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Bridging alkyls in *d*-transition metal chemistry: Reactions of $(\mathrm{cod})_2\mathrm{M}_2(\mu\text{-R})_2$ with organolithium reagents to give $(\mathrm{cod})_2\mathrm{M}_2(\mathrm{R})_4\mathrm{Li}_2$, where M is Rh or Ir, and the crystal structure of $(\mathrm{cod})_2\mathrm{Rh}_2(\mathrm{CH}_2\mathrm{SiMe}_3)_4\mathrm{Li}_2$ and $(\mathrm{cod})\mathrm{Rh}(\mathrm{CH}_2\mathrm{SiMe}_3)_2\mathrm{Li}(\mathrm{Me}_2\mathrm{NCH}_2\mathrm{CH}_2\mathrm{NMe}_2)$

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Abstract

The bridging alkyls, $(\mathrm{cod})_2\mathrm{Rh}_2(\mu\text{-R})_2$ where R is Me or $\mathrm{Me_3SiCH_2}$, react with one molar equivalent of RLi to generate the thermally stable dialkylrhodates, $(\mathrm{cod})\mathrm{Rh}(\mathrm{R})_2\mathrm{Li}$, which may be crystallized from hydrocarbons. X-Ray crystallography of the compound with $\mathrm{R = CH_2SiMe_3}$ shows that the complex is a centrosymmetric dimer with space group *C2/c*, *a* 24.370(6), *b* 9.946(2), *c* 17.791(5) Å, γ 106.62(2)°, and *V* 4132(2) Å^3. The dimer is cleaved by reaction with the Lewis base, $\mathrm{Me_2NCH_2CH_2NMe_2}$, to give $(\mathrm{cod})\mathrm{Rh}(\mathrm{CH_2SiMe_3})_2\mathrm{Li}(\mathrm{tmed})$ as shown by X-ray crystallography. The space group is *Pbca*, *a* 16.532(5), *b* 19.239(5), *c* 18.141(4), and *V* 5770(3) Å^3. The coordination geometry about the square planar $\mathrm{Rh^I}$ atom is similar in both compounds; $\mathrm{Rh^I}$ is bonded to cod and two $\mathrm{CH_2SiMe_3}$ groups and the lithium atom is oriented ca. 30° off a normal to the rhodium atom towards the $\mathrm{CH_2SiMe_3}$ groups with a Li···Rh distance of ca. 2.6 Å. Solution NMR spectroscopy as a function of temperature and solvent on these and the related iridates, $(\mathrm{cod})\mathrm{Ir}(\mathrm{CH_2SiMe_3})_2\mathrm{Li}(\mathrm{tmed})$ and $(\mathrm{cod})\mathrm{Ir}(\mathrm{R})_2\mathrm{Li}$ where R is Me or $\mathrm{CH_2SiMe_3}$, are interpreted relative to the solid state structures.

Two principal reactivity patterns of bridging alkyls in main group organometallic chemistry are (i) bridge cleavage reactions with Lewis bases to give mononuclear

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coordination complexes and (ii) reactions with lithium alkyls to give anionic or "ate" complexes [1]. The small number of bond cleavage reactions in *d*-transition metal chemistry [2] is doubtless related to the rather small number of bridging alkyls that are known for the *d*-transition metals [3]. We recently described reactions of the bridging alkyls of rhodium, $(cod)_2Rh_2(\mu\text{-}R)_2$ where R is Me or Me_3SiCH_2, with a variety of Lewis bases to give mononuclear $(cod)Rh(R)(PR_3)$ [4]. In this paper we describe the reactions of the bridging alkyls with lithium alkyls.

Synthetic studies

The anionic rhodium compounds may be prepared by the two synthetic routes shown in eq. 1, bridge cleavage of the neutral bridging alkyl, or more conveniently by the route shown in eq. 2. The iridates were prepared by the

$$(cod)_2Rh_2(\mu\text{-}R)_2 + 2\ RLi \rightarrow 2(cod)RhR_2Li \qquad (1)$$

$$(cod)_2M_2(\mu\text{-}Cl)_2 + 4\ RLi \rightarrow 2(cod)MR_2Li + 2\ LiCl \qquad (2)$$

second route since the bridging alkyls are as yet unknown for iridium [3f,5]. The second route is the preferred synthetic route to all of the anions; synthesis details are in the Experimental Section. The synthetic procedure involves addition of a lithium alkyl, R = Me, Me_3CCH_2, or Me_3SiCH_2, to $(cod)_2M_2(\mu\text{-}Cl)_2$ in diethyl ether at −70 °C followed by warming to room temperature and eventual crystallization from an aliphatic hydrocarbon. The base-free anions are freely soluble in aromatic hydrocarbon and ethereal solvents. They are stable at room temperature for prolonged periods of time in absence of air and moisture. The neopentyl compounds could not be obtained in analytically pure form, presumably due to their thermal sensitivity, though the similarity of spectroscopic properties (Table 1) suggests that they are similar to the other compounds prepared in this work. The $Me_2NCH_2CH_2NMe_2$ complexes, $(cod)M(CH_2SiMe_3)_2Li(tmed)$, can be isolated by addition of tmed to solutions of the anions followed by crystallization from an aliphatic hydrocarbon solvent. These complexes also are thermally stable at room temperature for prolonged periods of time.

It is of interest to compare the properties of the 1,5-cyclooctadiene metallates with those of the phosphine metallates, $(Me_3C)_2PCH_2CH_2P(CMe_3)_2MR_2Li(L)_x$ [6]. The cod complexes are obtained free of diethyl ether or any other coordinating solvent on crystallization from hydrocarbons. In contrast, the phosphine complexes could never be obtained free of coordinating ether and the complexes crystallize with one to two ether molecules per lithium. It is tempting to suggest that this difference is primarily a steric one since the cod complexes are dimeric in the solid state (see below) and that the bulky phosphine ligands prevent association. Thus, in the cod complexes the lithium atom achieves four (or greater) coordination by dimerizing; when dimerization is blocked by steric hindrance, the lithium atom achieves four (or greater) coordination by coordinating to an ether or another Lewis base.

The solution NMR spectra (Table 1) of the anions are complicated since they depend on solvent and temperature. The features due to the cod resonances, particularly those due to the cod-olefinic resonances are quite revealing relative to symmetry in solution. Given the complex nature of the solid state structure of

Table 1

NMR spectroscopic data [a]

(cod)Rh(CH$_2$SiMe$_3$)$_2$Li			
SiCH$_2$	SiMe$_3$	cod-olefin	cod-aliphatic
^{1}H, thf-d_8, 20 °C			
−0.52d	−0.02s	3.40	2.12m
*J*HRh = 1.5			1.61m
^{13}C			
11.3td			
*J*CH = 115	5.90q	73.4dd	32.8t
*J*CRh = 27.7	JCH = 116	*J*CH = 153	*J*CH = 123
		*J*CRh = 8.7	
^{1}H, PhMe-d_8, 20 °C			
−0.80s	0.32s	3.80s	2.24m
			1.80m
^{13}C{^{1}H}			
10.0d	4.70s	81.3s,br	31.4s
*J*CRh = 28.2			
^{1}H, PhMe-d_8, −80 °C			
−0.31s,br	0.48s	4.05s	2.25m
−0.80s,br		3.20s	1.67m
^{13}C{^{1}H}			
[b]	4.50s	83.6s,br	31.3s
		80.7s,br	30.5s
(cod)Ir(CH$_2$SiMe$_3$)$_2$Li			
^{1}H, thf-d_8, −60 °C			
0.34s	−0.07s	2.77s	1.88m
			1.26m
^{13}C			
18.0t	6.00q	58.0d	34.0t
*J*CH = 113	*J*CH = 114	*J*CH = 154	*J*CH = 124
^{1}H, PhMe-d_8, −60 °C			
0.76d	0.35s	3.55s	2.16s
*J*HH = 7		2.37s	1.40m
0.11d			
*J*HH = 7			
^{13}C{^{1}H}			
[b]	4.50s	68.6s	32.1s
		65.0s	31.2s

(cod)Rh(CH$_2$SiMe$_3$)$_2$Li(tmed)					
NCH$_2$	SiCH$_2$	SiMe$_3$	NMe$_2$	cod-olefin	cod-aliphatic
^{1}H, PhMe-d_8, −30 °C					
1.40s	−0.60d	0.49s	1.77s	4.12s,br	2.59m
	*J*HH = 8			4.03s,br	1.95m
	−1.30d				
	*J*HH = 8				
^{13}C{^{1}H}					
56.5t	8.24td	5.50q	45.8q	79.7dd	32.4t
*J*CH = 133	*J*CRh = 35	*J*CH = 118	*J*CH = 136	*J*CH = 155	*J*CH = 122
	*J*CH = 101			*J*CRh = 9	
				78.7dd	31.6t
				*J*CH = 155	*J*CH = 125
				*J*Crh = 9	

continued

Table 1 (continued)

NCH_2	$SiCH_2$	$SiMe_3$	NMe_2	cod-olefin	cod-aliphatic
(cod)Ir(CH_2SiMe_3)$_2$Li(tmed)					
^1H, PhMe-d_8, −40 °C					
1.32s	0.45d	0.55s	1.69s	3.73s,br	2.25m
	$JHH = 8$			3.35s,br	1.90m
	0.08d				
	$JHH = 8$				
$^{13}C\{^1H\}$, −50 °C					
55.4s	15.7s	5.40s	45.0s	62.4br	33.1s
				55.4br	32.2s
(cod)RhMe$_2$Li					
^1H, thf-d_8, 20 °C					
	−0.60d			3.50s	2.1m
^{13}C	$JHRh = 1.5$				1.75m
4.0qd				77.7dd	39.4t
$JCH = 120$				$JCH = 153$	$JCH = 127$
$JCRh = 38$				$JCRh = 8$	
(cod)IrMe$_2$Li					
^1H, thf-d_8, 20 °C					
0.32s				2.80s,br	1.86m
					1.31m
^{13}C					
13.0q				58.9d	34.1t
$JCH = 114$				$JCH = 152$	$JCH = 122$
^1H, PhMe-d_8, 18 °C					
0.71s				3.01s	2.04m
					1.50m
−60 °C					
0.70s				3.33s	2.18s
				2.49s	1.98s
					1.47m
$^{13}C\{^1H\}$, 20 °C					
11.5s				67.8s	32.1s

[a] Chemical shifts are in δ-units and coupling constants are in Hertz. [b] The low solubility at low temperature makes the unequivocal assignment of the methylene region difficult

$(cod)_2Rh_2(CH_2SiMe_3)_2Li_2$ and its tmed complex, see below, we will comment mainly on the apparent molecular symmetry in solution as judged by the cod-olefin resonances.

The ^1H and ^{13}C NMR spectra of the dialkylanions in thf-d_8 are similar to each other and they are temperature invariant from +20 to −80 °C. The ^1H NMR spectra show one type of alkyl resonance, one type of cod-olefin and two kinds of cod-aliphatic protons. The ^{13}C NMR spectra show one type of alkyl group, cod-olefin, and cod-aliphatic carbon. The spectra are consistent with a molecule of idealized C_{2v} symmetry, i.e., the mid-points of the chelating diolefin occupy two *cis*-sites and the alkyl groups occupy the other two *cis*-sites in a square planar geometry [7*]. It is reasonable to propose that the anions in tetrahydrofuran are

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* Reference number with asterisk indicates a note in the list of references.

either solvent separated ion-pairs or contact ion-pairs in which C_{2v} symmetry is maintained on average.

A comparison of the spectral properties of the four coordinate Rh^I compounds, (cod)Rh(R)(PMe_3) [4] and (cod)RhR_2Li(thf)$_x$, is revealing relative to electron density at the metal center. For the methyls, R = Me, the ^1H chemical shift (δ(H)) of the methyl group is shielded in the anion by ca. 0.4 ppm and the ^{13}C chemical shift (δ(C)) by ca. 0.8 ppm relative to the neutral complex. Further, the cod-olefin resonances in the anion, δ(H), are shielded by ca. 1 ppm and in δ(C) by 8 ppm relative to the neutral complex. In addition, δ(C) for the rhodium bound methyl groups in $(Me_3C)_2PCH_2CH_2P(CMe_3)_2RhMe_2Li(thf)_x$ [6] are shielded by ca. 5 ppm relative to the methyl groups in the analogous cod complexes. These chemical shift trends are consistent with the notion that the methyl groups in the phosphine anion carry more negative charge than those on the cod anion and both carry more negative charge than the methyl group on the neutral complex. This implies that cod is a better π-acceptor ligand than $(Me_3C)_2PCH_2CH_2P(CMe_3)_2$.

The carbon chemical shifts for the cod-olefin resonances also may be used to address the question of π-acceptance in analogous rhodium and iridium anions. In (cod)RhMe_2Li(thf)$_x$ and (cod)IrMe_2Li(thf)$_x$ the δ(C) of the cod-olefin resonance is deshielded by 9 ppm on going from rhodium to iridium. Similarly, in (cod)Rh$(CH_2SiMe_3)_2$Li(thf)$_x$ the δ(C) of the cod-olefin resonances are shielded by 15 ppm and the methylene resonances are deshielded by 7 ppm on going from rhodium to iridium. As suggested previously, this trend in carbon chemical shifts is indicative of iridium being a better π-donor than rhodium towards the π-accepting cod ligand [8], a view that has considerable experimental support [9].

The ^1H and ^{13}C NMR spectra of the isolated tmed complexes in PhMe-d_8 at 20 ° C are similar in form to those of the base-free complexes dissolved in thf-d_8 at 20 ° C. Further, δ(C) for the methylene and cod-olefin carbons are close to each other in the rhodium and iridium complexes. In contrast, the spectra of the tmed complexes are temperature dependent (Table 1). Two changes are observed for both rhodium and iridium complexes, (cod)M$(CH_2SiMe_3)_2$Li(tmed), on cooling to −30 to −40 ° C. Two cod-olefinic resonances appear in the ^1H and ^{13}C spectra whereas a single resonance was observed at +20 ° C, indicative of the cod ligand having top-bottom asymmetry, and the methylene resonances of CH_2SiMe_3 in the ^1H NMR spectra appear as AB patterns (coupling to rhodium is not observed). These observations may be explained by proposing that the average symmetry of (cod)M$(CH_2SiMe_3)_2$Li(tmed) is the same as that in thf, viz., C_{2v} at +20 ° C. If the symmetry is reduced by placing the Li(tmed) fragment on either side of the square plane defined by the midpoints of the cod-olefin ligands and the CH_2SiMe_3 groups, generating an idealized square pyramidal geometry about the transition metal atom, then the molecules will have idealized C_s symmetry. This postulate is consistent with the NMR data which assumes a fluxional process is occurring in solution at 20 ° C that averages the cod-olefinic resonances and the prochiral methylene resonances and that this process is slow by −30 ° C. Further, the NMR spectra are consistent with the overall molecular geometry found for the rhodium complex in the solid state (see below).

The ^1H and ^{13}C NMR spectra of the base-free compounds in PhMe-d_8 are quite related to those of the tmed compounds (Table 1). The spectra are temperature dependent, the high temperature spectra being consistent with a molecule of C_{2v}

symmetry and the low temperature spectra being consistent with a molecule of C_s symmetry and that the barrier to interconversion is ca. 10 kcal mole^{-1}. Again, the NMR results are consistent with the overall dimeric nature of the complexes found in the solid state (see below).

The base-free metallate, (cod)Rh$(CH_2SiMe_3)_2$Li, reacts with Me_3CCH_2Li or (cod)Rh$(CH_2CMe_3)_2$Li as shown in eqs. 3 and 4.

$$\text{(cod)Rh(CH}_2\text{SiMe}_3)_2\text{Li} + 2\ \text{LiCH}_2\text{CMe}_3 \rightleftharpoons \text{(cod)Rh(CH}_2\text{CMe}_3)_2\text{Li} + 2\ \text{LiCH}_2\text{SiMe}_3 \quad (3)$$

$$\text{(cod)Rh(CH}_2\text{SiMe}_3)_2\text{Li} + \text{(cod)Rh(CH}_2\text{CMe}_3)_2\text{Li} \rightleftharpoons 2\text{(cod)Rh(CH}_2\text{SiMe}_3)(\text{CH}_2\text{CMe}_3)\text{Li} \quad (4)$$

in either PhMe-d_8 or thf-d_8. The equilibria are set up rapidly at room temperature as monitored by ^{1}H and ^{13}C NMR spectroscopy. These studies suggest, though do not prove, that the fluxional mechanism for the base-free complexes is an intermolecular process. These exchange reactions may be contrasted with the lack of such exchange reactions with $(Me_3C)_2PCH_2P(CMe_3)_2RhMe_2Li(thf)_x$ [6]. Clearly, the cod metallates show rather different reactivity patterns than their analogous phosphine metallates, a difference that is being studied in this laboratory.

X-Ray crystallographic studies

The positional parameters for the tmed and base-free complexes are in Tables 2 and 3, respectively. Bond lengths and angles are in Tables 4 and 5 and crystal data are in Table 6. An ORTEP of the tmed complex is shown in Fig. 1 and Fig. 2 shows the atom numbering scheme for the base-free complex. Figures 3 and 4 shows views of the inner coordination sphere of the metal atoms in the base-free complex with the nonessential atoms omitted for clarity.

The tmed complex has idealized C_s symmetry with the Li(tmed) fragment sitting below the square planar (cod)Rh$(CH_2SiMe_3)_2$ fragment such that the LiC(CH_2SiMe_3) distances are 2.434(8) Å and 2.325(8) Å (average is 2.38 ± 0.03 Å), the Li–Rh distance is 2.563(9) Å and the Rh–C(a1, a2)–Li angles are 61.6(3)° and 59.3(2)° (average is 60.5 ± 0.6°). In addition, two long cod-olefin to lithium contacts are observed, Li $\cdots$ C(6) is 3.58(1) Å and Li $\cdots$ C(1) is 3.72(1) Å. The $Li(Me_2NCH_2CH_2NMe_2)$ fragment is normal and the bond lengths and angles within the fragment agree with other structures [10].

The average Li–C(CH_2SiMe_3) bond length of 2.38 ± 0.03 Å in the rhodate is longer than the equivalent bond in $(LiCH_2SiMe_3)_6$ of 2.23 ± 0.04 Å [11a] though it is equal to the Li–C bond length of 2.38(2) Å in o-$C_6H_4(CHSiMe_3)_2Li(tmed)$ [11b]. The four-hydrogen atoms on the methylene carbons of the CH_2SiMe_3 group were located and refined isotropically. Two of the hydrogens, one on each methylene group, have short Li $\cdots$ H distances of 1.92(4) Å and 2.17(4) Å. These distances are similar to the Li $\cdots$ H distances found in (cyclohexyllithium)$_6$ and $(LiMe_4B)_4$ [12].

The Rh–C(CH_2SiMe_3) distances of 2.117(5) Å and 2.134(5) Å [average is 2.126 ± 0.005 Å] are shorter by 0.084 Å than the homonuclear bridging methyl distance of 2.210 ± 0.012 Å in $(cod)_2Rh_2(\mu\text{-}Me)_2$ [3f] and 0.117 Å longer than the

Table 2

Fractional atomic coordinates for (cod)Rh(CH_2SiMe_3)$_2$Li(tmed) ($\times 10^4$)

Atom	x	y	z	Equivalent isotropic thermal parameter B ($Å^2$) [a]
Rh	1779(1)	979(1)	554(1)	37(1)
Si(a)	3720(1)	1100(1)	1223(1)	57(1)
Si(b)	2165(1)	−664(1)	11(1)	52(1)
C(a1)	3042(3)	1173(3)	425(3)	46(2)
C(a2)	3807(4)	1934(3)	1750(4)	77(2)
C(a3)	4765(4)	883(4)	899(4)	107(3)
C(a4)	3430(5)	416(4)	1915(4)	107(3)
C(b1)	1884(3)	209(2)	−274(3)	41(1)
C(b2)	1612(5)	−1005(4)	825(4)	92(3)
C(b3)	1985(5)	−1301(3)	−751(4)	88(3)
C(b4)	3264(4)	−702(3)	219(5)	95(3)
C(1)	1654(4)	1981(3)	1079(4)	57(2)
C(2)	1647(4)	1495(3)	1619(4)	61(2)
C(3)	901(4)	1258(4)	2024(4)	88(3)
C(4)	483(4)	645(4)	1660(4)	85(3)
C(5)	581(3)	597(3)	842(4)	56(2)
C(6)	512(3)	1142(3)	351(4)	58(2)
C(7)	240(4)	1860(3)	573(4)	77(2)
C(8)	930(4)	2349(3)	754(4)	80(3)
N(1)	1607(3)	1705(3)	−1583(3)	69(2)
N(2)	3283(3)	1269(2)	−1512(3)	61(2)
C(e1)	2195(6)	1882(6)	−2139(5)	120(4)
C(e2)	2861(6)	1453(5)	−2200(5)	105(4)
C(e3)	1168(5)	2343(4)	−1394(6)	127(4)
C(e4)	1012(5)	1216(4)	−1849(4)	108(4)
C(e5)	3889(5)	1782(4)	−1337(4)	105(3)
C(e6)	3670(5)	613(4)	−1620(5)	108(3)
Li	2312(6)	1275(5)	−735(5)	48(3)
H(a1a)	3146(27)	1611(22)	265(23)	81(15)
H(a1b)	3245(30)	913(24)	13(28)	77(18)
H(b1a)	2220(22)	288(18)	−647(19)	40(11)
H(b1b)	1345(25)	156(19)	−548(22)	57(13)

[a] For the nonhydrogen atoms this is one-third of the trace of the orthogonalized B_{ij} tensor. For hydrogen atoms, it is the refined value of the isotropic thermal parameter.

terminal Rh–C distance of 2.099(2) Å in (cod)RhMe(P-i-Pr_3) [9e]. The rhodium–cod-olefin distances, Rh–C(1, 2, 5, 6), average to 2.167 ± 0.013 Å and the averaged Rh to midpoint of the cod-olefin distance is 2.06 Å. The averaged Rh–C(1, 2, 5, 6) is longer than the equivalent distance in (cod)$_2$Rh$_2$(μ-Cl)$_2$ of 2.00 ± 0.04 Å [13] and in (cod)$_2$Rh$_2$(μ-Me)$_2$ of 2.120 ± 0.013 Å [3f].

The geometry of the complex may be viewed in the following manner. The Rh^I atom is in the center of a rectangle with an averaged Rh to midpoint of the C–C cod-olefin distance of 2.06 Å and a Rh–C distance of 2.13 Å. The lithium atom is located 2.38 Å from the bridging carbon atoms and 2.56 Å from the rhodium atom. Thus the lithium atom is displaced 27° away from a perpendicular from the rhodium atom towards the bridging carbon atoms. This position is presumably a

Table 3

Fractional atomic coordinates for $(cod)_2Rh_2(CH_2SiMe_3)_4Li_2$ $(\times 10^4)$

Atom	x	y	z	Equivalent isotropic thermal parameter B (Å^2) [a]
Rh	1671.7(1)	2022.1(2)	3996.8(1)	2.79
Si(a)	1371(1)	−1389(1)	4187(1)	4.2
Si(b)	992(1)	2616(1)	5371(1)	3.9
C(1)	2002(2)	1357(4)	3037(2)	4.7
C(2)	1420(2)	1167(4)	2795(2)	4.7
C(3)	1015(2)	2101(4)	2229(2)	6.7
C(4)	803(2)	3241(4)	2612(2)	5.8
C(5)	1206(1)	3720(4)	3371(2)	4.1
C(6)	1789(1)	3983(4)	3508(2)	4.4
C(7)	2112(2)	3877(5)	2894(2)	6.4
C(8)	2310(2)	2485(4)	2764(2)	6.3
C(a)	1850(1)	81(3)	4550(2)	3.3
C(a2)	1589(2)	−2305(4)	3401(3)	6.6
C(a3)	1446(2)	−2625(4)	5008(3)	7.3
C(a4)	591(2)	−958(5)	3805(3)	6.8
C(b1)	1663(1)	2894(4)	5082(2)	3.4
C(b2)	1007(2)	957(4)	5870(2)	5.6
C(b3)	929(2)	3936(5)	6093(3)	6.8
C(b4)	323(2)	2720(5)	4542(2)	6.6
H(a11)	1884(13)	132(31)	5078(18)	4.1(8)
H(a12)	2244(13)	−254(31)	4566(17)	5.5(8)
H(b11)	1714(13)	3808(36)	5101(18)	4.4(8)
H(b12)	1943(16)	2685(35)	5550(20)	4.2(8)
Cation				
Li	2531(2)	1336(6)	5222(4)	4.9

[a] For nonhydrogen atoms this is one-third of the trace of the orthogonalized B_{ij} tensor; for hydrogen atoms, it is the refined value of the isotropic thermal parameter.

Table 4

Bond lengths (Å) and angles (°) in $(cod)_2Rh(CH_2SiMe_3)_2Li(tmed)$

Rh–C(a1)	2.134(5)	Rh–C(1)	2.160(6)
Rh–C(b1)	2.114(5)	Rh–C(2)	2.183(6)
		Rh–C(5)	2.176(6)
Rh–Li	2.563(9)	Rh–C(6)	2.150(5)
Li–C(a1)	2.434(8)	Rh–C(1,2) [a]	2.063(–)
Li–C(b1)	2.325(8)	Rh–C(5,6) [a]	2.050(–)
C(a1)–Rh–C(b1)	89.7(2)	C(a1)–Rh–C(1,2) [a]	93.1(–)
		C(a1)–Rh–C(5,6) [a]	174.1(–)
C(1)–Rh–C(2)	36.3(2)	C(b1)–Rh–C(1,2) [a]	176.9(–)
C(5)–Rh–C6	37.2(2)	C(b1)–Rh–C(5,6) [a]	90.3(–)
C(a1)–Rh–C(1)	89.2(2)	C(b1)–Rh–C(1)	160.7(2)
C(a1)–Rh–C(2)	96.6(2)	C(b1)–Rh–C(2)	162.5(2)
C(a1)–Rh–C(5)	167.4(2)	C(b1)–Rh–C(5)	88.9(2)
C(a1)–Rh–C(6)	155.4(2)	C(b1)–Rh–C(6)	91.7(2)
Li–Rh–C(a1)	61.6(3)	Li–Rh–C(1)	103.7(3)
Li–Rh–C(b1)	59.3(2)	Li–Rh–C(2)	137.8(3)
		Li–Rh–C(5)	127.3(3)
Li–Rh–C(1,2) [a]	121.0(–)	Li–Rh–C(6)	98.4(3)
Li–Rh–C(5,6) [a]	113.5(–)		

[a] The symbols C(1,2) and C(5,6) are used to denote the centers of the C(1)–C(2) and C(5)–C(6) bonds, respectively, and are therefore listed without estimated standard deviations.

Table 5

Bond lengths (Å) and angles (°) in $(cod)_2Rh_2(CH_2SiMe_3)_4Li_2$

Rh-C(1)	2.189(5)	Rh-Li	2.644(6)
Rh-C(2)	2.219(5)	Rh-Li′ [b]	2.614(6)
Rh-C(5)	2.157(3)		
Rh-C(6)	2.187(4)	Li-H(a11)	1.94(3)
		Li-H(a12)	1.97(3)
Rh-C(1,2) [a]	2.095(-)	Li-H(b′11) [b]	2.09(4)
Rh-C(5,6) [a]	2.057(-)	Li-H(b′12) [b]	2.34(3)
Li-C(a1)	2.146(3)	Li-H(b12)	2.16(3)
Rh-C(a1)	2.154(3)	Li-H(6′) [b,c]	1.60(-)
Rh-C(b1)	2.122(4)		
Li-C(b1)	2.312(3)	Li···Li′ [b]	2.437(6)
C(1,2)-Rh-C(5,6) [a]	86.2(-)	Rh-Li-Rh′ [b]	124.8(1)
C(a1)-Rh-C(b1)	90.2(1)		
C(1,2)-Rh-C(a1) [a]	92.3(-)	Rh-Li-Li′ [b]	61.8(1)
C(5,6)-Rh-C(b1) [a]	91.3(-)	Rh′-Li-Li′ [b]	63.0(1)
		Rh-Li-H(a11)	68(1)
C(1,2)-Rh-C(b1) [a]	176.4(-)	Rh-Li-H(a12)	70(1)
C(5,6)-Rh-C(b1) [a]	178.5(-)	Rh-Li-H(b′11)	110(1)
		Rh-Li-H(b′12) [b]	81(1)
C(1,2)-Rh-Li [a]	115.5(-)	Rh-Li-H(b12)	68(1)
C(5,6)-Rh-Li [a]	129.1(-)		
C(1,2)-Rh-Li′ [a,b]	119.4(-)	H(a11)-Li-H(b′11) [b]	132(2)
C(5,6)-Rh-Li′ [a,b]	73.9(-)	H(a11)-Li-H(b′12) [b]	138(2)
		H(a11)-Li-H(b12)	82(2)
C(a1)-Rh-Li	51.9(1)	H(a11)-Li-Rh′ [b]	156(1)
C(b1)-Rh-Li	64.3(1)	H(a11)-Li-Li′ [b]	125(2)
C(a1)-Rh-Li′ [b]	107.2(1)		
C(b1)-Rh-Li′ [b]	57.3(1)	H(a12)-Li-H(b′11) [b]	88(2)
		H(a12)-Li-H(b′12) [b]	98(2)
H(6′)-Li-Rh [c]	172(-)	H(a12)-Li-H(b12) [b]	121(2)
H(6′)-Li-Rh′ [c]	63(-)	H(a12)-Li-Rh′ [b]	154(1)
H(6′)-Li-Li′ [c]	126(-)	H(a12)-Li-Li′ [b]	126(2)
H(6′)-Li-H(a11) [c]	104(-)		
H(6′)-Li-H(a12) [c]	104(-)	H(b′11)-Li-H(b12) [b]	145(2)
H(6′)-Li-H(b′11) [c]	74(-)	H(b′11)-Li-Rh′ [b]	67(1)
H(6′)-Li-H(b′12) [c]	105(-)	H(b′11)LiLi′ [b]	87(2)
H(6′)-Li-H(b12) [c]	112(-)		
		H(b′12)-Li-Rh′ [b]	67(1)
H(b12)-Li-H(b′12) [b]	115(2)		

[a] The symbols C(1,2) and C(5,6) are used to denote the centers of the C(1)-C(2) and C(5)-C(6) bonds, respectively, and therefore listed without estimated standard deviations. [b] Primed (′) atoms are related to nonprimed atoms by the symmetry operation $\frac{1}{2}-x$, $\frac{1}{2}-y$, $1-z$. [c] Values which are listed involving H(6) and H(6′) are given without estimated standard deviations since H(6) was included in the structure factor calculations as an idealized atom and was not varied.

reflection of steric effects, the N-methyls avoiding the Si-methyls, and electronic effects, the Li(tmed) fragment seeking out the sites of negative charge.

The geometry of the $(cod)Rh(CH_2SiMe_3)_2Li$ unit in the dimeric base-free complex is remarkably similar to that in the tmed complex. The base-free dimer can be generated by removing the tmed from the $(cod)Rh(CH_2SiMe_3)_2Li(tmed)$ and joining the two $(cod)Rh(CH_2SiMe_3)_2Li$ fragments so as to generate an inversion

Table 6

Crystal data

	I	II
a (Å)	16.532(5)	24.370(6)
b (Å)	19.239(5)	9.946(2)
c (Å)	18.141(4)	17.791(5)
$\alpha = \beta$ (°)	90.00	90.00
γ (°)	90.00	106.62(2)
Crystal system	orthorhombic	monoclinic
Space group	$Pbca$-D_{2h}^{15}(No. 61)	$C_{2/c}$-C_{2h}^{6} (No. 15)
Volume (Å^3)	5770(3)	4132(2)
d(calc) g cm^{-3})	1.17	1.25
Z	8	4(dimers)
temp (°C)	20 ± 1	20 ± 1
Empirical fmw	$C_{22}H_{50}LiN_2RhSi_2$	$C_{16}H_{34}LiRhSi_2$
Formula weight	508.8	388.4
Color	brown	orange
X-ray, (τ, Å)	0.71073	0.71073
Crystal size (mm)	0.50 × 0.50 × 0.70	irregular, min 0.45 max 0.95
Absorb coeff (cm^{-1})	6.7	9.2
2θ limits (°)	3.0–48.3	3.0–55.0
sin θ/τ (min, max)	0.00,0.567	0.00,0.650
no. stds	6	6
no. rflx between stds	300	300
no. independent rflx	4608	4725
no. unique rflx	2553	3343
no. parameters	300	216
R_1 [a]	0.037	0.030
R_2 [b]	0.034	0.030
GOF [c]	1.61	1.56

[a] $R_1 = \Sigma \| F_0 | - | F_c \| / \Sigma | F_0 |$. [b] $R_2 = \{\Sigma w (| F_0 | - | F_c |)^2 / \Sigma w | F_0 |^2 \}^{1/2}$. [c] $GOF = \{\Sigma w(|F_0| - |F_c|)^2/((NO - NV)\}^{1/2}$, where NO is the number of observations and NV is the number of variables.

center at the midpoint of the Li–Li vector. The molecule has idealized C_{2h} symmetry which can most readily be seen by inspection of Fig. 4.

Each lithium atom in the base-free dimer is four coordinate with LiC(CH_2SiMe_3) distances of 2.146(3) Å and 2.312(3) Å (average is 2.23 ± 0.04 Å). The averaged Li–C distance in the base-free dimer is ca. 0.15 Å shorter than that in the tmed complex. The shorter Li–C distance brings one of the cod-olefin carbon atom in each fragment, C(6), in close contact with a lithium atom with an Li $\cdots$ C distance of 2.410(5) Å. The two hydrogens on each methylene group were located and refined isotropically. Each hydrogen has short Li $\cdots$ H contact distances of 1.94(3), 1.97(3), 2.08(4) and 2.16(3) Å (average is 2.03 ± 0.08 Å). The averaged Rh–C (1,2,5,6), the cod-olefin carbons, distance of 2.180 ± 0.015 Å is similar to those in the tmed complex, as is the averaged Rh-C(CH_2SiMe_3) distance of 2.138 ± 0.008 Å.

As mentioned earlier, the geometry of each (cod)Rh(CH_2SiMe_3)$_2$Li fragment in the dimer is similar to that fragment in the tmed complex. In the dimer, the Rh^I atom is in the center of a rectangle with an averaged Rh to midpoint of the C–C

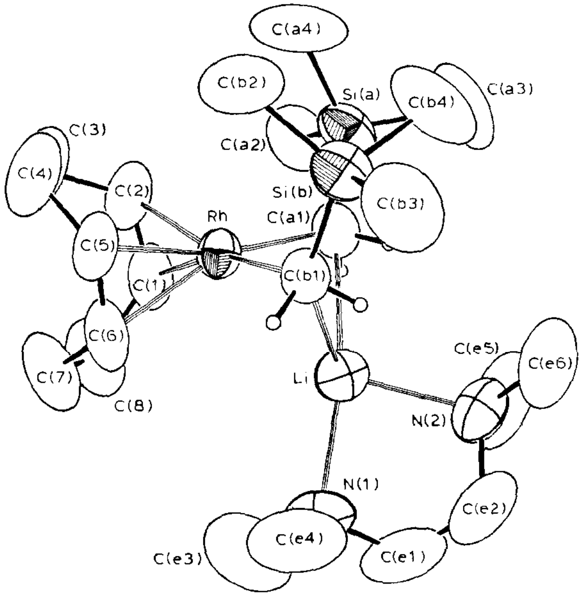


Fig. 1. ORTEP diagram of (cod)Rh$(CH_2SiMe_3)_2$Li(tmed), 50% thermal ellipsoids, except for hydrogen which are arbitrary.

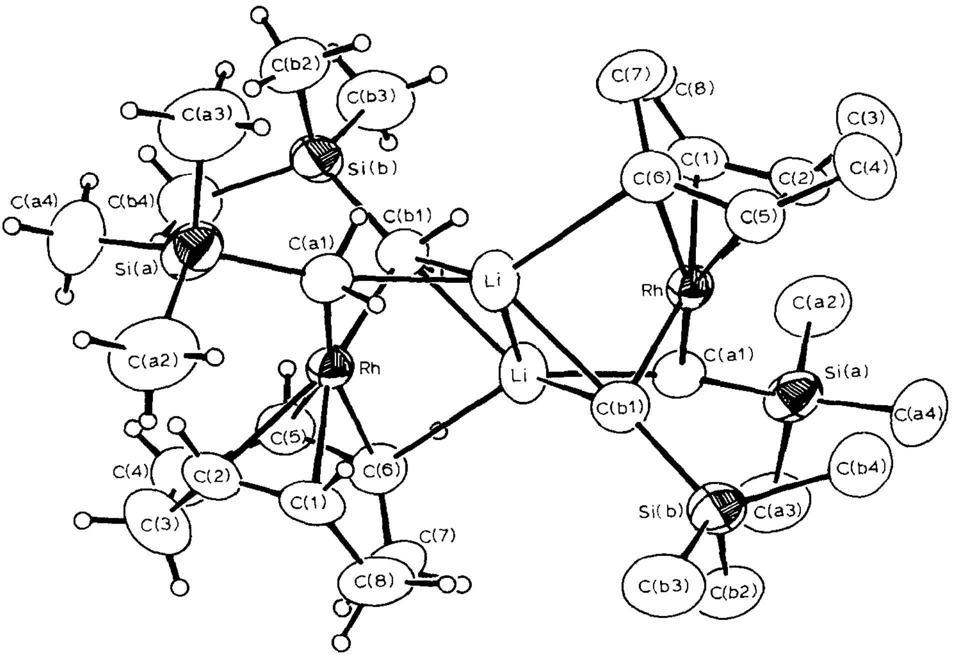
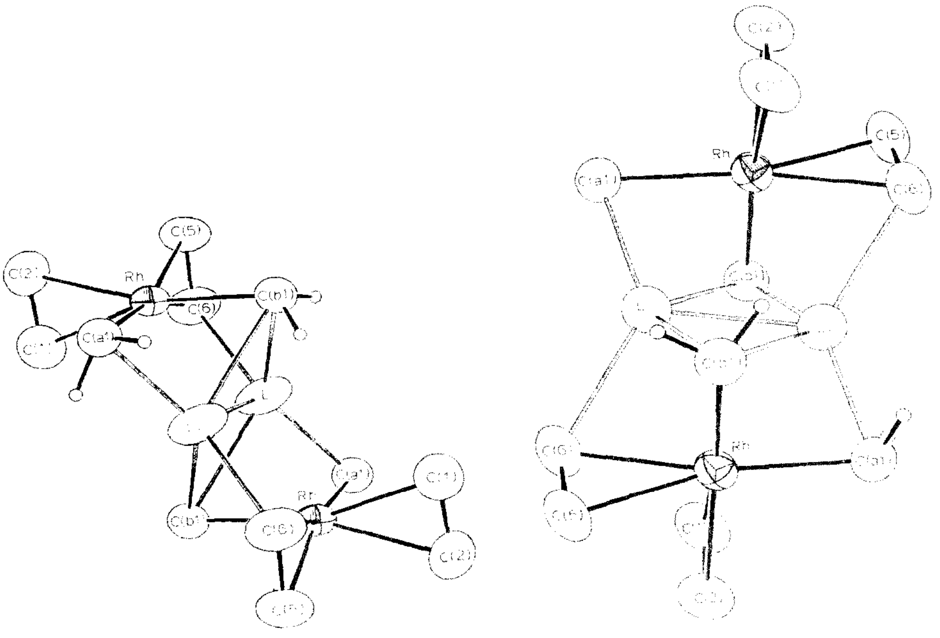
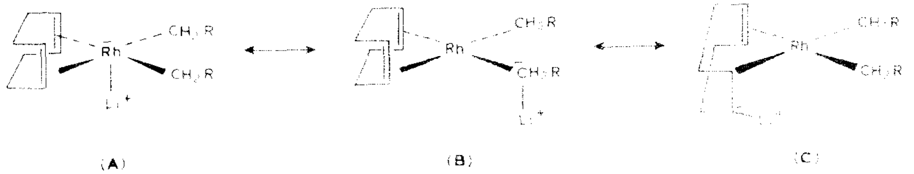


Fig. 2. ORTEP diagram of $(cod)_2Rh_2(CH_2SiMe_3)_4Li_2$ showing the atom numbering scheme, 50% thermal ellipsoids, except for hydrogen which are arbitrary.



Figs. 3 and 4. ORTEP diagram of $(cod)_2Rh_2(CH_2SiMe_3)_4Li_2$ showing two views of the inner coordination sphere of the metal atoms.

cod-olefin distance of 2.08 Å and an averaged Rh–C distance of 2.14 Å. The lithium atom is located 2.23 Å from the bridging carbon atoms and 2.63 Å from the rhodium atoms so that the lithium atom is displaced 32° off a normal to the Rh^I atom in the rectangle towards the bridging carbon atoms. In the base-free dimer the location of the lithium atoms is probably due to the Li atom seeking out the sites of negative electron density in order to achieve four coordination while minimizing ligand-ligand repulsions. This electronic effect may be viewed by writing the three



resonance structures **A**, **B**, and **C**. The most controversial is **A** since this shows a structure with a direct Li–Rh bond. The Li to rhodium distance in each rhodate is ca. 2.6 Å which is in the range found in other *d*-transition metal–lithium compounds [14]. Electron deformation density studies and theory have been applied to the question of the nature of the Li to *d*-transition metal bond with the net result that even though the orbitals are available for bonding the extent of orbital overlap is controversial [15].

Experimental

All manipulations were done under nitrogen or argon by using standard Schlenk techniques or in a Vacuum Atmospheres inert atmosphere box. Elemental analyses were done by the microanalytical laboratory of this department. Nuclear magnetic resonance spectra were recorded on a Bruker AM500 spectrometer operating at 500 MHz (^{1}H) or on homebuilt machines operating at 180, 200, or 250 MHz (^{1}H). All ^{1}H and ^{13}C chemical shifts are relative to Me_4Si, $\delta = 0$, with positive values to high frequency.

(cod)Ir(CH$_2$SiMe$_3$)$_2$Li. Trimethylsilylmethyllithium (0.35 g, 3.7 mmol) and $(cod)_2Ir_2(\mu\text{-}Cl)_2$ (0.50 g, 0.75 mmol) were mixed together, then diethyl ether (50 ml) was added at $-70\,°C$. The suspension was stirred for 4 h at $-70\,°C$ then it was allowed to warm to room temperature. The diethyl ether was removed under reduced pressure and the yellow solid was crystallized from a saturated solution of cyclopentane by cooling ($-70\,°C$). The crystals were isolated in 77% (0.55 g) yield. Anal. Found: C, 39.5; H, 6.99; Li, 1.39. $C_{16}H_{34}IrLiSi_2$ calc: C, 39.9; H, 7.06; Li, 1.44%.

(cod)Rh(CH$_2$SiMe$_3$)$_2$Li. This compound was prepared from Me_3SiCH_2Li (0.23 g, 2.4 mmol) and $(cod)_2Rh_2(\mu\text{-}Cl)_2$ (0.20 g, 0.40 mmol) in diethyl ether in a manner similar to that described for the iridate and the yellow-orange complex was crystallized from cyclopentane ($-70\,°C$) in 76% (0.24 g) yield. Anal. Found: C, 49.0; H, 8.94; Li, 1.73. $C_{16}H_{34}RhLiSi_2$ calcd: C, 49.0; H, 8.67; Li, 1.77%.

(cod)Ir(CH$_2$SiMe$_3$)$_2$Li(Me$_2$NCH$_2$CH$_2$NMe$_2$). Tetramethylethylenediamine (0.04 ml, 0.43 mmol) was added to $(cod)Ir(CH_2SiMe_3)_2Li$ (0.40 mmol) in diethyl ether (50 ml) and the orange solution was stirred for 1 h at room temperature. The volatile material was removed under reduced pressure and the orange oil was crystallized as orange crystals from a minimum amount of cyclopentane ($-70\,°C$) in 80% yield. Anal. Found: C, 44.2; H, 8.27; N, 4.56; Li, 1.15. $C_{22}H_{50}IrLiN_2Si_2$ calcd: C, 44.3; H, 8.19; N, 4.70; Li, 1.16%.

(cod)Rh(CH$_2$SiMe$_3$)$_2$Li(Me$_2$NCH$_2$CH$_2$NMe$_2$). This compound was prepared in a manner analogous to that of its iridium analogue in 85% yield. Anal. Found: C, 5.20; H, 9.99; N, 5.38; Li, 1.41. $C_{22}H_{50}LiN_2RhSi_2$ calc: C, 52.0; H, 9.91; N, 5.51; Li, 1.36%.

(cod)IrMe$_2$Li. Methyllithium (9.0 ml of a 0.41 *M* diethyl ether solution, 3.7 mmol) was added to $(cod)_2Ir_2(\mu\text{-}Cl)_2$ (0.50 g, 1.0 mmol) in diethyl ether (50 ml) at $-70\,°C$. The suspension was stirred at $-70\,°C$ for 1 h then the flask was allowed to slowly warm to room temperature. The diethyl ether was removed under reduced pressure and the orange residue was crystallized as orange crystals from cyclopentane at $-70\,°C$ in a yield of 60% (0.30 g). Anal. Found: C, 35.5; H, 5.34; Li, 1.88. $C_{10}H_{18}IrLi$ calcd: C, 35.6; H, 5.38; Li, 2.06.

(cod)RhMe$_2$Li. This compound was prepared in a manner analogous to that of its iridium analogue as a pale yellow powder. Crystallization resulted in substantial decomposition and analytically pure material could not be obtained.

(cod)Ir(CH$_2$CMe$_3$)$_2$Li. Neopentyllithium (0.12 g, 1.6 mmol) and $(cod)_2Ir_2(\mu\text{-}Cl)_2$ (0.024 g, 0.36 mmol) were mixed and diethyl ether (50 ml) was added at $-70\,°C$ and the suspension was stirred at that temperature for 4 h then warmed to room temperature. The suspension was filtered and the filtrate was evaporated to dryness to yield an orange powder in 45% (0.32 g) yield. Attempts to crystallize the powder led to decomposition and the compound was characterized by solution spectroscopy only. ^{1}H NMR (20 °C, thf-d_8): δ 2.77 (s, cod-olefin, 4 H), 1.80 (m, cod-aliphatic, 4 H), 1.42 (s, CH_2CMe$_3$, 4 H), 1.19 (m, cod-aliphatic, 4 H), 1.04 (s, CH$_2$CMe_3, 18 H). ^{1}H NMR (PhMe-d_8, +20 °C): δ 3.5 (s, br, cod-olefin, 4 H), 2.1

(s, br, cod-aliphatic, 4 H), 1.55 (s, br, CH_2CMe$_3$, 4 H), 1.50 (m, cod-aliphatic, 4 H), 1.22 (s, CH$_2$CMe_3, 18 H). ^{13}C{^{1}H} NMR (thf-d_8, +20 °C): 59.1 (s, cod-olefin), 46.3 (s, CH_2CMe$_3$), 39.3 (s, CH$_2$$CMe_3$), 38.5 (s, CH$_2CMe_3$), 34.1 (s, cod-aliphatic).

(cod)Rh(CH$_2$CMe$_3$)$_2$Li. This compound was prepared in a manner analogous to that used to prepare the iridium analogue. The orange-yellow powder was characterized by solution spectroscopy since the molecule is somewhat thermally sensitive. ^{1}H NMR (PhMe-d_8, +20 °C): δ 4.31 (s, cod-olefin, 4 H), 2.23 (m, cod-aliphatic, 4 H), 1.99 (m, cod-aliphatic, 4 H), 1.28 (s, CH$_2$CMe_3, 18 H), 0.45 (s, CH_2CMe$_3$, 4 H).

X-Ray crystallography of (cod)Rh(CH$_2$SiMe$_3$)$_2$Li(tmed) (I). The air- and moisture-sensitive crystals were loaded into glass capillaries inside an inert atmosphere glovebox. The capillaries were removed from the box and flame sealed. The X-ray crystallographic procedures and programs used were as previously described [16]. Accurate cell parameters were determined by a least squares fit to the setting angles of the unresolved Mo-K_α component of 15 reflections with $2\theta > 25$°. The 4608 reflections were obtained. Analysis of the psi-scan data showed a range of relative transmission factors of 0.815–1.000. The intensity data were corrected, empirically, for absorption effects using psi-scans for 6 reflections having 2θ between 12.3° and 34.5° and then corrected for Lorentz and polarization effects. Rejection of redundant data gave a unique set of 2553 data which were used to solve the structure. The rhodium atom position was found by analysis of a three-dimensional Patterson map and the remaining atoms were found by conventional Fourier and difference Fourier methods. The rhodium and silicon atoms were corrected for anomalous dispersion. The 10 methyl groups (C(a2), C(a3), C(a4), C(b2), C(b3), C(b4), C(e3), C(e4), (C(e5) and C(e6) and their hydrogens) were refined as rigid rotors with idealized sp^3-hybridized geometry and a C–H bond length of 0.96 Å. The initial orientation of each methyl group was determined from difference Fourier positions for the hydrogen atoms. The final orientation was determined by three rotational parameters. With the exception of the silyl ligand methylene hydrogens (H_{a1a}, H_{a1b}, H_{b1a} and H_{b1b}) which were refined as independent isotropic atoms, the remaining hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp^3- or sp^2-hybridization of the carbon atoms with a C–H bond length of 0.96 Å) "riding" on their respective carbon atoms. The isotropic thermal parameters of all hydrogens except the silyl ligand methylene hydrogens were fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which they are bonded. Table 2 lists the thermal parameters (isotropic) of the silylmethylene hydrogens. In the final least-squares the maximum shift for all parameters is 0.15 σ_p and the average shift for all parameters is 0.04 σ_p where σ_p is the esd of the parameter in question. No peaks were present in the final difference Fourier map above the noise level of 0.46 electron Å^{-3}.

X-ray crystallography on (cod)$_2$Rh$_2$(CH$_2$SiMe$_3$)$_4$Li$_2$ (II). The air- and moisture-sensitive crystals were put into glass capillaries as described above. The diffractometer, programs, etc. were the same as that described above. Accurate cell dimensions were determined by a least squares fit to the setting angles of unresolved Mo-K_α component of 15 reflections with $2\theta > 25$°. The 4728 reflections were collected. The intensity data showed a range of relative transmission factors of 0.70–1.00. The intensity data were corrected, empirically, for absorption effects using psi-scans for 6 reflections have 2θ between 12.8° and 39.7° and were corrected for Lorentz and polarization effects. Rejection of redundant data gave a unique set of 3343 data which were used to solve the structure. The rhodium atom position was found by analysis of a three-dimensional Patterson map and the remaining atoms were formed by conventional Fourier and difference Fourier methods. The rhodium and silicon atoms were corrected for anomalous dispersion. The terminal methyl groups were refined as rigid rotors assuming sp^3-hybridization of the carbon atom and a C–H bond length of 0.96 Å. The initial orientation of each methyl group was determined from difference Fourier positions for the hydrogen atoms. The final orientation of each group was determined by 3 rotational parameters. The hydrogen atoms of the cod ligand were included in the structure factor calculations as idealized atoms (assuming sp^3- or sp^2-hybridization of the carbon atoms and a C–H bond length of 0.96 Å) "riding" on their respective carbon atoms. With the exception of the silyl ligand, methylene hydrogens (H(a11), H(a12), H(b11) and H(b12)) which were refined as independent isotropic atoms, the isotropic thermal parameters of all hydrogen atoms were fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded. The isotropic thermal parameters of H(a11), H(a12), H(b11) and H(b12) refined to final values of 4.1(8), 5.5(8), 4.4(8) and 4.2(8) Å^2, respectively. In the final least squares cycle, the maximum shift for all parameters was 0.31 σ_p and the average shift for all parameters was 0.05 σ_p. No peaks were present in the final difference Fourier map above the noise level of 0.45 electron Å^3.

Supplementary material available. Anisotropic thermal parameters, atomic coordinates for idealized hydrogen atom positions and additional bond lengths and angles (11 pages). The structure factors are available from Dr. Day upon request.

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