exchange of carbonyl groups. As shown in Scheme III there are several plausible intermediates which would allow for carbonyl group migration between Fe and Rh. We favor the doubly bridged structure F since it is easily achieved from both isomeric C and D and it maintains the favored μ - η^4 , η^3 -C₇H₇ bonding functionality. Furthermore, the process is related to the well-established merry-goround mechanism for carbonyl group migration in di- and polynuclear metal carbonyl compounds.³² An often observed feature in these systems is increased facility for carbonyl group migration upon phosphine substitution.^{32,36} This is well illustrated in the present context as well. The parent pentacarbonyl la shows no line broadening in the ¹³C NMR spectrum up to 70 °C whereas in 1b this temperature represents the coalescence point with an associated ΔG^*_{343} of 15.4 kcal/mol.

Conclusion

It is apparent from this first reactivity study on 1a that the bridging cycloheptatrienyl moiety is capable of exhibiting a variety of bonding capabilities. This flexible nature can be manifested in two distinct manners. The ability to create coordinative unsaturation is responsible for the facile carbonyl substitution reaction and may promote other reactions as well. The capacity for bonding

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Further studies are underway to delineate the scope of the reactivity of 1a. The synthesis of related $(\mu$ -C₇H₇)-MM'(CO)₅ (M = Fe, Ru, Os and M' = Co, Rh, Ir) compounds are also being explored in order to probe the effect of the metal on the structure, fluxionality, and reactivity in this class of molecules.

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Registry No. 1a, 51608-48-1; 1b, 100190-09-8; 2a, 91868-00-7; 2b, 91855-30-0; 3a, 91855-31-1; 3b, 91855-32-2; 3c, 91855-33-3; 3d, 91855-34-4; 3e, 100190-10-1; 3f, 100190-11-2; $Na(C_7H_7)Fe(CO)_3$, 62313-81-9; $[RhCl(COD)]_2$, 12092-47-6; Rh, 7440-16-6; Fe, 7439-89-6.

Supplementary Material Available: A table of thermal parameters for 1b (Table VIII) and listings of observed and calculated structure amplitudes for 1b and 3b (31 pages). Ordering information is given on any current masthead page.

Synthesis, Molecular Structure, Solution Dynamics, and Reactivity of $(\eta$ -C₅H₅)₂M(μ -PR₂)₂Rh(η -indenyl) (M = Zr, Hf; R = Et, Ph)[†]

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The "metal-containing diphosphines", $Cp_2M(PR_2)_2$ ($Cp = \eta - C_5H_5$; M = Zr, Hf; R = Et, Ph), displace both coordinated ethylenes from $(\eta - C_2H_4)_2Rh(\eta$ -indenyl), yielding the early-late heterobimetallic complexes $Cp_2M(\mu-PR_2)_2Rh(\eta$ -indenyl). The molecular structure of $Cp_2Zr(\mu-PPh_2)_2Rh(\eta$ -indenyl) (1c), determined by X-ray diffraction, consists of edge-shared, pseudotetrahedral 16e Zr(IV) and distorted, square-planar Rh(I) centers with a planar ZrP₂Rh bridging unit and a Zr. Rh separation of 3.088 (1) Å. The indenyl ligand exhibits a pronounced "slip-fold" distortion toward η^3 -coordination and high barriers (14-15 kcal/mol) to indenyl rotation are observed by ¹H DNMR. Addition of CH₃I to $Cp_2M(\mu-PEt_2)_2Rh(\eta$ -indenyl) affords the cationic d⁰-d⁶ heterobimetallics [$Cp_2M(\mu-PEt_2)_2Rh(CH_3)(\eta$ -indenyl)]I. Red crystals of 1c are monoclinic, $P2_1/m$ (no. 11), with two molecules per unit cell of dimensions a = 9.700 (1) Å, b = 18.855 (3) Å, c = 10.185(1) Å, and $\beta = 112.95$ (1)°. The structure was refined to R = 0.029 and $R_w = 0.031$ for 2928 observed reflections.

Transition-metal complexes containing the η -indenyl ligand undergo ligand substitution much more readily than their η -cyclopentadienyl analogs due to the stability of the η^3 bonding mode in the former, suggested to result from the aromatization of the indenyl benzene ring.¹ The recently reported^{2,3} "metal-containing diphosphines", Cp₂M-(PR₂)₂ (Cp = η -C₅H₅; M = Zr, Hf; R = Et, Ph, cyclohexyl (Cy)), contain both 1e and 3e donor PR₂ ligands. Donation of both phosphorus lone pairs to a second metal center thus creates an electronically unsaturated early metal center in the resulting PR₂-bridged heterobimetallic com-

plex. We have previously described the binding of various metal carbonyl⁴ and ML_n^5 fragments, where M = Ni, Pd,

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Table I. Elemental Analyses and Melting Point Data

	elemental analyses ^{a,b}							
<u> </u>	no.	mp, °C	С	Н	Р	Rh	М	I
				$Cp_2M(\mu$	-PR ₂) ₂ Rh(η-indenyl))		
M = Zr, R = Et	1 a	295-297	51.97, 52.17 (52.50)	6.08, 6.11 (6.04)	9.91, 10.10 (10.03)	16.6, 16.8 (16.66)	14.8, 14.9 (14.77)	
M = Hf, R $= Et$	1 b	295-297	45.77, 45.70 (46.00)	5.21, 5.23 (5.29)	8.68, 8.73 (8.79)	14.5, 14.5 (14.60)	24.6, 24.7 (25.32)	
M = Zr, R = Ph	1c	270-272	63.17, 62.88 (63.77)	4.66, 4.60 (4.61)	7.40, 7.51 (7.65)	12.7, 12.6 (12.71)	11.8, 11.7 (11.26)	
M = Hf, R $= Ph$	1d	280285	57.79, 57.82 (57.57)	4.48, 4.53 (4.16)	6.53, 6.71 (6.91)	11.0, 11.0 (11.47)	18.4, 18.6 (19.90)	
				$[Cp_{2}M(\mu - PE]$	t ₂) ₂ Rh(CH ₂)(<i>n</i> -inder	nyl)]I		
M = Zr	2a	162-165	$44.12, \ 43.99$ (44.27)	5.28, 5.29 (5.31)	7.94, 7.95 (8.16)	13.5, 13.5 (13.55)	12.0, 12.0 (12.01)	16.6, 16.7 (16.71)
M = Hf	2b	165-168	39.10, 39.13 (39.71)	4.75, 4.75 (4.76)	7.32, 7.17 (7.31)	12.2, 11.9 (12.15)	20.9, 20.2 (21.08)	14.3, 14.3 (14.99)

^a Found; calculated in parentheses. ^bHf analyses are low due to significant quantities of Cp₂ZrCl₂ in commercial Cp₂HfCl₂.

and Pt, L = diene, alkyne, phosphine, diphosphine, and phosphite, and n = 1 and 2. We now report (i) the binding of the Rh(η -indenyl) fragment, (ii) the X-ray structural determination of $Cp_2Zr(\mu-PPh_2)_2Rh(\eta-indenyl)$, (iii) the observation of hindered indenyl ligand rotation in solution by ¹H DNMR, and (iv) the oxidative addition of CH_3I to the Rh(I) center without disruption of the MP₂Rh bridge system.

Experimental Section

All operations were conducted in a Vacuum Atmospheres glovebox with continuous nitrogen flush. Solvents were purified by standard techniques⁶ and distilled from sodium- or potassium-benzophenone ketyl. $(\eta$ -Indenyl)Rh $(\eta$ -C₂H₄ $)_2^{1d,e}$ and Cp₂M- $(PR_2)_2^{2,4}$ were prepared by literature methods. CH_3I , $CH_3C(O)Cl$, NH_4PF_6 (Aldrich), and research purity H_2 and CO (Matheson) were used as received. NMR spectra were recorded on a Nicolet NMC-300-WB (121-MHz ³¹P and 76-MHz ¹³C) spectrometer. ¹³C and ³¹P NMR chemical shifts are positive downfield from external SiMe₄ and 85% H₃PO₄, respectively. IR spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 983 spectrometer. Elemental analyses were performed by Pascher Mikroanalytisches Labor, Bonn, West Germany. Melting points were determined in sealed, nitrogen-filled capillaries using a Thomas-Hoover apparatus and are uncorrected. Elemental analyses and melting points are listed in Table I, and IR and NMR data are compiled in Tables II-V.

 $Cp_2Zr(\mu-PEt_2)_2Rh(\eta-indenyl)$ (1a). To a solution of 1.199 g (3.0 mmol) of $Cp_2Zr(PEt_2)_2$ in 60 mL of hexane was added dropwise a solution of 823 mg (3.0 mmol) (η -indenyl)Rh(η -C₂H₄)₂ in 20 mL of hexane, over 10 min. The solution turned red-brown and slowly precipitated an orange solid. After the solution was stirred for 12 h, the product was filtered off, washed with 2×10 mL of cold (-30 °C) pentane, and dried in vacuo, yielding 1.333 g. Concentration of the filtrate to 5 mL yielded a second crop of 270 mg, for a combined yield of 1.603 g (87%). The Hf analogue 1b was prepared similarly by using 1.461 g (3.0 mmol) of Cp₂Hf(PEt₂)₂, affording 1.814 g of product (86%). Red crystals of both complexes were obtained in good yield from tolueneheptane

 $Cp_2Zr(\eta-PPh_2)_2Rh(\eta-indenyl)$ (1c). To a solution of 1.775 g (3.0 mmol) of Cp₂Zr(PPh₂)₂ in 40 mL of THF was added dropwise a solution of 823 mg (3.0 mmol) of $(\eta$ -indenyl)Rh $(\eta$ - $C_2H_4)_2$ in 40 mL of THF, over 10 min. The resulting dark red

Table II. Infrared Spectral Data^a

- $Cp_2Zr(\mu-PEt_2)_2Rh(\eta-indenyl)$ (1a): 1316 (m), 1228 (m), 1208 (w), 1168 (w), 1146 (w), 1120 (w), 1066 (w), 1030 (s), 1022 (s), 1010 (s, sh), 975 (m), 924 (m), 885 (m), 877 (m), 851 (w), 843 (w), 823 (m, sh), 800 (s, sh), 791 (vs), 780 (vs), 765 (s), 736 (s), 721 (s), 673 (m), 633 (m), 438 (s), 398 (w), 386 (w, sh), 338 (m), 280 (w), 248 (w) cm⁻¹
- $Cp_2Hf(\mu-PEt_2)_2Rh(\eta-indenyl)$ (1b): 1315 (m), 1227 (m), 1208 (w), 1167 (w), 1158 (w), 1145 (w), 1120 (w), 1067 (w), 1029 (s), 1021 (s), 1010 (s), 976 (m), 924 (m), 884 (m), 875 (m), 851 (w), 844 (w), 828 (m), 805 (s, sh), 796 (vs), 780 (vs), 763 (vs), 735 (vs), 721 (s), 672 (m), 633 (m), 610 (w), 437 (s), 400 (w), 340 (w), 302 (w, sh), 286 (m), 246 (w) cm⁻¹
- $Cp_2Zr(\mu-PPh_2)_2Rh(\eta-indenyl)$ (1c): 1579 (m), 1564 (w), 1322 (w), 1310 (m), 1223 (m), 1213 (w), 1185 (w), 1174 (w), 1154 (w), 1120 (w), 1087 (w), 1070 (m, sh), 1062 (m), 1017 (s), 975 (m), 928 (m), 920 (m, sh), 892 (w), 854 (w), 843 (w), 831 (m), 811 (s), 790 (s), 781 (s), 736 (vs), 705 (s), 696 (s), 618 (w), 515 (s), 484 (s), 459 (m), 442 (w), 432 (w), 400 (m), 375 (w), 341 (w), 325 (w), 273 (w), 241 (w) cm⁻¹
- $Cp_2Hf(\mu-PPh_2)_2Rh(\eta-indenyl)$ (1d): 1577 (m), 1562 (w), 1321 (w), 1309 (m), 1222 (w), 1231 (w), 1184 (w), 1173 (w), 1153 (w), 1119 (w), 1087 (w), 1068 (w, sh), 1061 (m), 1015 (s), 978 (m), 926 (m), 890 (w), 845 (w, sh), 836 (m), 814 (s), 787 (s, sh), 782 (vs), 731 (vs), 703 (s, sh), 694 (s), 619 (w), 515 (s), 483 (s), 459 (m), 443 (m), 433 (m), 399 (m), 375 (w), 337 (w), 302 (w), 275 (w), 239 (w) cm^{-1}
- $[Cp_2Zr(\mu-PEt_2)_2Rh(CH_3)(\eta-indenyl)]I$ (2a): 3049 (m), 1541 (w), 1323 (w), 1237 (m), 1192 (w), 1183 (w), 1149 (m), 1121 (w), 1037 (s), 1020 (s), 975 (m), 946 (w), 926 (w), 892 (w), 861 (m), 850 (m), 838 (m), 828 (s), 809 (vs), 778 (m), 758 (s), 733 (s), 684 (s), 639 (m), 546 (w), 512 (w), 459 (m), 423 (w), 404 (w), 387 (w), 364 (w), 339 (w), 283 (w), 250 (w) cm⁻¹
- $[Cp_2Hf(\mu-PEt_2)_2Rh(CH_3)(\eta-indenyl)]I$ (2b): 3050 (m), 1540 (w). 1324 (w), 1237 (m), 1213 (w), 1192 (w, sh), 1184 (m), 1170 (w), 1151 (m), 1123 (w), 1036 (s), 1020 (s), 975 (m), 945 (w), 931 (w), 920 (w), 890 (w), 863 (m, sh), 854 (m), 841 (s, sh), 833 (s), 812 (vs), 777 (m), 758 (s), 731 (s), 684 (m), 640 (m), 545 (w), 512 (s), 456 (m), 421 (m), 404 (m), 386 (w), 336 (w), 315 (w), 281 (w), 247 (w) cm⁻¹

^a Recorded as mineral oil mulls between CsI plates. Underlined absorptions are assigned to M-P vibrations.

solution was stirred for 3 days and evaporated to dryness. The residue was stirred with 25 mL of hexane, filtered off, and dried in vacuo, yielding 2.191 g of the title product (90%). The Hf analogue 1d was prepared similarly by using 2.037 g (3.0 mmol) of Cp₂Hf(PPh₂)₂, affording 2.415 g of product (90%). Red crystals of both complexes were obtained in good yield from THF-heptane.

 $[Cp_2Zr(\mu-PEt_2)_2Rh(CH_3)(\eta-indenyl)]I$ (2a). To a solution of 93 mg (0.15 mmol) of 1a in 10 mL of hexane was added 21 mg (0.15 mmol) of CH₃I. The solution lightened and precipitated a yellow powder. After the solution was stirred for 12 h, the

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Table	, III.	301-MHz	H	NMR	Data ^a
1.	Cp ₂ N	$\Lambda(\mu-\mathrm{PEt}_2)_2\mathrm{I}$	Rh(η-inder	nyl)

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ср
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	19 26, 4.65
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	16 !5, 4.65
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	
Hf 1d 05^{f} 7.46 7.29 7.20 6.56 6.13 5.67 (2.5) 6.30 (2.5) 4.80	83
$-60^{s} 7.81, 7.11 7.44, 7.27 7.32, 7.25 6.59, 5.96 5.61 6.45 5.25, 4.85$.65
3. $[Cp_2M(\mu-PEt_2)_2Rh(CH_3)(\eta-indenyl)]I^i$	
Et indenyl	
M no. CH_2 CH_3^b H_{4-7}^c $H_{1,3}^d$ H_2^e CH_3^j C_1	F
Zr 2a 3.08 (mult), 2.15 (mult), 1.73 (mult), 1.37 1.46 (17.0, 7.5), 1.29 7.42, 7.21 6.48 5.79 (3.0) -0.60 (3.5, 3.0) 5.61, 4.89 (ov mult) (13.5, 7.0)	
Hf 2b $3.17 \text{ (mult)}, 2.07 \text{ (mult)}, 1.74 \text{ (mult)}, 1.31 1.45 (17.0, 7.5), 1.27 7.42, 7.21 6.43 5.75 (3.0) -0.58 (3.5, 2.5) 5.59, 4.90 (3.5, 2.5) 1.59 + 0.58 (3.5, 2.5) 1.59 +$	tr, ³ J _{Р-Н} ;)
4. DNMR Data for Hindered Indenyl Rotation ^k	

complex	T _c , K	$\Delta \nu$, Hz	$k_{T_{c}}, \mathrm{s}^{-1}$	$\Delta G^*_{T_c}$, kcal/mol	
la	320	181	402	15.0 ± 0.2	
1 b	317	182	404	14.8 ± 0.2	
1c	291	77	171	14.0 ± 0.3	
1d	285	59	131	13.9 ± 0.3	

^a Chemical shifts in ppm. Abbreviations: d = doublet; tr = triplet; br = broad; ov = overlapping; mult = multiplet. ^bd tr; ³J_{P-H}, ³J_{H-H} in Hz in parentheses. ^cMultiplets due to AA'BB' spin system. ^dd; ³J_{H-H} in Hz in parentheses. ^etr; ²J_{Rh-H} \approx ³J_{H-H} in Hz in parentheses. ^fRun in p-dioxane-d₈. ^gRun in THF-d₈. ^hVirtual triplets with ³J_{H-H} \approx 7-8 Hz. ⁱRun in CD₃CN at 25 °C. ^jtr d; ³J_{P-H}, ²J_{Rh-H} in Hz in parentheses. ${}^{k}T_{c}$ = coalescence temperature ±5 K; $\Delta \nu$ = chemical shift difference of exchanging sites ±5 Hz.

Table IV, 121-MIRZ "P NMR	Data
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	no.	chem shift, ^b ppm
$Cp_0M(\mu-P)$	R.).Rh(n-ir	ndenvl)
M = Zr, R = Et	1a	181.6 (129)
M = Hf, R = Et	1b	169.1 (125)
M = Zr, R = Ph	1 c	177.3 (137)
M = Hf, R = Ph	1 d	169.7 (133)
$[Cp_2M(\mu-PEt_2)]$	$_{2}\mathbf{Rh}(\mathbf{CH}_{3})(1$	η-indenyl)]I
M = Zr	2a	158.5 (82)
M = Hf	2b	145.4 (81)

^aRun at 25 °C with proton decoupling; 1a-d in THF-d₈ and 2a,b in CD₃CN. ^bAll resonances are doublets; J_{Rh-P} in Hz in parentheses.

product was filtered off, washed with 5 mL of hexane, and dried in vacuo, yielding 80 mg of the title complex (71%). The Hf analogue 2b was prepared similarly by using 106 mg (0.15 mmol) of 1b, affording 93 mg of product (74%).

X-ray Data Collection and Structure Solution and Refinement. Red crystals of complex 1c suitable for diffraction studies were grown by slow diffusion of *n*-heptane into a THF solution of the complex. A crystal of appropriate dimensions (see Table VI for crystallographic details) was encapsulated in a glass capillary under N₂ and mounted on a Syntex P3 diffractometer. The crystal proved to be suitable based on Ω scans having peak widths at half-height of 0.24° at -100 °C. Preliminary photographic examination revealed the space group and approximate cell constants. The latter were refined to the values shown in Table VI by using 47 reflections chosen from diverse regions of reciprocal space.

Intensity data were collected by using the Ω scan technique (0.90° scan range, scan rates of 8-20° min⁻¹, and total background time = scan time). The intensities of three standard reflections were monitored at 200 reflection intervals and were found to vary insignificantly. The data were corrected for absorption by using the DIFABS program⁷ and processed by using counting statistics and a p value of 0.02 to derive standard deviations.

The solution and refinement were accomplished by using local modifications of the SDP-Plus software supplied by the Enraf-Nonius Corp. The Zr and Rh atoms were located in an originremoved Patterson synthesis, and the positions of the remaining non-hydrogen atoms were determined by the usual combination of structure factor and Fourier syntheses and least-squares refinements. The function minimized was $\sum w(|F_0| - |F_c|)^2$, where $|F_0|$ and $|F_c|$ are the observed and calculated structure amplitudes where $w = 1/\sigma^2(F_0)$. The atomic scattering factors used were taken from the compilations of Cromer and Waber,^{9a} and the anomalous dispersion terms used were Cromer's.9b All hydrogen atoms were located, placed in idealized positions [d(CH) = 0.95 Å], and included in the final refinements as a fixed contribution $(B_{\rm H} =$ 4.0 $Å^2$). Final convergence led to the agreement indices shown in Table VI where $R = \sum ||F_0| - |F_c|| / \sum |F_0|$ and $R_w = \sum w(|F_0|)$ $|F_c|^2 / \sum wF_0|^{1/2}$. The highest peak in a final difference map was adjacent to the Zr atom and corresponded to $1.58 \text{ e} \text{ Å}^{-3}$. Other residual peaks were less than 0.35 e $Å^{-3}$.

Selected bond lengths and angles are compiled in Table VII. Positional and equivalent isotropic thermal parameters for the non-hydrogen atoms are collected in Table VIII. Positional and thermal parameters for the idealized hydrogen atoms (Table IX), general temperature factors (Table X), dihedral angles between calculated planes (Table XI), and structure factor amplitudes

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								1. ($Dp_2M($	μ -PEt ₂)	2Rh	(η-indeny	l) ^b				
									- <u></u>	inde	nyld	1				ethyl ^e	
	М	no.		$\mathbf{C}\mathbf{p}^{c}$		C(1,5	3) ^f	C	(2) ^g		C(5	,6)	C(4,7)	C(3a,7a)	CH ₂		CH ₃
	Zr Hf	la 1b	99 98	.5 (172 .4 (173	2, 7) 3, 7)	73.9 (2.5 73.7 (2,	, 169) 172)	96.9 97.1	(7, 168) (4, 172)	$ \begin{array}{ccc} 8) & 11 \\ 2) & 11 \end{array} $	3.8 3.8	(161) (161)	120.7 (159 120.5 (159	121.3 121.1	25.0 (12 24.9 (12	9) 1 7) 1	3.6 (129) 3.6 (127)
								2. C	$p_2M(p_2)$	u-PPh ₂)	$_2$ Rh	(η-indeny	1) ^b				
							i	indenyl ^d							ohenyl		
Μ	no.	Ср		C(1	1,3) ^f	C(2)	g	C(5,	6)	C(4,7)	C(3a,7a)) ipso ^h	ortho ⁱ	m	eta ^j	para
Zr	lc	103.3 (174)	br,	77.4 17:	(3.5, 3)	100.3 (6.5	, 170)	117.5 (157)	123.2 (1	57)	127.1	145.5 (2	(6, 16) 134.6)) 127.9	(5, 159)	127.5 (159)
Hf	ld	102.2 (174)	br,	76.9 17	(3.5, 1)	100.4 (5.5	, 173)	117.6 (157)	123.0 (1	57)	127.5	145.6 (2	21) 135.0 (4, 16)) 127.8	(4, 160)	127.6 (160)
							;	B. [Cp ₂]	Μ(μ-Ρ	Et ₂) ₂ Rh	(CH	3)(η-inde	$nyl)]I^k$				
								i	ndeny] ^d						eth	nyl
М	no.		Cp ^c			C(1,3) ^f	C	(2) ^g	C	(5,6)	(C(4,7)	C(3a,7a)	CH_{3}^{l}		H_2^m	CH ₃
Zr	2a	104.4 (103.3	175, 3 (17	7), '5, 7)	79.6	(3.5, 179)	110.3	(6, 177)	122.	6 (167)	128	3.2 (162)	119.8	-9.8 (26, 2.5, 13	9) 24.5	(17, 132) 13.9 (128)
Hf	2b	103.7 (102.8	176, 5 (17	6), (6.6)	79.3	(180)	110.0	(179)	122.	6 (167)	128	8.0 (163)	119.5	-9.8 (26, 2.5, 13	17.2 (39) 24.4 ((14, 128 (8, 130)) 10.8 (128) 13.9 (128)
		1010		-,-,											17.1 (9, 131)	10.9 (127)

Table V. 75.6-MHz ¹³C NMR Data^a

^aChemical shifts in ppm. Numbering scheme:

^bRun in THF-d₈ at 60 °C with gated decoupling. ^cDoublet of virtual quintets: J_{CH} , ${}^{2}J_{CH} \approx {}^{3}J_{CH}$ in Hz in parentheses. ^d J_{CH} in Hz in parentheses; ${}^{2}J_{CH}$ of 5-8 Hz was also observed. ^eBroad, J_{CH} in Hz in parentheses. ^fDoublet of doublet of triplets; $J_{Rh-C} \approx {}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; $J_{Rh-C} \approx {}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; ${}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; ${}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; ${}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; ${}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; ${}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; ${}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; ${}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; ${}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; ${}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; ${}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; ${}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; ${}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; ${}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; ${}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; ${}^{2}J_{P-C}$, J_{CH} in Hz in parentheses. ^fDoublet of doublets; {}^{2}J_{P-C}, J_{CH} in Hz in parentheses. ^fDoublet of doublets; {}^{2}J_{P-C}, J_{CH} in Hz in parentheses. ^fDoublet of doublets; {}^{2}J_{P-C}, J_{CH} in Hz in parentheses. ^fDoublet of doublets; {}^{2}J_{P-C}, J_{CH} in Hz in parentheses. triplet of quartets; $J_{\text{Rb-C}}$, ${}^{2}J_{\text{P-C}}$, J_{CH} in Hz in parentheses. "Doublet of triplets; $J_{\text{P-C}}$, J_{CH} in Hz in parentheses.

Table	VI.	Summary	of	X-rav	Diffraction Data	
ranc	V 4.	o ummar y	υı	A-Lay	Dilliaction Data	

	•
complex	$(\eta^5 - C_5 H_5)_2 Zr[\mu - P(C_6 H_5)_2]_2$
	$Rh(\eta - C_9H_7)$ (1c)
formula	C ₄₃ H ₃₇ P ₂ RhZr
fw	809.85
space group	$C_{2h}^2 - P_{2_1}/m$ (no. 11)
a, Å	9.700 (1)
b, Å	18.855 (3)
c, Å	10.185 (1)
β , deg	112.95 (1)
V, Å ³	1715.3 (6)
Ζ	2
ρ (calcd), g cm ⁻³	1.568
cryst dimens, mm	$0.19 \times 0.25 \times 0.29$
temp, °C	-100
radiatn	Mo Kα (0.71069Å) from
	graphite monochromator
$\mu, {\rm cm}^{-1}$	8.94
absorptn correctn factors	0.86-1.07; av 0.99
2θ limits, deg.	4.0-55.0
total no. of unique observns	4065
data, $F_0^2 > 3\sigma(\bar{F}_0^2)$	2928
final no. of variables	219
R	0.029
$R_{\mathbf{w}}$	0.031
error in obsvn of unit wt, electrons	1.296

(Table XII) are available as supplementary material.

Results and Discussion

Synthesis of $Cp_2M(\mu - PR_2)_2Rh(\eta - indenyl)$. The reaction of $Cp_2M(PR_2)_2$ with $(\eta$ -indenyl) $Rh(\eta$ - $C_2H_4)_2$ in hexane or THF liberates ethylene, affording the new heterobimetallic complexes $Cp_2M(\mu-PR_2)_2Rh(\eta-indenyl)$ (1a-d) in excellent yield. The products are red-orange to brown-orange, air-sensitive crystalline solids which are soluble in nonpolar organic solvents (1c,d are only slightly soluble in alkanes). Monitoring the reactions by ³¹P NMR spectroscopy showed the reactions to be quantitative, although formation of 1c,d was slow (ca. 2 days) and reaction with $Cp_2M(PCy_2)_2$ was still not clean after 1 week. Complexes 1a-d were characterized by full elemental analysis and IR and ¹H, ³¹P, and ¹³C NMR spectroscopy and, for 1c, by single-crystal X-ray diffraction.



Molecular Structure of $Cp_2Zr(\mu-PPh_2)_2Rh(\eta$ indenyl) (1c). The molecular structure of 1c, shown in Figure 1, consists of edge-shared pseudotetrahedral 16e Zr(IV) and distorted square-planar Rh(I) centers with a planar ZrP₂Rh bridge system and a Zr...Rh separation of 3.088 (1) Å. A crystallographic mirror plane contains the Zr and Rh atoms and bisects the indenyl and cyclopentadienyl ligands. The indenyl ligand exhibits a pronounced "slip-fold" distortion¹⁰ relative to a planar, η^5 indenyl ligand,^{11,12} such that the Rh-C distances to the

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Table VI	. Selected	Distances	(A) a	and A	Angles	(deg) in
	Cp ₂ Zr(µ	-PPh ₂) ₂ Rh(n	-C.F	H7) (1	c) ^a	

	Bond I	Distances	
Rh-Zr	3.088 (1)		
Rh–P	2.264 (1)	Zr-P	2.590 (1)
Rh-C(21)	2.249 (4)	Zr-C(31-33)	2.512-2.540 (4)
Rh-C(22)	2.242 (3)	Zr-C(41-43)	2.495 - 2.550(4)
Rh-C(23)	2.469 (3)		
D. 0(1)	1 000 (0)	D ((11)	1.040 (0)
P-C(1)	1.838 (3)	P-C(11)	1.842 (3)
C(1-5)-C(2-6)	1.382-1.406	(5)	
C(11-15)-C(12-16	i) 1.377–1.402 ((5)	
C(21)-C(22)	1.415 (4)	C(23)-C(24)	1.395 (4)
C(22) - C(23)	1.456 (4)	C(24) - C(25)	1.382 (4)
$C(22) = C(23)^{\prime}$	1 443 (4)	C(25) = C(25)'	1 408 (4)
	1.110 (1)	(10)	1.100 (1)
C(31-33)-C(32-33	i) 1.410–1.414 ((4)	
C(41-43)-C(42-43	i) 1.400-1.408 ((4)	
	Bond	Angles	
Zr-Rh-P	55.33 (2)	P-Rh-P'	110.66 (3)
Zr-Rh-C(21)	151.6 (1)	P-Rh-C(21)	120.04 (4)
$7_{r-Bh-C(22)}$	148 63 (8)	P-Rh-C(22)	93.81 (8)
C(21) = Dh = C(22)	26 79 (0)	$D_{D_{1}}$	154 89 (8)
C(21) = MI = C(22)	50.72 (8)	$C(22) = Rh = C(22)^{\prime}$	61.3(2)
	15.00 (0)		01.05 (2)
Rh-Zr-P	45.98 (2)	P-Zr-P	91.95 (3)
Rh-Zr-C(31-33)	89.9-138.9 (1)	P-Zr-C(31-33)	82.6-136.5 (1)
Rh-Zr-C(41-43)	85.6-134.0 (1)	P-Zr-C(41-43)	80.5-133.6 (1)
Rh-P-Zr	78.70 (2)	Zr-P-C(1)	118.67 (9)
Rh-P-C(1)	114.99 (9)	Zr-P-C(11)	129.40 (9)
Rh-P-C(11)	111.48 (9)	C(1) - P - C(11)	101.9 (1)
P_C(1)_C(9)	190 5 (9)	$P_{-}C(11)_{-}C(19)$	110.6 (9)
P = O(1) = O(2)	120.0(2)	P = O(11) = O(12)	119.0 (2)
P = C(1) = C(6)	121.1(2)	P = U(11) = U(10)	123.2 (2)
C(2) - C(1) - C(6)	118.3 (3)	C(12) - C(11) - C(16)	117.0 (3)
C-C-C(Ph)	119.0-121.1 (3)		
Rh-C(21)-C(22)	71.4 (2)	Rh-C(22)-C(21)	71.9 (2)
C(22)-C(21)-	107.8 (4)	Bh-C(22)-C(23)	80.7 (2)
C(22)'	20110 (1)		0001 (2)
C(22) = C(23) =	106.8 (2)	C(21) = C(22) = C(23)	108 7 (3)
C(99)/	100.0 (2)	O(21) O(22) O(20)	100.7 (0)
C(20) $C(20)$	199.9 (9)		
C(22) = C(23) = C(23	100.2 (0)		
0(24)			
C-C-C-	119.0-121.1 (3)		
(benzenoid)			
C-C-C(Cn)	107 5-109 5 (4)		
U-U-U(Up)	107.0-108.0 (4)		

^a The prime indicates symmetry-related atoms.



(42) C (41)

Figure 1. Molecular structure of $(\eta - C_5H_5)_2 Zr(\mu - PPh_2)_2 Rh(\eta - indenyl)$ (1c). Only the ipso carbon atoms of the phenyl rings are shown, and hydrogen atoms are omitted for clarity.

quaternary carbons (C(23), C(23')) are >0.2 Å longer than those to the "allylic" carbons (C(22), C(22')); $\Delta MC = 0.23$



Figure 2. ¹H DNMR of $(\eta$ -C₅H₆)₂Zr(μ -PPh₂)₂Rh(η -indenyl) (1c) in THF- d_8 .

Å. The dihedral "fold" angle between the allyl and arene planes is 8.5° and the "hinge" angle about the C(22)–C(22') vector is 10.6°, with the arene folded away from the Rh center. Although similar distortions have been observed in other rhodium- and iridium-indenyl complexes,¹³ 1c contains the most distorted indenyl ligand yet observed crystallographically,^{14,34} with the exception of the η^3 -indenyl ligand in (CO₂)W(η^5 -indenyl)(η^3 -indenyl)¹² in which $\Delta MC = 0.72$ Å and the "fold" angle is 26°.

Spectroscopic Characterization and Hindered Indenyl Ligand Rotation. The 300-MHz ¹H NMR spectra of complexes 1a-d at 25 °C contain sharp resonances for the indenyl ligand protons and broad resonances for the cyclopentadienyl and PR₂ protons. The series of ¹H DNMR spectra of 1c, shown in Figure 2, show that there are two types of phenyl and cyclopentadienyl proton environments at the low-temperature limit, as expected from the observed solid-state molecular structure. At the high-temperature limit, the effective symmetry is C_{2v} , due to rapid rotation of the indenyl ligand about the Rh-Zr vector. Similarly, for 1a,b there are two cyclopentadienyl

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⁽¹⁴⁾ For $[Rh(CO)(\eta-indenyi)]_2(\mu-C=CH_2)$, $\Delta MC = 0.19$ Å; the fold and hinge angles average 9.0 and 8.0°, respectively.^{13c} For $[IrH(PPh_3)_2(\eta-indenyi)]BF_4$, $\Delta MC = 0.19$ Å; the fold and hinge angles are 7.6 and 6.0°, respectively.^{13f}

Table VIII. Positional Parameters and Their Estimated Standard Deviations

atom	x	у	z	$B, Å^2$	atom	x	у	z	<i>B</i> , Å ²
Rh	0.31972 (3)	0.250	0.64577 (3)	1.292 (6)	C(15)	0.2329 (4)	-0.0227 (2)	0.8107 (4)	2.98 (8)
Zr	0.000	0.250	0.41166(4)	1.386 (8)	C(16)	0.2340(3)	0.0206(2)	0.7014 (3)	2.27(7)
Р	0.18637(7)	0.15123(4)	0.54808 (8)	1.39 (1)	C(21)	0.5701(4)	0.250	0.7157(5)	2.2(1)
C(1)	0.2675 (3)	0.0949 (2)	0.4492 (3)	1.49 (6)	C(22)	0.5280 (3)	0.1894(2)	0.7731(3)	2.05 (7)
C(2)	0.3994 (3)	0.1149(2)	0.4349(3)	1.76 (6)	C(23)	0.4843(3)	0.2117(2)	0.8883(3)	1.79 (6)
C(3)	0.4569(3)	0.0742(2)	0.3539 (3)	1.98 (6)	C(24)	0.4416(3)	0.1748(2)	0.9850 (3)	2.29 (7)
C(4)	0.3849 (3)	0.0130(2)	0.2866(3)	2.09 (7)	C(25)	0.4000(4)	0.2127(2)	1.0799(3)	2.71(8)
C(5)	0.2525(3)	-0.0074(2)	0.2998 (3)	2.09 (7)	C(31)	-0.1077 (4)	0.250	0.6025 (5)	2.10 (9)
C(6)	0.1943 (3)	0.0331(2)	0.3793 (3)	1.84 (6)	C(32)	-0.1657(3)	0.1891(2)	0.5177(3)	2.07 (6)
C(11)	0.1792(3)	0.0899 (2)	0.6861(3)	1.56(6)	C(33)	-0.2595 (3)	0.2126(2)	0.3803(4)	2.38(7)
C(12)	0.1258(3)	0.1140(2)	0.7878(3)	2.13 (7)	C(41)	0.1258(5)	0.250	0.2396 (5)	2.9(1)
C(13)	0.1234(3)	0.0697 (2)	0.8962 (3)	2.63(7)	C(42)	0.0329 (4)	0.1898(2)	0.2049 (3)	2.63 (7)
C(14)	0.1762(4)	0.0012(2)	0.9076 (4)	2.79 (8)	C(43)	-0.1162 (4)	0.2127(2)	0.1505 (3)	2.45 (7)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\binom{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.





 $\Delta MC = d_{MC3a, 7a} - d_{MC1,3}$ (Å) in parentheses

rigure 3. Correlation of ¹³C NMR chemical shift difference, $\Delta\delta(C)$, with indenyl ligand hapticity: complex 1, Fe(ind)₂;¹⁷ 2, [Co(ind)₂]^{+,17} 3, [Rh(η -C₅Me₅)(ind)]^{+,29} 4, Co[P(OEt)₃]₂(ind);¹ⁱ 5, Co(1,5-COD)(ind);³⁰ 6, Rh(duroquinone)(ind);^{31,32} 7, [IrH(PPh₃)₂(ind)]^{+,13} 8, [Rh(Me)(PMe₃)₂(ind)]^{+,32} 9, [Cp₂Zr(μ -PEt₂)₂Rh(Me)(ind)]⁺ (**2a**); 10, Ir(1,5-COD)(ind);^{33,34} 11, Rh(μ -C₂H₄)₂(ind);^{1d,32} 12, [Rh(ind)]₂-(μ -CO)(μ -1,3-CHD);^{13a} 13, [Rh(CO)(ind)]₂(μ -C=CH₂);^{13c} 14, Rh(CO)₂(ind);^{1k} 15, Rh(CN-t-Bu₂)₂(ind);²³ 16, Rh(PMe₃)₂(ind);²³ 217, Cp₂Zr(μ -PEt₂)₂Rh(ind) (1a); 18, Cp₂Zr(μ -PEt₂)₂Ir(ind);³⁵ 19, Cp₂Zr(μ -PPh₂)₂Rh(ind) (1c); 20, Ni(ind)₂;¹⁷ 21, [PdCl(ind)]₂;³⁶ 22, Ir-(PMe₂Ph)₃(ind)³⁴ (COD = cyclooctadiene and CHD = cyclohexadiene). Δ MC value for complex 1 is for Ru(ind)₂^{11b} as X-ray data for Fe(ind)₂^{11a} are of insufficient accuracy.

and four methylene proton environments at low temperature, which average to one and two unique environments, respectively, at 90 °C. Application of the Eyring equation¹⁵ for two-site exchange of the cyclopentadienyl protons gives the following values of the free energy of activation: $\Delta G^*_{T_c}$ = 15.0 ± 0.2, 14.8 ± 0.2, 14.0 ± 0.3, and 13.9 ± 0.3 kcal/mol, respectively, for 1a–d. The only other report¹⁶ of hindered indenyl rotation is for the thermally unstable heterobimetallic complex (η -mesityl)Cr(CO)(μ -CO)₂Rh(CO)(η -indenyl), for which $\Delta G^*_{T_c}$ = 10.8 ± 0.2 kcal/mol. It was suggested that the magnitude of the observed barrier is a result of the "slip-fold" distortion of the η -indenyl ligand.

The ¹³C NMR spectra of **1a-d** are consistent with the above analysis and suggest that the "slip-fold" distortion of the coordinated indenyl ligand persists in solution. Kohler¹⁷ has noted that the hapticity of the indenyl ligand

can be assessed spectroscopically by comparing the NMR chemical shifts of the five-membered ring carbon atoms in the metal complex with those of indene; for η^3 -indenyl ligands C(1-3) are shielded while C(3a,7a) are not. For more quantitative comparisons, we have calculated the chemical shift difference, $\Delta\delta(C) = \delta(C(\eta \text{-indenyl})) - \delta(C \text{-}$ (indenyl sodium)), for those d^6 and d^8 complexes for which ¹³C NMR data are available (Figure 3). The $\Delta\delta(C)$ values for C(3a,7a) correlate well with the hapticity of the indenyl ligand for those examples for which structural and/or theoretical results are also available. $\Delta\delta(C(3a,7a)) = -20$ to -40 ppm for planar η^5 -indenyl, -10 to -20 ppm for distorted η^5 -indenyl, and +5 to +30 ppm for η^3 -indenyl ligands. The values for 1a-d range from 0 to -10 ppm, again pointing to a severely distorted η^5 -indenyl ligand. While we may speculate that the severity of the "slip-fold" distortion is responsible for the large observed barriers to indenyl ligand rotation, more structural and theoretical

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The ³¹P NMR spectra of complexes 1a-d consist of a doublet at 170–180 ppm ($J_{Rh-P} = 125-137$ Hz), in good accord with other $Cp_2M(\mu-PR_2)_2M'L_n$ complexes.^{4,6,19,20} The low value of J_{Rh-P} is typical for $Rh(\mu-PR_2)M'$ bridges.²¹⁻²³

The IR spectra of 1a-d contain absorptions due to cyclopentadienyl,^{24,25} indenyl,²⁵ and PR₂ ligands.² The only absorptions that change significantly going from Zr to Hf complexes are observed below 400 cm⁻¹ (Table II) and presumably involve M-P vibrations.^{24,26}

Synthesis and Characterization of $[Cp_2M(\mu PEt_2)_2Rh(CH_3)(\eta$ -indenyl)]I. Werner and Feser²⁷ showed that $Rh(PMe_3)_2(\eta$ -indenyl) undergoes oxidative addition reactions with CH_3I and $CH_3C(0)Cl$, affording the cationic Rh(III) complexes $[RhR(PMe_3)_2(\eta-indenyl)]^+$ $(R = CH_3, C(O)CH_3)$. Addition of 1 equiv of CH_3I to complexes 1a,b in benzene led to precipitation of the yellow 1:1 adducts in quantitative yield. Elemental analysis and infrared and NMR spectroscopic characterization showed the adducts to be iodide salts of the d^0-d^6 heterobimetallic cations $[Cp_2M(\mu-PEt_2)_2Rh(CH_3)(inde-$

(18) A combined theoretical (EHMO), X-ray structural, and DNMR spectroscopic (with the η -1-Me-indenyl ligand) study is presently underway: Marder, T. B.; Calabrese, J. C.; Roe, D. C.; Tulip, T. H., to be submitted for publication.

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nyl)]I (2a,b). The Rh-CH₃ moiety was characterized by a doublet of triplets at δ -0.6 ($J_{\rm HRh} \approx {}^{3}J_{\rm HP}$ = 3 Hz) in the ¹H NMR and a quartet of doublets of triplets at -10 ppm $(J_{CH} = 139, J_{CRh} = 26, \text{ and } {}^2J_{CP} = 2.5 \text{ Hz})$ in the ¹³C NMR. The ³¹P NMR spectra of **2a** (**2b**) in CD₃CN consisted of a doublet at 158.5 (145.4) ppm with $J_{PRh} = 82$ (81) Hz. Although 1a,b do not react with 1 atm of H_2 or CO or with $CH_3C(O)Cl$, reactions are observed with $CH_3C(O)Br$ and with NH₄PF₆ which alter the MP₂Rh bridge system without complete disruption.²⁸ These studies will appear separately.

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Registry No. 1a, 100113-58-4; 1b, 100113-59-5; 1c, 100113-60-8; 1d, 100113-61-9; 2a, 100113-62-0; 2b, 100113-63-1; Cp₂Zr(PEt₂)₂, 86013-23-2; $(\eta$ -indenyl)Rh $(\eta$ -C₂H₄)₂, 63428-46-6; Cp₂Hf(PEt₂)₂, 86013-26-5; Cp₂Zr(PPh₂)₂, 86013-25-4; Cp₂Hf(PPh₂)₂, 86013-28-7.

Supplementary Material Available: Tables of non-hydrogen atom thermal parameters (Table IX), idealized hydrogen atom positions (Table X), plane data (Table XI), and a listing of observed and calculated structure factor amplitudes (Table XII) and the data (Table XIII) for Figure 3 (23 pages). Ordering information is given on any current masthead page.

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