid transition metals are bridged by the $^{-}C_5H_4CH_2CH_2PPh_2$ ligands. Metal−metal separations

(24) (a) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, 1984. (b) Values given are for coordination number 12; for pseudotetrahedral geometries these values should be multiplied by 0.88.

Table 5. Selected Bond Lengths and Angles for Compound 12

(a) Selected Interatomic Distances (Å)

atom 1	atom 2	distance	atom 1	atom 2	distance
Mo	P(1)	2.539(2)	P(2)	C(12)	1.837(8)
Mo	P(2)	2.540(2)	P(2)	C(41)	1.826(9)
Mo	C(1)	1.991(12)	P(2)	C(51)	1.838(9)
Mo	C(2)	2.071(11)	O(1)	C(1)	1.155(13)
Mo	C(3)	1.997(11)	O(2)	C(2)	1.146(12)
Mo	C(4)	2.006(10)	O(3)	C(3)	1.148(12)
Zr	Cl(1)	2.431(3)	O(4)	C(4)	1.132(11)
Zr	Cl(2)	2.412(2)	C(5)	C(6)	1.542(13)
Zr	C(7)	2.554(9)	C(6)	C(7)	1.497(13)
Zr	C(8)	2.542(9)	C(7)	C(8)	1.404(13)
Zr	C(9)	2.513(9)	C(7)	C(11)	1.413(13)
Zr	C(10)	2.474(9)	C(8)	C(9)	1.382(14)
Zr	C(11)	2.487(9)	C(9)	C(10)	1.412(15)
Zr	C(14)	2.541(9)	C(10)	C(11)	1.402(13)
Zr	C(15)	2.511(9)	C(12)	C(13)	1.536(12)
Zr	C(16)	2.475(9)	C(13)	C(14)	1.515(12)
Zr	C(17)	2.502(9)	C(14)	C(15)	1.412(12)
Zr	C(18)	2.541(8)	C(14)	C(18)	1.408(13)
P(1)	C(5)	1.824(9)	C(15)	C(16)	1.415(13)
P(1)	C(21)	1.823(10)	C(16)	C(17)	1.401(14)
P(1)	C(31)	1.833(9)	C(17)	C(18)	1.389(13)

(b) Selected Interatomic Angles (deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
P(1)	Mo	P(2)	100.87(8)	Mo	C(3)	O(3)	174.9(9)
P(1)	Mo	C(1)	90.3(3)	Mo	C(4)	O(4)	177.6(9)
P(1)	Mo	C(2)	90.9(3)	P(1)	C(5)	C(6)	119.8(6)
P(1)	Mo	C(3)	83.2(3)	C(5)	C(6)	C(7)	113.1(8)
P(1)	Mo	C(4)	172.8(3)	C(6)	C(7)	C(8)	127.1(9)
P(2)	Mo	C(1)	168.7(3)	C(6)	C(7)	C(11)	126.5(9)
P(2)	Mo	C(2)	88.9(3)	C(8)	C(7)	C(11)	106.3(9)
P(2)	Mo	C(3)	94.1(3)	C(7)	C(8)	C(9)	109.5(9)
P(2)	Mo	C(4)	85.6(3)	C(8)	C(9)	C(10)	108.2(8)
C(1)	Mo	C(2)	89.3(4)	C(9)	C(10)	C(11)	107.0(9)
C(1)	Mo	C(3)	88.9(4)	C(7)	C(11)	C(10)	109.0(9)
C(1)	Mo	C(4)	83.3(4)	P(2)	C(12)	C(13)	112.2(6)
C(2)	Mo	C(3)	173.8(4)	C(12)	C(13)	C(14)	113.6(7)
C(2)	Mo	C(4)	92.3(4)	C(13)	C(14)	C(15)	123.2(8)
C(3)	Mo	C(4)	93.3(4)	C(13)	C(14)	C(18)	128.4(8)
Cl(1)	Zr	Cl(2)	96.30(10)	C(15)	C(14)	C(18)	107.7(8)
Mo	P(1)	C(5)	112.2(3)	C(14)	C(15)	C(16)	107.1(8)
Mo	P(2)	C(12)	125.1(3)	C(15)	C(16)	C(17)	108.5(8)
Mo	C(1)	O(1)	173.9(9)	C(16)	C(17)	C(18)	107.9(8)
Mo	C(2)	O(2)	178.3(9)	C(14)	C(18)	C(17)	108.8(8)

of 6.895 and 6.945 Å in compounds **11** and **12**, respectively, rule out any metal−metal interaction. As shown in Figure 3, the cyclopentadienyl groups are staggered, where the angle subtended by the C(13)−C(14) and C(6)−C(7) vectors is 32.9° for both compounds, indicating that these groups rotate about the Cp−early-metal bond to find the most sterically favorable orientation. This drawing also shows that the molybdenum atom is located to the side of the pocket created by the canted cyclopentadienyl rings, with Mo−M−X angles (X is the bisector of the Cl−M−Cl angle) of 103.1° for compound **11** (M = Ti) and 104.4° for **12** (M = Zr), indicating that the early-metal substituents are directed essentially perpendicular to the early-metal−Mo vector. Also shown in Figures 2 and 3, access between the early metals and Mo is inhibited by the orientations of the C_2H_4 spacer between the PPh_2 and C_5H_4 groups, in which the methylene hydrogens block access to this cavity. Despite the coordination of the phosphine substituents to the Mo center, the Cp(centroid)−M−Cp(centroid) angles of 128.9° and 128.3° for these compounds are remarkably similar to those found in Cp'_2TiCl_2 (130.2°), in Cp'_2ZrCl_2 (128.9°),[17] and in the Zr precursor (**7**) (130.9°). Some asymmetry is noted in the M−Cl bond lengths, with M−Cl(1)/M−Cl(2) distances of 2.351(3) Å/2.325(4) Å for M = Ti and 2.431(3) Å/2.412(2) Å for M = Zr. The M−Cl(1) distances are similar to the corresponding bond lengths in Cp'_2TiCl_2 and Cp'_2ZrCl_2,[17] suggesting that this bond length is normal. Furthermore, it may be recalled that in the early-metal precursor (**7**) the Zr−Cl distances were identical (by symmetry) at 2.4448(6) Å. We suggest that the somewhat shorter M−Cl(2) distances may be due to intramolecular nonbonded contacts, since the intermolecular contacts are similar for both Cl(1) and Cl(2). However, Cl(2) has additional intramolecular nonbonded contacts with H(5A), H(6B), and H(12A), ranging from 2.75 to 2.76 Å, which act in a direction tending to compress the M−Cl(2) distances. The M−C bond lengths around the Cp′ rings show some distortion, presumably due to the presence of the diphenylphosphinoalkyl substituent, with the longest bond being to the cyclopentadienyl carbon connected to this substituent; for M = Zr these distances are Zr−C(7) = 2.554(9) and Zr−C(14) = 2.541(9) Å, whereas the Zr−C distance for the unsubstituted carbons ranges from 2.474(9) to 2.542(9) Å. These metal−carbon separations decrease with distance from the alkyl substituent, suggesting that the phosphinoalkyl group is forcing

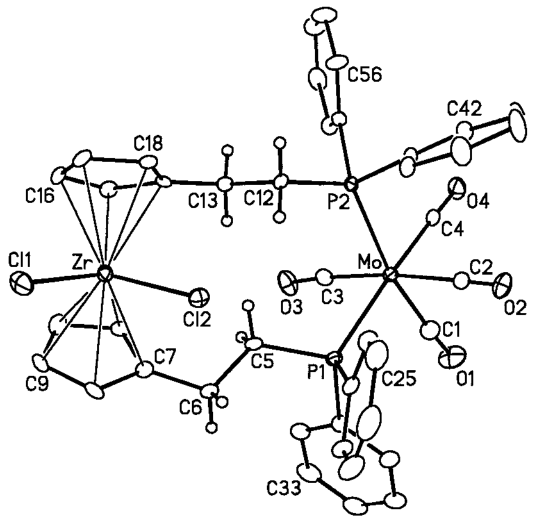


Figure 2. Perspective view of [(μ-η^5:η^1-$C_5H_4C_2H_4PPh_2$)$_2$-$ZrCl_2Mo(CO)_4$] (**12**). Thermal parameters and numbering convention as described in Figure 1. Numbering scheme for the Ti analogue (**11**) is identical.

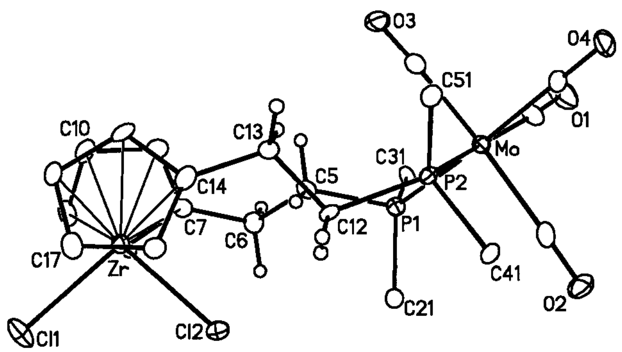


Figure 3. Alternate view of compound **12** viewed along the vector joining the Cp centroids.

the Cp rings apart. The structure of **11** shows similar effects in the Ti−Cp′ carbon bond lengths, and these deviations have also been observed in [(μ-η^5:η^1-C_5H_4-PPh_2)$_2ZrCl_2Mo(CO)_4$] (**E**),[6b] as well as in the precursor **7**. About molybdenum, the geometry in **11** and **12** is pseudooctahedral, with significant distortions due to the presence of the two cis phosphine substituents, which result in a P−Mo−P angle of 100.6(1)° in compound **11** and a similar value of 100.87(8)° for compound **12**. The large P−M−P angles result in a corresponding decrease of the C(1)−Mo−C(4) bond angle to 84.0(5)° and 83.3(4)° for the two compounds. These distortions were not nearly as pronounced in compounds **E** and **F** and are likely due to the preference of the phosphinoalkyl arms of the metalloligands **6** and **7** to be as far apart as possible, as was evidenced by the solid-state structure of compound **7** (vide supra). Although one would expect a trans influence in the Mo−C bond lengths, with the carbonyls opposite the phosphines differing from those opposite each other, there is no obvious correlation.

A comparison of the Ti and Zr compounds **11** and **12** with compounds **F** and **E**, in which the PPh_2 groups are directly bound to the C_5Me_4 or C_5H_4 rings, and which also involve Ti (**F**) and Zr (**E**), is enlightening. Although some of the significant differences between **E** and **F** were attributed to the smaller radius of Ti versus Zr,[6d] the structures of **11** and **12**, which are almost superimposable despite the different group 4 metals, indicate that the most significant structural differences are probably not attributable to metal differences. More likely the differences between **E** and **F** arise from the methyl substituents on the cyclopentadienyl ring in **F**, which put severe restrictions on the favored tilt angles of the C_5Me_4 groups. Consistent with this argument, the relative orientations of the MCl_2 group and the M−Mo vector (M = Ti, Zr) in compounds **11**, **12**, and **E** are all comparable, whereas for **F** the $TiCl_2$ group is aimed away from the Mo center; this $TiCl_2$ orientation is a direct function of the C_5Me_4 tilt angles.

Attempts to thermally induce the isomerization of the phosphine groups from a cis to a trans arrangement were unsuccessful and resulted in significant amounts of decomposition. Similarly, a convenient mononuclear Mo synthon having labile groups in a trans orientation was not available for the direct synthesis of a M/Mo compound (M = Ti, Zr) having a trans phosphine arrangement.

Discussion

Cyclopentadienyl rings having a variety of functional groups have been reported in the literature,[6,7,16,24] a number of them containing the desired pendent phosphine moieties.[6,7,16] However, at the time this study was initiated few had been reported[7a,c,16] in which the C_5H_4 and PR_2 moieties were linked with C_1 or C_2 spacers. More recently a number of reports of similar ligands have appeared.[7b,19,25] We began with the synthesis of the (diphenylphosphino)ethylcyclopentadienyl ligand, because it had been briefly reported as yielding heterobinuclear complexes of the type desired.[7c] We have prepared the C_2-spaced ligand by the reaction of $KPPh_2$ with spiro[2.4]hepta-4,6-diene (eq 1), a modification of an earlier procedure,[16] and we have used the fulvene route[26] for the synthesis of our C_1-spaced ligand since nucleophiles are known to add readily to the positively polarized C(6) carbon of fulvenes, as shown in eq 2; an analogous route was described by Erker[19] while our work was in progress.

We were concerned that in a metallocene-like species the rotational flexibility of the cyclopentadienyl rings might hinder the formation of binuclear ELHB complexes, leading instead to oligomeric compounds; consequently we investigated the use of the Me_2C-bridged difulvene (**4**) to form an *ansa*-metallocene, based on the idea that in such a structure the pendent phosphines would be held in the same general direction, suitable for binding to a single late metal, unlike the structure found for **D**, for example, in which these arms were directed in opposite directions on each side of the metallocene complex. We again chose the fulvene route, analogous to the method used by Little and Stone,[27] due to the ease of preparing the fulvene shown in Scheme

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1. Subsequent addition of 2 equiv of diphenylphosphide anion provided the precursor to *ansa*-metallocenes, compound **5**, in good yield. Reaction of this ligand with $ZrCl_4$ afforded the *ansa*-zirconocene dichloride **10**.

Preparation of the metallocene dichlorides proceeded smoothly for all ligands synthesized, and the structure determination of $[(C_5H_4C_2H_4PPh_2)_2ZrCl_2]$, together with the structure of $[(C_5H_4C(CH_3)_2PhMe_2)_2ZrCl_2]$ (**D**), reported by Erker, clearly shows the potential pitfalls in attempts to obtain heterobinuclear complexes based on these early-metal−ligand frameworks. Although these solid-state structures say little about the conformations in solution, they clearly indicate that such structures are accessible in solution and demonstrate two different conformations that can give rise to oligomeric species rather than the targeted heterobinuclear complexes. Even in **7,** in which the pendent phosphine arms are close-to-eclipsed, rotation about the $C_5H_4-CH_2CH_2-PPh_2$ bond orients the arms in opposite directions. In **D** these arms are in opposite directions by virtue of rotation of the Cp′ units themselves. Combinations of these rotational freedoms should arise in solution, possibly complicating attempts to obtain heterobinuclear species.

It seemed that synthesis of heterobinuclear complexes had the best chance for success if the phosphine arms coordinated to the second metal in a cis arrangement; the approach of two $(C_5H_4C_2H_4PPh_2)_2MCl_2$ units to a single metal in a cis arrangement should be unfavorable, so the formation of oligomeric products seemed unlikely. We therefore started with the synthesis of *cis*-$[(C_5H_4C_2H_4PPh_2)_2MCl_2Mo(CO)_4]$ (M = Ti, Zr). These compounds had been briefly reported previously; however their characterization had relied solely on IR and NMR spectroscopy.[7c]

Our structure determinations of **11** and **12** clearly confirm the heterobinuclear formulations previously proposed and offer useful comparisons to two related compounds $[(C_5R_4PPh_2)_2MCl_2Mo(CO)_4]$ (R = Me, M = Ti (**F**);[7d] R = H, M = Zr (**E**)[7b]) in which no spacer was used between the C_5R_4 and PPh_2 units. Inclusion of the C_2H_4 spacer between the two functional groups has had little effect except to increase the metal−metal separation, as expected on the basis of the greater length of the resulting bridging ligand. The major difference in the different structures has resulted from the severe crowding that results in **F** from the methyl substituents on the cyclopentadienyl groups, which suggests that the flexibility needed in these bifunctional ligands to accommodate different geometries in heterobinuclear complexes may be inhibited by substituents on the cyclopentadienyl ring which may result in unfavorable tilts of the cyclopentadienyl groups.

Although the structures of **11** and **12** confirm that heterobinuclear complexes can be obtained with the $-C_5H_5C_2H_4PPh_2$ ligand, the cis-phosphine arrangement at the later metal results in too great a metal−metal separation and an arrangement of spacer methylene groups that inhibits access between the metals. In the next paper[21] we present results in which ELHB complexes of the metalloligands **6**−**9** with Rh and Pd are described, in which a trans-phosphine arrangement is expected at the late metals.

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Supporting Information Available: Tables of X-ray experimental details, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for compounds **7**, **11,** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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