Syntheses of Dinuclear Metal Complexes of Rhodium, Iridium, Iron, Molybdenum, and Cobalt with Novel Bridged 2,2′-Bis(indenyl) Systems

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The first unsymmetric monosilanylene-bridged 2,2′-bis(indenyl) system, 1,1′-(2,2′-C_9H_6)$_2$-Si(Me)(*t*-Bu) (**3c**), was synthesized in the same manner as the disilanylene and disiloxanylene systems. Furthermore, a series of dinuclear complexes with these double-bridged ligands were reacted with appropriate metal fragments, yielding 1,1′-[(2,2′-η^5-C_9H_5)Rh(cod)]$_2$Si(Me)-(*t*-Bu) (**4c**), 1,1′-[(2,2′-η^5-C_9H_5)Rh(nbd)]$_2$(SiMe$_2$)$_2$ (**5b**), and 1,1′-[(2,2′-η^5-C_9H_5)Rh(CO)$_2$]$_2$(SiMe$_2$)$_2$ (**6b**) for rhodium, 1,1′-[(2,2′-η^5-C_9H_5)Ir(cod)]$_2$(SiMe$_2$)$_2$O (**7a**), 1,1′-[(2,2′-η^5-C_9H_5)Ir(cod)]$_2$(SiMe$_2$)$_2$ (**7b**), and 1,1′-[(2,2′-η^5-C_9H_5)Ir(cod)]$_2$Si(Me)(*t*-Bu) (**7c**) for iridium, 1,1′-[(2,2′-η^5-C_9H_5)Fe(Cp)]$_2$-(SiMe$_2$)$_2$O (**8a**), 1,1′-[(2,2′-η^5-C_9H_5)Fe(Cp)]$_2$(SiMe$_2$)$_2$ (**8b**), 1,1′-[(2,2′-η^5-C_9H_5)Fe(Cp)]$_2$Si(Me)-(*t*-Bu) (**8c**) for iron, 1,1′-[(2,2′-η^5-C_9H_5)Mo(CO)$_2$(allyl)]$_2$(SiMe$_2$)$_2$ (**9b**) for molybdenum, 1,1′-[(2,2′-η^5-C_9H_5)Co(CO)$_2$]$_2$(SiMe$_2$)$_2$ (**10b**) for cobalt. All compounds were obtained as the antifacial isomer, except complex **8a**, where a mixture of the syn and anti species was obtained. The redox behavior of **8a** was investigated by cyclic voltammetry in CH_2Cl_2. The structures of **6b** and **8a** were determined by X-ray diffractometry.

In the past few years, considerable attention has been focused on dinuclear organometallic compounds. This is based on the expectation that their chemical behaviors both in stoichiometric synthesis and in catalysis may differ significantly from those of the analogous mononuclear species.[1,2] The concerted effects of two metals in close proximity promise to offer a cooperative interaction which causes a significant increase in reaction rates or leads to transformations not occurring when monometallic species are involved. Additionally, an expanded range of oxidation states is accessible to dinuclear complexes as a result of stabilizing metal−metal interactions. Extensive work has been focused on complexes with linked Cp ligands, because the cyclopentadienyl unit is a ligand that can bind strongly to a large number of metals in different oxidation states without showing a tendency to dissociate into the mononuclear species. Different linking bridges of alkenes, alkynes, and silylenes with various chain lengths and asymmetric bridged compounds are well-known.[3] The fulvalene system occupies a special position based on the direct connection of two rings and the premise that many bimetallic complexes[4] could mediate the electronic communication between metal centers through ligands, even in the absence of a direct metal−metal bond.[5] The kinetic inertia of η^5-bonding cyclopentadienyl rings leads to less catalytic activity in contrast to (η^5-indenyl)metal compounds. These complexes display enhanced reactivity in ligand substitution reactions. Basolo and co-workers called it the “indenyl effect” and attributed it to the ease of slippage from a nominally 18-electron η^5 structure to a 16-electron η^3 species, assisted by restoration of full aromaticity to the benzene

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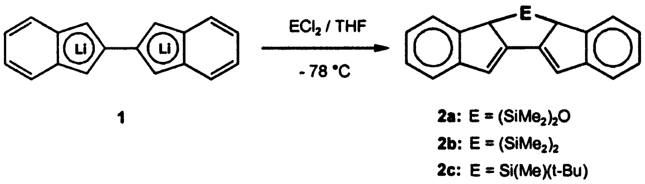
Scheme 1



ring.[6] In a few cases η^3-indenyl complexes have been isolated and characterized as stable compounds.[7] The first scientific approach on bridged indenyl systems began with the discovery of the stereoselective polymerization of propene with *ansa*-bis(indenyl)zirconocenes documented by Brintzinger and Kaminsky.[8] In a previous work we described the syntheses of the novel double-bridged indenyl systems **2a** and **2b** according to Scheme 1 and their reactions with rhodium compounds.[9] The second bridge introduced to the bis(indenyl) system inhibits rotation of both indenyl rings and causes a splitting into two isomers for the bimetallic complexes, the syn- and antifacial species. An influence has been determined between chain lengths and isomer ratios, but the anti isomer was always the major product. In this paper we describe our work on forcing the isomer ratio to the side of the synfacial product by introducing an asymmetric substituted silyl bridge to the bis(indenyl) system with the intention to block one side of the ligand by a sterically demanding substituent on the silicon. Furthermore, we present the synthesis of new homobimetallic complexes of these ligands with rhodium, iridium, iron, molybdenum, and cobalt moieties.

Table 1. Crystal Data for 6b and 8a

	4c	8a
	Crystal Parameters	
chem formula	$C_{26}H_{22}Rh_2Si_2O_4$	$C_{32}H_{32}OFe_2Si_2$
fw	660.44	600.46
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	14.77300(10)	11.6260(3)
b (Å)	11.95120(10)	14.6367(4)
c (Å)	15.11280(10)	17.2662(4)
α (deg)	90	90
β (deg)	101.1730(10)	104.2370(10)
γ (deg)	90	90
V (Å^3)	2617.67(3)	2847.89(13)
Z	4	4
D(calcd) (g cm^{-3})	1.676	1.400
μ(Mo Kα) (mm^{-1})	1.382	1.127
	Data Collection	
cryst size (mm^{-3})	0.48 × 0.38 × 0.35	0.33 × 0.23 × 0.06
θ range, deg	$2.82 \le 2\theta \le 60.90$	$3.6 \le 2\theta \le 50.0$
index range (*h*, *k*, *l*)	$-10 \le h \le 21$, $-17 \le k \le 16$, $-21 \le l \le 21$	$-16 \le h \le 13$, $-17 \le k \le 20$, $-24 \le l \le 24$
transmissn, max/min	0.5636/0.70158	0.5820/0.9507
no. of data	23 521	17 406
no. of indep obsd rflns (R_{int})	7886 (R_{int} = 0.0501)	5012 (R_{int} = 0.1158)
no. of indep rflns	1144	5006
no. of params	311	441
	Refinement	
Δ(ρ) (e Å^{-3})	0.781, −1.044	0.437, −0.448
GOF[a]	1.005	0.966
R1[a]	0.0323 (0.0466)[b]	0.0478 (0.1051)[b]
wR2[a]	0.0662 (0.0726)[b]	0.0858 (0.1040)[b]

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]^2]^{1/2}$; $GOF = S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. [b] Based on all data.

Experimental Section

Reactions were carried out under nitrogen and with conventional Schlenk techniques in dry, oxygen-free solvents. Melting points were measured in sealed capillaries with a Gallenkamp melting point determination apparatus under normal conditions without correction. The NMR spectra were recorded on a Bruker ARX 200 spectrometer (^{1}H, 200.13 MHz; ^{13}C, 50.32 MHz) at room temperature. Chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C residue of the deuterated solvents. The IR spectra were recorded on a Nicolet Magna System 750 spectrometer. Mass spectra (EI, 70 eV) were obtained by using a Varian MAT 311 A/AMD instrument. Only characteristic fragments containing the isotopes of the highest abundance are listed. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O 2400 analyzer. The X-ray diffraction structural analyses were performed with Mo Kα radiation (λ = 0.710 73 Å, graphite monochromator) at 293 K using a Siemens SMART CCD area detector diffractometer. All crystal structures were solved using direct methods (SHELXS 86) and subsequently refined by full-matrix least-squares methods (SHELXL 93).[10] The data for structure refinement of **6b** and **8a** are listed in Table 1, and selected bond lengths are summarized in Table 2. 2,2′-Bis(indenyl)dilithium (**1**),[9] 2,2′-(1,1′-tetramethyldisiloxyl)bis(indene) (**2a**),[9] 2,2′-(1,1′-tetramethyldisilyl)bis(indene) (**2b**),[9] bis(η^4-cycloocta-1,5-diene)[1,1′-tetramethyldisiloxyl-2,2′-bis(η^5-indenyl)]dirhodium(I) (**4a**),[9] bis(η^4-cycloocta-1,5-diene)[1,1′-tetramethyldisilyl-2,2′-bis(η^5-indenyl)]dirhodium(I) (**4b**)[9], [CpFe(fluorene)]PF$_6$,[24] bis(μ-chloro)bis(η^4-cycloocta-1,5-diene)dirhodium(I),[11] bis(μ-chloro)bis(η^4-norborna-1,4-diene)dirhodium(I),[11] tetracarbonylbis(μ-chloro)dirhodium(I),[12] bis(μ-chloro)bis(η^4-cycloocta-1,5-diene)diiridium(I),[13] and [(Py)$_3$Mo(CO)$_3$][14] were prepared according to published procedures. Octacarbonyldicobalt(0) and allyl chloride were used as purchased.

The electrochemical measurements were performed on a Metrohm VA693 instrument with a three-electrode configuration in methylene chloride with scan rates from 50 to 200 mV/s. The supporting electrolyte was tetrabutylammonium tetrafluoroborate (TBAB; 0.1 M). A Ag/AgCl/KCl$_{aq}$ half-cell was used as the reference electrode, which was separated from the sample cell by a second integrated electrolyte (saturated LiCl in ethanol) to avoid a large liquid junction and contamination of the nonaqueous cell. A glass frit and a glass membrane separate the electrolytes from each other. A polished platinum-disk electrode with a 2 mm diameter was used as the working electrode and a Pt wire as the auxiliary electrode. All potentials were referred to ferrocene/ferrocenium, for which the value was obtained by subsequent measurement under the same conditions.[15]

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Table 2. Selected Bond Lengths (Å) from the Crystal Structures of 6b and 8a

bond	**4c**	**8a**
M(1)−C(1)	2.233(2)	2.066(4)
M(1)−C(2)	2.270(2)	2.042(4)
M(1)−C(3)	2.238(2)	2.021(4)
M(1)−C(4)	2.440(2)	2.096(4)
M(1)−C(9)	2.408(2)	2.103(4)
Si(1)−C(1)	1.885(2)	1.845(5)
Si(1)−C(Me)[a]	1.880(3)	1.870(7)
Si(1)−O(1)		1.621(3)
Si(2)−O(1)		1.608(3)
Si(1)−Si(2)	2.3554(9)	
M(2)−C(11)	2.255(2)	2.070(4)
M(2)−C(12)	2.281(2)	2.064(4)
M(2)−C(13)	2.225(2)	2.049(4)
M(2)−C(14)	2.389(2)	2.098(4)
M(2)−C(19)	2.388(2)	2.076(4)
Si(2)−C(11)	1.889(2)	1.865(4)
Si(2)−C(Me)[a]	1.880(3)	1.846(5)
C(2)−C(12)	1.471(3)	1.488(5)
C(1)−C(2)	1.453(3)	1.461(5)
C(1)−C(9)	1.473(3)	1.459(6)
C(2)−C(3)	1.428(3)	1.431(6)
C(3)−C(4)	1.458(3)	1.415(5)
C(4)−C(5)	1.408(3)	1.431(6)
C(4)−C(9)	1.431(3)	1.431(6)
C(5)−C(6)	1.382(3)	1.354(7)
C(6)−C(7)	1.407(4)	1.414(8)
C(7)−C(8)	1.378(3)	1.364(7)
C(8)−C(9)	1.413(3)	1.438(6)
C(11)−C(12)	1.441(3)	1.457(6)
C(11)−C(19)	1.485(3)	1.458(5)
C(12)−C(13)	1.439(3)	1.438(5)
C(13)−C(14)	1.450(3)	1.422(5)
C(14)−C(15)	1.410(3)	1.432(5)
C(14)−C(19)	1.436(3)	1.439(6)
C(15)−C(16)	1.375(3)	1.359(6)
C(16)−C(17)	1.409(4)	1.424(7)
C(17)−C(18)	1.380(3)	1.357(6)
C(18)−C(19)	1.407(3)	1.433(6)
Rh(1)−C(CO)[a]	1.870(3)	
Rh(2)−C(CO)[a]	1.875(2)	
C(CO)-O(CO)[a]	1.144(3)	
C(CO)-O(CO)[a]	1.141(3)	
Fe(1)−C(Cp^1)[a]		2.041(6)
Fe(2)−C(Cp^2)[a]		2.033(6)
C(Cp^1)−C(Cp^1)[a]		1.405(8)
C(Cp^2)−C(Cp^2)[a]		1.385(9)

[a] Average value.

Synthesis of 2,2′-(1,1′-Methyl-*tert*-butylsilyl)bis(indene) (2c). A 5.43 mL (16.5 mmol) portion of dichloromethyl-*tert*-butylsilane was added to a solution of 3.8 g (15.7 mmol) of 2,2′-bis(indenyl)dilithium (**1**) in 120 mL of THF at −78 °C. The resulting solution was stirred overnight by warming to room temperature. After evaporation of the solvent, the residue was suspended in 10 mL of *n*-hexane and 1 mL of diethyl ether and then chromatographed on silica gel by eluting with *n*-hexane. The solvent of the orange fraction was removed under vacuum, yielding 2.8 g (54%) of an orange oil. ^{1}H NMR (d_6-acetone): δ 7.4−7.2 (m, 4H, arom), 7.2−7.0 (m, 4H, arom), 7.01 (s, 2H, $H^{3,3'}$), 3.74 (s, 2H, $H^{1,1'}$), 1.28 (s, 3H, CH_3), 0.93 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.1, 144.7, 143.6 ($C^{2/4/9}$), 125.8, 123.9, 123.3, 122.3, 119.6 ($C^{1/5/6/7/8}$), 47.28 (C^3), 31.58 (*t*-Bu, CH_3), 27.05 (*t*-Bu, C), 0.84 (SiMe). MS (182 °C; *m*/*z* (%)): 328 (25) $[M]^+$, 271 (39) $[M - C_4H_9]^+$, 228 (100) $[C_{18}H_{12}]^+$, 172 (85) $[M - C_{10}H_9Si]^+$, 115 (94) $[C_9H_7]^+$.

Synthesis of Bis(η^4-cycloocta-1,5-diene)[1,1′-methyl-*tert*-butylsilyl-2,2′-bis(η^5-indenyl)]dirhodium(I) (4c). To a stirred solution of 0.16 g (0.48 mmol) of 2,2′-(1,1′-methyl-*tert*-butylsilyl)bis(indene) (**2c**) in 20 mL of THF at 0 °C was added 0.4 mL of *n*-BuLi (2.5 M in hexane) via syringe. After it was stirred for 2 h at room temperature, the suspension was treated with 0.24 g (0.48 mmol) of $[(cod)RhCl]_2$ and refluxed overnight. The solvent was evaporated, and the residue was suspended in *n*-pentane (10 mL) and chromatographed on alumina. Eluting with *n*-hexane/diethyl ether (10:1) led to a light yellow fraction containing the product. Yield: 125 mg (35%). Mp: 177 °C dec. ^{1}H NMR (C_6D_6): δ 7.2 (m, 4H, $H^{6/7}$), 7.09 (m, 4H, $H^{5/8}$), 5.28 (s, 2H, H^3), 4.11 (m, 4H, CH(cod)), 4.0 (m, 4H, CH(cod)), 2.0−1.8 (m, 12H, CH_2(cod)), 1.7−1.6 (m, 4H, CH_2(cod)), 1.30 (m, 3H, Me), 1.01 (s, 9H, *t*-Bu). ^{1}H NMR ($CDCl_3$): δ 7.3−7.2 (m, 4H, $H^{6/7}$), 7.0 (m, 4H, $H^{5/8}$), 5.42 (s, 2H, H^3), 4.01 (m, 4H, CH(cod)), 3.7 (m, 4H, CH(cod)), 1.9−1.6 (m, 16H, CH_2(cod)), 1.30 (m, 3H, Me), 0.91 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR (C_6D_6): δ 122.48, 122.19 ($C^{5/8}$), 119.31, 118.82 ($C^{6/7}$), 113.53 (d, $^1J_{RhC} = 2.4$ Hz, $C^{4/9}$), 113.13 (d, $^1J_{RhC} = 2.1$ Hz, $C^{4/9}$), 108.69 (d, $^1J_{RhC} = 5.1$ Hz, C^2), 76.00 (d, $^1J_{RhC} = 4.3$ Hz, C^1), 73.96 (d, $^1J_{RhC} = 4.6$ Hz, C^3), 68.80 (d, $^1J_{RhC} = 13.6$ Hz, CH(cod)), 67.60 (d, $^1J_{RhC} = 13.6$ Hz, CH(cod)), 31.30, 29.69 (CH_2(cod)), 31.24 (*t*-Bu), 1.08 (SiMe). MS (208 °C; *m*/*z* (%)): 650 (81) $[M - Si(Me)(t\text{-}Bu)]^+$, 540 (100) $[M - (C_8H_{14}) - Si(Me)(t\text{-}Bu)]^+$, 437 (31) $[M - Rh - (C_8H_{14}) - Si(Me)(t\text{-}Bu)]^+$, 327 (40) $[M - Rh - (C_8H_{14})_2 - Si(Me)(t\text{-}Bu)]^+$. Anal. Calcd for $C_{39}H_{46}SiRh_2$ (mol wt 748.64): C, 63.56; H, 6.19. Found: C, 64.02; H, 6.15.

Synthesis of Bis(η^4-norbornadiene)[1,1′-tetramethyldisilyl-2,2′-bis(η^5-indenyl)]dirhodium (I) (5b). Reaction, in analogy to **4c**, of $[(nbd)RhCl]_2$ (0.19 g, 0.4 mmol) with 0.15 mg (0.4 mmol) of [1,1′-tetramethyldisilyl-2,2′-bis(indenyl)]dilithium (**3b**) in THF (15 mL) led to 272 mg (87%) of a yellow crystalline powder after chromatography and recrystallization from *n*-hexane. Mp: 198 °C dec. ^{1}H NMR (C_6D_6): δ 7.2 (m, 4H, $H^{6/7}$), 7.1−7.0 (m, 4H, $H^{5/8}$), 5.4 (s, 2H, H^3), 3.28 (m, 8H, CH(nbd)), 2.92 (m, 4H, CH(nbd)), 0.85 (s, 4H, CH_2(nbd)), 0.4 (s, 6H, $SiMe_2$), 0.11 (s, 6H, $SiMe_2$). ^{1}H NMR ($CDCl_3$): δ 7.3−7.2 (m, 4H, $H^{6/7}$), 7.1−7.0 (m, 4H, $H^{5/8}$), 5.44 (s, 2H, H^3), 3.27 (m, 8H, CH(nbd)), 3.11 (m, 4H, CH(nbd)), 0.84 (s, 4H, CH_2(nbd)), 0.34 (s, 6H, $SiMe_2$), 0.07 (s, 6H, $SiMe_2$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 122.39, 122.25, 120.84, 120.08 ($C^{5/6/7/8}$), 119.32 (d, $^1J_{RhC} = 3.5$ Hz, $C^{4/9}$), 115.68 (d, $^1J_{RhC} = 3.2$ Hz, $C^{4/9}$), 113.59 ($^1J_{RhC} = 5.1$ Hz, C^2), 76.58 (d, $^1J_{RhC} = 4.6$ Hz, $C^{1/3}$), 73.58 (d, $^1J_{RhC} = 4.9$ Hz, $C^{1/3}$), 58.05 (d, $^1J_{RhC} = 6.8$ Hz, CH_2(nbd)), 47.25 (d, $^1J_{RhC} = 2.4$ Hz, CH(nbd)), 38.29 (d, $^1J_{RhC} = 10.35$ Hz, CH(nbd)), 37.77 (d, $^1J_{RhC} = 10.35$ Hz, CH(nbd)), −1.71 ($SiMe_2$), −4.32 ($SiMe_2$). MS (240 °C; *m*/*z* (%)): 732 (100) $[M]^+$, 640 (60) $[M - (nbd)]^+$, 582 (55) $[M - SiMe_2 - (nbd)]^+$, 524 (58) $[M - (SiMe_2)_2 - (nbd)]^+$, 421 (28) $[M - (SiMe_2)_2 - Rh(nbd)]^+$, 73 (44) $[SiMe_3]^+$. Anal. Calcd for $C_{36}H_{38}Si_2Rh_2$ (mol wt 732.63): C, 59.01; H, 5.22. Found: C, 58.87; H, 5.41.

Synthesis of Tetracarbonyl[1,1′-tetramethyldisilyl-2,2′-bis(η^5-indenyl)]dirhodium(I) (6b). The reaction was carried out in analogy to **4c** by using $[(CO)_2RhCl]_2$ (0.19 g, 0.5 mmol) with 0.17 mg (0.5 mmol) of [1,1′-tetramethyldisilyl-2,2′-bis(indenyl)]dilithium **(3b)** in THF (10 mL) at room temperature instead of heating, and led after chromatography and recrystallization from *n*-hexane to 180 mg (56%) of a red crystalline powder. Mp: 144 °C dec. ^{1}H NMR (C_6D_6): δ 7.2−7.1 (m, 4H, $H^{6/7}$), 7.0−6.9 (m, 4H, $H^{5/8}$), 5.73 (s, $J_{RhH} = 0.6$ Hz, 2H, H^3), 0.45 (s, 6H, $SiMe_2$), 0.12 (s, 6H, $SiMe_2$) ppm. ^{1}H NMR ($CDCl_3$): δ 7.3−7.2 (m, 4H, $H^{6/7}$), 7.1−7.0 (m, 4H, $H^{5/8}$), 6.18 (s, $J_{RhH} = 0.86$ Hz, 2H, H^3), 0.81 (s, 6H, $SiMe_2$), 0.55 (s, 6H, $SiMe_2$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 190.57 (d, $^1J_{RhC} = 85.5$ Hz, CO), 125.8, 125.18 ($C^{5/8}$), 119.7, 119.16 ($C^{6/7}$), 120.33 (d, $^1J_{RhC} = 3.8$ Hz, $C^{4/9}$), 119.56 (d, $^1J_{RhC} = 2.9$ Hz, $C^{4/9}$), 103.37 (d, $^1J_{RhC} = 5.1$ Hz, C^2), 78.1 (d, $^1J_{RhC} = 3.5$ Hz, C^1), 73.95 (d, $^1J_{RhC} = 3.5$ Hz, C^3), − 2.3 ($SiMe_2$), − 3.52 ($SiMe_2$). MS (145 °C; *m*/*z* (%)): 660 (52) $[M]^+$, 604 (47) $[M - (CO)_2]^+$, 576 (55) $[M - (CO)_3]^+$, 548 (50) $[M - (CO)_4]^+$, 445 (27) $[M - Rh(CO)_4]^+$, 333 (18) $[M - Rh(CO)_4 - C_9H_5]^+$, 73 (28) $[SiMe_3]^+$. IR (KBr): $\tilde{\nu}$ 2040 (s), 1981 (s). Anal. Calcd for $C_{26}H_{22}O_4Si_2Rh_2$ (mol wt 660.40): C, 47.26; H, 3.35. Found: C, 46.47; H, 3.31.

Synthesis of Bis(η^4-cycloocta-1,5-diene)[1,1′-tetramethyldisiloxyl-2,2′-bis(η^5-indenyl)]diiridium(I) (7a). General Procedure. To a solution of 0.23 g (0.64 mmol) of [1,1′-

tetramethyldisiloxyl-2,2′-bis(indenyl)]dilithium (**3a**) in 20 mL of THF was added 0.42 g (0.64 mmol) of $[(cod)IrCl]_2$, and the resulting suspension was refluxed overnight. After the mixture was cooled to room temperature, the solvent was evaporated and the crude product was redissolved in 10 mL of diethyl ether. Purification as described for **4c** yields 380 mg (62%) as a light yellow crystalline powder. Mp: 204 °C dec. ^{1}H NMR ($CDCl_3$): δ 7.36−7.25 (m, 4H, $H^{6/7}$), 7.15−7.10 (m, 4H, $H^{5/8}$), 5.37 (s, 2H, H^3), 3.89 (m, 4H, CH(cod)), 3.76 (m, 4H, CH(cod)), 1.8−1.65 (m, 12H, CH_2(cod)), 1.4 (m, 4H, CH_2(cod)), 0.26 (s, 6H, $SiMe_2$), 0.19 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 123.88, 123.36 ($C^{5/8}$), 120.97, 120.39 ($C^{6/7}$), 114.22 ($C^{4/9}$), 113.17 ($C^{4/9}$), 91.71 (C^2), 73.74 (C^1), 70.14 (C^3), 50.65, 50.02 (CH(cod)), 33.26, 33.17 (CH_2(cod)), −1.49 ($SiMe_2$), −4.23 ($SiMe_2$). MS (197 °C; *m*/*z* (%)): 960 (37) $[M]^+$, 945 (100) $[M - CH_3]^+$, 828 (100) $[M - (SiMe_2)_2O]^+$, 718 (58) $[M - (SiMe_2)_2O - (C_8H_{14})]^+$, 528 (45) $[M - (SiMe_2)_2O - Ir(cod)]^+$, 413 (56) $[C_9H_5Ir(cod)]^+$, 73 (67) $[SiMe_3]^+$. Anal. Calcd for $C_{38}H_{46}OSi_2Ir_2$ (mol wt 959.32): C, 47.57; H, 4.83. Found: C, 47.41; H, 4.55.

Synthesis of Bis(η^4-cycloocta-1,5-diene)[1,1′-tetramethyldisilyl-2,2′-bis(η^5-indenyl)]diiridium(I) (7b). Reaction was carried out in analogy to **7a** by using 0.34 g (0.52 mmol) of $[(cod)IrCl]_2$ with 0.18 g (0.52 mmol) of **3b** in 15 mL of THF. Purification and chromatography gave 402 mg (82%) of an orange powder. Mp: 208 °C dec. ^{1}H NMR ($CDCl_3$): δ 7.3−7.2 (m, 4H, $H^{6/7}$), 7.1−7.0 (m, 4H, $H^{5/8}$), 5.24 (s, 2H, H^3), 3.88 (m, 4H, CH(cod)), 3.75 (m, 4H, CH(cod)), 1.7−1.6 (m, 12H, CH_2(cod)), 1.5 (m, 4H, CH_2(cod)), 0.35 (s, 6H, $SiMe_2$), 0.06 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 123.49, 123.04 ($C^{5/8}$), 121.43, 120.97 ($C^{6/7}$), 113.95 ($C^{4/9}$), 112.07 ($C^{4/9}$), 89.53 (C^2), 75.19 (C^1), 74.20 (C^3), 50.09, 49.86 (CH(cod)), 33.57, 32.45 (CH_2(cod)), −3.49 ($SiMe_2$), −3.94 ($SiMe_2$). MS (178 °C; *m*/*z* (%)): 944 (22) $[M]^+$, 834 (8) $[M - (C_8H_{14})]^+$, 778 (8) $[M - (cod) - SiMe_2]^+$, 471 (100) $[(C_9H_5)(SiMe_2)_2Ir(cod)]^+$. Anal. Calcd for $C_{38}H_{46}Si_2Ir_2$ (mol wt 943.32): C, 48.38; H, 4.91. Found: C, 48.01; H, 4.84.

Synthesis of Bis(η^4-cycloocta-1,5-diene)[1,1′-methyl-*tert*-butylsilyl-2,2′-bis(η^5-indenyl)]diiridium(I) (7c). Reaction, in analogy to **7a**, of $[(cod)IrCl]_2$ (0.33 g, 0.50 mmol) with **3c** (0.17 g, 0.50 mmol) in 15 mL of THF yielded 383 mg (83%) of an orange powder after purification and chromatography. Mp: 194 °C dec. ^{1}H NMR ($CDCl_3$): δ 7.30−7.23 (m, 4H, $H^{6/7}$), 7.13−7.08 (m, 4H, $H^{5/8}$), 5.33 (s, 2H, H^3), 3.95 (m, 4H, CH(cod)), 3.88 (m, 4H, CH(cod)), 1.9−1.6 (m, 16H, CH_2(cod)), 1.28 (s, 3H, SiMe), 0.9 (s, 9H, *t*-Bu) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 123.5, 123.4 ($C^{5/8}$), 120.5, 120.18 ($C^{6/7}$), 109.87 ($C^{4/9}$), 109.71 ($C^{4/9}$), 99.99 (C^2), 71.83 (C^1), 71.0 (C^3), 51.44, 50.06 (CH(cod)), 32.80, 32.71 (CH_2(cod)), 26.86 (CH_3, *t*-Bu), 0.95 (SiMe) ppm. MS (197 °C; *m*/*z* (%)): 928 (7) $[M]^+$, 828 (70) $[M - Si(Me)(t\text{-}Bu)]^+$, 718 (24) $[M - Si(Me)(t\text{-}Bu) - (C_8H_{14})]^+$, 528 (48) $[M - Si(Me)(t\text{-}Bu) - Ir(cod)]^+$, 416 (22) $[C_9H_5Ir(cod)]^+$, 73 (78) $[SiMe_3]^+$. Anal. Calcd for $C_{39}H_{46}SiIr_2$ (mol wt 927.24): C, 50.51; H, 5.00. Found: C, 48.87; H, 4.88.

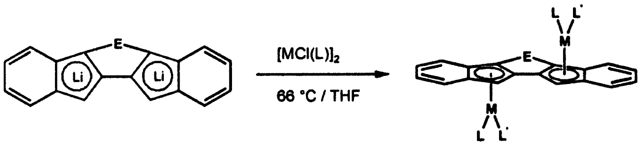
Synthesis of Bis(η^5-cyclopentadienyl)[1,1′-tetramethyldisiloxyl-2,2′-bis(η^5-indenyl)]diiron(II) (8a). General Procedure. Compound **3a** (0.19 g, 0.5 mmol) dissolved in 10 mL of THF was cooled to 0 °C and transferred via syringe to another flask containing the deprotonated form of [CpFe(fluorene)]PF_6 at the same temperature (generated in situ by the reaction of [CpFe(fluorene)]PF_6 (0.45 g, 1.05 mmol) with *n*-BuLi (0.7 mL of 2.5 M in hexane) in 10 mL of THF at 0 °C for 2 h). Then the reaction mixture was heated to reflux for 14 h. After it was cooled to room temperature, the suspension was filtered on neutral alumina and the filtrate concentrated and then chromatographed on neutral alumina by eluting with *n*-hexane/diethyl ether (10:1). The undesirable byproducts ferrocene and fluorene were sublimed off under high vacuum, and the dark red solid was recrystallized from *n*-hexane/diethyl ether (10:1). A mixture of the isomers was obtained. Yield: 217 mg (72%). Mp: 144 °C dec. Data for the anti isomer are as follows. ^{1}H NMR (C_6D_6): δ 7.6−7.5 (m, 4H, $H^{6/7}$), 6.9−6.8 (m, 4H, $H^{5/8}$) 5.45 (s, 2H, C^3), 3.57 (s, 10H, Cp), 0.97 (s, 6H, $SiMe_2$), 0.59 (s, 6H, $SiMe_2$). Data for the syn isomer are as follows. ^{1}H NMR (C_6D_6): δ 7.6−7.5 (m, 4H, $H^{6/7}$), 6.9−6.8 (m, 4H, $H^{5/8}$), 5.53 (s, 2H, C^3), 3.64 (s, 10H, Cp), 0.88 (s, 6H, $SiMe_2$), 0.25 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 129.91, 128.95 ($C^{5/8}$), 123.69, 123.31 ($C^{6/7}$), 93.04 ($C^{4/9}$), 92.35 ($C^{4/9}$), 90.33 (C^2), 70.15 (C^1), 69.98 (Cp), 64.56 (C^3), 4.44 ($SiMe_2$), 3.55 ($SiMe_2$). MS (57 °C; *m*/*z* (%)): 600 (100) $[M]^+$, 479 (14) $[M - FeCp]^+$, 414 (15) $[M - Fe(Cp)_2]^+$. Anal. Calcd for $C_{32}H_{32}OSi_2Fe_2$ (mol wt 600.44): C, 64.00; H, 5.37. Found: C, 64.04; H, 5.69.

Synthesis of Bis(η^5-cyclopentadienyl)[1,1′-tetramethyldisilyl-2,2′-bis(η^5-indenyl)]diiron(II) (8b). Reaction was carried out, in analogy to **8a,** by using 0.52 g (1.2 mmol) of [CpFe(fluorene)]PF_6, *n*-BuLi (0.6 mL of 2.5 M in hexane), and **3b** (0.21 g, 0.59 mmol) in 20 mL of THF to give 291 mg (84%) of a dark red crystalline solid after purification, chromatography, and sublimation. Mp: 178 °C. ^{1}H NMR (C_6D_6): δ 7.6 (m, 4H, $H^{6/7}$), 6.9−6.8 (m, 4H, $H^{5/8}$), 5.35 (s, 2H, H^3), 3.47 (s, 10H, Cp), 0.96 (s, 6H, $SiMe_2$), 0.56 (s, 6H, $SiMe_2$). ^{1}H NMR ($CDCl_3$): δ 7.7−7.6 (m, 4H, $H^{6/7}$), 7.0−6.9 (m, 4H, $H^{5/8}$), 5.48 (s, 2H, H^3), 3.49 (s, 10H, Cp), 0.56 (s, 6H, $SiMe_2$), 0.08 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 129.45, 129.27 ($C^{5/8}$), 124.09, 123.71 ($C^{6/7}$), 93.64 ($C^{4/9}$), 92.21 ($C^{4/9}$), 90.93 (C^2), 70.10 (C^1), 69.89 (Cp), 62.52 (C^3), −0.71 ($SiMe_2$), −1.68 ($SiMe_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 130.27, 129.17 ($C^{5/8}$), 123.74, 123.28 ($C^{6/7}$), 93.14 ($C^{4/9}$), 91.83 ($C^{4/9}$), 90.40 (C^2), 69.49 (Cp), 68.31 (C^1), 62.16 (C^3), −0.91 ($SiMe_2$), −1.79 ($SiMe_2$). MS (166 °C; *m*/*z* (%)): 584 (100) $[M]^+$, 519 (12) $[M - Cp]^+$, 463 (8) $[M - FeCp]^+$, 398 (8) $[M - Fe(Cp)_2]^+$. Anal. Calcd for $C_{32}H_{32}Si_2Fe_2$ (mol wt 584.44): C, 65.75; H, 5.52. Found: C, 65.77; H, 5.48.

Synthesis of Bis(η^5-cyclopentadienyl)[1,1′-methyl-*tert*-butylsilyl-2,2′-bis(η^5-indenyl)]diiron(II) (8c). Reaction, in analogy to **8a**, of [CpFe(fluorene)]PF_6 (0.58 g, 1.3 mmol) with *n*-BuLi (0.84 mL of 2.5 M in hexane) and with **3c** (0.22 g, 0.66 mmol) in 20 mL of THF gave 307 mg (82%) of a dark red crystalline solid after purification, chromatography, and sublimation. Mp: 199 °C. ^{1}H NMR (C_6D_6): δ 7.6−7.5 (m, 4H, $H^{6/7}$), 6.95−6.8 (m, 4H, $H^{5/8}$) 5.22 (s, 2H, H^3), 3.58 (s, 10H, Cp), 1.29 (s, 3H, SiMe), 0.92 (s, 9H, *t*-Bu) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 130.22, 129.87 ($C^{5/8}$), 123.99, 123.57 ($C^{6/7}$), 93.44 ($C^{4/9}$), 92.85 ($C^{4/9}$), 91.47 (C^2), 70.12 (C^1), 69.84 (Cp), 65.23 (C^3), 31.2 (CH_3, *t*-Bu), 0.90 (SiMe) ppm. MS (178 °C; *m*/*z* (%)): 568 (13) $[M]^+$, 468 (100) $[M - Si(Me)(t\text{-}Bu)]^+$, 347 (33) $[M - Si(Me)(t\text{-}Bu) - FeCp]^+$, 282 (28) $[M - Si(Me)(t\text{-}Bu) - Fe(Cp)_2]^+$, 234 (25) $[IndFeCp]^+$. Anal. Calcd for $C_{33}H_{32}SiFe_2$ (mol wt 568.36): C, 69.73; H, 5.67. Found: C, 69.12; H, 5.61.

Synthesis of Bis[(η^3-allyl)dicarbonyl][1,1′-tetramethyldisilyl-2,2′-bis(η^5-indenyl)]dimolybdenum(II) (9b). To a solution of 0.23 g (0.65 mmol) of **3b** in 25 mL of THF was added 0.54 g (1.3 mmol) of $[(Py)_3Mo(CO)_3]$ at room temperature. The resulting suspension was heated to reflux for 20 h. After the mixture was cooled to 0 °C, 0.12 mL (1.5 mmol) of allyl chloride was added slowly via syringe and the solution was stirred for an additional 20 h. The solvent was removed under vacuum, and the residue was suspended in 15 mL of *n*-hexane. Chromatography on neutral alumina by eluting with *n*-hexane/diethyl ether (10:1) gave a yellow fraction containing the product. Evaporation of the solvent yielded 311 mg (65%) of a yellow solid. Mp: 208 °C dec. ^{1}H NMR ($CDCl_3$): δ 7.26−7.2 (m, 4H, $H^{6/7}$), 7.06−6.9 (m, 4H, $H^{5/8}$), 6.0 (m, 2H, H^3), 5.09 (m, 2H, $CHH'CHCHH'$), 3.34 (m, 4H, $CHH'CHCHH'$), 2.31 (m, 4H, $CHH'CHCHH'$), 0.53 (s, 6H, $SiMe_2$), −0.07 (s, 6H, $SiMe_2$).$^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$): δ 239.35, 237.43 (CO), 137.53, 136.91 ($C^{5/8}$), 124.47, 123.78 ($C^{6/7}$), 116.70, 115.46 ($C^{4/9}$), 111.74 (C^2), 88.47 (C^1), 83.40 (C^3), 80.16 ($CHH'CHCHH'$), 48.63, 37.25 ($CHH'CHCHH'$), −0.62 ($SiMe_2$), −3.78 ($SiMe_2$). MS (183 °C; *m*/*z* (%)): 728 (16) $[M]^+$, 687 (24) $[M - C_3H_5]^+$, 646 (36) $[M - C_6H_{10}]^+$, 534 (20) $[M - C_6H_{10} - (CO)_4]^+$, 440 (14) $[M - C_6H_{10} - Mo(CO)_4]^+$, 342 (50) $[M - C_6H_{10} - Mo_2(CO)_4]^+$, 284 (33) $[M - C_6H_{10} - Mo_2(CO)_4 - SiMe_2]$, 73 (100) $[SiMe_3]^+$. IR (KBr): $\tilde{\nu}$ 2024 (w), 1980 (s). Anal. Calcd for $C_{32}H_{32}O_4Si_2Mo_2$ (mol wt 728.62): C, 52.74; H, 4.42. Found: C, 51.28; H, 4.44.

Scheme 2



3a: E = $(SiMe_2)_2O$
3b: E = $(SiMe_2)_2$
3c: E = Si(Me)(t-Bu)

4a: E = $(SiMe_2)_2O$, L+L' = cod, M = Rh
4b: E = $(SiMe_2)_2$, L+L' = cod, M = Rh
4c: E = Si(Me)(t-Bu), L+L' = cod, M = Rh
5b: E = $(SiMe_2)_2$, L+L' = nor, M = Rh
6b: E = $(SiMe_2)_2$, L,L' = CO, M = Rh
7a: E = $(SiMe_2)_2O$, L+L' = cod, M = Ir
7b: E = $(SiMe_2)_2$, L+L' = cod, M = Ir
7c: E = Si(Me)^{t}Bu, L+L' = cod, M = Ir

Synthesis of Tetracarbonyl[1,1′-tetramethyldisilyl-2,2′-bis(η^5-indenyl)]dicobalt(I) (10b). To a green suspension of octacarbonyldicobalt(0) (0.2 g, 0.6 mmol) and iodine (0.15 mg, 0.6 mmol) in 20 mL of THF was added **3b** (0.21 g, 0.6 mmol) at 0 °C. The suspension was heated to reflux overnight, and the solution color changed from green to red. After the mixture was cooled to room temperature, the solvent was removed under vacuum and then the crude product was suspended in *n*-hexane (10 mL) and chromatographed on neutral alumina. Elution with *n*-hexane/diethyl ether (10:1) gave a yellow fraction, followed by an orange fraction and finally a deep red fraction. The solvent of the red fraction was evaporated under vacuum, and 194 mg (56%) of the expected product was obtained. ^{1}H NMR ($CDCl_3$): δ 7.5−7.4 (m, 4H, $H^{6/7}$), 7.2−7.1 (m, 4H, $H^{5/8}$), 4.13 (s, 2H, H^3), 0.23 (s, 6H, $SiMe_2$), −0.15 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 203.83 (CO), 126.56, 124.91 ($C^{5/8}$), 123.94, 121.28 ($C^{6/7}$), 107.29, 106.69 ($C^{4/9}$), 100.73 (C^2), 85.13 (C^1), 72.74 (C^3), 2.48 ($SiMe_2$), −4.10 ($SiMe_2$). MS (162 °C; *m/z* (%)): 572 (7) $[M]^+$, 516 (10) $[M - (CO)_2]^+$, 457 (12) $[M - Co(CO)_2]^+$, 401 (20) $[M - Co(CO)_4]^+$, 342 (18) $[M - Co_2(CO)_4]^+$, 228 (68) $[C_{18}H_{10}]^+$, 73 (100) $[SiMe_3]^+$. IR (KBr): $\tilde{\nu}$ 2014 (w), 1954 (s).

Results and Discussion

Ligand Design. In the same manner as for the indenyl systems **2a** and **2b**,[9] the Si_1-bridged compound **2c** can be synthesized by the reaction of **1** with 1.2 molar equiv of the dihalosilane (*t*-Bu)(Me)$SiCl_2$ (Scheme 1). After column chromatography on silica gel **2c** was isolated as an orange oil, while the separation on alumina failed to obtain the desired compound. The ^{1}H NMR investigation showed six signals: four resonances at 7.4, 7.2, 7.0, and 3.7 ppm for the hydrogen atoms of the indenyl moieties and two resonances at 1.28 and 0.93 ppm for the different methyl- and *tert*-butyl substituents on silicon. The free ligand was deprotonated in benzene with 2.2 molar equiv of butyllithium to give the dilithio compound **3c**. The product precipitated as a white powder.

Rhodium and Iridium Complexes. To prepare the rhodium and iridium complexes, the dilithio compounds **3a**−**c** were mixed with 1 molar equiv of the appropriate binuclear transition-metal complex $[(\mu\text{-Cl})ML_2]_2$ (M = Rh, Ir; L = CO, L_2 = nbd, cod) in THF with refluxing for 10−24 h. At room temperature no reaction was observed. The crude products were isolated by removing the solvent under vacuum and purified by chromatography on neutral alumina with *n*-hexane/diethyl ether (10:1) as eluents. The yields for the complexes **4**−**7** were in the range of 50−85% (Scheme 2). The compounds **4c** and **7c** seemed to decompose in solution over a period of a few days by fragmentation at the silyl bridge. In contrast to that behavior, the complexes **4a**,**b**−**7a**,**b** are stable in solution under inert conditions and air and moisture stable as pure crystalline species. The low stability of the complexes with the single-atom bridge might be attributed to the ring tension in the five-membered sila ring. The complexes are quite soluble in nonpolar solvents such as *n*-hexane and polar solvents such as THF and diethyl ether as well as in aromatic solvents such as benzene and toluene. In chlorinated solvents all complexes showed the tendency to decompose.

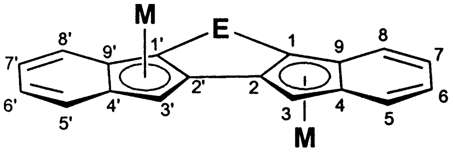


Figure 1. Numbering scheme for **4**−**10**.

As required by the ligand symmetry, only three and nine signals were obtained for the indenyl moieties in ^{1}H and ^{13}C NMR spectroscopy, respectively. The low number of signals in the proton spectra is reduced by comparable resonances of the hydrogen atoms at the diene systems of the indenyl moieties (Figure 1). All NMR spectroscopic data showed only one set of signals attributed to the antifacial isomer, except for complexes **4a** and **8a.** In those cases a 4:1 mixture of the anti- and synfacial isomers has been determined.[9] Even the approach of forcing the isomer ratio to prefer the synfacial coordination by blocking one side of the ligand by a *t*-Bu group on the silicon led to the anti isomer. In general, the isomer ratios found showed an unusual behavior that is comparable to the results of Ceccon et al.[16] They had investigated the dependence of the syn- and antifacial isomer ratio on *as*-indacene complexes. These systems are geometrically and electronically comparable to our compounds, especially those of the tetramethyldisilyl-bridged system. Looking at the deprotonated ligands, both are flat ligand systems with nearly the same distances between the five-membered-ring centers. Furthermore, it has been described in the literature that complexes with *as*-indacenediyl ligands must be considered as additional bridged fulvalenyl systems without any π-delocalization of the central double bond.[17] In our unpublished work on dinuclear metal complexes with analogous silyl-bridged 1,1′-fulvalene systems, we obtained the same preference for the antifacial isomers as with the bis(indenyl) species presented in this paper. This indicates that no electronic influence of the indenyl system affects the direction of the metal reagent attack on the ligand. The *as*-indacene, bridged-fulvalene, and bridged-indenyl systems appeared comparable in steric rigid properties as well as in intramolecular alterations

Nevertheless, Ceccon et al. obtained nearly exclusively the synfacial product by metalation with rhodium and iridium cyclooctadiene units. They explained this behavior by a concerted reaction mechanism favored by

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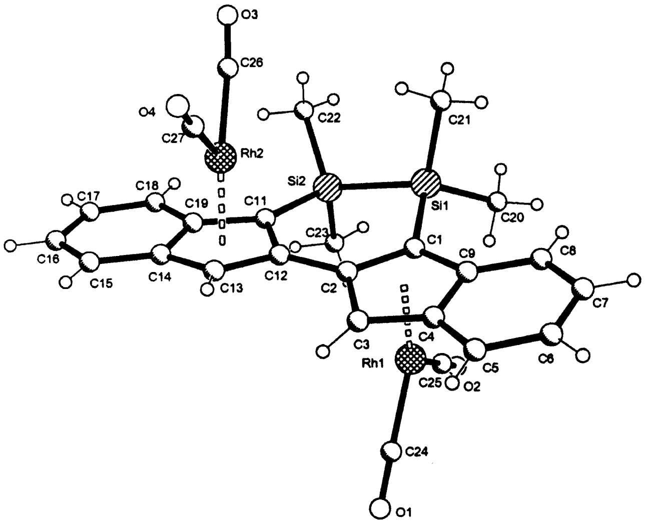

Figure 2. Crystal structure of **6b**.

the planarity of the dinuclear metal reagents $[(cod)MCl]_2$. Due to the similarities of the ligand framework, the preference of the antifacial species in the complexes **4b**,**c**−**7b**,**c** can result not only from the repulsion of the metal fragments in the synfacial complex but also from the minor degree of freedom in the strongly strained Si_1- or Si_2-bridged systems. The required space for both metal moieties by twisting the ligands against each other is provided by the three atomic bridging system, as demonstrated in the crystal structure of synfacial **4a**.[9] Also, the molecular structures of (*as*-indacene)$Rh_2(cod)_2$ and the analogous iridium compound show the metal fragment interaction by bending away the interacting cod ligands. Furthermore, we presume that the substituents on the silicon bridge have generally a low steric but a strong kinetic influence among the metalation steps, in which a higher reaction temperature is required for the syntheses of **4**−**7**. This higher temperature favors a solvent-supported dissociation step of $[(\mu\text{-Cl})ML_2]_2$ (M = Rh, Ir; L_2 = nbd, cod), which seemed essential for the anti formation[18] and resets the concerted mechanism.

The NMR spectra of all complexes **4**−**7** showed one peak between 5.4 and 5.1 ppm assignable to the protons $H^{3,3'}$ of the five-membered rings of the indenyl moieties, except for **6b**. The influence of the electron density of withdrawing CO ligands coordinated to the rhodium centers was observed in a peak displacement to lower field at 6.2 ppm. All NMR data comply with those from similar indenylrhodium and indenyliridium complexes.[18]

Crystals of **6b** suitable for a single-crystal X-ray diffraction analysis were obtained by recrystallization from *n*-pentane. The solid-state structure was determined by X-ray diffraction methods and is depicted in Figure 2. Selected bond distances and angles are listed in Table 1. The complex **6b** crystallized in the monoclinic space group $P2_1/c$. The $Rh(CO)_2$ moieties are η^5-coordinated to the five-membered rings of the polycyclic ligand, and antifacial coordination occurs. The indenyl planes are tilted slightly against each other (with an angle of 11.1°), similar to the case for **4a**. The silicon atoms are bent out of the indenyl planes to the opposite side of the metal to minimize the interaction of their bounded methyl groups with the $Rh(CO)_2$ units. The average bonding distance of rhodium to the CO ligands is 1.87 Å, and the average angle of CO−Rh−CO is 91.2°, both being in agreement with literature values.[18] The bond lengths of the carbon atoms C(1), C(11), C(2), C(12), C(3), C(13) to the metal are significantly shorter (0.15 Å) than those to the quarternary carbon atoms C(4), C(14), C(9), and C(19). This is typical for slight ring slippage to η^3. This common effect is accompanied by the slip distortion Δ[19] and the hinge angle HA.[20] The calculated values for Δ are 0.172 and 0.122 Å, and for HA are 4.08 and 4.4°, respectively. The values are in the expected range for distorted η^5 coordinations such as those found in $(CO)_2(\eta^5\text{-indenyl})Rh$ and $(CO)_2(\eta^5\text{-2-menthylindenyl})Rh$[18,21] (Δ = 0.186 Å, HA = 10.6°) and do not exhibit the characteristics of η^3-coordinations such as those found in $(PMe_2Ph)_3(\eta^3\text{-indenyl})Rh$[22] (Δ = 0.790 Å, HA = 25°). The ^{13}C NMR chemical shift values of the quarternary carbon atoms C(4) and C(9) have been found to be indicative of the extent of ring slippage in rhodium complexes.[23] Following this theory, the slippage from η^5 to η^3 coordination should be monitored by a stronger deshielding of the less coordinated atoms and therefore to a low-field shift, including smaller $^1J_{RhC}$ coupling constants. This theory can be confirmed, as the chemical shifts of complex **6b** have been determined at 120.3 and 119.6 ppm with smaller $^1J_{RhC}$ coupling constants of 2.9 Hz compared to 5.1 Hz for Rh−C(2).

Iron Complexes. To synthesize the CpFe complexes **8a**−**c**, the procedure of Lee et al.[24] was used, because the common synthetic route with $FeCl_2$ and NaCp failed to produce the desired complexes. Instead, only ferrocene has been isolated from that reaction. After lithiation of $[CpFe(fluorene)]PF_6$, the dilithio salts **3a**−**c** were introduced and the suspensions were refluxed in THF overnight (Scheme 3). The byproducts ferrocene and fluorene were sublimed from the reaction mixture, and the red resistant solids were chromatographed on neutral alumina with *n*-hexane/diethyl ether (10:1) as eluents to give the red complexes **8a**−**c** in 72−85% yields. NMR investigations showed for **8b** and **8c** only the antifacial isomers. In comparison to **4a,** the iron complex **8a** has been determined as a mixture of syn- and antifacial isomers in the ratio 1:4. Crystals of **8a** suitable for single-crystal X-ray diffraction analysis were obtained by recrystallization from *n*-pentane. The solid-state structure is shown in Figure 3. The dinuclear antifacial iron complex crystallized in the monoclinic space group $P2_1/c$. Both FeCp moieties are η^5 coordinated to the five-membered rings of the polycyclic

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(20) The hinge angle (HA) is the angle between the normals to the least-squares planes defined by C(1), C(2), C(3) and C(1), C(9), C(4), C(3). Kakkar, A. K.; Taylor, N. J.; Marder, T. B.; Shen, J. K.; Hallinan, B.; Basolo, F. *Inorg. Chim. Acta* **1992**, *198*, 219.

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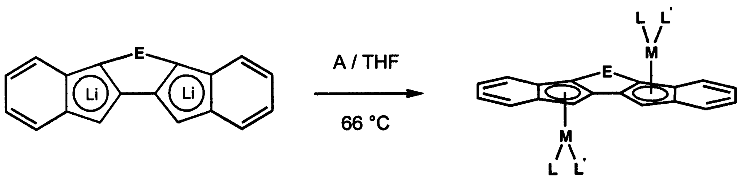
Scheme 3



3a: E = $(SiMe_2)_2O$ A = 2 [CpFe(fluorene)]PF_6 / 2 BuLi
3b: E = $(SiMe_2)_2$ A = $Co_2(CO)_8$ / I_2
3c: E = Si(Me)(t-Bu) A = 2 [$(Py)_3Mo(CO)_3$] / 2 (C_3H_5Cl)

8a: E = $(SiMe_2)_2O$, L+L' = Cp, M = Fe
8b: E = $(SiMe_2)_2$, L+L' = Cp, M = Fe
8c: E = Si(Me)(t-Bu), L+L' = Cp, M = Fe
9b: E = $(SiMe_2)_2$, L, L' = CO, M = Co
10b: E = $(SiMe_2)_2$, L = Allyl, L' = $(CO)_2$, M = Mo

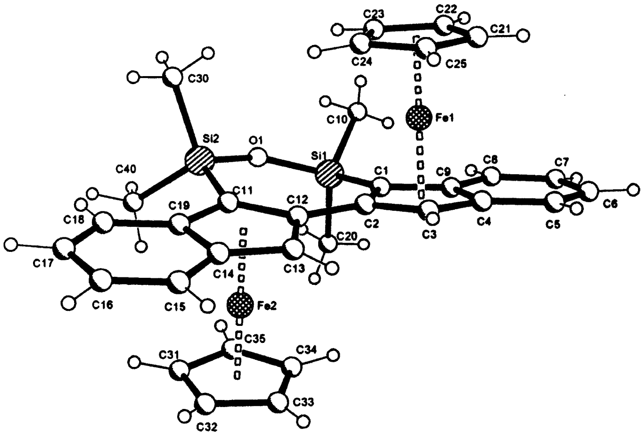


Figure 3. Crystal structure of **8a**.

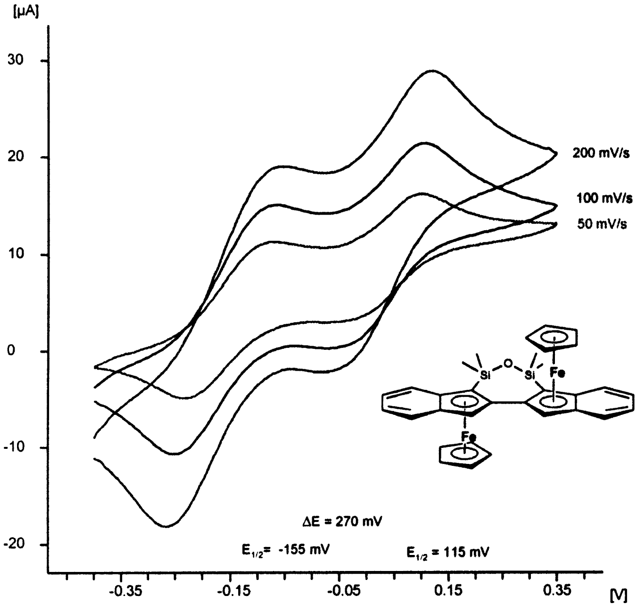


Figure 4. Cyclic voltammograms of **8a** recorded in CH_2Cl_2 at different scan rates.

system similar to ferrocene. The Cp planes are nearly coplanar with the indenyl planes, demonstrated by the plane angles of 4.46 and 1.22°. The average bonding distances of Fe−C(Cp) are 2.04 and 2.03 Å, while the average bond lengths of Fe−C(indenyl) are 2.06 and 2.07 Å. Thus, values are lying in the normal range similar to those of known compounds.[18,24] In this conformation, the indenyl planes are tilted against each other by an angle of 12.03°, comparable to the anti compounds **4a** and **6b**. The silicon atoms are pointed away from the metal to minimize the interaction of their bonded methyl groups with the FeCp units. The bond distances of the carbon atoms C(1), C(2), C(3) and C(11), C(12), C(13) to the metals are 0.05 Å shorter than those to C(4), C(9) and C(14), C(19). In conclusion, **8a** shows a weaker tendency toward a $\eta^2 + \eta^3$ coordination ($\Delta = 0.045$ and 0.020 Å; HA = 3.75 and 2.05°) than the rhodium complexes. This is based on a stronger back-bonding of the metal into the antibonding orbitals of Cp, which give a stronger ligand−metal bond and a smaller tendency to distortion of the η^5 coordination.

The extent of electronic interaction between two metal centers in a ligand-bridged complex can be quantified by cyclic voltammetry. This has been described for symmetric compounds in the literature: mostly for bis(ferrocenyl) species.[1] In the CV, two one-electron-transfer signals were found. The difference in potential between these two one-electron steps corresponds to the magnitude of the intermetallic electronic interaction. In homobimetallic systems containing two equivalent redox centers, the ΔE separation between the two reversible redox events is indicative of an interaction among the metal centers. Certainly, in the case of ΔE values close to zero, no interaction takes place. The diiron species **8a** shows two reversible redox events at $E_{1/2} = -155$ and 115 mV separated by a ΔE value of 270 mV (Figure 4). The redox potential corresponds well with the value for (Ind)FeCp ($E_{1/2} = -130$ mV) recorded under same conditions. The ΔE value must be compared with those of similar systems such as [(fulvalene)$Fe_2(Cp)_2$] (330 mV, acetonitrile),[25] [(*as*-indacene)Fe_2Cp_2] (410 mV, CH_2Cl_2)[26] or the double-bridged species [$(CpSiMe_2)_2(FeCp^*)_2$] (272 mV, CH_2Cl_2).[27] Even when ΔE is influenced by different electrolytes or solvents,[28] it is unambiguous that the value is smaller, as expected for this kind of strongly linked system. One reason for the minor ΔE might be the decreasing overlap due to the torsional effect by the indenyl planes. Additionally, the organic backbone might influence the communication as well, due to the weaker bonding to the metal fragment as a Cp-like system.

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Cobalt and Molybdenum Complexes. The cobalt complex **9b** was synthesized by a metathesis reaction from **3b** and [Co(CO)$_4$I], which was prepared in situ by oxidation of Co$_2$(CO)$_8$ with iodine in THF at 0 °C (Scheme 3). Chromatography on neutral alumina with *n*-hexane/diethyl ether (10:1) as eluents gave **9b** as a red oil in 56% yield. The NMR studies showed the formation of the antifacial isomer with one signal for the CO's at 203.83 ppm. IR absorption of the CO groups occurs at $\tilde{\nu}$ 2014 and 1954 cm^{-1}.

As described in Scheme 3, the molybdenum complex bis[(η^3-allyl)dicarbonyl][1,1′-tetramethyldisilyl-2,2′-bis-(η^5-indenyl)]dimolybdenum(II) (**10b**) was synthesized by adding **3b** to 2 molar equiv of [(Py)$_3$Mo(CO)$_3$] in THF and refluxing the solution. Quenching with 2.2 molar equiv of allylic chloride yielded 65% of the desired yellow complex **10b**. In contrast, oxidation with methyl iodide failed to produce the corresponding complex with two Mo(CO)$_3$Me units. In the ^{13}C NMR spectrum only one signal was detected for the CO groups. This seems to be a dynamic phenomenon at room temperature, due to free rotation around the Mo bond and the C_2-symmetric ligand backbone. The overall analytical studies unambiguously confirmed the formation of the molybdenum complex **10b** with an antifacial conformation.

Conclusion

Metathesis reactions of appropriate transition-metal fragments with the novel double-bridged indenyl systems led to a variety of new homonuclear bimetallic complexes of rhodium, iridium, iron, molybdenum, and cobalt. X-ray diffraction analyses of **6b** and **8a** confirm the suggested structures and the $\eta^2 + \eta^3$coordination of the ligand moieties. Furthermore, the preference for the antifacial conformation must be attributed to the required higher reaction temperature, which favors the formation of the thermodynamically more stable anti isomer. All attempts to displace the isomer ratio into the synfacial species by introducing a bulky *tert*-butyl substituent on the silicon atom were unsuccessful. The *tert*-butyl group is too small to displace the isomer ratio to favor the synfacial coordination. This fact shows that the steric repulsion of the metal fragments must be stronger than their steric interaction with the substituents on the silicon atom, even in the one-atom-bridged system, which provides a minimum in flexibility of the central ring system. We plan to investigate other bulky groups such as cyclohexyl and adamantyl to block one coordination side of the ligand.

The electrochemistry of **8a** shows a smaller intermetallic communication than related compounds. The reason might be the decreasing orbital overlap due to torsional effects of the indenyl planes, as well as the indenyl group itself, which is bonded more weakly to the metal than a similar Cp system.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (DFG) for financial support.

Supporting Information Available: Tables giving all crystallographic data and figures giving ORTEP diagrams for the structural analysis of the compounds **6b** and **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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