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Flexible Building Blocks for Transition Metal Early−Late Chemistry. Synthesis of Heterobimetallic Tetranuclear Metallomacrocycles

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The reaction of $LiOCH_2PPh_2$ with the metallocene compounds $[Cp_2MCl_2]$ yields the metallodiphosphines $[Cp_2M(OCH_2PPh_2)_2]$ (M = Ti (**1**), Zr (**2**)). Compound **2** has also been prepared by reaction of $HOCH_2PPh_2$ with $[Cp_2ZrMe_2]$, although the reaction with $[Cp^{tt}{}_2ZrMe_2]$ ($Cp^{tt} = \eta^5$-1,3-di-*tert*-butylcyclopentadienyl) stops at the complex $[Cp^{tt}{}_2ZrMe(OCH_2PPh_2)]$ (**3**). The mononuclear late transition metal complexes containing (diphenylphosphanyl)methanol ligands, *cis*-$[M(cod)(Ph_2PCH_2OH)_2]BF_4$ (M = Rh (**4**), Ir (**5**)) and *cis*-$[Pt(p\text{-tolyl})_2(Ph_2PCH_2OH)_2]$ (**6**), have been prepared by reaction of $[M(cod)(NCCH_3)_2]BF_4$ and $[Pt(\mu\text{-}SEt_2)(p\text{-tolyl})_2]_2$ with $HOCH_2PPh_2$. The reaction of the metallodiphosphines **1** and **2** with the compounds $[M(diolef)(NCCH_3)_2]BF_4$ (M = Rh, Ir) afforded the tetranuclear d^0-d^8 early−late heterobimetallic (ELHB) metallomacrocycles $[Cp_2M(OCH_2PPh_2)_2Ir(cod)]_2{}^{2+}$ (M = Zr (**7**), Ti (**8**)) and $[Cp_2Zr(\mu\text{-}OCH_2PPh_2)_2Rh(nbd)]_2{}^{2+}$ (**9**). The crystal structures of the 16-membered metallomacrocycles **7** and **9** have been determined by X-ray diffraction and show a rhomboidal arrangement of the metal centers with a conformation that is largely determined on steric grounds.

Introduction

Coordination-driven self-assembly has shown remarkable potential in the construction of solid-state architectures with interesting physicochemical properties.[1] The application of the directional bonding approach to supramolecular synthesis has produced a great variety of discrete geometrically shaped molecular architectures known as metallacyclic polygons and polyhedra with predesigned geometries.[2] For example, molecular squares, one of the simplest members of the polygon family, have been typically assembled using square-planar Pd(II) or Pt(II) complexes having two accessible coordination sites in *cis* position and rigid or semirigid aromatic bifunctional ligands as connectors.[3] However, this methodology is not applicable to the synthesis of heterometallic metallocycles for which the modular self-assembly strategy is more convenient. In this context, mononuclear complexes with strong covalently bound ligands and accessible donor sites have been used as building blocks for the synthesis of mixed Pd/Pt,[4] Pd/Re,[5] Pd/Ru,[6] and Ni/Pd[7] heterobimetallic squares using the modular approach.

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The self-assembly of mixed-metallic molecular squares requires predesigned angular modules with turning angles close to 90°. However, early transition metal metallocenes have also been successfully assembled into homometallic molecular squares because of their usually distorted tetrahedral geometry.[8] On the other hand, it has been shown that highly flexible ligands are required to bring about square-planar and tetrahedral metal centers into a molecular square, as was evidenced by the synthesis of a Rh/Zn heterobimetallic molecular square with a polydentate ligand containing salicylaldiminato and hemilabile thioether-phosphine moieties.[9] Very few heterobimetallic macrocycles containing metallocenes and late transition metals have been described. The pre-eminent examples are the tetranuclear Ti/Pt metallomacrocycles,[10] which were assembled using the flexible bis(pyridine-4-carboxylate)titanocene entity as building block, although titanocene or zirconocene dihalide complexes containing phophinoalkylcyclopentadienyl ligands have also been assembled into tetranuclear M/Rh (M = Ti, Zr) metallomacrocycles.[11]

In view of that, we envisage the preparation of angular flexible metalloligands based on the (alkoxymethy)diphenylphosphine (μ-OCH_2PPh_2) ligand for the modular self-assembly of heterobimetallic d^0−d^8 early−late metallomacrocycles. This bridging ligand should be compatible with both electron-rich and electron-poor metals because of their ambivalent hard−soft character. Thus, the hard alkoxide end will link preferably to early metals and the softer phosphine end to late metals (HSAB principle). In addition, the strong alkoxy−early metal linkage should avoid ligand transfer reactions between the electronically disparate metal centers, an undesirable reaction in the synthesis of heterobimetallic complexes.[12] In fact, the ability of (oxyalkyl)phosphine bridging ligands to stabilize dinuclear Zr/Rh, Zr/Pt, and Zr/Ni heterobimallic complexes that mimic the interface of heterogeneous catalysts has been demonstrated by Wolczanski et al.[13]

We report herein the synthesis of complementary early and late metalloligands containing the (alkoxymethy)diphenylphosphine and (diphenylphosphanyl)methanol ligands, respectively, and their successful application in the construction of tetranuclear heterobimatallic d^0−d^8 early−late metallomacrocycles.

Results and Discussion

Synthesis of Early Transition Metal Metallophosphine Ligands. The synthesis of early metalloligands containing the (alkoxymethy)diphenylphosphine ligand was readily accomplished from the lithium salt $LiOCH_2PPh_2$, which was obtained in situ by reaction of $HOCH_2PPh_2$ with n-BuLi in tetrahydrofuran. The reaction of $LiOCH_2PPh_2$ with the dichloro compounds [Cp_2MCl_2] in a 2:1 molar ratio led to the formation of the metallocene complexes [$Cp_2M(OCH_2PPh_2)_2$] (M = Ti (**1**), Zr (**2**)), which were isolated as highly moisture-sensitive yellow oils in good yield. An alternative synthesis for compound **2** involves an alcoholysis procedure. Thus, the reaction of [Cp_2ZrMe_2] with $HOCH_2PPh_2$ (1:2 molar ratio) resulted in the immediate evolution of CH_4 and the formation of [$Cp_2Zr(OCH_2PPh_2)_2$] (**2**) in comparable yield. The metallodiphosphines **1** and **2** were characterized by microanalysis, mass spectra, and NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectra of both complexes showed a single resonance at δ −6.50 (**1**) and −9.68 ppm (**2**) indicative of an uncoordinated phosphine moiety by comparison with that of $HOCH_2PPh_2$ (δ −11.84 ppm).[14] In addition, the methylene fragments of the alcoxy groups for compounds **1** and **2** were observed as characteristic doublets, at δ 4.98 and 4.78 ppm in the ^1H NMR spectra and at δ 78.9 and 75.1 ppm in the $^{13}C\{^1H\}$ NMR spectra, respectively, due to the coupling to phosphorus.

The synthesis of related metallodiphosphines with a more protected early metal center prompted us to utilize the compound [$Cp^{tt}_2ZrMe_2$] that contains the bulky η^5-1,3-di-*tert*-butylcyclopentadienyl ligand. The reaction of [$Cp^{tt}_2ZrMe_2$] with $HOCH_2PPh_2$ in toluene at 60 °C gave the compound [$Cp^{tt}_2ZrMe(OCH_2PPh_2)$] (**3**) independently of the molar ratio used. Thus, the steric shield at the metal center after the introduction of 1 molar equiv of $HOCH_2PPh_2$ prevents the alcoholysis of the second Zr−Me bond even after prolonged heating with an excess of ligand at reflux in toluene. Compound **3** was obtained as a moderately stable white solid in high yield. The $^{31}P\{^1H\}$ NMR spectrum of **3** exhibited a single resonance at δ −15.9 ppm, and it is consistent with an uncoordinated phosphine fragment. The ^1H NMR spectrum of **3** showed three triplets for the C−H protons and two single resonances for the ^tBu protons of the two equivalent Cp^{tt} rings, in agreement with the C_s symmetry of the molecule. It is noticeable that no rotamers were observed in solution due the relative disposition of the *tert*-butyl substituents, indicating free rotation of the Cp^{tt} groups.[15] The equivalent methylene protons of the alkoxy-phosphine moiety were observed as a doublet at δ 5.14 ppm in the ^1H NMR spectrum. The

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Zr−Me fragment was observed at δ 0.59 ppm in the ^{1}H NMR spectrum and at δ 23.6 ppm in the ^{13}C{^{1}H} NMR spectrum.

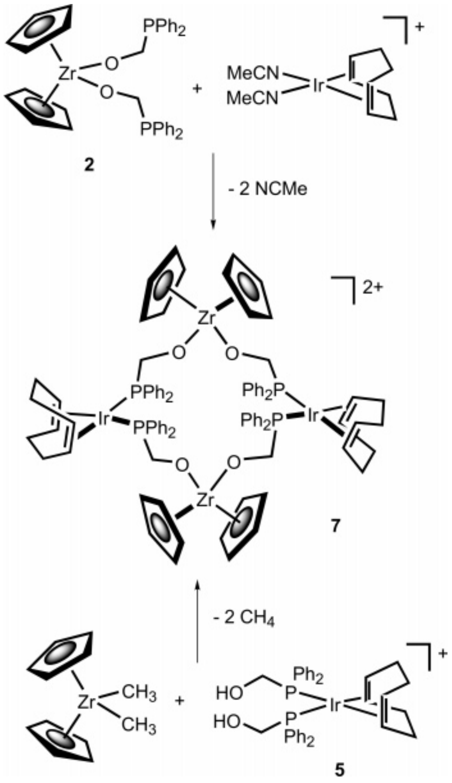
Synthesis of (Diphenylphosphanyl)methanol Late Transition Metal Complexes. The cationic d^8 mononuclear square-planar $[M(cod)(NCCH_3)_2]BF_4$ (M = Rh, Ir) complexes with two *cis*-coordinated labile acetonitrile ligands are convenient precursors for the synthesis of late metalloligands containing two (diphenylphosphanyl)methanol ligands in *cis* disposition. The reaction of $[M(cod)(NCCH_3)_2]BF_4$ with 2 molar equiv of $HOCH_2PPh_2$ afforded the bisphosphine derivatives *cis*-$[M(cod)(Ph_2PCH_2OH)_2]BF_4$ (M = Rh (**4**), Ir (**5**)), which were isolated as yellow and red microcrystalline solids, respectively, in high yield. Both compounds behaved as 1:1 electrolytes in acetone and displayed the molecular ion in the FAB+ mass spectra. The spectroscopic data for both complexes are very similar. In particular, the ^{1}H NMR spectra showed the expected 2:1 ratio for the $HOCH_2PPh_2$:cod ligands. The ^{31}P{^{1}H} NMR spectra consisted of a doublet at δ 21.6 ppm (J_{P-Rh} = 141.9 Hz) for **4** and a single resonance at δ 12.3 ppm for compound **5**, which are indicative of a P-coordination of the (diphenylphosphanyl)methanol ligands. The −OH resonance was observed as a broad resonance at 3.3 ppm in both complexes. In addition, the CH_2P fragment in compound **4** was observed a doublet of doublets in the ^{13}C{^{1}H} NMR spectrum by additional coupling to rhodium.

The dinuclear compound $[Pt(\mu\text{-}SEt_2)(p\text{-tolyl})_2]_2$ containing the labile diethyl sulfide ligands behaves as a source of unsaturated *cis*-PtR_2 fragments.[16] Thus, the reaction with 4 molar equiv of $HOCH_2PPh_2$ gave the compound *cis*-$[Pt(p\text{-tolyl})_2(Ph_2PCH_2OH)_2]$ (**6**), which was isolated as a white solid in excellent yield. The spectroscopic data for compound **6** are in agreement with a mononuclear formulation having equivalent (diphenylphosphanyl)methanol and *p*-tolyl ligands. The P-coordination of the Ph_2PCH_2OH ligands is supported by the ^{31}P{^{1}H} NMR spectrum that consisted of a singlet at δ 8.06 ppm exhibiting the characteristic ^{195}Pt satellites (J_{Pt-P} = 1804 Hz).

Synthesis of Early−Late Heterobimetallic Metallomacrocycles. Molecular models indicate that the compounds $[Cp_2M(OCH_2PPh_2)_2]$ are capable of behaving as both chelating and/or bridging metallodiphosphines due to their adequate flexibility. However, we have found a preference for the bridging coordination mode that allowed us to prepare early−late heterobimetallic tetranuclear complexes.

The reaction of $[Cp_2Zr(OCH_2PPh_2)_2]$ (**2**) with $[Ir(cod)(NCCH_3)_2]BF_4$ in a 1:1 molar ratio in dichloromethane gave an insoluble pink microcrystalline solid, isolated in moderate yield, which was characterized as the tetranuclear compound $[Cp_2Zr(\mu\text{-}OCH_2PPh_2)_2Ir(cod)]_2(BF_4)_2$ (**7**). Noteworthy, this compound can also be prepared from $[Ir(cod)(Ph_2PCH_2OH)_2]BF_4$ (**5**). Thus, the reaction of **5** with $[Cp_2ZrMe_2]$ in a 1:1 molar ratio gave **7** in similar yield upon evolution of methane (Scheme 1). In the same way, the compound $[Cp_2Ti(\mu\text{-}OCH_2PPh_2)_2Ir(cod)]_2(BF_4)_2$ (**8**) was obtained from the reaction of $[Cp_2Ti(OCH_2PPh_2)_2]$ (**1**) with $[Ir(cod)(NCCH_3)_2]BF_4$ under similar conditions.

Scheme 1



To get precise insight into the macrocycle conformation and details of molecular parameters of $[Cp_2Zr(\mu\text{-}OCH_2PPh_2)_2Ir(cod)]_2(BF_4)_2$ (**7**), suitable crystals for X-ray diffraction were obtained by slow diffusion of a dichloromethane solution of **5** into a solution of compound $[Cp_2ZrMe_2]$ in toluene at 4 °C. A molecular diagram of the cation $[Cp_2Zr(\mu\text{-}OCH_2PPh_2)_2Ir(cod)]_2^{2+}$ is shown in Figure 1 and confirms the formation of a Zr/Ir tetranuclear heterobimetallic metallomacrocycle. The crystallographic study has shown that only half the tetranuclear molecule is independent, as the whole dication is positioned around an inversion center of symmetry; selected bond lengths and angles are given in Table 1. The heterobimetallic macrocycle contains alternating zirconium and iridium metal atoms and displays a rhomboidal arrangement of the metal centers. The longest intermetallic separation has been detected between iridium centers (10.4134(4) Å), whereas the Zr···Zr distance is significantly shorter, 8.5502(8) Å. The Zr···Ir separations are too long, 6.7353 and 6.7385(6) Å, to display any intermetallic cooperativity. The ligand arrangement around the zirconium center is distorted tetrahedral by coordination of two η^5-cyclopentadienyl rings and two oxygen atoms of the (alkoxymethyl)diphenylphosphine ligands. The geometry around the iridium atoms is square-planar by coordination of two phosphorus atoms of the two bridging phosphines and two olefinic bonds of a η^4-1,5-cyclooctadiene ligand. The interatomic bond distances and angles in the 16-membered metallomacrocycle ring show values in the usual ranges for these types of atoms and hybridizations;[17] this is indicative of an unstrained conformation and of a facile assembly process. In particular, the P(1)−

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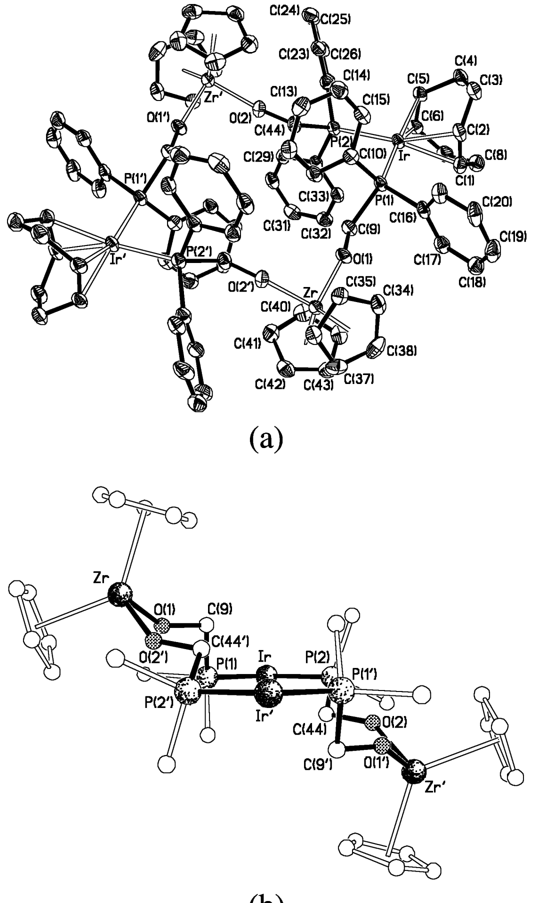

Figure 1. Molecular diagrams showing the structure of the cation of $[Cp_2Zr(\mu\text{-}OCH_2\text{-}PPh_2)_2Ir(cod)]_2(BF_4)_2$ (**7**): (a) ellipsoid representation together with labeling scheme used; (b) schematic view of the 16-membered metallacycle conformation (olefins and phenyl groups have been omitted).

Ir−P(2) bond angle, 95.16(4)°, is very close to the ideal value expected for a square-planar coordination, bearing also in mind the presence of a chelate diolefinic ligand; in the zirconium environment the O(1)−Zr−O(2′) bond angle (95.74(15)°) clearly reflects the high space requirement of the two coordinated Cp ligands (G(3)−Zr−G(4), 127.73(10)°). The conformational geometry of the metallomacrocycle seems to be dictated by the steric repulsions of the bulky diphenylphosphino groups that, in this way (see torsional angles in Table 1), are placed further apart from the Cp and cod ligands. Figure 1b displays a schematic view of the metallocycle along the coplanar iridium coordination environments and shows both "Cp_2ZrOCH_2-" fragments located up and down of this plane, resembling an analogue of a classical chair conformer. It is worth mentioning that the accessibility of the metallomacrocyclic cavity is significantly reduced by the steric influence of both Cp and phenyl rings of the phosphine groups. In fact, neither the solvent dichloromethane molecules nor the tetrafluoroborate counteranions are found to be into this cavity.

The spectroscopic data for complexes **7** and **8** evidenced a higher symmetry than that observed for the molecular framework in the solid state (C_{2h}). This fact is straightforwardly explained assuming a dynamic process in solution involving a conformational change of the flexible 16-membered metallomacrocycle. This dynamic process makes the four Cp ligands equivalent, and as a consequence, a single resonance was observed for the cyclopentadienyl protons in the ^{1}H NMR spectra of both compounds. Similarly, the cyclooctadiene ligands in both complexes displayed a broad resonance for the equivalent =CH protons. The $^{31}P\{^1H\}$ NMR spectra of **7** and **8** consisted of a single resonance, at δ 23.45 and 27.0 ppm, respectively, in agreement with the chemical equivalence of the four (alkoxymethy)diphenylphosphine ligands.

On the other hand, the FAB+ spectra of both complexes showed the heterodinuclear ions $[Cp_2M(OCH_2\text{-}PPh_2)_2Ir(cod)]^+$ (M = Ti, Zr) at *m/z* 951 and 909, respectively, but not the tetranuclear molecular ions. However, the tetranuclear ion $[Cp_2Ti(OCH_2PPh_2)_2Ir\text{-}(cod)]_2(BF_4)^+$ was detected in the FAB+ spectrum of compound **8**, and the molecular ion was observed in the MALDI-TOF spectrum of compound **7**. These data strongly support that the heterobimetallic tetranuclear structures are sustained in solution and rule out any fragmentation into dinuclear species.

The related heterobimetallic tetranuclear macrocycles Ti/Rh and Zr/Rh have been prepared following the same synthetic protocols used in the preparation of the iridium metallomacrocycles. The compounds were obtained directly as yellow solids in moderate yields. Despite that the FAB+ showed the heterodinuclear ions $[Cp_2M(OCH_2PPh_2)_2Rh(cod)]^+$ (M = Ti, Zr), at *m/z* 819 and 863, respectively, their characterization in solution became difficult because of their low solubility in a wide range of solvents, where they gradually decomposed to give an unidentified mixture of many different species, as confirmed by the $^{31}P\{^1H\}$ and ^{1}H NMR spectra. Additionally, these compounds were too air-sensitive to give satisfactory elemental analysis.

Nevertheless, more conclusive results were obtained when shifting to another diolefin such as norborna-2,5-diene (nbd). The reaction of $[Cp_2Zr(OCH_2PPh_2)_2]$ (**2**) with $[Rh(nbd)(NCCH_3)_2]BF_4$ in a 1:1 molar ratio in dichloromethane gave an orange solution, from which an orange solid could be isolated in moderate yield. The spectroscopic analysis by NMR of this solid showed the presence of two compounds. However, the crystallization of this mixture from dichloromethane/hexane resulted in red crystals of the tetranuclear heterobimetallic metallomacrocycle $[Cp_2Zr(\mu\text{-}OCH_2PPh_2)_2Rh(nbd)]_2(BF_4)_2$ (**9**), as was confirmed by an X-ray diffraction study. The NMR data for compound **9** compare well with those for the metallomacrocycles **7** and **8**. In particular, the ^{1}H NMR spectrum showed a single resonance for the equivalent cyclopentadienyl rings at δ 6.37 ppm and the expected 2:1 ratio for the OCH_2PPh_2:nbd ligands. The $^{31}P\{^1H\}$ NMR spectrum displayed a sole doublet at δ 19.3 ppm ($J_{P-Rh} = 153.9$ Hz) for the equivalent alkoxyphosphine ligands. Additionally, the FAB+ mass spectrum showed the heterodinuclear ion $[Cp_2Zr(OCH_2\text{-}PPh_2)_2Rh(nbd)]^+$ at *m/z* 847, and the MALDI-TOF an ion at *m/z* 1991 that resulted from the interaction of the heterotetranuclear ion with the matrix (ditranol). On the other hand, the second minority species, which could not be isolated and characterized, displayed a doublet at 32.54 ppm ($J_{P-Rh} = 145.3$ Hz) in the $^{31}P\{^1H\}$

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Table 1. Selected Bond Lengths (Å) and Bond and Torsion Angles (deg) for 7 and 9[a]

	7 (M = Ir)	**9** (M = Rh)[b]	
M−P(1)	2.3285(13)	2.312(3)	2.294(3)
M−P(2)	2.3408(13)	2.314(3)	2.322(3)
M−C(1)	2.218(5)	2.209(11)	2.194(10)
M−C(2)	2.197(5)	2.208(10)	2.190(10)
M−C(5)	2.219(5)	2.208(10)	2.202(10)
M−C(6)	2.203(5)	2.192(11)	2.188(10)
C(1)−C(2)	1.390(8)	1.396(15)	1.372(15)
C(5)−C(6)	1.372(7)	1.365(16)	1.370(15)
P(1)−C(9)	1.846(5)	1.830(10)	1.853(11)
P(2)−C(44)	1.858(5)	1.871(10)	1.853(11)
O(1)−C(9)	1.398(6)	1.391(11)	1.392(12)
O(2)−C(44)	1.387(6)	1.388(12)	1.388(12)
Zr−O(1)	1.973(3)	1.997(7)	1.960(7)
Zr−O(2′)	2.007(3)	1.984(7)	2.008(7)
Zr−C(Cp1)[c]	2.533−2.566(5)	2.502−2.558(11)	2.474−2.562(13)
Zr−C(Cp2)[c]	2.516−2.545(6)	2.506−2.586(11)	2.535−2.546(11)
Zr−G(3)[d]	2.254(2)	2.219(6)	2.225(8)
Zr−G(4)[d]	2.231(3)	2.242(5)	2.245(5)
P(1)−M−P(2)	95.16(4)	97.38(10)	97.12(10)
P(1)−M−G(1)[d]	91.05(12)	96.9(2)	97.5(2)
P(1)−M−G(2)[d]	173.22(10)	162.9(2)	166.5(2)
P(2)−M−G(1)[d]	173.73(13)	165.7(2)	165.3(2)
P(2)−M−G(2)[d]	89.36(10)	96.4(2)	95.5(2)
G(1)−M−G(2)[d]	84.54(15)	69.8(3)	70.1(3)
O(1)−Zr−O(2′)	95.74(15)	96.7(3)	97.5(3)
O(1)−Zr−G(3)[d]	106.64(12)	106.1(3)	105.3(3)
O(1)−Zr−G(4)[d]	106.24(12)	105.0(3)	105.9(3)
O(2′)−Zr−G(3)[d]	104.24(12)	110.6(3)	110.8(3)
O(2′)−Zr−G(4)[d]	111.56(13)	105.9(3)	104.4(2)
G(3)−Zr−G(4)[d]	127.73(10)	128.1(2)	128.6(2)
M−P(1)−C(9)	116.10(17)	120.9(3)	115.0(3)
P(1)−C(9)−O(1)	110.7(3)	112.2(7)	111.3(7)
C(9)−O(1)−Zr	147.8(3)	139.0(6)	151.6(6)
M−P(2)−C(44)	116.87(16)	116.4(3)	118.4(3)
P(2)−C(44)−O(2)	114.3(3)	114.9(7)	114.2(7)
C(44)−O(2)−Zr(1′)	145.6(3)	146.7(6)	141.1(6)
O(2′)−Zr(1)−O(1)−C(9)	−85.4(6)	−75.7(10)	−92.5(14)
Zr(1)−O(1)−C(9)−P(1)	172.9(4)	164.8(6)	177.3(9)
O(1)−C(9)−P(1)−M	172.9(3)	174.7(5)	173.8(6)
C(9)−P(1)−M−P(2)	58.4(2)	52.8(4)	62.9(4)
P(1)−M−P(2)−C(44)	34.0(2)	36.0(4)	33.0(4)
M−P(2)−C(44)−O(2)	167.7(3)	166.9(6)	172.1(6)
P(2)−C(44)−O(2)−Zr(1′)	−155.3(4)	−143.3(8)	−162.8(6)
C(44)−O(2)−Zr(1′)−O(1′)	−77.6(6)	−92.1(12)	−70.2(11)

[a] Primed atoms are related to the unprimed ones by the symmetry transformation $-x$, $2-y$, $2-z$ (**7**), $1-x$, $2-y$, $-z$ and $1-x$, $2-y$, $1-z$ (**9**). [b] Complex **9** presents two independent half-molecules. [c] Range values for the Zr−C bond distances of the C(34)−C(38) (Cp1) and C(39)−C(43) (Cp2) cyclopentadienyl rings. [d] G(1) and G(2) represent the midpoints of the C(1)−C(2) and C(5)−C(6) olefinic double bonds; G(3) and G(4), the centroids of the two Cp rings.

NMR spectrum and a single resonance for the Cp ligands at 5.59 ppm in the ^{1}H NMR spectrum in CD_2Cl_2.

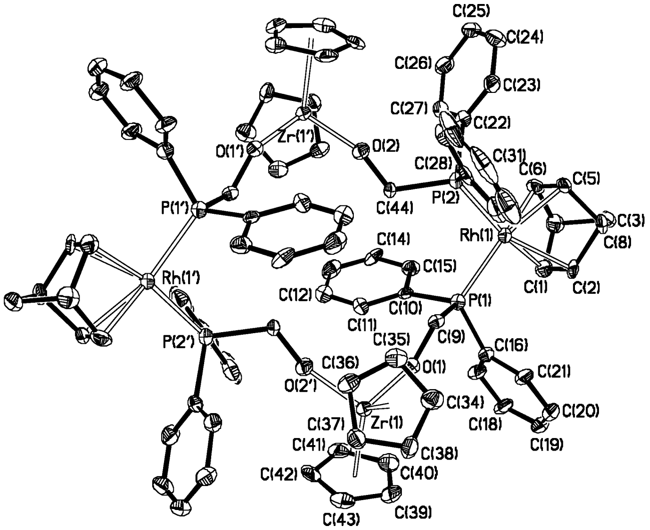

Figure 2. Molecular diagram showing the structure of the cation of $[Cp_2Zr(\mu\text{-}OCH_2PPh_2)_2Rh(nbd)]_2(BF_4)_2$ (**9**). Only one of the two independent molecules is shown.

The molecular structure of the cation of $[Cp_2Zr(\mu\text{-}OCH_2PPh_2)_2Rh(nbd)]_2(BF_4)_2$ (**9**) is shown in Figure 2, and selected bond distances and angles are collected in Table 1. The crystal structure shows the existence of two independent dinuclear moieties that generate two slightly different tetranuclear complexes through symmetry-related atoms (inversion centers). The molecular structures of both molecules show the expected 16-membered Zr/Rh tetranuclear heterobimetallic macrocycle with an alternated rhomboidal disposition of the metal centers analogous to that observed in **7**. The structural parameters of the metallomacrocycles **7** and **9** are comparable, and actually both cycles roughly exhibit the same conformation (see Table 1). This conformation seems to be the more adequate to accommodate the bulky tetrahedral zirconium centers and the square-planar rhodium fragments. The distance between the zirconium atoms (8.6385 and 8.5019(14) Å) is slightly longer than that found in compound **7**, and the separation between the rhodium atoms (10.2954 and 10.3717(16) Å) is also somewhat longer than the separation between the iridium atoms in compound **7**. The Zr−

Rh distances lie in the range 6.6529−6.7577(15) Å. It is also interesting to mention that the average Zr−O distances in **7** (1.990(2) Å) and in **9** (1.987(4) Å) are short enough to propose a weak zirconium−oxygen π interaction,[12e,18] which is corroborated by the large Zr−O−C bond angles observed in both compounds (mean values: 146.7(2)° in **7** and 144.6(3)° in **9**).

Ligand Transfer Reactions. The synthesis of Ti/Pt or Zr/Pt heterobimetallic compounds following a similar synthetic strategy has been unsuccessful. First, the compound [Pt(p-tolyl)$_2$(Ph$_2$PCH$_2$OH)$_2$] (**6**) is less reactive than the related rhodium and iridium counterparts, and second, ligand transfer or exchange reactions between the divergent metals have been observed. It is interesting that these undesirable reactions are believed to proceed through heterobimetallic intermediates where the ligand redistribution takes place.[12b]

The compound *cis*-[Pt(p-tolyl)$_2$(Ph$_2$PCH$_2$OH)$_2$] (**6**) was unreactive toward [Cp$^{tt}_2$ZrMe$_2$] and [Cp$_2$ZrMe$_2$] at room temperature. However, the reaction took place gradually at higher temperature to give a complex mixture of species as deduced from the ^{31}P{^{1}H} NMR spectra. On the other hand, monitoring of the reaction between the compounds [Cp$_2$M(OCH$_2$PPh$_2$)$_2$] (**1**, **2**) and 0.5 molar equiv of [Pt(μ-SEt$_2$)(p-tolyl)$_2$]$_2$ in benzene-d_6 evidenced the immediate formation of *cis*-[Pt(p-tolyl)$_2$(Ph$_2$PCH$_2$OH)$_2$] (**6**) along with other unidentified titanium- or zirconium-containing species. As the driving force for the ligand transfer could not be attributed to the hard/soft mismatching between the donor atoms of the alkoxy-phosphine bridging ligands in the heterobimetallic intermediates, we suggest that the formation of **6** is a consequence of the extreme sensitivity to the adventitious water in the reaction media of these intermediate compounds.

Concluding Remarks

We have applied the HSAB principle for the design of flexible early transition metal metallodiphosphines containing (alkoxymethy)diphenylphosphine ligands. These complexes behave as metalloligands for late transition metals and are useful for the A$_2$^{2a}A$_2$^{2d} assembly[19] of d^0−d^8 early−late heterobimetallic (ELHB) macrocycles of composition Ti/Ir, Zr/Rh, and Zr/Ir. This modular synthetic strategy overcomes the ligand redistribution reactions frequently observed in the synthesis of ELHB complexes. Interestingly, the zirconium metallomacrocycles can also be assembled using an alternative covalent strategy using rhodium and iridium complexes containing (diphenylphosphanyl)methanol ligands.

Experimental Section

General Methods. All manipulations were performed under a dry argon atmosphere using Schlenk-tube techniques. Solvents were dried by standard methods and distilled under argon immediately prior to use. The reactions involving the metallodiphosphines [Cp$_2$M(OCH$_2$PPh$_2$)$_2$] (M = Ti, Zr) were carried out in a drybox. The compounds [Pt(μ-SEt$_2$)(p-tolyl)$_2$]$_2$,[20] [Cp$_2$ZrMe$_2$],[21] [Cp$^{tt}_2$ZrMe$_2$],[22] and (hidroxymethyl)diphenylphosphine[23] were prepared as described previously. [M(diolef)(NCCH$_3$)$_2$]BF$_4$ (diolef = cod, M = Rh, Ir; diolef = nbd, M = Rh) were obtained following a slight modification of the literature procedure.[24] The compounds [Cp$_2$MCl$_2$] (M = Ti, Zr) were purchased from Aldrich and used as received.

Physical Measurements. Elemental C, H, and N analyses were performed in a 240-C Perkin-Elmer microanalyzer. Conductivities were measured in ca. 5 × 10^{-4} M acetone solutions using a Phillips PW 9501/01 conductimeter. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB$^+$ or EI$^+$ mode. MALDI-TOF spectra were recorded in a REFLEX MALDI spectrometer operating in the linear and reflector modes using dithranol as matrix. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300.08, 75.46, and 121.47 MHz, respectively. Chemical shifts are reported in ppm and referenced to SiMe$_4$ using the signal of the deuterated solvent (^{1}H and ^{13}C) and 85% H$_3$PO$_4$ (^{31}P) as external reference, respectively.

Synthesis of the Complexes. [Cp$_2$Ti(OCH$_2$PPh$_2$)$_2$] (1). To a solution of HOCH$_2$PPh$_2$ (1.0 g, 4.625 mmol) in THF (20 mL) was added a solution of n-BuLi 1.6 M in hexanes (2.9 mL, 4.640 mmol) to give a pale orange solution of LiOCH$_2$PPh$_2$. The addition of solid [Cp$_2$TiCl$_2$] (0.548 g, 2.202 mmol) gave a yellow-greenish solution, which was stirred for 10 min. The solvent was removed under vacuum and the residue extracted with toluene (20 mL) and filtered through a short pad of kiesselghur under argon to give a yellow solution. The solution was brought to dryness to give the compound as a yellow oil, which was dried in vacuo. Yield: 1.165 g (87%). ^{1}H NMR (C$_6$D$_6$, 293 K): δ 7.31 (m, 8H), 7.22 (m, 12H) (Ph), 5.72 (s, 10H, Cp), 4.98 (d, 4H, $^2J_{H-P}$ = 8.4 Hz, CH$_2$P). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 293 K): δ − 6.50 (s). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 137.7 (d, $^1J_{C-P}$ = 14.3 Hz, C$_i$ Ph), 133.9 (d, $^2J_{C-P}$ = 17.9 Hz, C$_o$ Ph), 128.7−128.4 (set of m, Ph), 114.5 (s, Cp), 78.9 (d, J_{C-P} = 12.4 Hz, CH$_2$P). Anal. Calcd for C$_{36}$H$_{34}$O$_2$P$_2$Ti: C, 71.06; H, 5.63. Found: C, 70.89; H, 5.45. MS (EI+, CH$_2$Cl$_2$, m/z): 543 (M$^+$ − Cp, 13%), 328 (M$^+$ − Cp − OCH$_2$PPh$_2$, 10%), 263 (M$^+$ − 2Cp − OCH$_2$PPh$_2$, 28%).

[Cp$_2$Zr(OCH$_2$PPh$_2$)$_2$] (2). *Method A.* To a solution of LiOCH$_2$PPh$_2$ (2.312 mmol), prepared as described previously, in THF (20 mL) was added solid [Cp$_2$ZrCl$_2$] (0.338 g, 1.156 mmol) to give a pale yellow solution, which was stirred for 20 min. Workup as described above gave the compound as a pale yellow oil, which was dried in vacuo. Yield: 0.700 g (93%). *Method B.* A Schlenk tube was charged with [Cp$_2$ZrMe$_2$] (0.087 g, 0.347 mmol) and PPh$_2$CH$_2$OH (0.150 g, 0.694 mmol) and the solid mixture dissolved in toluene (10 mL) to give a colorless solution with evolution of methane. The solution was stirred for 1.5 h and the solvent removed under vacuum to give a pale yellow oil, which was dried in vacuo. Yield: 0.190 g (84%). ^{1}H NMR (C$_6$D$_6$, 293 K): δ 7.58 (m, 8H), 7.16 (m, 12H) (Ph), 5.82 (s, 10H, Cp), 4.78 (d, 4H, $^2J_{H-P}$ = 8.1 Hz, CH$_2$P). ^{31}P{^{1}H} (C$_6$D$_6$, 293 K): δ −9.68 (s). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 138.4 (d, J_{C-P} = 15.2 Hz, C$_i$ Ph), 134.0 (d, $^2J_{C-P}$ = 17.5 Hz, C$_o$ Ph), 128.7 (s, C$_m$ Ph), 128.6 (s, C$_p$ Ph), 112.2 (s, Cp), 75.1 (d, J_{C-P} = 8.3 Hz, CH$_2$P). Anal. Calcd for C$_{36}$H$_{34}$O$_2$P$_2$Zr: C, 66.33; H, 5.26. Found: C, 66.25; H, 5.21. MS (FAB$^+$, CH$_2$Cl$_2$, m/z): 585 (M$^+$ − Cp, 10%), 435 (M$^+$ − OCH$_2$PPh$_2$, 57%), 370 (M$^+$ − Cp − OCH$_2$PPh$_2$, 10%), 220 (M$^+$ − 2 OCH$_2$PPh$_2$, 80%).

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[Cp$^{tt}{}_2$ZrMe(OCH$_2$PPh$_2$)] (3). A Kontes tube was charged with [Cp$^{tt}{}_2$ZrMe$_2$] (0.200 g, 0.420 mmol) and PPh$_2$CH$_2$OH (0.909 g, 0. 420 mmol) and the solid mixture dissolved in toluene (10 mL) to give a colorless solution, which was stirred for 6 h at 60 °C. The solution was cooled to room temperature and the solvent removed under vacuum to give a colorless oil, which solidified after 2 days at 4 °C. Yield: 0.126 g (93%). ^{1}H NMR (C$_6$D$_6$, 293 K): δ 7.65 (m, 4H), 7.23 (m, 6H) (Ph), 6.51 (t, 2H, $J_{\mathrm{H-H}}$ = 2 Hz), 5.87 (t, 2H, $J_{\mathrm{H-H}}$ = 2.7 Hz), 5.65 (t, 2H, $J_{\mathrm{H-H}}$ = 2.5 Hz) (Cp^{tt}), 5.14 (d, 2H, $^3J_{\mathrm{H-P}}$ = 3.7 Hz, CH$_2$P), 1.39 (s, 18H, ^{t}Bu), 1.36 (s, 18H, ^{t}Bu), 0.59 (s, 3H, Me). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 293 K): δ −15.9 (s). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 138.3−128.6 (set of m, Ph), 139.5, 137.9 (s, *C*CMe), 112.0, 102.8, 102.1 (s, *C*H, Cp^{tt}), 78.0 (d, $J_{\mathrm{C-P}}$ = 5.0 Hz, CH$_2$P), 33.6, 32.9 (s, *C*Me$_3$), 31.5, 31.3 (s, *C*H$_3$), 23.6 (s, Zr−*C*H$_3$). Anal. Calcd for C$_{40}$H$_{57}$OPZr: C, 71.06; H, 8.40. Found: C, 70.38; H, 8.22. MS (FAB+, toluene, *m/z*): 676 (M$^+$, 24%), 660 (M$^+$ − CH$_3$, 100%), 445 (M$^+$ − CH$_3$ − OCH$_2$PPh$_2$, 72%).

[Rh(cod)(Ph$_2$PCH$_2$OH)$_2$]BF$_4$ (4). Solid [Rh(cod)(NCCH$_3$)$_2$]BF$_4$ (0.100 g, 0.263 mmol) was added to a solution of HOCH$_2$PPh$_2$ (0.114 g, 0.527 mmol) in CH$_2$Cl$_2$ (10 mL) to give an orange solution. This solution was stirred for 30 min and then concentrated under vacuum to ca. 2−3 mL. Slow addition of diethyl ether (20 mL) gave a yellow oily solid. The solution was decanted and the residue stirred with diethyl ether (20 mL). The resulting yellow solid was filtered, washed with diethyl ether, and dried under vacuum. Yield: 0.159 g (83%). ^{1}H NMR (CDCl$_3$, 293 K): δ 7.60−7.25 (set of m, 20H, Ph), 4.69 (br m, 4H, =CH, cod), 4.29 (br s, 4H, CH$_2$P), 3.35 (m, 2H, OH), 2.38 (m, 4H), 2.19 (m, 4H) (CH$_2$ cod). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ 21.6 (d, $J_{\mathrm{P-Rh}}$ = 141.9 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K): δ 134−128 (set of m, Ph), 98.6 (m, =CH, cod), 61.7 (dd, $J_{\mathrm{C-P}}$ = 17 Hz, $^2J_{\mathrm{C-Rh}}$ = 17 Hz, CH$_2$P), 30.6 (s, CH$_2$, cod). Anal. Calcd for C$_{34}$H$_{38}$BF$_4$O$_2$P$_2$Rh: C, 55.92; H, 5.24. Found: C, 55.89; H, 5.17. MS (FAB$^+$, CH$_2$Cl$_2$, *m/z*): 643 (M$^+$, 5%), 535 (M$^+$ − cod, 11%), 427 (M$^+$ − HOCH$_2$PPh$_2$, 62%). Λ_{M} (Ω^{-1} cm^2 mol^{-1}): 99.1 (acetone, 5.38 × 10^{-4} M).

[Ir(cod)(Ph$_2$PCH$_2$OH)$_2$]BF$_4$ (5). Solid HOCH$_2$PPh$_2$ (0.092 g, 0.426 mmol) was added to a solution of [Ir(cod)(NCCH$_3$)$_2$]BF$_4$ (0.100 g, 0.213 mmol) in CH$_2$Cl$_2$ (10 mL) to give a red solution. This solution was stirred for 30 min and then concentrated under vaccum to ca. 2−3 mL. Workup as described above gave the compound as a red microcrystalline solid, which was filtered, washed with diethyl ether, and dried under vacuum. Yield: 0.145 g (83%). ^{1}H NMR (CDCl$_3$, 293 K): δ 8.0−6.8 (set of m, 20H, Ph), 4.39 (br s, 4H, CH$_2$P), 4.28 (m, 4H, =CH, cod), 3.30 (br s, 2H, OH), 2.20 (m, 4H), 1.44 (m, 4H) (CH$_2$ cod). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ 12.3 (s). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K): δ 133.7−128.6 (set of m, Ph), 86.5 (m, =CH, cod), 61.7 (m, CH$_2$P), 30.8 (s, CH$_2$, cod). Anal. Calcd for C$_{34}$H$_{38}$BF$_4$IrO$_2$P$_2$: C, 49.82; H, 4.67. Found: C, 49.19; H, 5.08. MS (FAB$^+$, acetone, *m/z*): 733 (M$^+$, 100%). Λ_{M} (Ω^{-1} cm^2 mol^{-1}): 91.7 (acetone, 5.27 × 10^{-4} M).

***cis*-[Pt(*p*-tolyl)$_2$(Ph$_2$PCH$_2$OH)$_2$] (6).** A Schlenk tube was charged with [Pt(μ-SEt$_2$)(*p*-tolyl)$_2$]$_2$ (0.100 g. 0.107 mmol) and PPh$_2$CH$_2$OH (0.0925 g, 0.428 mmol) and the solid mixture dissolved in CH$_2$Cl$_2$ (10 mL) to give a colorless solution. The solution was stirred for 1 h and the solvent removed under vacuum to give a white solid, which was washed with *n*-hexane and dried in vacuo. Yield: 0.151 g (87%). ^{1}H NMR (C$_6$D$_6$, 293 K): δ 7.86−6.96 (set of m, 28H, Ph and *p*-tolyl), 4.07 (d, 4H, $^2J_{\mathrm{H-P}}$ = 7.8 Hz, CH$_2$P), 2.39 (t, 2H, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, OH), 2.09 (s, 6H, CH$_3$ *p*-tolyl). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 293 K): δ 8.06 (s, $J_{\mathrm{Pt-P}}$ = 1804 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K): δ 136.4−128.8 (set of m, Ph + *p*-tolyl), 63.9 (d, CH$_2$P), 20.9 (s, CH$_3$ *p*-tolyl). Anal. Calcd for C$_{40}$H$_{40}$O$_2$P$_2$Pt: C, 59.33; H, 4.98. Found: C, 58.95; H, 4.84. MS (FAB$^+$, CH$_2$Cl$_2$, *m/z*): 809 (M$^+$, 13%), 627 (M$^+$ − 2 *p*-tolyl, 53%), 502 (M$^+$ − *p*-tolyl − HOCH$_2$PPh$_2$, 17%), 411 (M$^+$ − 2 *p*-tolyl − HOCH$_2$PPh$_2$, 33%).

[Cp$_2$Zr(μ-OCH$_2$PPh$_2$)$_2$Ir(cod)]$_2$(BF$_4$)$_2$ (7). *Method A.* [Cp$_2$Zr(OCH$_2$PPh$_2$)$_2$] (**2**) (0.148 g, 0.227 mmol) was reacted with [Ir(cod)(NCCH$_3$)$_2$]BF$_4$ (0.106 g, 0.227 mmol) in dichloromethane (20 mL) to give a pink suspension within 5 min. The suspension was stirred for 2 h and the pink solid filtered, washed with dichloromethane, and dried under vacuum. Yield: 0.120 g (51%). *Method B.* To a solution of [Ir(cod)(Ph$_2$PCH$_2$OH)$_2$]BF$_4$ (**5**) (0.100 g, 0.122 mmol) in dichloromethane (7 mL) was added solid [Cp$_2$ZrMe$_2$] (0.031 g, 0.122 mmol) to give a pink suspension within 5 min upon evolution of methane, which was stirred for 1 h. Workup as described above gave the compound as a reddish pink microcrystalline solid. Yield: 0.072 g (59%). ^{1}H NMR (CD$_3$CN, 293 K): δ 7.9−7.4 (m, 40H, Ph), 5.52 (s, 20H, Cp), 4.41 (d, $^2J_{\mathrm{H-P}}$ = 3.9 Hz, 8H, CH$_2$P), 4.16 (m, 8H, =CH), 2.19 (m, 8H, CH$_2$), 2.03 (m, 4H, CH$_2$) (cod). ^{31}P{^{1}H} NMR (CD$_3$CN, 293 K): δ 23.45 (s). ^{13}C{^{1}H} NMR (CD$_3$CN, 293 K): δ 134.4−128.5 (set of m, Ph), 112.6 (s, Cp), 86.3 (s, C=C cod), 62.5 (m, CH$_2$P), 31.4 (s, CH$_2$ cod). Anal. Calcd for C$_{88}$H$_{92}$B$_2$F$_8$Ir$_2$O$_4$P$_4$Zr$_2$: C, 50.86; H, 4.46. Found: C, 50.79; H, 4.28. MS (FAB+, CH$_3$CN, *m/z*): 951 (M/2$^+$, 12%). MALDI-TOF (CH$_3$CN, *m/z*): 1991 [M^{2+} + BF$_4^-$]$^+$.

[Cp$_2$Ti(μ-OCH$_2$PPh$_2$)$_2$Ir(cod)]$_2$(BF$_4$)$_2$ (8). A solution of [Ir(cod)(NCCH$_3$)$_2$]BF$_4$ (0.125 g, 0.266 mmol) in dichloromethane (10 mL) was added to a solution of [Cp$_2$Ti(OCH$_2$PPh$_2$)$_2$] (**1**) (0.162 g, 0.266 mmol) in toluene (10 mL) to give a pink suspension. The suspension was stirred for 30 min and the pink solid filtered, washed with acetone, and dried under vacuum. Yield: 0.127 g (48%). ^{1}H NMR (CD$_3$CN, 293 K): δ 8.00−7.20 (set of m, 40H, Ph), 6.36 (s, 20H, Cp), 4.67 (d, 8H, $^2J_{\mathrm{H-P}}$ = 4.35 Hz, CH$_2$P), 4.18 (m, 8H, =CH cod), 2.23 (m, 8H, CH$_2$), 1.98 (m, 8H, CH$_2$) (cod). ^{31}P{^{1}H} NMR (CD$_3$CN, 293 K): δ 27.0 (s). Anal. Calcd for C$_{88}$H$_{92}$B$_2$F$_8$Ir$_2$O$_4$P$_4$Ti$_2$: C, 53.08; H, 4.66. Found: C, 52.00; H, 4.62. MS (FAB+, acetone, *m/z*): 1903 ([M^{2+} + BF$_4^-$]$^+$, 35), 909 ([M/2]$^+$, 93%), 801 ([M/2 − cod]$^+$, 39%).

[Cp$_2$Zr(μ-OCH$_2$PPh$_2$)$_2$Rh(nbd)]$_2$(BF$_4$)$_2$ (9). A solution of [Rh(nbd)(NCCH$_3$)$_2$]BF$_4$ (0.111 g, 0.304 mmol) in dichloromethane (10 mL) was added to a solution of [Cp$_2$Zr(OCH$_2$PPh$_2$)$_2$] (**2**) (0.198 g, 0.304 mmol) in dichloromethane (10 mL) to give an orange solution, which was stirred for 30 min. Concentration of the volume to ca. 2 mL under vacuum and slow addition of diethyl ether gave an orange solid, which was isolated by filtration, washed with diethyl ether, and then dried under vacuum. The crude solid was dissolved in CH$_2$Cl$_2$ (3 mL) and layered with hexanes (30 mL). The mixture was allowed to stand at 4 °C for 3 days, affording the compound as red crystals. Yield: 0.127 g (45%). ^{1}H NMR (CD$_2$Cl$_2$, 293 K): δ 7.63−7.38 (set of m, 40H, Ph), 6.37 (s, 20H, Cp), 4.58 (m, 4H, CH nbd), 4.39 (m, 8H, CH$_2$P), 3.98 (m, 8H, =CH), 1.60 (s, 4H, CH$_2$) (nbd). ^{31}P{^{1}H} NMR (CD$_3$CN, 293 K): δ 19.3 (d, $J_{\mathrm{P-Rh}}$ = 153.9 Hz). Anal. Calcd for C$_{86}$H$_{84}$B$_2$F$_8$O$_4$P$_4$Rh$_2$Zr$_2$: C, 55.31; H, 4.53. Found: C, 55.15; H, 4.14. MS (FAB+, CH$_2$Cl$_2$, *m/z*): 847 ([M/2]$^+$, 28%). MALDI-TOF (CH$_3$CN, *m/z*): 1991 [M^{2+} + 2BF$_4^-$ + dithranol]$^+$.

Crystal Structure Determination of [Cp$_2$Zr(μ-OCH$_2$PPh$_2$)$_2$Ir(cod)]$_2$(BF$_4$)$_2$·4CH$_2$Cl$_2$ (7) and [Cp$_2$Zr(μ-OCH$_2$PPh$_2$)$_2$Rh(nbd)]$_2$(BF$_4$)$_2$·2CH$_2$Cl$_2$ (9). A summary of crystal data and data collection and refinement parameters is given in Table 2. Preliminary crystal quality checks revealed the presence of twinned crystals in the case of **9**; eventually a tiny sample with no more than 10% twinned reflections was used in the analysis. Intensity data were collected for both compounds at low temperature (100(2) K) on a CCD Bruker SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) by using ω rotations (0.3°). Instrument and crystal stability were evaluated by measuring equivalent reflections at different times; no significant decay was observed. Data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction was applied.[25] The structures were solved by Patterson and difference Fourier methods.[26] For **7**, only half the tetranuclear complex was observed as a crystallographic independent moiety (together with one BF$_4^-$ anion and two dichloromethane molecules). The BF$_4^-$ anion and one of the two CH$_2$Cl$_2$ solvent

Table 2. Crystal Data, Data Collection, and Refinement Parameters for the X-ray Analysis of Complexes 7 and 9

	7	**9**
formula	$C_{88}H_{92}B_2F_8Ir_2O_4P_4Zr_2 \cdot 4CH_2Cl_2$	$C_{86}H_{84}B_2F_8O_4P_4Rh_2Zr_2 \cdot 2CH_2Cl_2$
M_r	2417.66	2037.14
cryst size, mm	0.328 × 0.260 × 0.251	0.090 × 0.085 × 0.070
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	15.4325(10)	19.703(2)
b, Å	15.4098(10)	17.9741(18)
c, Å	19.5915(13)	25.627(3)
β, deg	97.8530(10)	110.236(2)
Z	2	4
V, Å^3	4615.4(5)	8515.4(15)
D_{calc}, g·cm^{-3}	1.740	1.589
μ, mm^{-1}	3.461	0.888
θ range, deg	3.2−56.8	2.3−52.2
no. measd rflns	29 387	49 707
no. unique rflns	10 544 (R_{int} = 0.0261)	16 821 (R_{int} = 0.0806)
min./max. transm fact	0.3488/0.4197	0.9244/0.9405
no. rflns/restr/params	10 544/16/533	16 821/12/1022
$R_1(F)$ ($F^2 \geq 2\sigma(F^2)$)	0.0425	0.0963
$wR_2(F^2)$ (all data)	0.1178	0.2220
S (all data)	1.055	1.147

molecules were observed as disordered and were modeled with two moieties with complementary occupancy factors. In the case of **9**, two half tetranuclear complexes were observed in the asymmetric unit, together with the corresponding BF_4^- counterions and two additional solvation dichloromethane molecules; one of the BF_4^- anions and the two CH_2Cl_2 molecules were found to be disordered and refined from two moieties with complementary factors. Anisotropic displacement parameters were applied for all non-hydrogen nondisordered atoms. Hydrogen atoms were included in calculated positions in the final cycles of refinement only for the cations; they were refined with a typical riding model. Refinements were carried out by full-matrix least-squares on F^2 (SHELXL-97).[26] The highest residuals were found close to the metal centers or in proximity to disordered atoms; they have no chemical sense.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of complexes **7** and **9**. The molecular diagram of the structure and schematic view showing the conformation of the second independent cation of compound **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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