Synthesis, Molecular Structure, and Reactivity of Indenylrhodium Complexes Containing Diphenylcarbene as Ligand†

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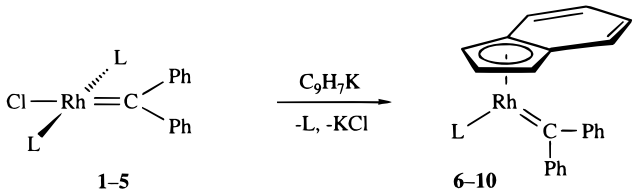
(η^5-Indenyl)rhodium(I) complexes of the general composition [(η^5-C_9H_7)Rh(=CPh_2)(L)] (L = Sb*i*Pr_3 (**6**), P*i*Pr_3 (**7**), PPh_3 (**8**), P*i*$PrPh_2$ (**9**), P*i*Pr_2Ph (**10**)) were prepared from the square-planar precursors *trans*-[RhCl(=CPh_2)$(L)_2$] (**1**−**5**) and C_9H_7K in THF. Treatment of **6**−**10** with carbon monoxide resulted in an unusual migratory insertion of the carbene ligand into one of the C−H bonds of the five-membered ring of the indenyl unit to give the compounds [{η^5-$C_9H_6(CHPh_2)$}Rh(CO)(L)] (**12**−**16**) in 78−87% yield. The X-ray crystal structure analyses of **6** and **13** revealed that in both complexes the slip distortion from a η^5 to a η^3 coordination mode of the indenyl ligand is nearly the same, independent of the bulky $CHPh_2$ group in the ring-substituted species.

Introduction

Recently, we described a simple and very efficient synthesis of square-planar (carbene)rhodium(I) complexes of the general composition *trans*-[RhCl(=CRR′)$(L)_2$], in which the ligands L could be tertiary phosphines, arsines, or stibines.[1,2] The key to success was the use of the bis(stibine) compound *trans*-[RhCl(C_2H_4)$(Sb$*i*$Pr_3)_2$] as the starting material, which reacts with a variety of diazoalkanes $RR'CN_2$ to give the complexes *trans*-[RhCl(=CRR′)$(Sb$*i*$Pr_3)_2$] in excellent yield. The two triisopropylstibine ligands can be easily displaced by several phosphines and arsines without cleavage of the rhodium−carbene bond. The square-planar compounds *trans*-[RhCl(=CRR′)$(L)_2$] also undergo ligand substitution reactions with various anionic nucleophiles, which led not only to the structurally related derivatives *trans*-[RhX(=CRR′)$(L)_2$] with X = F, Br, OPh, OC(O)R, $OS(O)_2CF_3$ etc.[1,3] but, by using NaC_5H_5 or $LiC_5H_4SiMe_3$ as the substrates, also to the cyclopentadienyl complexes [(η^5-C_5H_5)Rh(=CRR′)(L)] and [(η^5-$C_5H_4SiMe_3$)Rh(=CRR′)(L)], respectively.[1,4]

Taking into account that η^5-indenyl transition-metal complexes are sometimes more reactive toward nucleophiles than their η^5-cyclopentadienyl analogues,[5,6] we set out to prepare half-sandwich type compounds of the type [(η^5-C_9H_7)Rh(=CPh_2)(L)]. In this paper we describe the synthesis of a series of corresponding tertiary phosphine and stibine complexes and the molecular structure of the compound with L = Sb*i*Pr_3 and report on the reactivity of the molecules [(η^5-C_9H_7)Rh(=CPh_2)(ER_3)] (E = P, Sb) toward CO, which leads to an unusual migratory insertion of the carbene ligand into a C−H bond of the indenyl ring. Some preliminary results have already been communicated.[7]

Scheme 1



L	
Sb*i*Pr_3	**1, 6**
P*i*Pr_3	**2, 7**
PPh_3	**3, 8**
P*i*$PrPh_2$	**4, 9**
P*i*Pr_2Ph	**5, 10**

Results and Discussion

1. Preparation of (η^5-Indenyl)(carbene)rhodium(I) Complexes. The square-planar (diphenylcarbene)rhodium(I) compounds **1**−**5** react with C_9H_7K in THF at room temperature to give the η^5-indenyl complexes **6**−**10** in 62−87% yield (Scheme 1). After chromatographic workup, the analytically pure products were

† Dedicated to Professor Fred Basolo on the occasion of his 80th birthday.

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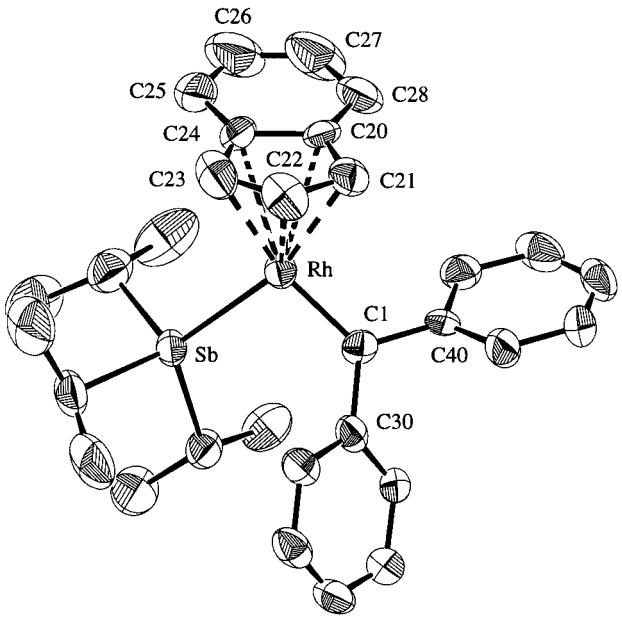


Figure 1. ORTEP drawing of **6**.

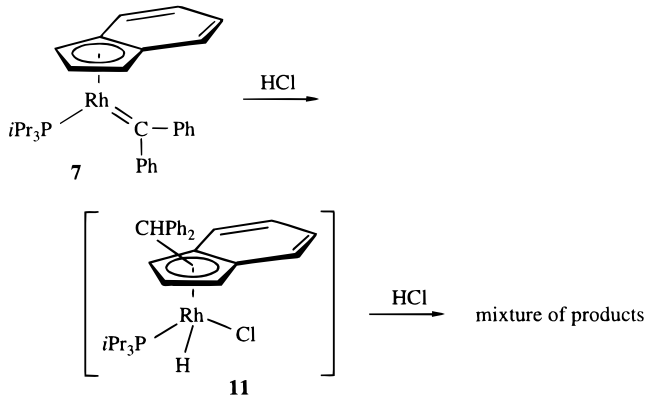
Table 1. Selected Bond Distances and Angles with Esd's for Compound 6

	Bond Distances (Å)		
Rh−C1	1.885(7)	Rh−C22	2.199(8)
Rh−Sb	2.559(7)	Rh−C23	2.274(8)
Rh−C20	2.45(1)	Rh−C24	2.46(1)
Rh−C21	2.210(8)		
	Bond Angles (deg)		
C1−Rh−Sb	96.7(2)	Rh−C1−C40	120.5(5)
Rh−C1−C30	127.0(4)	C30−C1−C40	112.2(5)

obtained as deeply colored solids which are only moderately air-sensitive and readily soluble in common organic solvents. The ^{13}C NMR spectra of the η^5-indenyl compounds display a resonance for the carbene carbon atom in the low-field region at δ 281−289, which compared with the square-planar precursors **1**−**5** are shifted upfield by 26−37 ppm. The signals for the bridging carbon atoms C^8 and C^9 appear at δ 117−120, indicating that the indenyl ligand is coordinated in a η^5 fashion. For compounds in which a η^3 bonding mode predominates, the corresponding resonances are usually observed at somewhat lower fields.[8] In the case of the phosphine derivatives **7**−**10**, the signals of the carbon atoms C^1, C^3, C^8, and C^9 appear as doublets of doublets due to $^{13}C-^{31}P$ and $^{13}C-^{103}Rh$ coupling, whereas the resonance for C^2 is a doublet with $J(RhC) = 5.0-6.1$ Hz. Characteristic features of the ^1H NMR spectra of **7**−**10** are the multiplet for the ring proton H^2 at δ 4.9−5.2 and the doublet of doublets for the adjacent protons H^1 and H^3 at δ 5.1−5.8, which seems to be a quartet due to almost identical $^1H-^1H$ and $^1H-^{103}Rh$ couplings.

The molecular structure of compound **6** is shown in Figure 1, and bond distances and angles are given in Table 1. The molecule possesses the expected two-legged piano-stool configuration with a Rh−Sb distance (2.559(7) Å) that differs only slightly from the Rh−Sb bond lengths in the square-planar complex **1** (2.5843(5) and 2.5633(5) Å). Similarly to **1**, also the Rh−C1 distance is rather short (1.885(7) Å), which points to a relatively high degree of back-bonding between the metal and the carbene ligand. The slip-fold parameter Δ,[9] which results from the difference between the distances Rh−C20, Rh−C24 and Rh−C21, Rh−C23, is 0.213 Å and is thus nearly the same as in $[(\eta^5\text{-}C_9H_7)Rh(C_2H_4)_2]$ (0.161 Å) and $[(\eta^5\text{-}C_9H_7)Rh(PMe_3)_2]$ (0.201 Å).[10] The parameter Δ, together with the hinge angle HA (6.3°) and the fold angle FA (8.9°), indicates that in **6** a significant slippage of the indenyl moiety from a η^5 to a η^3 bonding mode occurred.

Scheme 2



2. CO-Initiated Migratory Insertion Reactions. In the context of our studies on the reactivity of half-sandwich complexes of the general type $[(\eta^5\text{-}C_5H_5)M(PR_3)(L)]$ (M = Co, Rh, Ir),[11] we recently observed that, upon treatment of $[(\eta^5\text{-}C_5H_5)Rh(=CPh_2)(PiPr_3)]$ with HX (X = Cl, CF_3CO_2), instead of the expected addition of the electrophile to the rhodium−carbon double bond a migratory insertion of the carbene ligand into one of the C−H bonds of the cyclopentadienyl ring occurs.[12] The analogous reaction of the related η^5-indenyl complex **7** with HCl is less straightforward. If an equimolar amount of HCl is added to a solution of **7** in benzene, the formation of a new compound is observed, the ^1H NMR spectrum of which displays a signal in the hydride region at δ −12.70. Since the ^{31}P NMR spectrum of the solution exhibits a doublet resonance at δ 77.6 with a $^{31}P-^{103}Rh$ coupling of 145.7 Hz that is typical for a (triisopropylphosphine)rhodium(III) species,[13] we assume that the product of the reaction of **7** with HCl is the chloro hydrido compound **11** (Scheme 2). If the insertion of the carbene would occur adjacent to the benzene ring, diastereomers could be produced. However, we found no evidence for this. In contrast to the cyclopentadienyl analogue $[\{\eta^5\text{-}C_5H_4(CHPh_2)\}RhHCl(PiPr_3)]$,[12] the substituted indenyl complex is quite labile; therefore, attempts to isolate **11** failed. Addition of an excess of HCl did not yield the supposedly more stable dichlororhodium(III) derivative $[\{\eta^5\text{-}C_9H_6(CHPh_2)\}RhCl_2(PiPr_3)]$ but led to a mixture of products which could not be separated by fractional crystallization or chromatographic techniques.

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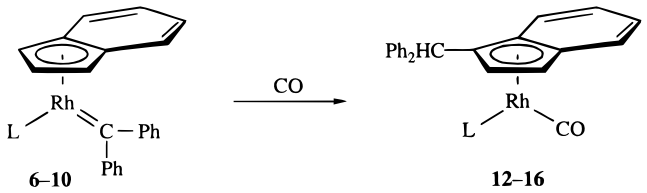
Scheme 3



L	
Sb*i*Pr$_3$	**6**, **12**
P*i*Pr$_3$	**7**, **13**
PPh$_3$	**8**, **14**
P*i*PrPh$_2$	**9**, **15**
P*i*Pr$_2$Ph	**10**, **16**

Quite unexpectedly, a migratory insertion of the CPh_2 ligand not only of **7** but also of **6** and **8**−**10** can be initiated by carbon monoxide (Scheme 3). Passing a slow stream of CO through a solution of the η^5-indenyl complex in pentane at −78 °C leads, upon warming to room temperature, to a change of color from dark green to yellow and gives, after removal of the solvent and recrystallization from pentane, the complexes **12**−**16** as yellow, moderately air sensitive solids in 78−87% yield. The IR spectra of **12**−**16** show a strong ν(CO) band at 1930−1980 cm^{-1}, while the ^{1}H NMR spectra display as a typical feature a resonance at δ 5.6−6.1 for the methine proton of the $CHPh_2$ unit. The two nonequivalent protons H^2 and H^3 of the five-membered ring give rise to two separate signals, indicating that the insertion of the carbene ligand took place into one of the C−H bonds next to the bridging carbon atoms C^8 and C^9. With regard to the mechanism of the migratory insertion, we assume that the initial step consists of a bimolecular process leading to a 1:1 adduct of the starting material and CO. This 20-electron intermediate could afford via a ring slippage an isomer with an η^3-indenyl ligand and an 18-electron configuration at rhodium which finally would yield the isolated product.

To confirm the structural proposal for the insertion products, an X-ray crystal structure analysis of **13** was carried out. The ORTEP plot (Figure 2) illustrates the unsymmetrical substitution of the five-membered ring of the indenyl ligand. The $CHPh_2$ moiety is pointing away from the triisopropylphosphine, which minimizes the steric repulsion between the two bulky moieties. The plane [P, Rh, C20] lies almost exactly perpendicular to the plane defined by the carbon atoms C1, C2, C3, C4, and C9, the dihedral angle being 88.6(1)°. The bond lengths Rh−C4 and Rh−C9 (see Table 2) are ca. 0.2 Å larger than those between the metal center and C1, C2, and C3, which confirms the slip distortion of the indenyl ligand. The slip-fold parameter Δ (0.196 Å), the hinge angle HA (9.5(3)°), and the fold angle FA (10.6(3)°) are similar to those of the nonsubstituted complex **6**, which means that the substituent $CHPh_2$ has no influence on the slippage from a η^5 to a η^3 coordination mode.

The influence of CO on the migratory insertion of the diphenylcarbene ligand seems rather unique. We attempted to generate the trimethylphosphine complex [{η^5-C$_9$H$_6$(CHPh$_2$)}Rh(PMe$_3$)(Sb*i*Pr$_3$)] by treatment of **6** with PMe$_3$ but, apart from small amounts of the substitution product [(η^5-C$_9$H$_7$)Rh(=CPh$_2$)(PMe$_3$)] (δ(^{31}P) −12.7, d, J(RhP) = 255.8 Hz), mainly observed decomposition. It should be noted, however, that the reaction of [(η^5-C$_5$H$_5$)Rh(=CPh$_2$)(P*i*Pr$_3$)] with PF$_3$ led to the migration of the diphenylcarbene ligand to the ring and afforded the insertion product [{η^5-C$_5$H$_4$(CHPh$_2$)}-Rh(PF$_3$)(P*i*Pr$_3$)].[12]

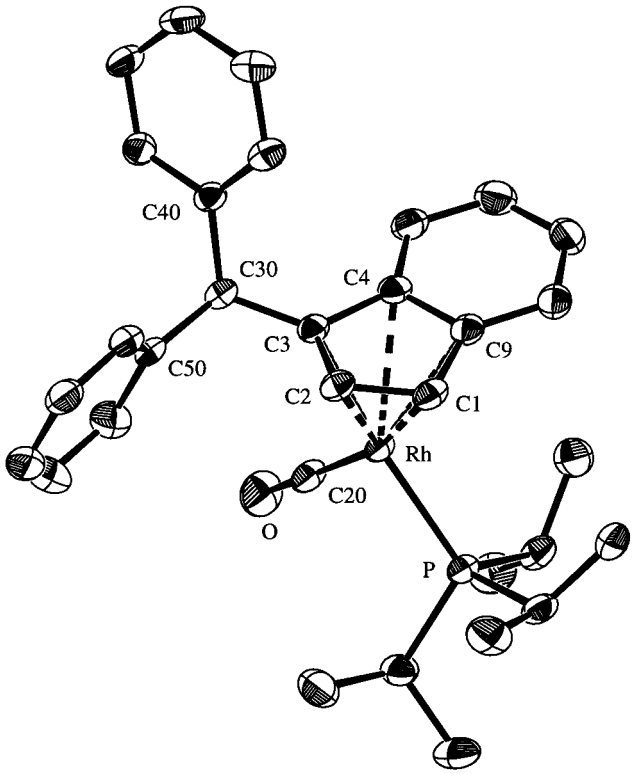


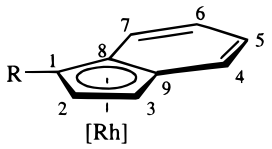
Figure 2. ORTEP drawing of **13**.

Table 2. Selected Bond Distances and Angles with Esd's for Compound 13

Bond Distances (Å)			
Rh−P	2.2714(7)	Rh−C2	2.244(2)
Rh−C20	1.816(3)	Rh−C3	2.238(2)
C20−O	1.156(3)	Rh−C4	2.426(2)
Rh−C1	2.254(2)	Rh−C9	2.458(2)
Bond Angles (deg)			
P−Rh−C20	88.91(8)	C4−C3−C30	124.1(2)
Rh−C20−O	178.1(2)	C40−C30−C50	111.1(2)
C2−C3−C30	126.8(2)		

Conclusions

The present investigations have shown that the analogous (η^5-cyclopentadienyl)- and (η^5-indenyl)rhodium(I) compounds [(η^5-C$_5$H$_5$)Rh(=CPh$_2$)(P*i*Pr$_3$)] and [(η^5-C$_9$H$_7$)Rh(=CPh$_2$)(P*i*Pr$_3$)] (**7**) behave completely differently toward carbon monoxide. While the η^5-cyclopentadienyl derivative upon treatment with CO affords exclusively the substitution product [(η^5-C$_5$H$_5$)Rh(CO)-(P*i*Pr$_3$)] and diphenylketene,[1,2] the η^5-indenyl complex **7** reacts with CO by migratory insertion of the carbene ligand into one C−H bond of the indenyl unit to give the ring-substituted compound [{η^5-C$_9$H$_6$(CHPh$_2$)}Rh-(CO)(P*i*Pr$_3$)] in excellent yield. A striking difference in the reactivity toward CO has also been observed for the corresponding *triisopropylstibine* complexes [(η^5-C$_5$H$_5$)-Rh(=CPh$_2$)(Sb*i*Pr$_3$)] and [(η^5-C$_9$H$_7$)Rh(=CPh$_2$)(Sb*i*Pr$_3$)] (**6**), respectively. Treatment of the η^5-cyclopentadienyl



R = H, $CHPh_2$

Figure 3.

compound with carbon monoxide leads to the formation of $[(\eta^5\text{-}C_5H_5)Rh(=CPh_2)(CO)]$ and uncoordinated $SbiPr_3$,[13] while the reaction of **6**, similar to that of **7**, with CO yields the insertion product $[\{\eta^5\text{-}C_9H_6(CHPh_2)\}Rh(CO)(SbiPr_3)]$ (**12**).

Therefore, the final conclusion is that structurally related η^5-cyclopentadienyl and η^5-indenyl transition-metal complexes differ not only in the *rate* of ligand substitution processes[5] but also in the *course* of the reactions with Lewis bases. It is conceivable that in both cases the reason is the same and lies in the slip distortion of the more unsymmetrical indenyl moiety.

Experimental Section

General Considerations. All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by known procedures and distilled before use. The starting materials **1**−**5** were prepared as described in the literature.[1,2]

Physical Measurements. NMR spectra were recorded at room temperature on Bruker AC 200 and Bruker AMX 400 instruments. Chemical shifts are expressed in ppm downfield from $SiMe_4$ (^1H and ^{13}C) and (85%) H_3PO_4 (^{31}P). Abbreviations used: s, singlet; d, doublet; q, quartet; sept, septet; m, multiplet; br, broadened signal. Coupling constants *J* are given in hertz. Melting points were measured by DTA. For assignment of indenyl protons and carbon atoms see Figure 3.

Preparation of $[(\eta^5\text{-}C_9H_7)Rh(=CPh_2)(SbiPr_3)]$ (6). A solution of **1** (161 mg, 0.20 mmol) in THF (10 mL) was treated at −78 °C with C_9H_7K (154 mg, 1.00 mmol) and then slowly warmed to room temperature. After the mixture was stirred for 30 min, the solvent was evaporated in vacuo, and the dark green residue was extracted with pentane (30 mL). The extract was concentrated to ca. 2 mL and then chromatographed on Al_2O_3 (neutral, activity grade V, height of column 4 cm). With pentane, a dark green fraction was eluted, which was brought to dryness in vacuo. The residue was recrystallized from pentane (3 mL) at −78 °C to give dark green crystals, which were separated from the mother liquor, washed twice with pentane (2 mL, −30 °C), and dried: yield 103 mg (81%); mp 62 °C dec. ^1H NMR (400 MHz, C_6D_6): δ 7.28−6.97 (br m, 14H, C_6H_5 and H^{4-7}), 5.37 (m, 3H, H^{1-3}), 1.44 (sept, J(HH) = 7.3 Hz, 3H, SbC*H*CH_3), 1.02 (d, J(HH) = 7.3 Hz, 18H, SbCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 281.2 (d, J(RhC) = 46.3 Hz, Rh=C), 164.8 (s, *ipso*-C of C_6H_5), 128.3, 127.4, 126.6, 125.5 (all s, C_6H_5), 122.1, 119.4 (both s, C^{4-7}), 117.7 (s, $C^{8,9}$), 85.0 (d, J(RhC) = 5.5 Hz, *C*^{2}), 73.0 (d, J(RhC) = 3.8 Hz, *C*^{1,3}), 21.5 (s, SbCH*C*H$_3$), 18.3 (d, J(RhC) = 3.9 Hz, SbC*H*CH$_3$). Anal. Calcd for $C_{31}H_{38}RhSb$ (635.3): C, 58.61; H, 6.03. Found: C, 58.35; H, 6.05.

Preparation of $[(\eta^5\text{-}C_9H_7)Rh(=CPh_2)(PiPr_3)]$ (7). This was prepared as described for **6**, from **2** (99 mg, 0.16 mmol) and C_9H_7K (123 mg, 0.80 mmol) in THF (5 mL): dark green crystals; yield 75 mg (87%); mp 75 °C dec. ^1H NMR (200 MHz, C_6D_6): δ 7.37−7.02 (br m, 14H, C_6H_5 and H^{4-7}), 5.75 (dt, J(HH) = J(RhH) = 2.6 Hz, 1H, H^2), 5.20 (m, 2H, $H^{1,3}$), 1.52 (dsept, J(PH) = 13.3, J(HH) = 7.1 Hz, 3H, PC*H*CH_3), 0.87 (dd, J(PH) = 13.3, J(HH) = 7.1 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR (50.3 MHz, C_6D_6): δ 285.0 (dd, J(RhC) = 50.8, J(PC) = 12.8 Hz, Rh=C), 163.6 (d, J(RhC) = 1.2 Hz, *ipso*-C of C_6H_5), 128.3, 127.4, 127.0, 125.9 (all s, C_6H_5), 122.3, 121.8 (both s, C^{4-7}), 118.4 (s, $C^{8,9}$), 88.9 (d, J(RhC) = 6.1 Hz, C^2), 75.5 (br dd, J(RhC) = J(PC) = 3.7 Hz, $C^{1,3}$), 26.5 (d, J(PC) = 18.3 Hz, P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$). ^{31}P NMR (81.0 MHz, C_6D_6): δ 57.3 (d, J(RhP) = 245.6 Hz). Anal. Calcd for $C_{31}H_{38}PRh$ (544.5): C, 68.38; H, 7.03; Rh, 18.90. Found: C, 68.13; H, 7.35; Rh, 18.41.

Preparation of $[(\eta^5\text{-}C_9H_7)Rh(=CPh_2)(PPh_3)]$ (8). This was prepared as described for **6**, from **3** (99 mg, 0.12 mmol) and C_9H_7K (93 mg, 0.60 mmol) in THF (10 mL) at room temperature: blue green crystals; yield 48 mg (62%); mp 40 °C dec. ^1H NMR (200 MHz, C_6D_6): δ 7.44−6.74 (br m, 29H, C_6H_5 and H^{4-7}), 5.61 (dt, J(HH) = J(RhH) = 2.6 Hz, 1H, H^2), 4.92 (m, 2H, $H^{1,3}$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 163.0 (d, J(RhC) = 2.0 Hz, *ipso*-C of C_6H_5), 134.1 (d, J(PC) = 20.1 Hz, *meta*-C of C_6H_5P), 128.8, 128.7, 127.8, 127.3, 126.8, 125.6 (all s, C_6H_5), 122.7, 119.5 (both s, C^{4-7}), 119.1 (s, $C^{8,9}$), 90.6 (d, J(RhC) = 5.0 Hz, C^2), 78.7 (dd, J(RhC) = 5.0, J(PC) = 3.0 Hz, $C^{1,3}$); the signal of Rh=C could not be exactly located. ^{31}P NMR (81.0 MHz, C_6D_6): δ 48.7 (d, J(RhP) = 264.5 Hz). Anal. Calcd for $C_{40}H_{32}PRh$ (646.6): C, 74.31; H, 4.99. Found: C, 74.32; H, 5.00.

Preparation of $[(\eta^5\text{-}C_9H_7)Rh(=CPh_2)(PiPrPh_2)]$ (9). This was prepared as described for **6**, from **4** (221 mg, 0.29 mmol) and C_9H_7K (224 mg, 1.45 mmol) in THF (10 mL) at room temperature. For column chromatography, ether was used as the eluant: dark green crystals; yield 126 mg (71%); mp 40 °C dec. ^1H NMR (400 MHz, C_6D_6): δ 7.39−6.95 (br m, 24H, C_6H_5 and H^{4-7}), 5.15 (br dt, J(HH) = J(RhH) = 2.0 Hz, 1H, H^2), 4.98 (m, 2H, $H^{1,3}$), 1.23 (m, 1H, PC*H*CH$_3$), 1.06 (dd, J(PH) = 16.0, J(HH) = 7.2 Hz, 3H, PCHC*H*$_3$), 0.45 (dd, J(PH) = 15.6, J(HH) = 6.8 Hz, 3H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 284.4 (dd, J(RhC) = 48.8, J(PC) = 13.6 Hz, Rh=C), 162.9 (d, J(RhC) = 2.0 Hz, *ipso*-C of C_6H_5), 136.4 (d, J(PC) = 35.2 Hz, *ipso*-C of C_6H_5P), 133.8 (d, J(PC) = 11.1 Hz, *meta*-C of C_6H_5P), 131.2 (d, J(PC) = 9.1 Hz, *ortho*-C of C_6H_5P), 130.3, 129.0, 127.7, 127.6, 127.0, 125.8 (all s, C_6H_5), 122.7, 119.4 (both s, C^{4-7}), 119.9 (s, $C^{8,9}$), 91.1 (d, J(RhC) = 5.0 Hz, C^2), 78.0 (dd, J(RhC) = J(PC) = 3.5 Hz, $C^{1,3}$), 22.7 (br s, P*C*HCH$_3$), 17.9 (s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 53.3 (d, J(RhP) = 260.5 Hz). Anal. Calcd for $C_{37}H_{34}PRh$ (612.6): C, 72.55; H, 5.59. Found: C, 72.09; H, 5.97.

Preparation of $[(\eta^5\text{-}C_9H_7)Rh(=CPh_2)(PiPr_2Ph)]$ (10). This was prepared as described for **6**, from **5** (232 mg, 0.33 mmol) and C_9H_7K (258 mg, 1.67 mmol) in THF (10 mL) at room temperature. For column chromatography, ether was used as the eluant: dark green crystals; yield 150 mg (78%); mp 70 °C dec. ^1H NMR (400 MHz, C_6D_6): δ 7.25−6.80 (br m, 19H, C_6H_5 and H^{4-7}), 5.70 (dt, J(HH) = J(RhH) = 2.4 Hz, 1H, H^2), 5.11 (m, 2H, $H^{1,3}$), 1.57 (m, 2H, PC*H*CH$_3$), 0.66 (dd, J(PH) = 13.2, J(HH) = 6.8 Hz, 6H, PCHC*H*$_3$), 0.62 (dd, J(PH) = 15.4, J(HH) = 7.2 Hz, 6H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 289.3 (dd, J(RhC) = 49.3, J(PC) = 13.1 Hz, Rh=C), 163.1 (br s, *ipso*-C of C_6H_5), 134.3 (d, J(PC) = 10.1 Hz, *meta*-C of C_6H_5P), 133.1 (d, J(PC) = 31.2 Hz, *ipso*-C of C_6H_5P), 129.3 (d, J(PC) = 0.2 Hz, *ortho*-C of C_6H_5P), 127.3, 127.2, 127.1, 127.0, 126.0 (all s, C_6H_5), 122.4, 121.8 (both s, C^{4-7}), 118.8 (s, $C^{8,9}$), 89.9 (d, J(RhC) = 5.2 Hz, C^2), 76.2 (br dd, J(RhC) = J(PC) = 3.6 Hz, $C^{1,3}$), 23.5 (dd, J(PC) = 22.9, J(RhC) = 2.0 Hz, P*C*HCH$_3$), 18.8 (br s, PCH*C*H$_3$), 17.5 (s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 53.9 (d, J(RhP) = 256.6 Hz). MS (FAB): *m*/*z* 578 (M^+), 463 ($M^+ - C_9H_7$), 384 ($M^+ - PiPr_2Ph$). Anal. Calcd for $C_{34}H_{36}PRh$ (578.5): C, 70.59; H, 6.27. Found: C, 70.17; H, 6.32.

Preparation of $[\{\eta^5\text{-}C_9H_6(CHPh_2)\}Rh(CO)(SbiPr_3)]$ (12). A slow stream of CO was passed for 30 s through a solution of **6** (58 mg, 0.09 mmol) in pentane (10 mL) at −78 °C. Warming of the solution to room temperature was accompanied by a change of color from dark green via violet and red to yellow. The solvent was removed in vacuo, and the residue was dissolved in pentane (3 mL) which was saturated with CO.

Table 3. Crystallographic Data for 6 and 13

formula	$C_{31}H_{38}RhSb$ (**6**)	$C_{32}H_{38}OPRh$ (**13**) + $^1/_2C_6H_{14}$
fw	635.27	615.59
cryst size, mm^3	0.5 × 0.43 × 0.3	0.5 × 0.4 × 0.4
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
cell dimens determn	25 rflns, $12° < \theta < 18°$	25 rflns, $10° < \theta < 15°$
a, Å	17.66(5)	9.4450(6)
b, Å	9.73(3)	11.505(1)
c, Å	18.06(5)	14.9591(5)
α, deg	90	101.660(6)
β, deg	115.6(1)	99.720(4)
γ, deg	90	99.542(6)
V, $Å^3$	2800(2)	1535.1(2)
Z	4	2
d_{calcd}, g cm^{-3}	1.508	1.332
temp, K	223(2)	173(2)
μ, mm^{-1}	1.571	0.627
scan method	*ω*/*θ*	*ω*/*θ*
2*θ*(max), deg	48	48
total no. of rflns	3142	5149
no. of unique rflns	2986 (*R*(int) = 0.0328)	4820 (*R*(int) = 0.0166)
no. of obsd rflns ($I > 2\sigma(I)$)	2406	4573
no. of rflns used for refinement	2984	4820
no. of params refined	298	354
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0304, wR2 = 0.0676[a]	R1 = 0.0265, wR2 = 0.0637[a]
R indices (all data)	R1 = 0.0493, wR2 = 0.0772[a]	R1 = 0.0283, wR2 = 0.0653
resid electron density, e $Å^{-3}$	0.519/−0.535	0.730/−0.705

[a] $w^{-1} = [\sigma^2F_o^2 + (0.0427P)^2 + 0.7682P]$ (**6**) and $w^{-1} = [\sigma^2F_o^2 + (0.0270P)^2 + 2.0493P]$ (**13**), where $P = (F_o^2 + 2F_c^2)/3$.

After the solution was stored for 3 days at −18 °C, yellow crystals precipitated which were separated from the mother liquor, washed with a small amount of pentane (−10 °C), and dried: yield 47 mg (78%); mp 42 °C dec. IR (C_6H_6): *ν*(CO) 1930 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): *δ* 7.23−6.70 (br m, 14H, C_6H_5 and H^{4-7}), 5.58 (br s, 1H, C*H*Ph_2), 5.52 (m, 1H, H^2), 5.11 (d, *J*(RhH) = 3.0 Hz, 1H, H^3), 2.08 (m, 3H, SbC*H*CH_3), 1.34 (m, 18H, SbCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): *δ* 190.8 (d, *J*(RhC) = 86.5 Hz, Rh−CO), 147.0, 144.9 (both s, *ipso*-C of C_6H_5), 132.1, 131.8, 130.7, 128.7, 128.1, 125.0 (all s, C_6H_5), 124.1, 121.2 (both s, $C^{4,7}$), 119.4 (s, C^5 or C^6), 118.3 (s, C^8 or C^9), 118.2 (s, C^5 or C^6), 117.3 (s, C^8 or C^9), 102.6 (d, *J*(RhC) = 3.0 Hz, C^1), 98.9 (d, *J*(RhC) = 6.1 Hz, *C*HPh_2), 71.7 (d, *J*(RhC) = 4.1 Hz, C^2), 50.3 (br s, C^3), 22.0 (s, SbCH*C*H$_3$), 21.3 (s, Sb*C*HCH$_3$). Anal. Calcd for $C_{32}H_{38}ORhSb$ (663.3): C, 57.94; H, 5.77. Found: C, 57.78; H, 5.59.

Preparation of [{*η*^{5}-C_9H_6(CH**Ph_2)}Rh(CO)(P*i*Pr_3)] (13).** This was prepared as described for **12**, from **7** (98 mg, 0.18 mmol) and CO: orange-yellow solid; yield 81 mg (79%); mp 56 °C dec. IR (hexane): *ν*(CO) 1944 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): *δ* 7.69 (m, 2H, C_6H_5), 7.24−6.89 (br m, 12H, C_6H_5 and H^{4-7}), 6.06 (d, *J*(RhH) = 3.2 Hz, 1H, C*H*Ph_2), 5.83 (m, 1H, H^2), 4.82 (d, *J*(RhH) = 3.2 Hz, 1H, H^3), 1.72 (br sept, *J*(HH) = 7.2 Hz, 3H, PC*H*CH_3), 0.84 (dd, *J*(PH) = 14.4, *J*(HH) = 7.2 Hz, 9H, PCHC*H*$_3$), 0.81 (dd, *J*(PH) = 14.0, *J*(HH) = 7.2 Hz, 9H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): *δ* 196.0 (dd, *J*(RhC) = 89.0, *J*(PC) = 21.6 Hz, Rh−CO), 144.3, 144.0 (both s, *ipso*-C of C_6H_5), 130.4, 128.9, 128.5, 128.1, 126.5, 126.4 (all s, C_6H_5), 122.9, 121.2 (both s, $C^{4,7}$), 119.3 (s, C^8 or C^9), 118.6 (s, C^5 or C^6), 117.6 (s, C^8 or C^9), 117.3 (s, C^5 or C^6), 98.5 (dd, *J*(RhC) = 5.2, *J*(PC) = 1.7 Hz, *C*HPh_2), 97.3 (dd, *J*(RhC) = 13.0, *J*(PC) = 3.8 Hz, C^1), 72.3 (d, *J*(RhC) = 3.3 Hz, C^2), 51.0 (d, *J*(RhC) = 1.5 Hz, C^3), 28.0 (d, *J*(PC) = 21.2 Hz, P*C*HCH$_3$), 19.8, 19.7 (both s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): *δ* 74.3 (d, *J*(RhP) = 194.7 Hz). MS (FAB): *m*/*z* 572 (M^+), 544 (M^+ − CO), 384 (M^+ − CO − P*i*Pr_3), 291 (M^+ − C_9H_6(C**H**Ph_2)). Anal. Calcd for $C_{32}H_{38}OPRh$ (572.5): C, 67.13; H, 6.69; Rh, 17.97. Found: C, 66.84; H, 6.90; Rh, 18.60.

Preparation of [{*η*^{5}-C_9H_6(CH**Ph_2)}Rh(CO)(P**P**h_3)] (14).** This was prepared as described for **12**, from **8** (72 mg, 0.11 mmol) and CO: orange-yellow crystals; yield 65 mg (87%); mp 68 °C dec. IR (C_6H_6): *ν*(CO) 1948 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): *δ* 7.61 (m, 2H, C_6H_5), 7.42−6.50 (br m, 27H, C_6H_5 and H^{4-7}), 5.91 (m, 2H, C*H*Ph_2 and H^2), 4.48 (m, 1H, H^3). ^{13}C NMR (100.6 MHz, C_6D_6): *δ* 195.4 (dd, *J*(RhC) = 90.1, *J*(PC) = 22.4 Hz, Rh−CO), 144.0, 143.8 (both s, *ipso*-C of C_6H_5), 136.7 (d, *J*(PC) = 44.8 Hz, *ipso*-C of C_6H_5P), 134.1 (d, *J*(PC) = 12.4 Hz, *meta*-C of C_6H_5P), 132.4 (d, *J*(PC) = 9.5 Hz, *ortho*-C of C_6H_5P), 130.3, 128.9, 128.6, 128.4, 128.2, 128.1 (all s, C_6H_5), 129.8 (d, *J*(PC) = 2.9 Hz, *para*-C of C_6H_5P), 123.0, 122.7 (both s, $C^{4,7}$), 118.5 (s, C^8 or C^9), 117.9, 117.5 (both s, $C^{5,6}$), 116.8 (s, C^8 or C^9), 99.0 (dd, *J*(RhC) = 5.7, *J*(PC) = 1.9 Hz, *C*HPh_2), 98.7 (dd, *J*(RhC) = 13.4, *J*(PC) = 3.8 Hz, C^1), 76.6 (br s, C^2), 50.8 (br s, C^3). ^{31}P NMR (162.0 MHz, C_6D_6): *δ* 47.9 (d, *J*(RhP) = 201.8 Hz). Anal. Calcd for $C_{41}H_{32}OPRh$ (674.6): C, 73.00; H, 4.78. Found: C, 72.54; H, 5.04.

Preparation of [{*η*^{5}-C_9H_6(CH**Ph_2)}Rh(CO)(P*i***P**rPh_2)] (15).** This was prepared as described for **12**, from **9** (85 mg, 0.14 mmol) and CO: orange-yellow crystals; yield 75 mg (84%); mp 41 °C dec. IR (C_6H_6): *ν*(CO) 1943 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): *δ* 7.65 (m, 2H, C_6H_5), 7.43−6.66 (br m, 22H, C_6H_5 and H^{4-7}), 5.94 (br s, 1H, C*H*Ph_2), 5.85 (m, 1H, H^2), 4.44 (m, 1H, H^3), 2.24 (m, 1H, PC*H*CH_3), 0.85 (dd, *J*(PH) = 17.0, *J*(HH) = 7.0 Hz, 3H, PCHC*H*$_3$), 0.81 (dd, *J*(PH) = 15.8, *J*(HH) = 7.0 Hz, 3H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): *δ* 196.0 (dd, *J*(RhC) = 89.5, *J*(PC) = 21.4 Hz, Rh−CO), 144.5, 144.1 (both s, *ipso*-C of C_6H_5), 137.4 (d, *J*(PC) = 39.7 Hz, *ipso*-C of C_6H_5P), 133.5 (d, *J*(PC) = 10.5 Hz, *meta*-C of C_6H_5P), 130.7, 129.8, 128.9, 128.6, 128.3, 128.1, 128.0 (all s, C_6H_5), 126.5 (d, *J*(PC) = 9.5 Hz, *ortho*-C of C_6H_5P), 123.1, 122.3 (both s, $C^{4,7}$), 118.7 (s, C^8 or C^9), 117.9, 117.4 (both s, $C^{5,6}$), 117.0 (s, C^8 or C^9), 98.7 (dd, *J*(RhC) = 5.7, *J*(PC) = 1.9 Hz, *C*HPh_2), 98.6 (dd, *J*(RhC) = 13.2, *J*(PC) = 4.1 Hz, C^1), 75.6 (br s, C^2), 50.9 (br s, C^3), 29.2 (d, *J*(PC) = 29.5 Hz, P*C*HCH$_3$), 19.4, 19.2 (both d, *J*(PC) = 4.1 Hz, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): *δ* 58.3 (d, *J*(RhP) = 201.8 Hz). Anal. Calcd for $C_{38}H_{34}OPRh$ (640.6): C, 71.25; H, 5.35. Found: C, 71.13; H, 5.17.

Preparation of [{*η*^{5}-C_9H_6(CH**Ph_2)}Rh(CO)(P*i*Pr_2**P**h)] (16).** This was prepared as described for **12**, from **10** (61 mg, 0.11 mmol) and CO: orange-yellow crystals; yield 55 mg (86%); mp 78 °C dec. IR (C_6H_6): *ν*(CO) 1945 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): *δ* 7.68 (m, 2H, C_6H_5), 7.34 (m, 2H, *ortho* H of C_6H_5P), 7.24−6.92 (br m, 15H, C_6H_5 and H^{4-7}), 6.07 (d, *J*(RhH) = 3.2 Hz, 1H, C*H*Ph_2), 5.80 (m, 1H, H^2), 4.64 (m, 1H, H^3), 1.95 (m, 2H, PC*H*CH_3), 0.79 (dd, *J*(PH) = 16.7, *J*(HH) = 6.8 Hz, 3H, PCHC*H*$_3$), 0.69 (dd, *J*(PH) = 16.9, *J*(HH) = 6.8 Hz, 3H, PCHC*H*$_3$), 0.66 (dd, *J*(PH) = 17.2, *J*(HH) = 6.8 Hz, 3H, PCHC*H*$_3$), 0.62 (dd, *J*(PH) = 17.6, *J*(HH) = 6.8 Hz, 3H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): *δ* 195.0 (dd, *J*(RhC) = 89.0, *J*(PC) = 21.9 Hz, Rh−CO), 144.4, 143.8 (both s, *ipso*-C of C_6H_5), 134.5 (d, *J*(PC) = 10.2 Hz, *meta*-C of C_6H_5P), 130.4, 128.9, 128.7, 128.6, 128.1, 126.5 (all s, C_6H_5), 129.9 (d, *J*(PC) = 2.0 Hz, *para*-C of C_6H_5P), 127.5 (d, *J*(PC) = 9.2 Hz, *ortho*-C of C_6H_5P), 123.5, 121.3 (both s, $C^{4,7}$), 119.2 (s, C^5 or C^6), 118.7 (br s, $C^{8,9}$), 117.4 (s, C^5 or C^6), 98.5 (dd, *J*(RhC) = 5.1, *J*(PC) = 2.0 Hz, *C*HPh_2), 98.3 (dd, *J*(RhC) = 13.2, *J*(PC) = 4.1 Hz, C^1), 73.5 (d, *J*(RhC) = 4.1 Hz, C^2), 51.0 (d, *J*(RhC) = 2.0 Hz, C^3), 26.1 (br d, *J*(PC) = 19.3 Hz, P*C*HCH$_3$), 25.9 (br d, *J*(PC) = 17.3 Hz, P*C*HCH$_3$), 18.5, 18.4 (both d, *J*(PC) = 6.1 Hz, PCH*C*H$_3$), 17.8, 17.3 (both br s, PCH*C*H$_3$); signal of *ipso*-C of C_6H_5P could not be exactly located. ^{31}P NMR (162.0 MHz, C_6D_6): *δ* 67.8 (d, *J*(RhP) = 201.7 Hz). Anal. Calcd for $C_{35}H_{36}$-OPRh (606.6): C, 69.31; H, 5.98; C, 69.61; H 6.33.

X-ray Structural Determination of Compounds 6 and 13. Single crystals of **6** were grown from pentane at −18 °C and those of **13** from hexane (saturated with CO) at −18 °C.

Crystal data collection parameters are summarized in Table 3. Intensity data were corrected by Lorentz and polarization effects, and an empirical absorption correction was applied in each case (minimum transmission 83.47% (**6**) and 96.35% (**13**)). The structure of **6** was solved by the Patterson method (SHELXS-86)[14] and that of **13** by direct methods (SHELXS-86). Atomic coordinates and the anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-93).[15] In **13**, half of a molecule of hexane was found in the asymmetric unit and refined anisotropically with restraints on the anisotropic displacement parameters and interatomic distances. The center of the central C−C bond lies on the crystallographic center of symmetry. The positions of all hydrogen atoms in **6** and **13** were calculated according to ideal geometry and were refined by using the riding method, except for H6 of **13**, which was found and refined isotropically.

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Supporting Information Available: Tables of data collection parameters, bond lengths and angles, positional and thermal parameters, and least-squares planes for **6** and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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