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Synthesis of homo- and heterodinuclear metal complexes with dimethylsilylene bridged unsymmetrical bis(cyclopentadienyl) ligand

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Abstract

The reaction of the dilithium salt $Li_2[Me_2Si(C_5H_4)(C_5Me_4)]$ (**2**) of $Me_2Si(C_5H_5)(C_5HMe_4)$ (**1**) with $[MCl(C_8H_{12})]_2$ (M = Rh, Ir) and $[RhCl(CO)_2]_2$ afforded homodinuclear metal complexes $[\{Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5Me_4)\}\{M(C_8H_{12})\}_2]$ (M = Rh: **3**; M = Ir: **4**) and $[\{Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5Me_4)\}Rh_2(CO)_2(\mu\text{-}CO)]$ (**5**), respectively. The reaction of **2** with $RhCl(CO)(PPh_3)_2$ afforded a mononuclear metal complex $[\{Me_2Si(C_5HMe_4)(\eta^5\text{-}C_5H_4)\}Rh(CO)PPh_3]$ (**6**) leaving the C_5HMe_4 moiety intact. Taking advantage of the difference in reactivity of the two cyclopentadienyl moieties of **2**, heterodinuclear complexes were prepared in one pot. Thus, the reaction of **2** with $RhCl(CO)(PPh_3)_2$, followed by the treatment with $[MCl(C_8H_{12})]_2$ (M = Rh, Ir) afforded a homodinuclear metal complex $[Rh(CO)PPh_3\{(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5Me_4)\}Rh(C_8H_{12})]$ (**7**) consisting of two rhodium centers with different ligands and a heterodinuclear metal complex $[Rh(CO)(PPh_3)\{(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5Me_4)\}Ir(C_8H_{12})]$ (**8**). The successive treatment of **2** with $[IrCl(C_8H_{12})]_2$ and $[RhCl(C_8H_{12})]_2$ provided heterodinuclear metal complex $[Ir(C_8H_{12})\{(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5Me_4)\}Rh(C_8H_{12})]$ (**9**). The reaction of **2** with $CoCl(PPh_3)_3$ and then with PhC≡CPh gave a mononuclear cobaltacyclopentadiene complex $[\{Me_2Si(C_5Me_4H)(\eta^5\text{-}C_5H_4)\}Co(CPh{=}CPh{-}CPh{=}CPh)(PPh_3)]$ (**10**). However, successive treatment of **2** with $CoCl(PPh_3)_3$, PhC≡CPh and $[MCl(C_8H_{12})]_2$ in this order afforded heterodinuclear metal complexes $[M(C_8H_{12})\{(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5Me_4)\}Co(\eta^4\text{-}C_4Ph_4)]$ (M = Rh: **11**; M = Ir: **12**) in which the cobalt center was connected to the C_5Me_4 moiety. Although the heating of **10** afforded a tetraphenylcyclobutadiene complex $[\{Me_2Si(C_5Me_4H)(\eta^5\text{-}C_5H_4)\}Co(\eta^4\text{-}C_4Ph_4)]$ (**13**), in which the cobalt center was connected to the C_5H_4 moiety, simple heating of the reaction mixture of **2**, $CoCl(PPh_3)_3$ and PhC≡CPh resulted in the formation of a tetraphenylcyclobutadiene complex $[\{Me_2Si(C_5H_5)(\eta^5\text{-}C_5Me_4)\}Co(\eta^4\text{-}C_4Ph_4)]$ (**14**), in which the cobalt center was connected to the C_5Me_4 moiety. The mechanism of the cobalt transfer was suggested based on the electrophilicity of the formal trivalent cobaltacyclopentadiene moiety. In the presence of 1,5-cyclooctadiene, the reaction of **2** with $CoCl(PPh_3)_3$ provided a mononuclear cobalt cyclooctadiene complex $[\{Me_2Si(C_5Me_4H)(\eta^5\text{-}C_5H_4)\}Co(C_8H_{12})]$ (**15**). The reaction of **15** with *n*-BuLi followed by the treatment with $[MCl(C_8H_{12})]_2$ (M = Rh, Ir) afforded the heterodinuclear metal complexes of $[Co(C_8H_{12})\{(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5Me_4)\}M(C_8H_{12})]$ (M = Rh: **16**; M = Ir: **17**). Treatment of **6** with $Fe_2(CO)_9$ at room temperature afforded a heterodinuclear metal complex $[\{Me_2Si(C_5HMe_4)(\eta^5\text{-}C_5H_4)\}\{Rh(PPh_3)(\mu\text{-}CO)_2Fe(CO)_3\}]$ (**18**) in which the C_5HMe_4 moiety was kept intact. Treatment of dinuclear metal complex **5** with $Fe_2(CO)_9$ afforded a heterotrinuclear metal complex $[\{(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5Me_4)\}\{Rh(CO)Rh(\mu\text{-}CO)_2Fe(CO)_3\}]$ (**19**) having a triangular metal framework. The crystal and molecular structures of **3**, **11**, **12**, **18** and **19** have been determined by single-crystal X-ray diffraction analysis. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Homodinuclear metal complexes; Heterodinuclear metal complexes; Cyclopentadienyl metal complexes

1. Introduction

In recent years, considerable attention has been focused on polynuclear transition-metal complexes because a multi-metal center may provide reaction pathways not available to a single metal one. However, true polynuclear reactions have not been seen frequently, because of the ready fragmentation of the metal framework. In order to quench cleavage of the inherently weak metal–metal bonds, bridging ligands have been used as the support. For this purpose, bridged bis(η^5-cyclopentadienyl) ligands such as $[X(C_5H_4)_2]$ (X = CH_2, Me_2Si, Me_2C, C=O, etc.), $[Me_2C(C_5H_4)(C_9H_6)]$ and a fulvalendiyl ligand

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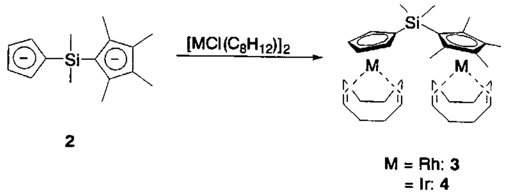


Scheme 1.

$[C_5H_4–C_5H_4]$ have often been employed [1–3]. We have been interested in the use of bridged unsymmetrical bis(η^5-cyclopentadienyl) ligands $[Me_2Si(C_5H_4)(C_5Me_4)]$ because differences in the steric and electronic effects of each of the cyclopentadienyl moieties may facilitate preparation of heterodinuclear metal complexes and make it possible to insert different reactivity into each metal center. We report here the synthesis of homo- and heterodinuclear metal complexes by metathesis reaction of the dianion of $[Me_2Si(C_5H_5)(C_5HMe_4)]$ with metal complex halides.

2. Results and discussion

2.1. Synthesis of homodinuclear metal complexes of rhodium and iridium

Dimethylsilylene-bridged unsymmetrical bis(cyclopentadiene) $[Me_2Si(C_5H_5)(C_5HMe_4)]$ (**1**), having a simple cyclopentadiene moiety and a bulky and electron-donating tetramethylcyclopentadiene moiety, was prepared by the literature method [4]. The dilithium derivative $Li_2[Me_2Si(C_5H_4)(C_5Me_4)]$ (**2**), prepared in situ from **1** and *n*-BuLi, reacted with $[MCl(C_8H_{12})]_2$ (M = Rh, Ir) to form dinuclear rhodium and iridium complexes $[\{Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5Me_4)\}\{M(C_8H_{12})\}_2]$ (M = Rh: **3**; M = Ir: **4**) (Scheme 1). The ^{1}H-NMR spectrum of rhodium complex **3** shows peaks at 3.94 and 2.97 ppm assignable to the olefinic protons of 1,5-cyclooctadiene coordinated to Rh centers. The corresponding peaks of $(C_8H_{12})Rh(\eta^5\text{-}C_5H_5)$ and $(C_8H_{12})Rh(\eta^5\text{-}C_5Me_5)$ are reported to appear at 3.97 and 2.95 ppm, respectively [5,6]. Therefore, the lower field peak at 3.94 is ascribed to the olefinic protons of the cyclopentadienylrhodium side and the higher field peak at 2.97 ppm to those of the tetramethylcyclopentadienylrhodium side. In the same way, the peaks at 3.76 and 2.80 ppm in iridium complex **4** are assigned to the olefinic protons of 1,5-cyclooctadiene coordinated to the $(\eta^5\text{-}C_5H_4)$Ir and $(\eta^5\text{-}C_5Me_4)$Ir centers, respectively, because the mononuclear iridium complexes $(C_8H_{12})Ir(\eta^5\text{-}C_5H_5)$ and $(C_8H_{12})Ir(\eta^5\text{-}C_5Me_5)$ show the corresponding peaks at 3.78 and 2.73 ppm, respectively

Table 1
Selected bond lengths (Å) and bond angles (°) for **3**

Bond lengths			
Rh1–C1	2.296(7)	Rh2–C6	2.276(7)
Rh1–C2	2.261(7)	Rh2–C7	2.219(7)
Rh1–C3	2.278(7)	Rh2–C8	2.288(7)
Rh1–C4	2.278(8)	Rh2–C9	2.281(8)
Rh1–C5	2.212(7)	Rh2–C10	2.224(8)
Rh1–C17	2.131(8)	Rh2–C25	2.119(7)
Rh1–C18	2.132(8)	Rh2–C26	2.119(7)
Rh1–C21	2.110(7)	Rh2–C29	2.139(10)
Rh1–C22	2.120(9)	Rh2–C30	2.132(9)
C1–Si	1.861(7)	C6–Si	1.840(7)
Bond angles			
C1–Si–C6	110.8(3)	C15–Si–C16	109.4(4)
Cp–Cp* [a]	85.31		

[a] Dihedral angle between least-squares planes.

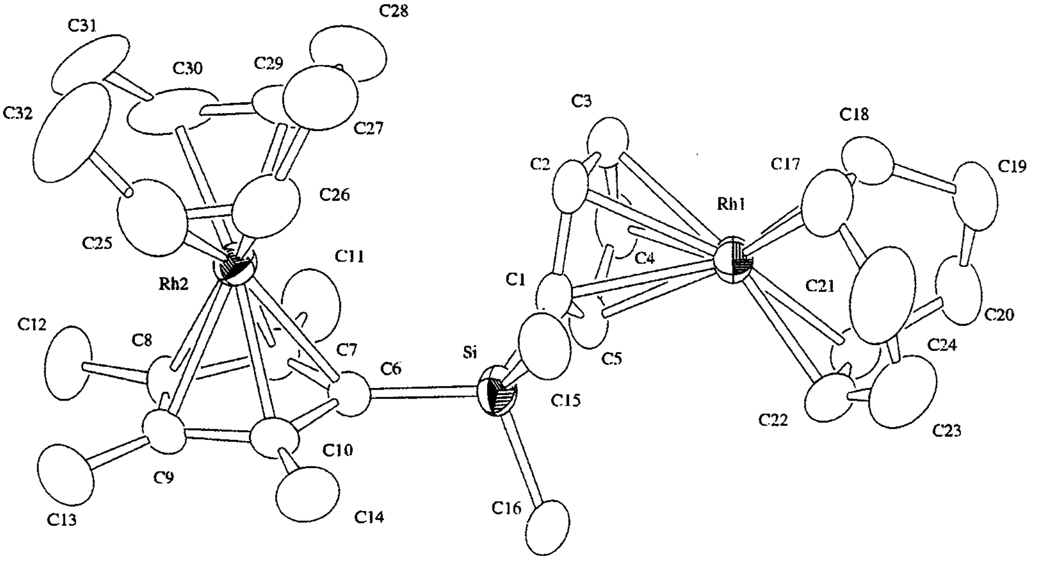


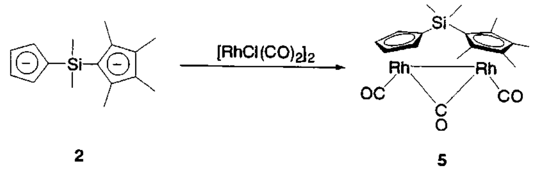
Fig. 1. ORTEP view of $[\{Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5Me_4)\}\{Rh(C_8H_{12})\}_2]$ (**3**).

[7]. The structure of **3** has been determined unequivocally by single-crystal X-ray diffraction analysis. The molecular structure is depicted in Fig. 1. Selected bond distances and angles are listed in Table 1. The two cyclopentadienyl rings are twisted with each other at a dihedral angle of 85.31°. No appreciable differences in the average Rh–C bond distances between the cyclopentadienyl and the tetramethylcyclopentadienyl parts are observed (2.265 and 2.258 Å in η^5-C_5R_4Rh and 2.123 and 2.127 Å in η^4-cod–Rh).

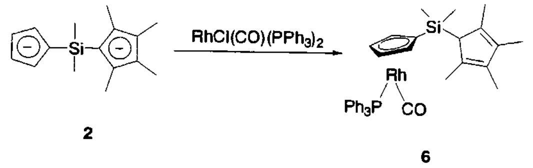
Complex **2** reacted with $[RhCl(CO)_2]_2$ at room temperature to form the dirhodium complex $[\{Me_2Si(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5Me_4)\}Rh_2(CO)_2(\mu\text{-}CO)]$ (**5**) bearing a Rh–Rh bond and a bridged carbonyl (Scheme 2). The IR spectrum of **5** shows strong absorptions at 1988, 1952 and 1792 cm^{-1} assignable to the stretching frequencies of the terminal and bridging carbonyls. The frequencies are lower than those reported for $[Me_2Si(\eta^5\text{-}C_5H_4)_2Rh_2(CO)_2(\mu\text{-}CO)]$ (2010, 1975, 1960 and 1800 cm^{-1} in KBr) [8], reflecting the existence of a stronger electron-donating tetramethylcyclopentadienyl group.

2.2. Synthesis of heterodinuclear metal complexes

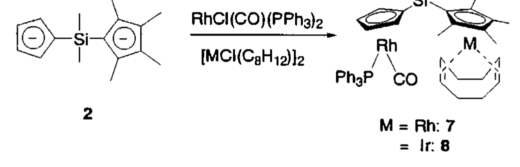
Reaction of **2** with two equivalents of $RhCl(CO)(PPh_3)_2$ failed to produce a dinuclear rhodium complex analogous to the known $[CH_2(\eta^5\text{-}C_5H_4)_2\{Rh(CO)(PPh_3)\}_2]$ [9] but afforded a mononuclear rhodium complex $[\{Me_2Si(C_5HMe_4)(\eta^5\text{-}C_5H_4)\}Rh(CO)PPh_3]$ (**6**) in which the tetramethylcyclopentadiene moiety (C_5HMe_4) was kept intact (Scheme 3). The IR spectrum shows only one strong absorption at 1933 cm^{-1} for the carbonyl group compared to that at 1942 cm^{-1} in $(\eta^5\text{-}C_5H_5)Rh(PPh_3)(CO)$. The ^{1}H-NMR spectrum shows a singlet peak at 0.12 ppm for the methyl protons of dimethylsilyl groups and two singlets at 1.72 and 1.79 ppm for the methyl protons of the non-coordinated tetramethylcyclopentadienyl groups. Two triplets ascribed to the cyclopentadienyl protons appeared at 4.80 and 5.13 ppm and a broad singlet to the proton of the uncoordinated tetramethylcyclopentadiene ring at 2.90 ppm, respectively. Failure of the formation of the expected dinuclear rhodium complex may be caused by the steric hindrance between the ancillary ligands of the rhodium halide complex and the tetramethylcyclopentadienyl anion. Previously, Werner prepared related mononuclear metal complexes from the monoanion of a bridged bis(cyclopentadiene) and employed them as the starting material to prepare heterodinuclear metal complexes through metallation of the remaining cyclopentadiene moiety [1]. However, the method requires several steps for completion. We attempted the synthesis of a dinuclear metal complex in a one-pot manner, taking advantage of the difference in reactivity of the two cyclopentadienyl moieties.



Scheme 2.



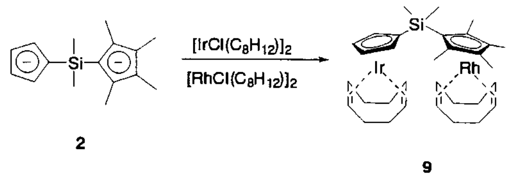
Scheme 3.



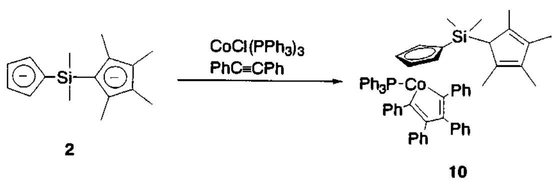
Scheme 4.

Treatment of a solution of **2** in THF with an equimolar amount of $RhCl(CO)(PPh_3)_2$ at room temperature overnight and then subsequent treatment of the resulting solution with $[RhCl(C_8H_{12})]_2$ at reflux for 5 h afforded a dinuclear rhodium complex $[Rh(CO)PPh_3\{(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5Me_4)\}Rh(C_8H_{12})]$ (**7**) in which the two rhodium centers carried different ligands (Scheme 4).

However, similar treatment of the dianion **2** with $RhCl(CO)(PPh_3)_2$ and $[IrCl(C_8H_{12})]_2$ failed to give the corresponding heteronuclear complex and provided **6** together with an iridium phosphine complex $IrCl(PPh_3)(C_8H_{12})$. It is reasonable to assume that the dissociated phosphine from $RhCl(CO)(PPh_3)_2$ in the initial step reacts with $[IrCl(C_8H_{12})]_2$ to afford $IrCl(PPh_3)(C_8H_{12})$ of low reactivity. We obtained the intended heterodinuclear metal complex $[Rh(CO)PPh_3\{(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5Me_4)\}Ir(C_8H_{12})]$ (**8**) by using excess $[IrCl(C_8H_{12})]_2$. The ^{1}H-NMR spectra of **7** and **8**, respectively, show peaks at 2.94 and 3.77 ppm for the olefinic protons of 1,5-cyclooctadiene. In comparison with the spectra of **3** and **4**, those resonances are assignable to the olefinic protons of 1,5-cyclooctadiene bound to the tetramethylcyclopentadienyl metal center. Similar treatment of **2** with $[RhCl(C_8H_{12})]_2$ and then with $[IrCl(C_8H_{12})]_2$ gave a mixture of the desired heterodinuclear metal complex and homodinuclear metal complex **3**. This may be due to the high reactivity of $[RhCl(C_8H_{12})]_2$ toward both cyclopentadieneyl moieties. We were not successful in separating them by column



Scheme 5.



Scheme 6.

chromatography or recrystallization. The treatment of **2** with $[IrCl(C_8H_{12})]_2$ and then with $[RhCl(C_8H_{12})]_2$ afforded the heterodinuclear complex $[Ir(C_8H_{12})\{(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5Me_4)\}Rh(C_8H_{12})]$ (**9**) in a good yield (Scheme 5).

It is well established that the reaction of $CoCl(PPh_3)_3$ with alkali metal cyclopentadienide provides bis(triphenylphosphine)(η^5-cyclopentadienyl)cobalt and that subsequent treatment of the complex with PhC≡CPh affords (triphenylphosphine)(η^5-cyclopentadienyl)tetraphenylcobaltacyclopentadiene [10]. However, the preparation of the corresponding bis-phosphine cobalt complex of the bulky C_5Me_5 ligand was not successful for steric reasons. In accord with these facts, the treatment of **2** with $CoCl(PPh_3)_3$ in the presence of PhC≡CPh afforded only the mononuclear cobalt complex $[\{Me_2Si(C_5HMe_4)(\eta^5\text{-}C_5H_4)\}Co(CPh{=}CPh{-}CPh{=}CPh)PPh_3]$ (**10**) in which the C_5HMe_4 moiety was kept intact (Scheme 6). The ^{1}H-NMR spectrum shows a singlet at 0.54 ppm for the six methyl protons of the dimethylsilyl group, two singlets at 1.67 and 1.79 ppm for the 12 methyl protons of the tetramethylcyclopentadiene groups, a broad singlet at 2.94 ppm for the one proton of the tetramethylcyclopentadiene ring and a broad singlet at 4.61 ppm for the four cyclopentadienyl protons. The X-ray crystal structure analysis of **10** resulted in poor resolution but revealed the structure unequivocally. We attempted the synthesis of a heterodinuclear complex containing cobalt and rhodium in a one-pot manner through the anion of **10** as the intermediate.

Reaction of **2** with $CoCl(PPh_3)_3$ and PhC≡CPh in THF for 8 h at room temperature and then with $[RhCl(C_8H_{12})]_2$ overnight afforded a reddish-brown crystalline compound. The IR and NMR spectra as well as the elemental analysis suggested the formation of a heterodinuclear complex of the formula $[\{(\eta^5\text{-}C_5H_4)Me_2Si(\eta^5\text{-}C_5Me_4)\}Rh(C_8H_{12})Co(\eta^4\text{-}C_4Ph_4)]$ (**11**), where the expected cobaltacyclopentadiene structure was transformed into the η^4-cyclobutadienecobalt structure. Similarly, the iridium analog $[(\eta^5\text{-}C_5H_4)Me_2Si(\eta^5\text{-}C_5Me_4)\}Co(\eta^4\text{-}C_4Ph_4)Ir(C_8H_{12})]$ (**12**) was prepared. The structures of **11** and **12** have been determined by single-crystal X-ray diffraction analysis. The molecular structures are depicted in Figs. 2 and 3. Selected bond distances and angles are listed in Tables 2 and 3. Originally, we considered structure **A** for these complexes, but unexpectedly, the X-ray crystallographic analysis revealed structure **B**, suggesting the involvement of an intraligand cobalt metal transfer reaction. Simple heating of mononuclear complex **10** at toluene reflux gave the (η^5-cyclopentadienyl)cobalt(η^4-cyclobu-

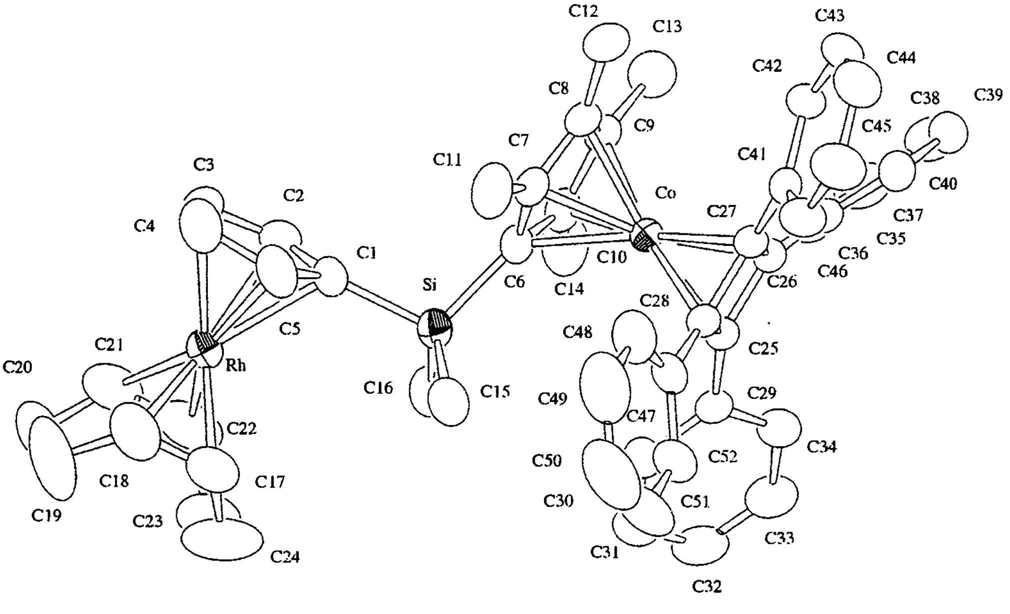


Fig. 2. ORTEP view of $[Rh(C_8H_{12})\{(\eta^5\text{-}C_5H_4)Me_2Si(\eta^5\text{-}C_5Me_4)\}Co(\eta^4\text{-}C_4Ph_4)]$ (**11**).

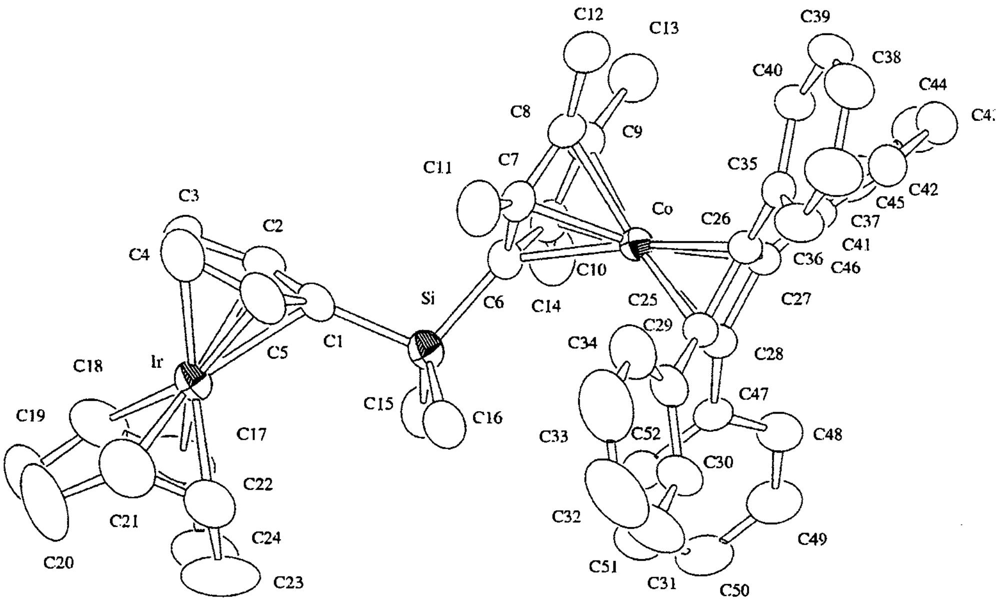
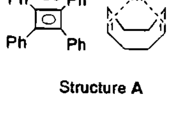
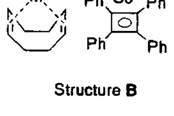


Fig. 3. ORTEP view of $[Ir(C_8H_{12})\{(\eta^5\text{-}C_5H_4)Me_2Si(\eta^5\text{-}C_5Me_4)\}Co(\eta^4\text{-}C_4Ph_4)]$ (**12**).

tadiene) complex $[Co(\eta^4\text{-}C_4Ph_4)\{(\eta^5\text{-}C_5H_4)Me_2Si(C_5Me_4H)\}]$ (**13**). However, when **2** was heated with $CoCl(PPh_3)_3$ and PhC≡CPh in THF or kept at ambient temperature for several days, $[\{(C_5H_5)Me_2Si(\eta^5\text{-}C_5Me_4)\}Co(\eta^4\text{-}C_4Ph_4)]$ (**14**) was obtained after hydrolysis, which had the same composition as **13** but a different structure. The ^{1}H-NMR spectrum of **13** shows peaks at 4.63 and 4.70 ppm assignable to the protons of the η^5-cyclopentadienyl ring; however, the spectrum of **14** shows no corresponding peaks but exhibits peaks at 6.20 and 6.50 ppm, which are assignable to the olefinic protons of the cyclopentadiene ring. The peaks ascribable to the aliphatic proton of the cyclopentadiene rings appear at 2.73 ppm in **13** and 3.42 ppm in **14**. The corresponding peak of **6** appeared at 2.90 ppm. Based on the NMR data, we deduced that the η^4-tetraphenylcyclobutadiene cobalt moiety was connected to the cyclopentadienyl site in **13** and to the tetramethylcyclopentadienyl site in **14** (Schemes 7 and 8).



Structure A



Structure B

We suggest the mechanism of the intraligand cobalt transfer from cyclopentadienyl to tetramethylcyclopentadienyl groups as shown in Scheme 9. The driving force of the cobalt transfer may arise from the formal trivalent state of cobalt in the cobaltacyclopentadiene structure, which prefers a more electron-rich tetramethylcyclopentadienyl site. The transformation may be assisted by the presence of $[MCl(C_8H_{12})]_2$ (M =

Table 2
Selected bond lengths (Å) and bond angles (°) for **11**

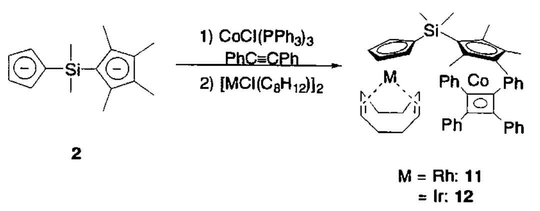
Bond lengths			
Rh–C1	2.287(4)	Rh–C17	2.116(4)
Rh–C2	2.257(4)	Rh–C18	2.099(4)
Rh–C3	2.276(5)	Rh–C21	2.089(5)
Rh–C4	2.250(5)	Rh–C22	2.111(5)
Rh–C5	2.191(4)		
Co–C6	2.092(3)	Co–C25	1.993(3)
Co–C7	2.075(3)	Co–C26	2.000(3)
Co–C8	2.098(4)	Co–C27	1.997(3)
Co–C9	2.084(4)	Co–C28	1.996(3)
Co–C10	2.066(4)		
Bond angle			
Cp–Cp* [a]	92.05		

[a] Dihedral angle between least-squares planes.

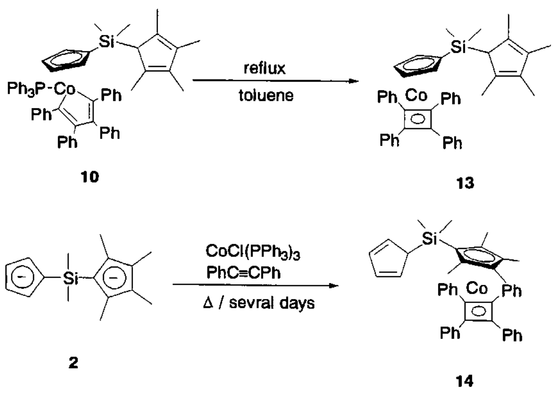
Table 3
Selected bond lengths (Å) and bond angles (°) for **12**

Bond lengths			
Ir–C1	2.266(3)	Ir–C17	2.115(4)
Ir–C2	2.270(4)	Ir–C18	2.080(4)
Ir–C3	2.292(4)	Ir–C21	2.109(4)
Ir–C4	2.254(4)	Ir–C22	2.114(4)
Ir–C5	2.190(4)		
Co–C6	2.088(3)	Co–C25	1.993(3)
Co–C7	2.080(3)	Co–C26	2.003(3)
Co–C8	2.093(3)	Co–C27	2.004(3)
Co–C9	2.086(3)	Co–C28	2.000(3)
Co–C10	2.064(3)		
Bond angle			
Cp–Cp* [a]	91.74		

[a] Dihedral angle between least-squares planes.

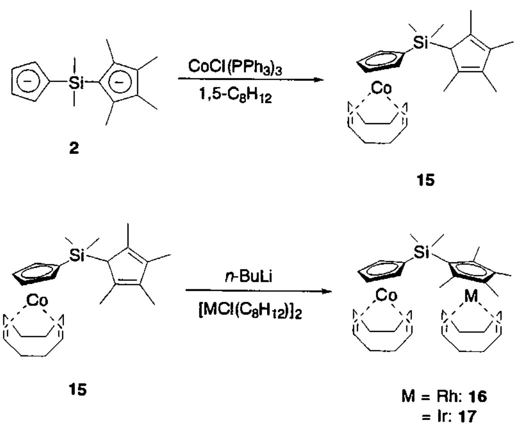


Scheme 7.



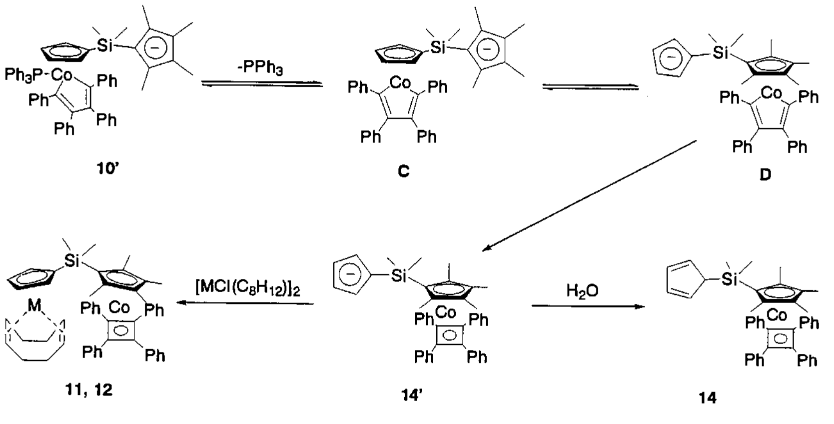
Scheme 8.

Rh, Ir) behaving as a phosphine sponge. Initial product of the reaction of **2** with $CoCl(PPh_3)_3$ and PhC≡CPh may be a cobaltacyclopentadiene complex (**10′**) in which the cobalt moiety is connected to the sterically less bulky cyclopentadienyl group and stabilized by the coordination of PPh_3. Dissociation of PPh_3 from **10′** gives an equilibrium mixture of cobaltacyclopentadienes in which the cobalt moiety is connected to the cyclopentadienyl and the tetramethylcyclopentadienyl groups, respectively (**C** and **D**). **D** cannot be stabilized by PPh_3 for steric reason and gradually changes to the corresponding cobalt cyclobutadiene complex (**14′**). The reaction of either **C** or **14′** with $[MCl(C_8H_{12})]_2$ may produce **11** and **12**.



Scheme 10.

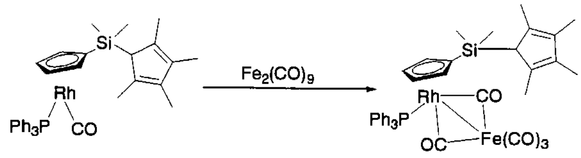
The dilithium anion **2** reacted with $CoCl(PPh_3)_3$ in the presence of 1,5-cyclooctadiene to yield mononuclear complex $[(C_5Me_4H)Me_2Si\{(\eta^5\text{-}C_5H_4)Co(C_8H_{12})\}]$ (**15**), in which the tetramethylcyclopentadiene moiety was left intact (Scheme 10). The ^{1}H-NMR spectrum of **15** shows a singlet at 0.89 ppm for the methyl protons of the dimethylsilyl group and two singlets at 1.79 and 2.73 ppm for the methyl protons of the tetramethylcyclopentadiene group. A broad singlet at 2.94 ppm for the aliphatic proton of the tetramethylcyclopentadiene ring has the same value as that in **10**. The treatment of mononuclear complex **15** with *n*-BuLi in THF solution at room temperature and then with $[MCl(C_8H_{12})]_2$ (M = Rh, Ir) afforded heterodinuclear metal cyclooctadiene complexes $[Co(C_8H_{12})\{(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5Me_4)\}M(C_8H_{12})]$ (M = Rh: **16**, M = Ir: **17**) (Scheme 10). The ^{1}H-NMR spectra of **16** and **17** are similar. In comparison with the spectrum of **15**, the resonance of the methyl protons of the dimethylsilyl group shifted to a lower field (0.46 (**15**), 0.89 (**16**) and 0.85 (**17**) ppm), and the resonances of the methyl protons for tetramethylcyclopentadienyl shifted to an upper field (1.79, 2.73 (**15**), 1.43, 1.87 (**16**) and 1.54, 1.90 (**17**) ppm).



Scheme 9.

2.3. Synthesis of heteronuclear metal complexes containing rhodium and iron

The reaction of **6** with $Fe_2(CO)_9$ at room temperature afforded a heterodinuclear complex containing both rhodium and iron, $[\{Me_2Si(C_5HMe_4)(\eta^5\text{-}C_5H_4)\}\{Rh(PPh_3)(\mu\text{-}CO)_2Fe(CO)_3\}]$ (**18**), in which the C_5HMe_4 moiety was left intact (Scheme 11). $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$ is reported to react with $Fe_2(CO)_9$ to form the dinuclear complex $[Fe(CO)_3(\mu\text{-}CO)_2Rh(CO)(\eta^5\text{-}C_5Me_5)]$ [11]. The IR spectrum of **18** shows strong absorptions at 2021, 1955, 1945, 1811 and 1782 cm^{-1} in KBr and 2030, 1961, 1806 and 1777 cm^{-1} in $CHCl_3$, assignable to terminal and bridging CO ligands. Lower frequencies than those of $[Fe(CO)_3(\mu\text{-}CO)_2Rh(CO)(\eta^5\text{-}C_5Me_5)]$ (2053, 2017, 1979, 1961, 1835 and 1825 cm^{-1}) are ascribed to the replacement of one CO by one triphenylphosphine ligand. Complex **18** has been characterized by X-ray analysis. The selected bond distances and angles are tabulated in Table 4. The molecular structure is depicted in Fig. 4. The C_5Me_4H moiety was kept intact and the sp^3 carbon bearing a hydrogen atom was connected to the silicon atom. The Fe–Rh bond length (2.612(2) Å) is slightly greater than that found in a similar complex $[(\eta^5\text{-}C_5H_5)(P^iPr_3)Rh(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)Fe(CO)_3]$ (2.604(1) Å) [12]. The metal-bridging carbonyl bond distances of Rh–C(35) (2.103(8) Å) and Rh–C(36) (2.090(9) Å) are longer than those of Fe–C(35) (1.901(9) Å) and Fe–C(36) (1.922(9) Å). Also, the angles of Rh–C(35)–O(1) (127.9(7)°) and Rh–C(36)–O(2) (133.2(7)°) are smaller than those of Fe–C(35)–O(1) (149.9(8)°) and Fe–C(36)–O(2) (145.3(8)°). The bridging carbonyls are semi-bridging to the Rh center, because the Rh core has a high electron density.



6 **18**

Scheme 11.

Table 4
Selected bond lengths (Å) and bond angles (°) for **18**

Bond lengths			
Rh–Fe	2.612(2)	Rh–C35	2.103(8)
Rh–C1	2.325(8)	Rh–C36	2.090(9)
Rh–C2	2.245(8)	Fe–C35	1.901(9)
Rh–C3	2.251(9)	Fe–C36	1.922(9)
Rh–C4	2.278(9)	Fe–C39	1.79(1)
Rh–C5	2.233(9)	C1–Si	1.865(9)
Rh–P	2.312(3)	C6–Si	1.913(9)
Bond angles			
C1–Si–C6	104.1(4)		
Rh–C35–Fe	81.2(3)	Rh–C36–Fe	81.3(3)
Rh–C35–O1	127.9(7)	Fe–C35–O1	149.9(8)
Rh–C36–O2	133.2(7)	Fe–C36–O2	145.3(8)
Cp–Cp* [a]	29.6		

[a] Dihedral angle between least-squares planes.

Dinuclear rhodium complex **5** reacted with $Fe_2(CO)_9$ at room temperature to form heterotrinuclear complex $[\{(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5Me_4)\}\{Rh(CO)Rh(\mu\text{-}CO)_2\text{-}Fe(CO)_3\}]$ (**19**) (Scheme 12). The IR spectra showed CO stretching absorptions at 2027, 1977, 1967, 1832 and 1784 cm^{-1} in KBr and 2043, 1990, 1826 and 1775 cm^{-1} in $CHCl_3$. Compared with the IR spectra of $[(\eta^5\text{-}C_5Me_5)_2Rh_2Fe(CO)_6]$ which has a face-capped carbonyl (2051, 2019, 1993, 1971, 1953, 1837, 1801 and 1690 cm^{-1} in hexane) [11] and those of $[(\eta^5\text{-}C_5H_5)_2Rh_2Fe(CO)_6]$ which has no such face-capped carbonyl (2054, 2002, 1989, 1980, 1839 and 1792 cm^{-1}) [13], the structure of **19** is estimated to consist of two bridging carbonyls and four terminal carbonyls. An unequivocal structure of **19** was obtained by X ray crystallographic analysis (Fig. 5). Selected bond distances and angles are listed in Table 5. The Rh–Rh bond length of 2.6600(5) Å is slightly greater than the lengths of 2.648(3) and 2.650(1) Å found in the tetranuclear complex $(\eta^5\text{-}C_5H_5)_2Rh_2Fe_2(CO)_8$ [13] and the dinuclear complex $[CH_2(\eta^5\text{-}C_5H_4)Rh_2(CO)_2(\mu\text{-}CO)]$ [12], respectively. The Rh(2)–Fe bond length (2.5922(9)) is shorter than the Rh(1)–Fe bond length (2.6960(8) Å), in accord with the location of the two bridging carbonyls between the Rh(2) and the Fe metal centers. It is reasonable to find a bridging carbonyl on the Rh(2) center bearing an electron-rich ancillary ligand because a bridging carbonyl draws more electrons than does a terminal one.

3. Experimental

3.1. General procedures

All reactions were carried out under an atmosphere of N_2 by Schlenk tube techniques. The starting materials $Me_2Si(C_5H_5)(C_5HMe_4)$ (**1**) [4], $Fe_2(CO)_9$ [14], $CoCl(PPh_3)_3$ [15], $[RhCl(C_8H_{12})]_2$ [16], $[RhCl(CO)_2]_2$ [17], *trans*-$RhCl(CO)(PPh_3)_2$ [18] and $[IrCl(C_8H_{12})]_2$ [19] were prepared according to the literature procedures. THF was distilled over sodium benzophenone ketyl under N_2.

^{1}H-NMR spectra were recorded on a JOEL JNM-GSX400 spectrometer. IR spectra were recorded on JASCO A-202 and Shimadzu FTIR-8100M. Elemental

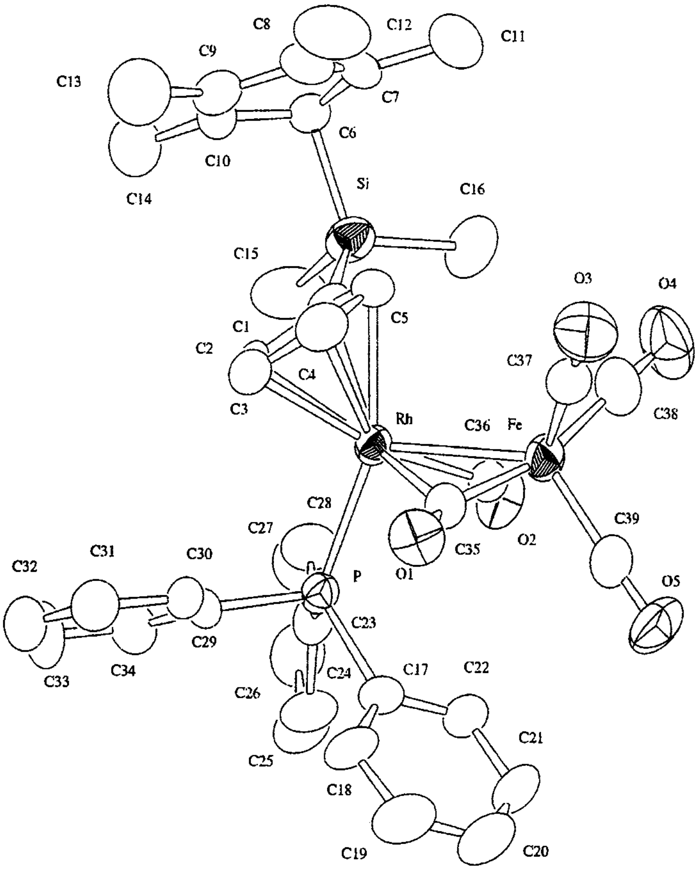


Fig. 4. ORTEP view of [{$Me_2Si(C_5HMe_4)(\eta^5$-$C_5H_4)$}{$Rh(PPh_3)(\mu$-$CO)_2Fe(CO)_3$}] (**18**).

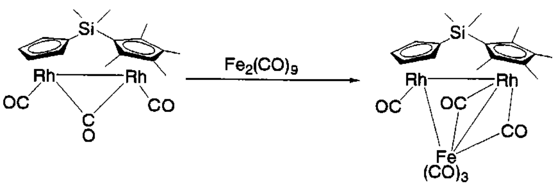
analyses were done with a Yanaco CHN CORDER MT-5.

3.2. [{$Me_2Si(\eta^5$-$C_5H_4)(\eta^5$-$C_5Me_4)$}{$Rh_2(C_8H_{12})_2$}] (3)

A solution of **1** (0.24 g, 0.98 mmol) in THF was treated with *n*-BuLi (1.63 M, 1.4 ml, 2.14 mmol) in hexane at 0 °C, and the resulting solution was stirred overnight at room temperature (r.t.). A solution of $[RhCl(C_8H_{12})]_2$ (0.51 g, 1.03 mmol) in THF was added to the above reaction mixture and heated at reflux for 5 h. After the reaction mixture was evaporated and dissolved in C_6H_6, the solution was hydrolyzed with a saturated aqueous solution of NH_4Cl, and the organic layer was separated and dried over Na_2SO_4. After concentration, the residue was chromatographed on alumina. The yellow eluate by hexane was concentrated and kept under refrigeration to give yellow crystals of **3**, 0.23 g (0.35 mmol, 36%); m.p. 168 °C. Anal. Found: C, 56.92; H, 6.72. Calc. for $C_{32}H_{46}SiRh_2$: C, 57.83; H, 6.98%. ^{1}H-NMR ($CDCl_3$): δ 0.67 (s, 6H, $SiMe_2$), 1.44 (s, 6H, C_5Me_4), 1.88 (s, 6H, C_5Me_4), 1.91 (m, 8H, C_8H_{12}), 2.19 (m, 8H, C_8H_{12}), 2.97 (m, 4H, C_8H_{12}), 3.94 (m, 4H, C_8H_{12}), 4.80 (s, 2H, C_5H_4), 5.43 (s, 2H, C_5H_4).

3.3. [{$Me_2Si(\eta^5$-$C_5H_4)(\eta^5$-$C_5Me_4)$}{$Ir_2(C_8H_{12})_2$}] (4)

The dilithium salt, prepared from **1** (0.26 g, 1.07 mmol) and *n*-BuLi (1.53 M, 1.4 ml, 2.14 mmol) in THF, was treated with $[IrCl(C_8H_{12})]_2$ (0.86 g, 1.28 mmol) and heated at reflux for 8 h. After the solvent was removed, the residue was dissolved in a small amount of C_6H_6 and chromatographed on alumina. The pale yellow eluate by hexane was concentrated and kept under refrigeration to give white crystals of **4**, 0.20 g (0.24 mmol, 22%); m.p. 172 °C. Anal. Found: C, 45.75; H, 5.65. Calc. for $C_{32}H_{46}SiIr_2$: C, 45.58; H, 5.50%. ^{1}H-NMR ($CDCl_3$): δ 0.59 (s, 6H, $SiMe_2$), 1.57 (s, 6H, C_5Me_4), 1.91 (s, 6H, C_5Me_4), 1.80 (m, 8H, C_8H_{12}), 2.05 (m, 8H, C_8H_{12}), 2.80 (m, 4H, C_8H_{12}), 3.76



5 **19**

Scheme 12.

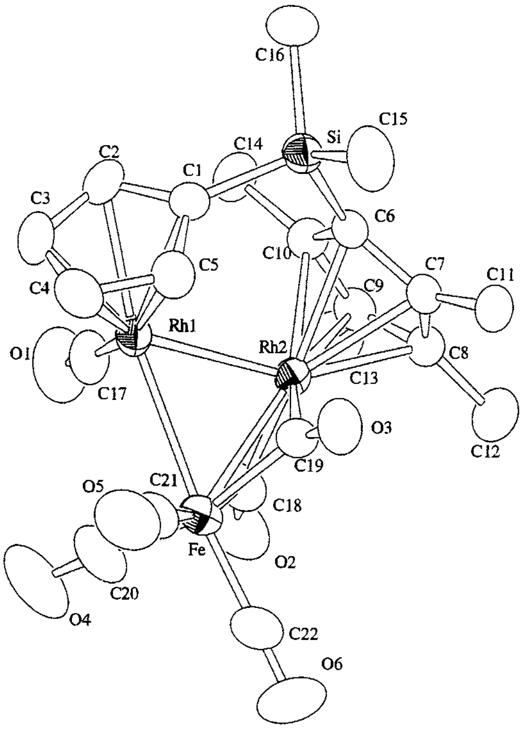


Fig. 5. ORTEP view of [Rh(CO){(η^5-C_5H_4)$SiMe_2$(η^5-C_5Me_4)}{Rh(μ-$CO)_2Fe(CO)_3$}] (**19**).

Table 5
Selected bond lengths (Å) and bond angles (°) for **19**

Bond lengths			
Rh1–Rh2	2.6600(5)	Rh1–Fe1	2.6960(8)
Rh2–Fe1	2.5922(9)		
Rh1–C1	2.277(4)	Rh2–C6	2.229(4)
Rh1–C2	2.216(5)	Rh2–C7	2.284(4)
Rh1–C3	2.245(5)	Rh2–C8	2.273(4)
Rh1–C4	2.282(5)	Rh2–C9	2.269(4)
Rh1–C5	2.238(5)	Rh2–C10	2.225(4)
Rh1–C17	1.823(6)	Rh2–C18	1.940(5)
Rh2–C19	2.018(4)	Rh2–C18	2.101(5)
Fe–C19	1.951(5)		
C1–Si	1.876(5)	C6–Si	1.880(4)
Bond angles			
Rh1–Fe–Rh2	60.36(2)	Rh1–Rh2–Fe	61.75(2)
Rh2–Rh1–Fe	57.88(2)	C1–Si–C6	108.6(2)
Fe–C18–Rh2	79.7(2)	Fe–C19–Rh2	81.5(2)
Rh2–C18–O2	144.0(4)	Rh2–C19–O3	134.9(4)
Fe–C18–O2	136.3(4)	Fe–C19–O3	143.6(4)
Cp–Cp* [a]	79.84		

[a] Dihedral angle between least-squares planes.

(m, 4H, C_8H_{12}), 4.80 (t, 2H, $J = 1.7$ Hz, C_5H_4), 5.46 (t, 2H, $J = 1.7$ Hz, C_5H_4).

3.4. [{Me_2Si(η^5-C_5H_4)(η^5-C_5Me_4)}$Rh_2(CO)_2$(μ-CO)] (**5**)

The dilithium salt, prepared from **1** (0.37 g, 1.52 mmol) and *n*-BuLi (1.66 M, 2.1 ml, 3.49 mmol) in THF, was treated with $[RhCl(CO)_2]_2$ (0.60 g, 1.54 mmol) overnight. After the solution was evaporated, the residue was dissolved in a small amount of C_6H_6 and chromatographed on alumina. The black eluate by hexane–C_6H_6 (1:2) was evaporated, and the residue was crystallized from hexane to give black crystals of **5**, 0.08 g (0.15 mmol, 10%). Anal. Found: C, 42.94; H, 4.19. Calc. for $C_{19}H_{22}O_3SiRh_2$: C, 42.87; H, 4.17%. ^{1}H-NMR ($CDCl_3$): δ 0.55 (s, 6H, $SiMe_2$), 1.96 (s, 6H, C_5Me_4), 2.15 (s, 6H, C_5Me_4), 5.36 (s, 2H, C_5H_4), 6.03 (s, 2H, C_5H_4). IR (nujol, cm^{-1}): ν_{CO} 1988, 1952, 1792.

3.5. [{Me_2Si(C_5HMe_4)(η^5-C_5H_4)}Rh(CO)PPh_3] (**6**)

The dilithium salt, prepared from **1** (1.27 g, 5.21 mmol) and *n*-BuLi (1.65 M, 4.8 ml, 7.92 mmol) in THF, was treated with $RhCl(CO)(PPh_3)_2$ (3.45 g, 5.00 mmol) at reflux for 6 h. The reaction mixture was removed and dissolved in C_6H_6, and the solution was hydrolyzed with a saturated aqueous solution of NH_4Cl. The organic layer was separated and dried over Na_2SO_4. After concentration, the solution was chromatographed on alumina. The red eluate by hexane was evaporated, and the residue was crystallized from hexane to give orange crystals of **6**, 1.89 g (2.81 mmol, 56%); m.p. 108 °C. Anal. Found: C, 65.17; H, 6.09. Calc. for $C_{35}H_{38}OPSiRh$: C, 65.03; H, 6.02%. ^{1}H-NMR ($CDCl_3$): δ 0.12 (s, 6H, $SiMe_2$), 1.72 (s, 6H, C_5Me_4), 1.79 (s, 6H, C_5Me_4), 2.90 (br, 1H, Me_4C_5H), 4.81 (s, 2H, C_5H_4), 5.13 (s, 2H, C_5H_4), 7.32–7.58 (m, 15H, P–Ph_3). IR (KBr, cm^{-1}): ν_{CO} 1933.

3.6. [Rh(CO)PPh_3{(η^5-C_5H_4)$SiMe_2$(η^5-C_5Me_4)}-Rh(C_8H_{12})] (7)

The dilithium salt, prepared from **1** (0.12 g, 0.49 mmol) and *n*-BuLi (1.63 M, 0.8 ml, 1.30 mmol) in THF, was treated with $RhCl(CO)(PPh_3)_2$ (0.36 g, 0.52 mmol) in C_6H_6 at r.t. for 1 day. The solution of $[RhCl(C_8H_{12})]_2$ (0.12 g, 0.24 mmol) in C_6H_6 was then added to the mixture and heated at reflux for 5 h. The reaction mixture was hydrolyzed with a saturated aqueous solution of NH_4Cl. The organic layer was separated and dried over Na_2SO_4. After concentration of the solution, the residue was chromatographed on alumina. The yellow eluate by hexane–C_6H_6 (1:1) was evaporated to dryness, and the residue was crystallized from hexane to give orange crystals of **7**, 0.09 g (0.11 mmol, 23%); m.p. 145 °C. Anal. Found: C, 61.49; H, 6.11. Calc. for $C_{43}H_{49}OPSiRh_2$: C, 61.00; H, 5.83%. IR (nujol, cm^{-1}): ν_{CO} 1952. ^{1}H-NMR ($CDCl_3$): δ 0.56 (s, 6H, $SiMe_2$), 1.41 (s, 6H, C_5Me_4), 1.87 (s, 6H, C_5Me_4), 4.95 (s, 2H, C_5H_4), 5.17 (s, 2H, C_5H_4), 1.92 (m, 4H, C_8H_{12}), 2.15 (m, 4H, C_8H_{12}), 2.94 (m, 4H, C_8H_{12}), 7.37–7.61 (m, 15H, P–Ph_3).

3.7. $[Rh(CO)PPh_3\{(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5Me_4)\}\text{-}Ir(C_8H_{12})]$ (**8**)

The dilithium salt, prepared from **1** (0.22 g, 0.90 mmol) and *n*-BuLi (1.53 M, 1.2 ml, 1.84 mmol) in THF, was treated with a solution of $RhCl(CO)(PPh_3)_2$ (0.90 g, 1.30 mmol) at reflux for 4 h. $[IrCl(C_8H_{12})]_2$ (0.90 g, 2.68 mmol) was added to the reaction mixture and heated at reflux for 8 h. After the solvent was removed, the residue was dissolved in a small amount of C_6H_6 and chromatographed on alumina. The dark yellow eluate by hexane–C_6H_6 (3:1) was evaporated and crystallized from hexane–C_6H_6 to give orange crystals of **8**, 0.31 g (0.33 mmol, 37%); m.p. 243 °C. Anal. Found: C, 55.50; H, 5.39. Calc. for $C_{43}H_{49}OPSiIrRh$: C, 55.18; H, 5.28%. IR (KBr, cm^{-1}): ν_{CO} 1953. ^1H-NMR ($CDCl_3$): δ 0.52 (s, 6H, $SiMe_2$), 1.53 (s, 6H, C_5Me_4), 1.90 (s, 6H, C_5Me_4), 4.92 (s, 2H, C_5H_4), 5.17 (s, 2H, C_5H_4), 1.80 (d, 4H, C_8H_{12}), 2.02 (m, 4H, C_8H_{12}), 2.76 (br, 4H, C_8H_{12}), 7.37 (m, 9H, PPh_3), 7.58 (m, 6H, PPh_3).

3.8. $[Ir(C_8H_{12})\{(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5Me_4)\}Rh(C_8H_{12})]$ (**9**)

The dilithium salt, prepared from **1** (0.15 g, 0.61 mmol) and *n*-BuLi (1.69 M, 0.7 ml, 1.18 mmol) in THF, was treated with $[IrCl(C_8H_{12})]_2$ (0.20 g, 0.30 mmol) in C_6H_5Me for 5 h. $[RhCl(C_8H_{12})]_2$ (0.12 g, 0.24 mmol) was added to the resulting mixture and stirred overnight. After the reaction mixture was removed and dissolved in C_6H_6, the solution was hydrolyzed with a saturated aqueous solution of NH_4Cl, and the organic layer was separated and dried over Na_2SO_4. After concentration, the residue was chromatographed on alumina. The pale yellow eluate by hexane was concentrated and kept in a refrigerator to give yellow crystals of **9**, 0.20 g (0.27 mmol, 56%); m.p. 175 °C. Anal. Found: C, 50.55; H, 6.07. Calc. for $C_{32}H_{46}SiIrRh$: C, 50.98; H, 6.15%. ^1H-NMR ($CDCl_3$): δ 0.62 (s, 6H, $SiMe_2$), 1.46 (s, 6H, C_5Me_4), 1.89 (s, 6H, C_5Me_4), 4.82 (s, 2H, C_5H_4), 5.46 (s, 2H, C_5H_4), 1.79 (m, 4H, C_8H_{12}), 1.92 (m, 4H, C_8H_{12}), 2.18 (m, 4H, C_8H_{12}), 2.05 (m, 4H, C_8H_{12}), 2.97 (m, 4H, C_8H_{12}), 3.77 (m, 4H, C_8H_{12}).

3.9. $[\{Me_2Si(C_5Me_4H)(\eta^5\text{-}C_5H_4)\}Co(CPh{=}CPh{-}CPh{=}CPh)PPh_3]$ (**10**)

The dilithium salt, prepared from **1** (0.44 g, 1.80 mmol) and *n*-BuLi (1.63 M, 2.5 ml, 4.07 mmol) in THF, was treated with $CoCl(PPh_3)_3$ (1.94 g, 2.20 mmol) and $PhC{\equiv}CPh$ (1.21 g, 6.80 mmol) for 4 h. The reaction mixture was evaporated to dryness and dissolved in C_6H_6. The solution was hydrolyzed with a saturated aqueous solution of NH_4Cl. The organic layer was separated and dried over Na_2SO_4. After the concentration of the solvent, the solution was chromatographed on alumina. The reddish-brown eluate by C_6H_6–hexane (3:1) was evaporated to dryness, and the residue was crystallized from hexane–CH_2Cl_2 to give reddish-brown crystals of **10**, 0.37 g (0.56 mmol, 31%); m.p. 128 °C. Anal. Found: C, 78.43; H, 6.42. Calc. for $C_{62}H_{58}PSiCo \cdot 1/3CH_2Cl_2$: C, 78.86; H, 6.23%. ^1H-NMR ($CDCl_3$): δ 0.54 (s, 6H, $SiMe_2$), 1.67 (s, 6H, C_5Me_4), 1.79 (s, 6H, C_5Me_4), 2.94 (br, 1H, Me_4C_5H), 4.61 (s, 4H, C_5H_4), 6.33–6.83 (m, 20H, C_4–Ph_4), 7.19, 7.33 (br, 15H, PPh_3).

3.10. $[Rh(C_8H_{12})\{(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5Me_4)\}Co\text{-}(\eta^4\text{-}C_4Ph_4)]$ (**11**)

The dilithium salt, prepared from **1** (0.24 g, 1.00 mmol) and *n*-BuLi (1.59 M, 1.3 ml, 2.1 mmol), was treated with $CoCl(PPh_3)_3$ (0.90 g, 1.02 mmol) and $PhC{\equiv}CPh$ (0.78 g, 4.38 mmol) for 8 h. $[RhCl(C_8H_{12})]_2$ (0.25 g, 0.51 mmol) was then added to the mixture. The reaction mixture was stirred overnight. The solvent was removed and the residue was dissolved in C_6H_6. The solution was hydrolyzed with a saturated solution of NH_4Cl, and the organic layer was separated and dried over Na_2SO_4. After concentration, the solution was chromatographed on alumina. The brown eluate by hexane–C_6H_6 (2:1) was evaporated, and the residue was crystallized from hexane–C_6H_6 to give reddish-brown crystals of **11**, 0.15 g (0.17 mmol, 18%); m.p. 238 °C. Anal. Found: C, 71.50; H, 6.40. Calc. for $C_{52}H_{54}SiCoRh$: C, 71.88; H, 6.26%. ^1H-NMR ($CDCl_3$): δ 0.26 (s, 6H, $SiMe_2$), 1.36 (s, 6H, C_5Me_4), 1.60 (s, 6H, C_5Me_4), 4.50 (s, 2H, C_5H_4), 5.35 (s, 2H, C_5H_4), 1.85 (m, 4H, C_8H_{12}), 2.11 (m, 4H, C_8H_{12}), 3.82 (m, 4H, C_8H_{12}), 7.19–7.37 (m, 20H, C_4-Ph_4).

3.11. $[Ir(C_8H_{12})\{(\eta^5\text{-}C_5H_4)SiMe_2(\eta^5\text{-}C_5Me_4)\}Co\text{-}(\eta^4\text{-}C_4Ph_4)]$ (**12**)

The dilithium salt, prepared from **1** (0.30 g, 1.23 mmol) and *n*-BuLi (1.53 M, 1.6 ml, 2.45 mmol) in THF, was treated with $CoCl(PPh_3)_3$ (1.08 g, 1.23 mmol) and $PhC{\equiv}CPh$ (0.55 g, 3.09 mmol) overnight. After the solvent was removed, the residue was washed with dry hexane several times to remove excess PPh_3 and again dissolved in THF. $[IrCl(C_8H_{12})]_2$ (1.01 g, 1.50 mmol) was added to the reaction solution and heated at reflux for 8 h. The solvent was evaporated, and the residue was dissolved in a small amount of C_6H_6 and chromatographed on alumina. The yellow eluate by hexane–C_6H_6 (7:1) was evaporated and crystallized from hexane–C_6H_6 to give reddish-brown crystals of **12**, 0.17 g (0.18 mmol, 15%); m.p. 243 °C. Anal. Found: C, 65.46; H, 5.80. Calc. for $C_{52}H_{54}SiCoIr$: C, 65.18; H, 5.68%. ^1H-NMR ($CDCl_3$): δ 0.23 (s, 6H, $SiMe_2$), 1.37 (s, 6H, C_5Me_4), 1.60 (s, 6H, C_5Me_4), 4.51 (t, 2H, $J = 1.7$

Hz, C_5H_4), 5.36 (s, 2H, $J = 1.8$ Hz, C_5H_4), 1.73 (m, 4H, C_8H_{12}), 1.98 (m, 4H, C_8H_{12}), 3.65 (m, 4H, C_8H_{12}), 7.21 (m, 12H, C_4–Ph_4), 7.36 (m, 8H, C_4–Ph).

3.12. [{$Me_2Si(C_5Me_4H)(\eta^5$-$C_5H_4)$}$Co(\eta^4$-$C_4Ph_4)$] (**13**)

A solution of **10** (0.80 g, 0.92 mmol) in C_6H_5Me was heated at 80 °C for 18 h. After concentration of the solution, the residue was chromatographed on alumina. The yellow eluate by hexane was evaporated to dryness. The residue was crystallized from hexane to give yellow orange crystals of **13**, 0.20 g (0.30 mmol, 33%); m.p. 150 °C. Anal. Found: C, 80.42; H, 6.76. Calc. for $C_{44}H_{43}CoSi$: C, 80.21; H, 6.58%. ^{1}H-NMR ($CDCl_3$): δ 0.31 (s, 6H, $SiMe_2$), 1.62 (s, 6H, C_5Me_4), 1.65 (s, 6H, C_5Me_4), 2.73 (br, 1H, C_5Me_4–H), 4.63 (t, 2H, $J = 1.7$ Hz, C_5H_4), 4.70 (t, 2H, $J = 1.8$ Hz, C_5H_4), 7.17–7.23 (m, 12H, C_4Ph_4), 7.44–7.46 (m, 8H, C_4Ph_4).

3.13. [{$Me_2Si(C_5H_5)(\eta^5$-$C_5Me_4)$}$Co(\eta^4$-$C_4Ph_4)$] (**14**)

The dilithium salt, prepared from **1** (0.29 g, 1.19 mmol) and *n*-BuLi (1.54 M, 1.6 ml, 2.46 mmol), was treated with $CoCl(PPh_3)_3$ (1.05 g, 1.19 mmol) and PhC≡CPh (0.74 g, 4.16 mmol) in THF for 2 days at r.t. The solution was hydrolyzed with a saturated aqueous solution of NH_4Cl, and the organic layer was dried over Na_2SO_4. The solution was concentrated and chromatographed on alumina. The first yellow band was eluted by hexane and a second reddish-brown band eluted by C_6H_6–hexane (1:2). The yellow elute was evacuated to dryness and crystallized from hexane to give yellow orange crystals of **14**, 0.12 g (0.18 mmol, 15%). From the reddish-brown elute reddish-brown crystals of **10** were obtained, 0.17 g (0.18 mmol, 15%); m.p. 180 °C. Anal. Found: C, 80.27; H, 6.70. Calc. for $C_{44}H_{43}CoSi$: C, 80.21; H, 6.58%. ^{1}H-NMR ($CDCl_3$): δ 0.22 (s, 6H, $SiMe_2$), 1.44 (s, 6H, C_5Me_4), 1.65 (s, 6H, C_5Me_4), 3.42 (br, 1H, C_5H_4–H), 6.20 (s, 2H, C_5H_4), 6.50 (s, 2H, C_5H_4), 7.20 (m, 12H, C_4Ph_4), 7.35 (m, 8H, C_4Ph_4).

3.14. [$(C_5Me_4H)Me_2Si(\eta^5$-$C_5H_4)Co(C_8H_{12})$] (**15**)

The dilithium salt, prepared from **1** (0.35 g, 1.43 mmol) and *n*-BuLi (1.54 M, 1.9 ml, 2.93 mmol) in THF, was reacted with $CoCl(PPh_3)_3$ (2.54 g, 2.89 mmol) and 1,5-C_8H_{12} (6 ml, 6.80 mmol) overnight. The reaction mixture was evacuated to dryness and the residue was dissolved in C_6H_6. The solution was hydrolyzed with a saturated aqueous solution of NH_4Cl, and the organic layer was dried over Na_2SO_4. After concentration, the resulting solution was chromatographed on alumina. The yellow–orange eluate by hexane was evacuated to dryness and the residue was crystallized from pentane–MeCN to yield orange crystals of **15**, 0.22 g (0.54 mmol, 38%); m.p. 82 °C. Anal. Found: C, 70.87; H, 9.16. Calc. for $C_{24}H_{35}SiCo$: C, 70.21; H, 8.59%. ^{1}H-NMR ($CDCl_3$): δ 0.46 (s, 6H, $SiMe_2$), 1.57 (pseudo-q, 4H, C_8H_{12}), 1.73 (s, 6H, C_5Me_4), 1.79 (s, 6H, C_5Me_4), 2.37 (br, 4H, C_8H_{12}), 2.94 (br, 1H, C_5Me_4H), 3.39 (br, 4H, C_8H_{12}), 3.50 (s, 2H, C_5H_4), 5.13 (s, 2H, C_5H_4).

3.15. [$(C_8H_{12})Rh${$(\eta^5$-$C_5Me_4)Me_2Si(\eta^5$-$C_5H_4)Co$-(C_8H_{12})}] (**16**)

Complex **15** (0.17 g, 0.41 mmol) was treated with *n*-BuLi (1.54 M, 0.27 ml, 0.42 mmol) in THF overnight. The reaction solution was reacted with $[RhCl(C_8H_{12})]_2$ (0.13 g, 0.53 mmol) at reflux for 5 h. After the solvent was removed and the residue was dissolved in C_6H_6, the solution was hydrolyzed with a saturated aqueous solution of NH_4Cl, and the organic layer was dried over Na_2SO_4. After concentration of the solution, the residue was chromatographed on alumina. The yellow–orange eluate by hexane was evaporated to dryness, and the residue was crystallized from hexane to give yellow–orange crystals of **16**, 0.18 g (0.29 mmol, 71%); m.p. 183 °C. Anal. Found: C, 61.09; H, 7.62. Calc. for $C_{32}H_{46}SiCoRh$: C, 61.93; H, 7.47%. ^{1}H-NMR ($CDCl_3$): δ 0.89 (s, 6H, $SiMe_2$), 1.43 (s, 6H, C_5Me_4), 1.87 (s, 6H, C_5Me_4), 1.60 (d, 4H, C_8H_{12}) 1.93 (d, 4H, C_8H_{12}), 2.19 (m, 4H, C_8H_{12}), 2.42 (m, 4H, C_8H_{12}), 2.96 (br, 4H, C_8H_{12}), 3.47 (br, 4H, C_8H_{12}), 3.69 (t, 2H, $J = 1.9$ Hz, C_5H_4), 5.17 (t, 2H, $J = 1.7$ Hz, C_5H_4).

3.16. [$(C_8H_{12})Ir${$(\eta^5$-$C_5Me_4)Me_2Si(\eta^5$-$C_5H_4)Co(C_8H_{12})$}] (**17**)

Complex **15** (0.20 g, 0.49 mmol) was treated with *n*-BuLi (1.54 M, 0.32 ml, 0.49 mmol) in THF overnight. The reaction solution was treated with $[IrCl(C_8H_{12})]_2$ (0.17 g, 0.51 mmol) at reflux for 5 h. The solvent was evaporated and the residue was dissolved in C_6H_6. The solution was hydrolyzed with a saturated aqueous solution of NH_4Cl, and the organic layer was dried over Na_2SO_4. After concentration of the solution, the residue was chromatographed on alumina. The orange eluate by hexane was evaporated to dryness, and the residue was crystallized from hexane to give orange crystals of **17**, 0.14 g (0.20 mmol, 41%); m.p. 199 °C Anal. Found: C, 54.03; H, 6.78. Calc. for $C_{32}H_{46}CoIrSi$: C, 54.14; H, 6.53%. ^{1}H-NMR ($CDCl_3$): δ 0.85 (s, 6H, $SiMe_2$), 1.54 (s, 6H, C_5Me_4), 1.60 (pseudo-q, 4H, C_8H_{12}), 1.84 (pseudo-q, 4H, C_8H_{12}), 1.90 (s, 6H, C_5Me_4), 2.06 (m, 4H, C_8H_{12}), 2.41 (m, 4H, C_8H_{12}), 2.79 (br, 4H, C_8H_{12}), 3.46 (br, 4H, C_8H_{12}), 3.67 (t, 2H, $J = 2.0$ Hz, C_5H_4), 5.18 (t, 2H, $J = 2.0$ Hz, C_5H_4).

3.17. *[{Me$_2$Si(C$_5$HMe$_4$)(η^5-C$_5$H$_4$)}-{Rh(PPh$_3$)(μ-CO)$_2$Fe(CO)$_3$}]* (**18**)

A suspension of **6** (0.53 g, 0.83 mmol) and $Fe_2(CO)_9$ (0.41 g, 1.13 mmol) in hexane was stirred at r.t. overnight. The resulting purple solution was evacuated to dryness. The residue was dissolved in a small amount of C_6H_6 and chromatographed on alumina. The purple eluate by hexane–C_6H_6 (3:1) was evacuated to dryness, and the residue was crystallized from CH_2Cl_2–hexane to give purple crystals of **18**, 0.51 g (0.63 mmol, 76%); m.p. 140 °C. Anal. Found: C, 57.59; H, 4.85. Calc. for $C_{39}H_{38}O_5PSiFeRh$: C, 58.22; H, 4.76%. ^{1}H-NMR ($CDCl_3$): δ 0.47 (s, 6H, $SiMe_2$), 1.59 (s, 6H, C_5Me_4), 1.75 (s, 6H, C_5Me_4), 2.83 (br, 1H, C_5Me_4H), 4.97 (s, 2H, C_5H_4), 5.19 (s, 2H, C_5H_4), 7.36–7.44 (m, 15H, PPh_3). IR (KBr, cm^{-1}): ν_{CO} 2021, 1955, 1945, 1811, 1782. IR ($CHCl_3$, cm^{-1}): ν_{CO} 2030, 1961, 1806, 1777.

3.18. *[{(η^5-C$_5$H$_4$)SiMe$_2$(η^5-C$_5$Me$_4$)}-{Rh(CO)Rh(μ-CO)$_2$–Fe(CO)$_3$}]* (**19**)

To a solution of **5** (0.08 g, 0.15 mmol) in Et_2O was added $Fe_2(CO)_9$ (0.25 g, 0.69 mmol) and stirred overnight at r.t. The color of the mixture turned deep green. After the solvent was evaporated to dryness, the residue was dissolved in a small amount of C_6H_6 and chromatographed on alumina. The green fraction eluted by hexane–C_6H_6 (3:1) was evacuated, and the residue was crystallized from hexane–C_6H_6 to give green crystals of **19**, 0.05 g (0.07 mmol, 47%); m.p. 159 °C. Anal. Found: C, 39.16; H, 3.32. Calc. for $C_{22}H_{22}O_6SiFeRh_2$: C, 39.31; H, 3.30%. ^{1}H-NMR ($CDCl_3$): δ 0.57 (s, 6H, $SiMe_2$), 1.80 (s, 6H, C_5Me_4), 1.83 (s, 6H, C_5Me_4), 4.89 (t, 2H, $J = 1.9$ Hz, C_5H_4), 5.65 (m, 2H, C_5H_4). IR (KBr, cm^{-1}): ν_{CO} 2027, 1977, 1967, 1832, 1784. IR ($CHCl_3$, cm^{-1}): ν_{CO} 2043, 1990, 1826, 1775.

3.19. *X-ray diffraction studies*

Single crystals suitable for X-ray analysis were mounted on a glass fiber, and all measurements were made on a Rigaku AFC7S diffractometer with graphite monochromatized Mo–K$_\alpha$ radiation ($\lambda = 0.71069$ Å). Cell constants and orientation matrixes were determined by a least-squares refinement of 25 centered reflections with $39.16 < 2\theta < 39.81°$ for **3**, $25.07 < 2\theta < 29.49°$ for **11**, $38.90 < 2\theta < 39.84°$ for **12**, $20.23 < 2\theta < 23.52°$ for **18**, $27.91 < 2\theta < 36.42°$ for **19**. The data collection was performed at r.t. using the ω–2θ scan technique. Details of crystal and data collection parameters are summarized in Table 6. The structure solution and refinements were carried out sing the TEXSAN program package. The positions of the non-hydrogen atoms were determined by Patterson methods

Table 6
Crystal data and structure refinement parameters for complexes **3**, **11**, **12**, **18** and **19**

Complex	**3**	**11**	**12**	**18**	**19**
Empirical formula	$C_{32}H_{46}SiRh_2$	$C_{52}H_{54}SiCoRh$	$C_{52}H_{54}SiCoIr$	$C_{39}H_{38}O_5PsiFeRh$	$C_{22}H_{22}O_6SiFeRh_2$
Formula weight	664.61	868.92	958.24	804.54	672.16
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$C2$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions					
a (Å)	19.829(1)	13.096(5)	13.096(4)	13.163(3)	9.261(2)
b (Å)	12.670(1)	14.112(8)	14.108(5)	13.216(3)	27.462(2)
c (Å)	15.938(1)	12.390(7)	12.385(3)	11.034(3)	9.822(2)
α (°)		101.88(7)	101.85(3)	90.98(2)	
β (°)	133.566(2)	105.77(4)	105.86(2)	100.29(2)	103.78(1)
γ (°)		97.69(4)	97.61(3)	73.24(2)	
V (Å^3)	2901.3(4)	2112(2)	2110(1)	1807.1(8)	2426.3(6)
Z	4	2	2	2	4
D_{calc} (g cm^{-3})	1.521	1.366	1.508	1.478	1.840
Crystal dimensions (mm)	0.40 × 0.30 × 0.40	0.15 × 0.13 × 0.30	0.38 × 0.20 × 0.35	0.08 × 0.04 × 0.30	0.12 × 0.12 × 0.20
μ, Mo–K$_\alpha$ (cm^{-1})	11.95	8.46	36.15	9.76	20.15
Scan type	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ
$2\theta_{max}$ (°)	55	55	55	50	55
Reflections collected	3591	10 110	10 099	6672	6036
Unique reflections	3491	9688	9675	6367	5701
Reflections observed [$I > 3.00\sigma(I)$]	3117	6144	7866	3488	3866
Number of parameters	314	496	496	433	289
Goodness-of-fit	2.35	1.57	1.80	1.66	1.19
R	0.030	0.039	0.030	0.058	0.032
R_w	0.027	0.034	0.027	0.043	0.033

(DIRDIF PATTY). All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. All hydrogen atoms were placed at calculated positions.

4. Supplementary material

Crystallographic date for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 160435–160439 for compounds **3**, **11**, **12**, **18** and C_5H_4, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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