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Tetranuclear, Early−Late Heterobimetallic Complexes Bridged by the Bifunctional Phosphinoalkylcyclopentadienyl Ligands $[Ph_2P(CH_2)_nC_5H_4]^-$ ($n = 1, 2$)

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Reaction of $(\eta^5\text{-}C_5H_4(CH_2)_nPPh_2)_2MCl_2$ ($n = 1$, M = Ti (**1**), Zr (**2**); $n = 2$, M = Ti (**3**), Zr (**4**)) with $[RhCl(CO)_2]_2$ at −80 °C and under conditions of high dilution yields the tetranuclear products $[(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_nPPh_2)_2MCl_2RhCl(CO)]_2$ ($n = 2$, M = Ti (**5**), Zr (**6**); $n = 1$, M = Ti (**7**), Zr (**8**)). Molecular weight measurements, mass spectral data, and the X-ray structures of **5b** (one isomer of **5**) and of **7** confirm the tetranuclear formulations. Compounds **5b** and **7** are shown to have two parallel Rh(I) square planes, in which these metals are approximately 11.88 and 9.01 Å apart, respectively, each bridged by the metallodiphosphine ligands, $(\eta^5\text{-}C_5H_4(CH_2)_nPPh_2)_2TiCl_2$, which are in trans positions at each Rh. The larger metallodiphosphine ligand ($n = 2$) gives rise to additional flexibility in compounds **5** and **6**, yielding two isomers of each, which appear to differ by a twist of the titanocene dichloride moiety about the metallodiphosphine backbone. Reaction of compound **1** with $(COD)PdCl_2$ gives the analogous Ti/Pd tetranuclear product $[(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2PdCl_2]_2$, which is assumed, on the basis of spectral similarities, to have a structure like those of **7** and **8**.

Introduction

In a previous article[1] we described the synthesis of a series of titanocene and zirconocene dihalide derivatives having a pendent phosphinoalkyl group attached to each cyclopentadienyl ring. Our goal was to utilize these $(\eta^5\text{-}C_5H_4(CH_2)_nPR_2)_2MCl_2$ moieties (M = Ti, Zr; $n = 1, 2$; R = Me, Ph) as bidentate ligands in which the pendent phosphines would bind to late metals to generate early−late heterobimetallic (ELHB) complexes.[2] In the earlier report[1] we demonstrated the success of this approach in the synthesis of the heterobinuclear complexes, $[(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4C_2H_4PPh_2)_2MCl_2Mo(CO)_4]$ (M = Ti, Zr). However the cis-phosphine arrangement at Mo results in a separation of the two metals of almost 7 Å, a distance that appears too great to allow significant metal−metal cooperativity. We therefore sought to incorporate these metallophosphine ligands into group 9 and 10 metal complexes in which the pendent phosphines would again chelate to the late metal but in a mutually trans arrangement. Several ELHB complexes involving the groups 4/9[3] or groups 4/10[4] metal combinations have been reported, but few have used the cyclopentadienyl phosphine ligands[3a,4c] addressed in this report.

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 except with CH_2Cl_2, which was distilled from P_2O_5. Deuterated THF and benzene were vacuum-distilled from sodium benzophenone and deuterated dichloromethane from calcium hydride. Hydrated rhodium trichloride was purchased from Johnston-Matthey Ltd. Group 4 metal salts and $[(COD)PdCl_2]$ were purchased from Strem or Aldrich. $TiCl_4$ was used as received, and $ZrCl_4$ was sublimed before use. $[RhCl(CO)_2]_2$[5] and the compounds $(\eta^5\text{-}C_5H_4(CH_2)_nPPh_2)_2MCl_2$ ($n = 1$, M = Ti (**1**), Zr (**2**); $n = 2$, M = Ti (**3**), Zr (**4**))[1] were prepared as previously reported, and 99% ^{13}CO was purchased from Isotec Inc. All other chemicals were purchased from Aldrich and used as received.

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Table 1. Spectroscopic Data for Compounds[a]

compound	IR (cm^{-1})[b]	NMR[c]	
		$\delta(^{31}P\{^1H\})$ (ppm)	$\delta(^1H)$ (ppm)[e]
$[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**5a**)	1974 (s)	26.3 (d, $^1J_{Rh-P}$ = 123.9 Hz, Rh-*P*)	6.40 (m, 8H, C_5H_4) 6.36 (m, 8H, C_5H_4) 3.09 (m, 8H $CH_2CH_2PPh_2$) 2.94 (m, 8H $CH_2CH_2PPh_2$)
$[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**5b**)	1974 (s)	31.2 (d, $^1J_{Rh-P}$ = 128.1 Hz, Rh-*P*)	7.22 (m, 4H, C_5H_4) 6.91 (m, 4H, C_5H_4) 6.67 (m, 4H, C_5H_4) 6.08 (m, 4H, C_5H_4) 3.09 (m, 8H, $CH_2CH_2PPh_2$) 2.94 (m, 8H, $CH_2CH_2PPh_2$)
$[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2RhCl(CO)]_2$ (**6a**)	1974	26.0 (d, $^1J_{Rh-P}$ = 124.0 Hz, Rh-*P*)	6.28 (m, 8H, C_5H_4) 6.25 (m, 8H, C_5H_4) 3.06 (m, 8H, $CH_2CH_2PPh_2$) 2.90 (m, 8H, $CH_2CH_2PPh_2$)
$[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2RhCl(CO)]_2$ (**6b**)	1968	30.8 (d, $^1J_{Rh-P}$ = 126.7 Hz, Rh-*P*)	7.01 (m, 4H, C_5H_4) 6.71 (m, 4H, C_5H_4) 6.46 (m, 4H, C_5H_4) 6.03 (m, 4H, C_5H_4) 3.11 (m, 8H, $CH_2CH_2PPh_2$) 2.90 (m, 8H, $CH_2CH_2PPh_2$)
$[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2RhCl(CO))_2]_2$ (**7**)	1973	31.9 (d, $^1J_{Rh-P}$ = 125.7 Hz, Rh-*P*)	6.59 (m, 8H, C_5H_4) 6.55 (m, 8H, C_5H_4) 3.94 (m, $^{2+4}J_{PH}$ = 3.5 Hz, 8H, CH_2PPh_2)
$[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2PPh_2)_2ZrCl_2RhCl(CO))_2]_2$[d] (**8**)	1977	31.6 (d, $^1J_{Rh-P}$ = 131.7 Hz, Rh-*P*)	6.44 (m, 8H, C_5H_4) 6.34 (m, 8H, C_5H_4) 3.99 (m, $^{2+4}J_{PH}$ = 3.5 Hz, 8H, CH_2PPh_2)
$[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2PdCl_2]_2$ (**9**)		22.5 (s, Pd-*P*)	6.50 (m, 8H, C_5H_4) 6.47 (m, 8H, C_5H_4) 3.80 (m, $^{2+4}J_{PH}$ = 3.3 Hz, 8H, CH_2PPh_2)

[a] Abbreviations used: for IR spectra, (vs) very strong; (s) strong; (m) medium, (sh) sharp; for NMR (m) multiplet, (dm) doublet of multiplets. [b] IR spectra recorded as a CH_2Cl_2 cast unless otherwise stated. [c] NMR spectra recorded in CD_2Cl_2. [d] IR spectra recorded in CH_2Cl_2 solution. [e] PPh_2-bound phenyl groups omitted.

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. All infrared spectra were run on a Nicolet 7199 FT interferometer as solids in Nujol or as dichloromethane casts on KBr. The elemental analyses were performed by the microanalytical service within the department. Spectroscopic data for all compounds are given in Table 1.

Mass spectrometric analyses were performed by positive mode electrospray ionization on a Micromass ZabSpec Hybrid Sector-TOF. The liquid carrier was infused into the electrospray source by means of a Harvard syringe pump at a flow rate of 10 μL/min. The sample solution was introduced via a 1 μL-loop injector. Prepurified nitrogen was used as a spray pneumatic aid and filtered air as the bath gas, heated at ca. 80 °C. For low resolution, the mass spectra were acquired by magnet scan at a rate of 5 s/decade. Data acquisition and processing was achieved by using the OPUS software package on a Digital Alpha station with VMS operating system.

Preparation of Compounds. (a) α- and β-$[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (5a and 5b, respectively). A 400 mg (0.594 mmol) sample of $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2TiCl_2]$ (**3**) in 125 mL of THF and 115.5 mg (0.297 mmol) of $[RhCl(CO)_2]_2$ in 125 mL of THF were simultaneously added dropwise to 250 mL of THF at −80 °C over 1.5 h. The solution was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo and the residue recrystallized by dissolving in 100 mL of CH_2Cl_2 and then by adding 100 mL of Et_2O. After 30 min of stirring, 40 mL of Et_2O was added, followed by stirring for an additional 30 min, and solvent was removed via cannula. The solid was washed with 3 × 10 mL of Et_2O and dried in vacuo. Yield: 145 mg of analytically pure **5**, 30%. Removal of the solvent from the supernatant and precipitation of the solid yielded a mixture of isomers **5a** and **5b**. Yield: 264 mg, total yield 80%. Anal. Calcd for $C_{78}H_{72}Cl_6O_2P_4Ti_2Rh_2$: C, 55.78; H, 4.32. Found: C, 55.58; H, 4.25. MS: $[M - Cl]^+$; 1640.9, 1641.9, 1642.9, 1643.8, 1644.8, 1645.9, 1686.9, 1647.9.

(b) α- and β-$[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2RhCl(CO)]_2$ (6a and 6b, respectively). A 127 mg (0.177 mmol) sample of $[(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)_2ZrCl_2]$ (**4**) in 35 mL of THF and 34.2 mg (0.088 mmol) of $[RhCl(CO)_2]_2$ in 35 mL of THF were simultaneously added to 75 mL of THF at −80 °C over 30 min. The solution was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo, and the yellow residue was recrystallized by dissolving in 10 mL of CH_2Cl_2, followed by the dropwise addition of 18 mL of Et_2O and stirring for 45 min. The solvent was removed via cannula, and the solid was washed with 3 × 5 mL of Et_2O and dried in vacuo, yielding 116 mg, 74% of pure **6**. After 3 days in solution, a 2:1 mixture of **6a/b** formed. Anal. Calcd for $C_{78}H_{72}Cl_6O_2P_4Zr_2Rh_2$: C, 53.04; H, 4.11. Found: C, 52.95; H, 3.86.

(c) $[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (7). A 37.9 mg (0.098 mmol) sample of $[RhCl(CO)_2]_2$ in 10 mL of THF was added to 126 mg (0.195 mmol) of $[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2TiCl_2]$ (**1**) in 5 mL of THF. The red solution was stirred for 1 h, during which time an orange precipitate formed. Et_2O (5 mL) was added dropwise, and then the solvent was removed via cannula. The solid was washed with 2 × 5 mL of Et_2O and dried in vacuo. Yield: 50 mg, 31%. Anal. Calcd for $C_{74}H_{64}P_4O_2Cl_6Ti_2Rh_2$: C, 54.75; H, 3.97. Found: C, 54.59; H, 3.89. MS: $[M - Cl]^+$; 1583.0, 1584.8, 1585.9, 1586.8, 1587.8, 1583.8, 1589.8, 1590.8, 1591.8, 1592.8, 1593.7, 1594.6.

(d) $[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2PPh_2)_2ZrCl_2RhCl(CO)]_2$ (8). A 50 mg (0.073 mmol) sample of $[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2ZrCl_2]$ (**2**) in 10 mL of THF was added to 13.9 mg (0.036 mmol) of $[RhCl(CO)_2]_2$ in 10 mL of THF, and the yellow solution was stirred

Table 2. Crystallographic Experimental Details for Compounds 5b and 7.

	$[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2\text{-}TiCl_2RhCl(CO)]_2]_2$ (**5b**)	$[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2PPh_2)_2\text{-}TiCl_2RhCl(CO)]_2]_2$ (**7**)·CH_2Cl_2
	A. Crystal Data	
formula	$C_{78}H_{72}Cl_6O_2P_4Rh_2Ti_2$	$C_{75}H_{66}Cl_8O_2P_4Rh_2Ti_2$
fw	1679.56	1708.38
crystal dimens (mm)	0.20 × 0.18 × 0.04	0.48 × 0.35 × 0.06
crystal system	monoclinic	triclinic
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
unit cell params[a]		
a (Å)	36.654(3)	13.955(3)
b (Å)	12.0072(12)	13.969(4)
c (Å)	16.332(3)	19.176(4)
α (deg)		89.70 (2)
β (deg)	92.771 (3)	88.57 (2)
γ (deg)		82.45 (2)
V ($Å^{3)}$	7179.6(18)	3704.6(14)
Z	4	2
$\rho_{\text{calcd (g cm}^{-3})}$	1.554	1.532
μ (mm^{-1})	1.026	1.065
	B. Data Collection and Refinement	
diffractometer	Enraf-Nonius KappaCCD[b]	Enraf-Nonius CAD4[b]
radiation (λ [Å])	Mo Kα (0.71073)	Mo Kα (0.71073)
monochromator	incident-beam, graphite crystal	incident-beam, graphite crystal
temperature (°C)	−173	−50
scan type	mixture of ϕ rotations and ω scans	$\theta-2\theta$
data collection 2θ limit (deg)	52.75	50.0
total data collected	7273 ($0 \le h \le 45$, $0 \le k \le 14$, $-20 \le l \le 20$)	12532 ($-16 \le h \le 16$, $-16 \le k \le 16$, $0 \le l \le 22$)
no. of indep reflns	7273	12119
no. of observations (NO)	4284 ($F_o^2 \ge 2\sigma(F_o^2)$)	6583 ($F_o^2 \ge 2\sigma(F_o^2)$)
structure solution method	direct methods (SHELXS-86)	direct methods (SHELXS-86)
refinement method	full-matrix least-squares on F^2 (SHELXL−93)	full-matrix least-squares on F^2 (SHELXL−93)
absorption correction method	SCALEPACK	semiempirical
range of transmission factors	0.9601−0.8211	0.9899−0.7648
no. of data/restraints/params	7273 [$F_o^2 \ge -3\sigma(F_o^2)$]/0/424	12119 [$F_o^2 \ge -3\sigma(F_o^2)$]/3[c]/838
goodness-of-fit (S)[d]	1.015 [$F_o^2 \ge -3\sigma(F_o^2)$]	1.041 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[g]		
$R_1[F_o^2 > 2\sigma(F_o^2)]$	0.0576	0.0827
wR_2(all data)	0.1232	0.2395
largest difference peak and hole (e $Å^{-3}$)	1.030 and −0.664	1.773 and −1.164

[a] For compound **7**, obtained from least-squares refinement of 24 reflections with 22.0° < 2θ < 25.8°. [b] Programs for diffractometer operation and data collection were those supplied by Enraf-Nonius. [c] Distances within the solvent dichloromethane molecule for compound **7** were fixed as follows: d(Cl(7)−C(111)) = d(Cl(8)−C(111)) = 1.80(1) Å; d(Cl(7)−Cl(8)) = 2.95(1) Å (to maintain an idealized Cl(7)−C(111)−Cl(8) bond angle of 110°). [d] $S = [\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (a_0P)^2 + a_1P]^{-1}$ where $a_0 = 0.0499$, $a_1 = 0$ for compound **5b** and $a_0 = 0.1141$, $a_1 = 1.7430$ for compound 7; where $P = [\max(F_o^2, 0) + 2F_c^2]/3$). [e] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

for 30 min. The solvent was removed in vacuo and the residue recrystallized from CH_2Cl_2/n-pentane. Yield: 47 mg, 77%. Elemental analyses showed that the compound crystallized with 0.5 molar equiv of CH_2Cl_2. Anal. Calcd for $C_{74.5}H_{65}P_4O_2Cl_7Zr_2Rh_2$: C, 51.06; H, 3.74; Cl, 14.16. Found: C, 51.01; H, 3.63; Cl, 13.71.

(e) $[(\mu\text{-}\eta^5:\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2PdCl_2]_2$ (9). A 9.5 mg (0.033 mmol) sample of $[(COD)PdCl_2]$ in 5 mL of CH_2Cl_2 was added to 21.5 mg (0.033 mmol) of $[(\eta^5\text{-}C_5H_4CH_2PPh_2)_2TiCl_2]$ (**1**) in 5 mL of CH_2Cl_2. The solution was stirred for 30 min, and then the solvent removed in vacuo. The red residue was recrystallized by dissolving in 2 mL of CH_2Cl_2 and adding 4 mL of MeOH dropwise, followed by stirring for 30 min. The solvent was removed via cannula, and the solid was washed with 3 × 5 mL of MeOH and dried in vacuo. Yield: 15 mg, 54%. Anal. Calcd for $C_{72}H_{64}P_4Cl_8Ti_2Pd_2$: C, 52.56; H, 3.92. Found: C, 52.22; H, 3.93. MW (osmometry, in CH_2Br_2) 1676 amu.

X-ray Data Collection. (a) Crystals of compound **5b** were obtained from slow diffusion of methanol into a CD_2Cl_2 solution of the compound. Data were collected to a maximum 2θ = 52.75° on an Enraf-Nonius KappaCCD diffractometer using Mo Kα radiation at −173 °C. The space group was determined to be $C2/c$ (No. 15). Absorption corrections were applied to the data during integration by the SCALEPACK[6] algorithm. See Table 2 for a summary of crystal data and X-ray data collection information.

The structure was solved by direct methods (SHELXS-86)[7a] and refined using the program SHELXL-93.[7b] 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 $R_1(F) = 0.0576$ (for 4284 data with $F_o^2 \ge 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.1232$ (for all 7273 independent data).

(b) Crystals of compound **7** were obtained from layering diethyl ether onto a CH_2Cl_2 solution of the compound. Data

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[7] (a) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (b) Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination; University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \ge -3\sigma(F_o^2)$). 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.

were collected to a maximum $2\theta = 50.0°$ on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation at −50 °C. Unit cell parameters were obtained from a least-squares refinement of the setting angles of 24 reflections with $22.0° < 2\theta < 25.8°$. The cell parameters suggested the triclinic space groups $P1$ or $P\bar{1}$; the latter was confirmed as the correct choice by the successful solution and refinement of the structure. Three reflections were chosen as intensity standards and were remeasured after every 7200 s of X-ray exposure time, 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),[7a] and refinement was completed using the program SHELXL-93.[7b] Hydrogen atoms were treated in a manner analogous to that used for compound **5b**. The final model refined to values of $R_1(F) = 0.0827$ (for 6583 data with $F_o^2 \geq 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.2395$ (for all 12119 independent data).

Results and Compound Characterization

As described previously,[1] the group 4 metal complexes $[(\eta^5\text{-}C_5H_4(CH_2)_nPPh_2)_2MCl_2]$ ($n = 1$, M = Ti (**1**), Zr (**2**); $n = 2$, M = Ti (**3**), Zr (**4**)) can function as bidentate metalloligands generating heterobinuclear complexes in which the Cp′ moiety (Cp′ = $C_5H_4(CH_2)_nPPh_2$) binds in an η^5-manner to the earlier metal and the phosphine moiety binds to the later metal. Our investigation of ELHB complexes, in which Rh or Pd is the late metal, began with the preparation of $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4(C_2H_4)PPh_2)_2TiCl_2RhCl(CO)]_2$ (**5**) by the slow addition of **3** to $[RhCl(CO)_2]_2$ at −80 °C under conditions of high dilution. Although a heterobinuclear Ti/Rh complex was targeted, the resulting product is tetranuclear, containing two Ti and two Rh atoms; all of the ELHB complexes reported herein are tetranuclear. In this reaction two isomers, **5a** and **5b**, are actually produced. Although isomer **5a** can be obtained free of **5b**, by careful recrystallization of the reaction mixture, it slowly converts to an approximate 2:1 mixture of isomers (**5a**/**5b**) over several days in solution. Isomer **5a** displays a doublet in the $^{31}P\{^1H\}$ NMR spectrum at δ 26.3 with 124 Hz coupling to Rh and shows AA′BB′ resonances centered at δ 6.38 in the ^1H NMR, corresponding to the C_5H_4 protons, with the two methylene resonances at δ 3.09 and 2.94 appearing as complex multiplets. $^{13}C\{^1H\}$ NMR spectroscopy shows a terminally bound carbonyl ligand at δ 188.1 with 75.6 Hz rhodium coupling and 14.3 Hz coupling to the two rhodium-bound phosphines. Compound **5b** displays a doublet at δ 31.2 in the $^{31}P\{^1H\}$ NMR spectrum with 128 Hz Rh coupling, with the carbonyl carbon resonance obscured by that of **5a** in the ^{13}C NMR spectrum. The ^1H NMR spectrum of this isomer differs from that of **5a** in that it displays four Cp′ hydrogen resonances instead of the two observed for **5a**. The structural differences giving rise to these ^1H NMR differences will be discussed later. The IR spectra of pure **5a** and a mixture of isomers are identical, each with a terminal carbonyl band at 1974 cm^{-1}. The extremely low solubility of these compounds precluded molecular weight determinations, so they were analyzed by electrospray mass spectroscopy. The mass spectrum of **5a** showed a number of signals around $m/z = 1644$, which corresponds to the molecular ion peak for $[M - Cl]^+$ if the compound contains two of each metal, and this spectrum is essentially identical to that calculated on the basis of the isotopic pattern for the formulation given. The mass spectrum of a mixture of isomers is exactly the same as that of pure **5a**. A single crystal suitable for X-ray diffraction was obtained from a mixture of isomers and is assumed to correspond to isomer **5b** on the basis of the correspondence between the X-ray-derived structure and the ^1H NMR spectrum (vide infra). Although redissolving the crystals showed the presence of both isomers in their equilibrium ratios, indicating that two crystal types must be present, it was not possible to identify the two crystal types in the mix, so their separation by this method was not possible. A representation of **5b** is shown in Figure 1, which clearly confirms the tetranuclear formulation in which two "RhCl(CO)" fragments are bridged by two $(\eta^5\text{-}C_5H_4C_2H_4PPh_2)_2TiCl_2$ metalloligands in a mutually trans arrangement at each Rh. As such, the complex resembles a number of group 9 metal complexes bridged by diphosphine ligands, $Ph_2P(CH_2)_nPPh_2$.[8] Each Rh has a square-planar geometry much like Vallarino's and Vaska's compounds and their analogues,[9,10] having a trans arrangement of phosphines and of the chloro and carbonyl groups. As shown in the alternate view depicted in Figure 2, the two Rh centers also have an anti arrangement in which the chloro ligand on one metal is aimed in the opposite direction of that on the other metal; again this is common in diphosphine-bridged compounds.[8a,b,e] This figure also shows the parallel arrangement of both Rh coordination planes, as required by the crystallographic inversion symmetry. All bond lengths and angles around Rh are typical for a square-planar Rh(I) system.

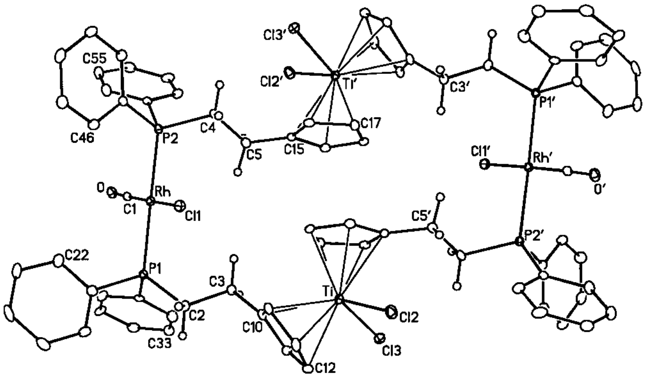

Figure 1. Perspective view of $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4C_2H_4PPh_2)_2TiCl_2RhCl(CO)]_2$ (**5b**) showing the atom-labeling scheme. Atoms are represented by Gaussian ellipsoids at the 20% probability level, except for methylene hydrogens, which are shown artificially small. Hydrogens on the cyclopentadienyl or phenyl groups are not shown. Numbering on the C_5 or C_6 rings starts at the ipso carbons. Primed atoms are related to unprimed ones by the crystallographic inversion center at (1/4, 1/4, 1/2).

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[8] (a) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500. (b) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1981**, *20*, 1534. (c) Guimerans, R. R.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 1677. (d) Wang, H.-H.; Pignolet, L. H.; Reedy, P. E., Jr.; Olmstead, M. M. *Inorg. Chem.* **1987**, *26*, 377. (e) Balch, A. L.; Davis, B. J.; Olmstead, M. M. *Inorg. Chem.* **1990**, *29*, 3068.

[9] (a) Vallarino, L. *J. Chem. Soc.* **1957**, 2287. (b) DeBoer, J. L.; Rogers, D.; Skapski, A. C.; Troughton, P. G. H. *Chem. Commun.* **1966**, 756. (c) Thorn, D. L.; Tulip, T. H.; Ibers, J. A. *J. Chem. Soc., Dalton Trans.* **1979**, 2022.

[10] (a) Rees, W. M.; Churchill, M. R.; Li, Y.-J.; Atwood, J. D. *Organometallics* **1985**, *4*, 1162. (b) Rees, W. W.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. D. *Organometallics* **1985**, *4*, 2179.

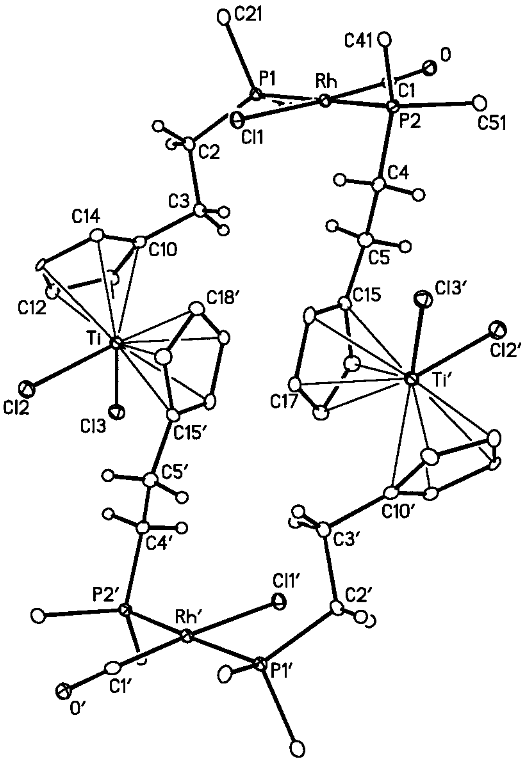

Figure 2. Alternate view of compound **5b** in which only the ipso carbons of the phenyl groups are shown.

The geometry of the Cp'_2TiCl_2 fragment is typically tetrahedral, and within each Cp'_2TiCl_2 ($Cp' = C_5H_4C_2H_4PPh_2$) unit the Cp′ ligands are aimed in opposite directions with one pendent phosphine moiety bound to one Rh and the other bound to Rh at the opposite end of the molecule. Figures 1 and 2 also show that there are two inequivalent environments for the Cp′ groups in which two face inward, effectively bisecting the elongated cavity between the two Rh centers, and two face outward. The inward-facing rings (C(15)−C(19) and its inversion equivalent) are parallel and approximately 3.20 Å apart, in line with a π-stacking interaction which is less than the predicted van der Waals separation of 3.40 Å.[11] In addition, the methylene hydrogens further bisect the two half cavities between Rh and the π-stacked Cp′ groups with a rather short H(3B)−H(5A) contact of 2.83 Å and appear to inhibit access to the inside face of the Rh plane.

Clearly in this structure the metals are too far apart for any direct cooperative interactions to occur. The longest separation, across the elongated length of the rectangular arrangement is between Rh centers, at 11.875(1) Å, whereas the Ti−Ti separation across the short dimension of the rectangle is 7.345(2) Å. Not only are the Rh−Ti separations (6.865(1) and 7.096(1) Å) far too long to display cooperativity between these disparate metals, they are separated by the organic ligand framework, which should also inhibit cooperativity.

As noted, the structure determined corresponds more closely to that of isomer **5b**, on the basis of the ^1H NMR resonances for the η^5-C_5H_4 moieties, and is therefore identified as such. Clearly, in the solid state the two symmetry-related rings on the inside of the complex are inequivalent to the pair on the outside. Assuming an analogous structure in solution, this would give rise to four sets of ^1H resonances for the C_5H_4 groups (two sets each for the α and the β protons on the two inequivalent rings). We assume that the structure of isomer **5a** is related to **5b** by rotation about the $Ph_2PC_2H_4(\eta^5\text{-}C_5H_4)TiCl_2(\eta^5\text{-}C_5H_4)C_2H_4PPh_2$ framework in such a way that the four Cp′ groups become equivalent. The slow transformation of **5a** into an equilibrium mix of **5a** and **5b** indicates that this rotation is not facile, presumably owing to the many nonbonded contacts involving the phenyl, methylene, and cyclopentadienyl groups, with each other and with the chloro ligands on the four metals.

We also considered that isomerization may result from rotation about a P−Rh−P vector, bringing both carbonyls to one side of the macrocycle and both Rh-bound chloro ligands to the other. However, this process has been dismissed since the resulting structure is inconsistent with the ^1H NMR spectrum, in which the isomer in question displays only two ^1H resonances for the C_5H_4 groups. The structure resulting from this isomerization at a Rh center would maintain two sets of inequivalent cyclopentadienyl groups, giving at least four ^1H NMR resonances for these groups. This isomerization process, which results in no significant change in the environments of the phosphine groups, is also inconsistent with the significantly different ^{31}P resonances observed for the two isomers. Conversely, the process suggested, in which major rearrangements of the macrocycle occur, would be expected to give rise to different ^{31}P environments in the two isomers.

The reaction of $(\eta^5\text{-}C_5H_4C_2H_4PPh_2)_2ZrCl_2$ (**4**) with $[RhCl(CO)_2]_2$ under the same conditions as for the preparation of **5** yields the Zr analogue, $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4C_2H_4PPh_2)_2ZrCl_2RhCl(CO)]_2$ (**6**). Although initially only one isomer is obtained, the two isomers **6a** and **6b** are obtained with time. This isomerization, like that of the Ti analogue, is extremely slow, requiring approximately 3 days to reach the equilibrium ratio of 2:1 (**6a** predominating). These isomers appear to be exactly analogous to those of **5a**/**5b**, displaying two and four ^1H resonances, respectively, for the C_5H_4 protons. The $^{31}P\{^1H\}$ parameters also match closely to those of the Ti compounds, strongly suggesting a tetranuclear formulation for the isomers of **6**.

Reaction of the metalloligands $(\eta^5\text{-}C_5H_4CH_2PPh_2)_2MCl_2$ (M = Ti (**1**), Zr (**2**)), having the shorter tether, with $[RhCl(CO)_2]_2$ under similar conditions as noted for **5** and **6** again yields tetranuclear species. However in each of these products only one species is observed. Therefore the reaction of 2 equiv of **1** with the rhodium dimer yields only $[(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2RhCl(CO)]_2$ (**7**), and no isomerization of this species occurs in solution, even after several days. This product displays a single resonance in the $^{31}P\{^1H\}$ NMR spectrum, much like those of either isomer of **5** and **6**, and the single carbonyl stretch in the IR spectrum is typical of all of these Rh(I) species. Two resonances are observed for the C_5H_4 protons, suggesting a structure that is related to the predominant isomers **5a** and **6a**. The methylene resonances appear as a pseudo-triplet due to virtual cou-

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(11) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, N.Y. 1960.

Table 3. Selected Bond Lengths and Angles for Compound 5b

(a) Selected Interatomic Distances (Å)

atom 1	atom 2	distance	atom 1	atom 2	distance
Rh	Cl(1)	2.3830(14)	P(2)	C(4)	1.857(5)
Rh	P(1)	2.336(2)	P(2)	C(41)	1.837(5)
Rh	P(2)	2.322(2)	P(2)	C(51)	1.822(5)
Rh	C(1)	1.816(6)	O	C(1)	1.148(6)
Ti	Cl(2)	2.382(2)	C(2)	C(3)	1.541(7)
Ti	Cl(3)	2.375(2)	C(3)	C(10)	1.507(7)
Ti	C(10)	2.435(5)	C(4)	C(5)	1.527(7)
Ti	C(11)	2.374(5)	C(5)	C(15)	1.501(7)
Ti	C(12)	2.321(6)	C(10)	C(11)	1.403(7)
Ti	C(13)	2.377(5)	C(10)	C(14)	1.418(7)
Ti	C(14)	2.378(5)	C(11)	C(12)	1.406(7)
Ti	C(15′)[a]	2.465(5)	C(12)	C(13)	1.384(8)
Ti	C(16′)	2.414(5)	C(13)	C(14)	1.421(7)
Ti	C(17′)	2.331(5)	C(15)	C(16)	1.402(7)
Ti	C(18′)	2.348(5)	C(15)	C(19)	1.423(7)
Ti	C(19′)	2.393(6)	C(16)	C(17)	1.419(7)
P(1)	C(2)	1.839(5)	C(17)	C(18)	1.412(7)
P(1)	C(21)	1.838(5)	C(18)	C(19)	1.416(7)
P(1)	C(31)	1.839(6)	P(2)	C(4)	1.857(5)

(b) Nonbonded Distances

atom 1	atom 2	distance	atom 1	atom 2	distance
Rh	Rh′	11.875(1)	Rh	Ti	6.865(1)
Ti	Ti′	7.345(2)	Rh	Ti′	7.096(1)

(c) Selected Interatomic Angles (deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cl(1)	Rh	P(1)	88.75(5)	Rh	C(1)	O	176.4(5)
Cl(1)	Rh	P(2)	87.44(5)	P(1)	C(2)	C(3)	115.9(4)
Cl(1)	Rh	C(1)	176.6(2)	C(2)	C(3)	C(10)	109.1(4)
P(1)	Rh	P(2)	176.05(5)	P(2)	C(4)	C(5)	111.7(4)
P(1)	Rh	C(1)	92.1(2)	C(4)	C(5)	C(15)	115.1(5)
P(2)	Rh	C(1)	91.6(2)	C(3)	C(10)	C(11)	126.7(5)
Cl(2)	Ti	Cl(3)	94.21(6)	C(3)	C(10)	C(14)	125.9(5)
Rh	P(1)	C(2)	116.1(2)	C(11)	C(10)	C(14)	107.1(5)
Rh	P(1)	C(21)	108.3(2)	C(10)	C(11)	C(12)	108.2(5)
Rh	P(1)	C(31)	118.5(2)	C(11)	C(12)	C(13)	109.1(5)
C(2)	P(1)	C(21)	103.3(2)	C(12)	C(13)	C(14)	107.4(5)
C(2)	P(1)	C(31)	104.9(3)	C(10)	C(14)	C(13)	108.1(5)
C(21)	P(1)	C(31)	104.0(2)	C(5)	C(15)	C(16)	127.8(5)
Rh	P(2)	C(4)	110.6(2)	C(5)	C(15)	C(19)	125.3(5)
Rh	P(2)	C(41)	115.1(2)	C(16)	C(15)	C(19)	106.8(4)
Rh	P(2)	C(51)	117.2(2)	C(15)	C(16)	C(17)	109.0(5)
C(4)	P(2)	C(41)	105.0(2)	C(16)	C(17)	C(18)	108.0(5)
C(4)	P(2)	C(51)	105.9(2)	C(17)	C(18)	C(19)	107.2(4)
C(41)	P(2)	C(51)	101.9(2)	C(15)	C(19)	C(18)	109.0(5)

[a] Primed atoms are related to unprimed ones via the inversion center at ($^1/_4$, $^1/_4$, $^1/_2$).

pling to both Rh-bound ^{31}P nuclei,[12] as is commonly seen in A-frame-type species having a trans arrangement of diphosphine ligands.[8a,13] Mass spectral data on this compound are again consistent with the tetranuclear formulation, which is confirmed by the X-ray structure determination as shown in Figure 3. Selected bond lengths and angles are given in Table 4. The structure of **7** is much like that of **5b**, apart from a number of subtle differences that arise as a consequence of the shorter length of the heterobifunctional ligand in which a single CH_2 spacer replaces the two methylene spacers in **5b**. At both Rh centers the geometry is square planar, although both metals are displaced 0.16 and 0.20 Å from their respective planes, toward the center of the molecule. As a result, the P−Rh−P angles (av 163.5°) are distorted significantly from the idealized 180°. The Cl and CO ligands, on the other hand, are almost exactly trans. As in all related complexes, the parameters at

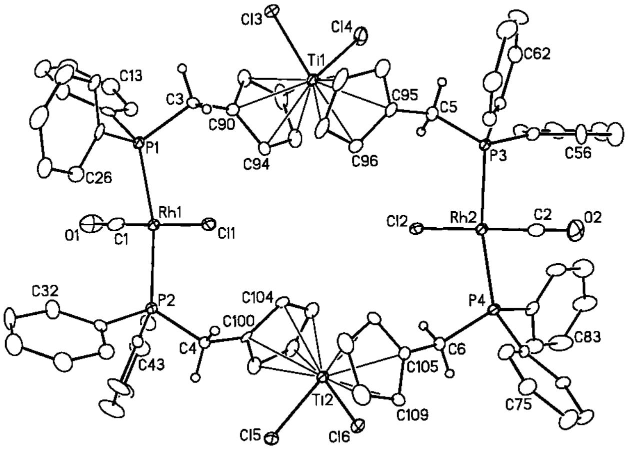

Figure 3. Perspective view of [(μ-η^5:η^1-$C_5H_4CH_2PPh_2$)$_2$-$TiCl_2RhCl(CO)$]$_2$ (**7**). Thermal parameters drawn as outlined in Figure 1.

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(12) Jenkins, J. M.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 770.

(13) See for example: (a) Balch, A. L.; Hunt, C. T.; Lee, C.-L.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764. (b) Berry, D. H.; Eisenberg, R. *Organometallics* **1987**, *6*, 1796. (c) Puddephatt, R. J.; Azam, K. A.; Hill, R. H.; Brown, M. P.; Nelson, C. D.; Moulding, R. P.; Seddon, K. R.; Grossel, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 5642. (d) Sterenberg, B. T.; McDonald, R.; Cowie, M. *Organometallics* **1997**, *16*, 2297.

Table 4. Selected Bond Lengths and Angles for Compound 7

(a) Selected Interatomic Distances (Å)

atom 1	atom 2	distance	atom 1	atom 2	distance
Rh(1)	Cl(1)	2.395(3)	Ti(2)	C(102)	2.409(13)
Rh(1)	P(1)	2.309(3)	Ti(2)	C(103)	2.352(13)
Rh(1)	P(2)	2.306(3)	Ti(2)	C(104)	2.384(11)
Rh(1)	C(1)	1.74(2)	Ti(2)	C(105)	2.386(11)
Rh(2)	Cl(2)	2.378(3)	Ti(2)	C(106)	2.385(11)
Rh(2)	P(3)	2.317(3)	Ti(2)	C(107)	2.331(13)
Rh(2)	P(4)	2.318(3)	Ti(2)	C(108)	2.405(14)
Rh(2)	C(2)	1.785(14)	Ti(2)	C(109)	2.422(12)
Ti(1)	Cl(3)	2.339(4)	P(1)	C(3)	1.852(11)
Ti(1)	Cl(4)	2.338(4)	P(1)	C(11)	1.824(13)
Ti(1)	C(90)	2.391(11)	P(1)	C(21)	1.830(11)
Ti(1)	C(91)	2.400(12)	P(2)	C(4)	1.834(11)
Ti(1)	C(92)	2.376(14)	P(2)	C(31)	1.827(11)
Ti(1)	C(93)	2.329(15)	P(2)	C(41)	1.797(13)
Ti(1)	C(94)	2.383(12)	P(3)	C(5)	1.847(11)
Ti(1)	C(95)	2.403(11)	P(3)	C(51)	1.824(12)
Ti(1)	C(96)	2.354(11)	P(3)	C(61)	1.827(14)
Ti(1)	C(97)	2.297(12)	P(4)	C(6)	1.857(10)
Ti(1)	C(98)	2.400(12)	P(4)	C(71)	1.830(12)
Ti(1)	C(99)	2.420(13)	P(4)	C(81)	1.825(11)
Ti(2)	Cl(5)	2.343(4)	O(1)	C(1)	1.20(2)
Ti(2)	Cl(6)	2.327(4)	O(2)	C(2)	1.160(15)
Ti(2)	C(100)	2.416(10)	C(3)	C(90)	1.492(14)
Ti(2)	C(101)	2.406(12)	C(4)	C(100)	1.518(14)
C(5)	C(95)	1.519(14)	C(98)	C(99)	1.41(2)
C(6)	C(105)	1.499(14)	C(100)	C(101)	1.42(2)
C(90)	C(91)	1.432(15)	C(100)	C(104)	1.39(2)
C(90)	C(94)	1.42(2)	C(101)	C(102)	1.39(2)
C(91)	C(92)	1.39(2)	C(102)	C(103)	1.42(2)
C(92)	C(93)	1.40(2)	C(103)	C(104)	1.40(2)
C(93)	C(94)	1.41(2)	C(105)	C(106)	1.40(2)
C(95)	C(96)	1.40(2)	C(105)	C(109)	1.41(2)
C(95)	C(99)	1.41(2)	C(106)	C(107)	1.40(2)
C(96)	C(97)	1.41(2)	C(107)	C(108)	1.42(2)
C(97)	C(98)	1.42(2)	C(108)	C(109)	1.42(2)

(b) Nonbonded Distances

Rh(1)	Rh(2)	9.009(2)	Cl(1)	H(3B)	3.09
Ti(1)	Ti(2)	8.245(3)	Cl(1)	H(4A)	2.86
Rh(1)	Ti(1)	5.917(3)	Cl(2)	H(5B)	2.78
Rh(1)	Ti(2)	6.310(2)	Cl(2)	H(6A)	2.79
Rh(2)	Ti(1)	6.248(2)	Cl(3)	H(3A)	2.89
Rh(2)	Ti(2)	5.975(3)	Cl(3)	H(3B)	3.21
P(1)	P(3)	9.455(4)	Cl(4)	H(5A)	2.76
P(2)	P(4)	9.440(5)	Cl(4)	H(5B)	3.18
H(94)	H(104)	2.713	Cl(5)	H(4B)	2.65
H(96)	H(106)	2.897	Cl(6)	H(6B)	3.05

(c) Selected Interatomic Angles (deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cl(1)	Rh(1)	P(1)	89.09(11)	C(4)	P(2)	C(31)	102.9(5)
Cl(1)	Rh(1)	P(2)	89.60(11)	C(4)	P(2)	C(41)	100.9(5)
Cl(1)	Rh(1)	C(1)	178.9(5)	C(31)	P(2)	C(41)	103.6(5)
P(1)	Rh(1)	P(2)	164.31(11)	Rh(2)	P(3)	C(5)	118.2(4)
P(1)	Rh(1)	C(1)	89.8(5)	Rh(2)	P(3)	C(51)	102.9(4)
P(2)	Rh(1)	C(1)	91.4(4)	Rh(2)	P(3)	C(61)	123.4(4)
Cl(2)	Rh(2)	P(3)	90.73(11)	C(5)	P(3)	C(51)	104.5(5)
Cl(2)	Rh(2)	P(4)	88.71(11)	C(5)	P(3)	C(61)	100.4(5)
Cl(2)	Rh(2)	C(2)	177.1(4)	C(51)	P(3)	C(61)	105.5(6)
P(3)	Rh(2)	P(4)	162.72(11)	Rh(2)	P(4)	C(6)	116.7(4)
P(3)	Rh(2)	C(2)	89.7(4)	Rh(2)	P(4)	C(71)	117.4(4)
P(4)	Rh(2)	C(2)	90.0(4)	Rh(2)	P(4)	C(81)	107.5(4)
Cl(3)	Ti(1)	Cl(4)	95.1(2)	C(6)	P(4)	C(71)	102.3(5)
Cl(5)	Ti(2)	Cl(6)	95.27(14)	C(6)	P(4)	C(81)	106.1(5)
Rh(1)	P(1)	C(3)	116.9(4)	C(71)	P(4)	C(81)	106.0(5)
Rh(1)	P(1)	C(11)	119.0(4)	Rh(1)	C(1)	O(1)	179.6(11)
Rh(1)	P(1)	C(21)	109.4(4)	Rh(2)	C(2)	O(2)	175.4(11)
C(3)	P(1)	C(11)	102.6(5)	P(1)	C(3)	C(90)	114.8(8)
C(3)	P(1)	C(21)	101.3(5)	P(2)	C(4)	C(100)	111.1(7)
C(11)	P(1)	C(21)	105.7(5)	P(3)	C(5)	C(95)	109.2(7)
Rh(1)	P(2)	C(4)	119.4(4)	P(4)	C(6)	C(105)	111.9(7)
Rh(1)	P(2)	C(31)	104.2(4)	C(3)	C(90)	C(91)	126.8(11)
Rh(1)	P(2)	C(41)	123.2(4)	C(3)	C(90)	C(94)	127.2(10)

Table 4 (Continued)

(c) Selected Interatomic Angles (deg)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C(91)	C(90)	C(94)	106.1(10)	C(4)	C(100)	C(104)	126.7(11)
C(90)	C(91)	C(92)	108.5(12)	C(101)	C(100)	C(104)	107.8(11)
C(91)	C(92)	C(93)	108.9(12)	C(100)	C(101)	C(102)	107.7(12)
C(92)	C(93)	C(94)	107.6(12)	C(101)	C(102)	C(103)	108.8(12)
C(90)	C(94)	C(93)	108.7(12)	C(102)	C(103)	C(104)	106.4(12)
C(5)	C(95)	C(96)	126.4(12)	C(100)	C(104)	C(103)	109.2(13)
C(5)	C(95)	C(99)	125.3(11)	C(6)	C(105)	C(106)	126.0(11)
C(96)	C(95)	C(99)	108.3(11)	C(6)	C(105)	C(109)	124.3(11)
C(95)	C(96)	C(97)	108.3(13)	C(106)	C(105)	C(109)	109.5(11)
C(96)	C(97)	C(98)	107.4(12)	C(105)	C(106)	C(107)	106.8(12)
C(97)	C(98)	C(99)	107.7(11)	C(106)	C(107)	C(108)	109.6(12)
C(95)	C(99)	C(98)	107.9(13)	C(107)	C(108)	C(109)	106.3(11)
C(4)	C(100)	C(101)	125.6(10)	C(105)	C(109)	C(108)	107.7(12)

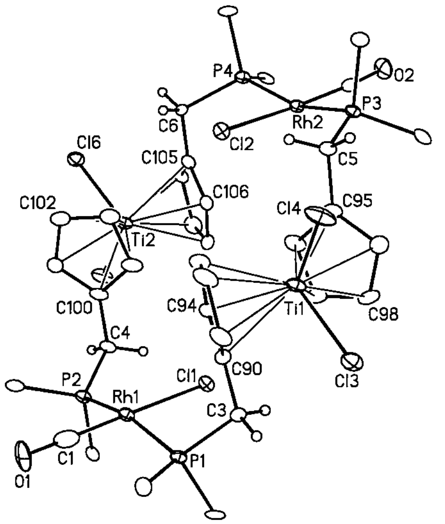

Figure 4. Alternate view of compound **7** in which only the ipso carbons of the phenyl rings are shown.

Ti change little from those of an isolated Cp'_2TiCl_2 system.[14] Unlike compound **5b**, there is no π stacking of C_5H_4 groups; instead all four have essentially equivalent environments. Their orientation forces the $TiCl_2$ moieties to the outside of the complex. The shorter tether between the cyclopentadienyl and phosphine moieties appears too short to allow a C_5H_4-ring orientation that would permit π stacking as in **5b**. Also as a result of this shorter tether, the rectangular molecular structure is not as elongated as in **5b**, having a Rh(1)−Rh(2) separation of 9.009(2) Å and a Ti(1)−Ti(2) separation of 8.245(3) Å. The Rh−Ti separations are between 5.917(3) and 6.310(2) Å. Figure 4 presents an alternate view of **7** in which the orientations of the Rh square planes become obvious. As in **5b**, these are essentially parallel, tipped from each other by only 2.4(1)°. Apart from the nonplanarity of the Rh coordination sphere, other structural features are similar to those of **5b** with an anti arrangement of Cl ligands at both metals and one phenyl group on each phosphine which is aimed away from the cavity between the metals, obstructing access to Rh from the outside of the complex. Access from inside the cavity appears again to be blocked, at least partially, although in this case it appears that the cyclopentadienyl rings and not the methylene groups are responsible.

The reaction of $(\eta^5\text{-}C_5H_4CH_2PPh_2)_2TiCl_2$ (**1**) with $(COD)PdCl_2$ also yields a single complex, formulated as $[(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2PdCl_2]_2$ (**9**), a tetranuclear complex analogous to compounds **5**−**8**. The spectral parameters of **9** very much resemble those of **7** and **8**, apart from the slight difference in the $^{31}P\{^1H\}$ chemical shift, which is expected based on binding of the phosphines to Pd instead of Rh. In particular, there is a very close correspondence between the ^1H NMR spectra for compounds **7**, **8**, and **9**. Molecular weight measurements are again consistent with a dimeric "Ti_2Pd_2" formulation, presumably having a structure much like that of **7**.

Discussion

Our approach to the synthesis of ELHB complexes was to use the bifunctional bridging groups $^-C_5H_4(CH_2)_nPR_2$ (n = 1, 2), which bind to the early metal by the cyclopentadienyl end and to the late metal by the phosphine end. It was reasoned that the use of bridging groups would allow the metals some flexibility, in which the integrity of the complex would not depend on the presence of metal−metal bonds. This approach was reported for the heterobinuclear complexes $[(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5R_4PPh_2)_2MCl_2Mo(CO)_4]$ (R = H, Me; M = Ti, Zr)[15,16] and $[(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5Me_4PMe_2)_2ZrCl_2Ru(H)_2(PPh_3)]$.[17] As noted earlier, the cis-phosphine arrangement at Mo was not ideal for allowing metal−metal cooperativity, so we sought to incorporate late metals, having the phosphines in a trans arrangement at these metals. However, the structure of the ZrRu complex, in which a trans-phosphine arrangement was achieved, demonstrated one potential drawback to the use of the bridging $^-C_5R_4PR'_2$ ligands, having too little separation between the two functional groups. The resulting complex displays significant internal strain as demonstrated by the significant deviation of the phosphines on Ru (P−Ru−P = 157°) from the idealized 180°. The use of the ligands shown above, in which the cyclopentadienyl and phosphine groups are linked by one or two carbon spacers, was intended to add some flexibility to this ligand type.

As noted in an earlier report,[1] the structures of a number of $(\eta^5\text{-}C_5H_4R)_2MX_2$ species (M = Ti, Zr; R =

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[14] (a) Petersen, J. L.; Egan, J. W., Jr. *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.

[15] Tikkanen, W.; Fujita, Y.; Petersen, J. L. *Organometallics* **1986**, *5*, 888.

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[17] Bakhmutov, V. I.; Visseaux, M.; Baudry, D.; Dormond, A.; Richard, P. *Inorg. Chem.* **1996**, *35*, 7316.

pendent group) clearly point out the potential dangers in using these early-metal complexes as chelating ligands to a late metal. The several different orientations of the pendent groups observed,[1,4e,18−20] in which the phosphine or amine functionalities are oriented in opposite directions to each other, suggest that oligomer formation might be problematic, with the two tethered phosphines (in our case) able to coordinate to different metals. Consistent with this idea, reactions of the early-metal-containing diphosphines, $(\eta^5\text{-}C_5H_4(CH_2)_nPPh_2)_2MCl_2$ ($n = 1$, M = Ti (**1**), Zr (**2**); $n = 2$, M = Ti (**3**), Zr (**4**)), with a variety of late-metal sources, including $[RhCl(CO)_2]_2$ and $(COD)PdCl_2$, under a range of conditions gave oligomeric mixtures as judged by their NMR spectra. Only under high dilution conditions at low temperature did we succeed in obtaining the single products $[(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_nPPh_2)_2MCl_2RhCl(CO)]_2$ ($n = 2$, M = Ti (**5**), Zr (**6**); $n = 1$, M = Ti (**7**), Zr (**8**)) and $[(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4CH_2PPh_2)_2TiCl_2PdCl_2]_2$ (**9**), although **5** and **6** were each obtained as an equilibrium mix of two isomers. Compounds **5** and **6** had previously been reported,[3a] although their characterization was based solely on spectroscopic techniques, and their formulations as either monomeric or dimeric (i.e., RhM or Rh_2M_2) were not established. Our data clearly establish their dimeric or tetranuclear natures. One puzzling aspect of the previous study, however, was the observation of only one species in each case; we are at a loss to explain why both isomers of **5** and **6** were apparently not observed.[3a]

Although our initial goal was to synthesize the monomeric ELHB complexes, containing just one group 4 metal together with a late metal (Rh or Pd in this study), we were unsuccessful in obtaining these heterobinuclear complexes. This is in contrast to the report of Erker and co-workers[4e] in which the analogous bridging bifunctional ligands, $^-C_5H_4(CRR')PAr_2$ (R = H, R′ = ^tBu; R = R′ = Me; Ar = Ph, Tol), were successfully utilized for the generation of heterobinuclear complexes involving groups 4 and 10 metals. On the basis of the structures of **5b** and **7**, described above, one can speculate on the reasons that tetranuclear complexes were obtained with our bifunctional ligands, yet binuclear complexes were obtained with the Erker ligands. The differences in these two ligand systems lie in the presence or absence of alkyl substituents on the carbon linking the cyclopentadienyl and phosphine groups. Considering compound **7**, which utilizes the unsubstituted analogue of Erker's ligands, we see in Figure 4 and Table 4 that the hydrogens of the linking methylene groups (C(3) to C(6)) come into close contacts with the chloro ligands on either Ti or Rh. The corresponding contacts, ranging between 2.65 Å (H(4B)−Cl(5)) and 3.21 Å (H(3B)−Cl(3)), are close to normal van der Waals contacts (2.9−3.3 Å).[21] Substituting either or both of the methylene hydrogens on the spacer carbons by more sterically demanding alkyl groups would bring these alkyl groups into unacceptably short contacts with the chloro ligands, destabilizing the tetranuclear structure and presumably favoring the heterobinuclear species instead. The same can be said for compound **5b**, shown in Figures 1 and 2, in which the methylene hydrogens adjacent to the C_5H_4 rings again aim inwardly. Substituting these hydrogens by larger substituents should again lead to destabilization of the tetranuclear framework. Using this logic, we have carried out preliminary studies involving the reaction of $(\eta^2\text{-}C_5H_4C(Me)_2PPh_2)_2TiCl_2$ with $[RhCl(CO)_2]_2$ and find evidence, in NMR and IR spectroscopy and in mass spectral data, for a mixture of binuclear and tetranuclear products. Currently we are attempting to optimize the experimental conditions to obtain the targeted heterobinuclear complexes in high yield.

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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 **5b** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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