Square-Planar Carbonylchlororhodium(I) Complexes Containing *trans*-Spanning Diphosphine Ligands as Catalysts for the Carbonylation of Methanol

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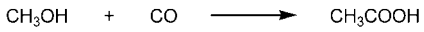
Dedicated to Professor *André Merbach* on the occasion of this 65th birthday

The rhodium(I) complexes *trans*-[Rh(diphos)(CO)Cl] **7** (diphos = pbpb), **8** (diphos = nbpb), and **9** (diphos = cbpb) were synthesized (*Scheme 4*) and used as catalysts for the carbonylation of MeOH to AcOH (*Scheme 1*). The *trans* coordination imposed by the rigid C-spacer framework of the diphos ligands pbpb, nbpb, and cbpb, demonstrated by ^{31}P-NMR and IR spectroscopy of **7**–**9** and unambiguously confirmed by single-crystal X-ray structure analysis of **7**, improved the thermal stability of the rhodium(I) system under carbonylation conditions and, hence, the catalytic performance of the complexes. For the catalytic carbonylation of MeOH, the active catalyst could be prepared *in situ* from the mixture of $[Rh(CO)_2Cl]_2$ and the corresponding diphos ligand pbpb, nbpb, or cbpb, giving the same results as carbonylation in the presence of the isolated complexes **7**, **8** or **9** (see *Table*). The highest activity was observed for complex **7** (or the mixture $[Rh(CO)_2Cl]_2$/pbpb, the catalytic turnover number (TON) being 950 after 15 min (170°, 22 bar).

Introduction. – The carbonylation of MeOH to generate AcOH is one of the most important homogeneously catalyzed industrial processes [1] (*Scheme 1*). The production of AcOH by the *Monsanto* process is based on soluble Rh-catalysts and operates at pressures of 30 to 60 bar and temperatures of 150 to 200°. The process gives selectivities of over 99% based on MeOH [2]. The reaction requires the presence of iodide, which converts MeOH prior to carbonylation into the actual substrate MeI [2]. The anion *cis*-$[Rh(CO)_2I_2]^-$ was found to be the initial catalytically active species [3]. As the rate-determining step of the catalytic cycle is the oxidative addition of MeI to *cis*-$[Rh(CO)_2I_2]^-$ [4], electron enrichment at the metal center is expected to facilitate this step and to improve the rate of AcOH formation. Consequently, square-planar rhodium(I) complexes with ligands that increase the electron density at the Rh-atom have been developed and studied as catalysts; they give better or at least comparable activities than the original *Monsanto* catalyst [5–8].

Scheme 1. *Production of Acetic Acid by Carbonylation of Methanol*



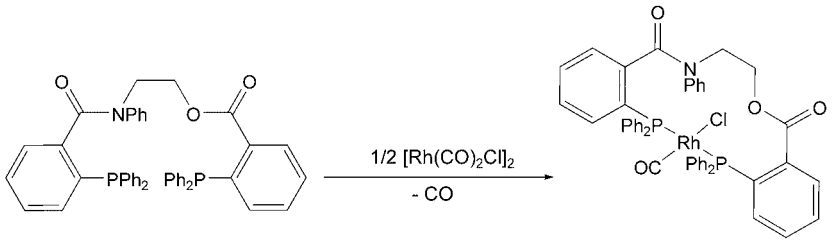
Cole-Hamilton and co-workers have investigated the use of strong electron-donating ligands (trialkylphosphines) as promoters for Rh-based carbonylation catalysts [9]. Complexes of the type *trans*-$[Rh(PEt_3)_2(CO)X]$ (X = Cl, Br, or I) have a CO absorption centered around 1960 cm^{-1}, as compared to 1988 and 2059 cm^{-1} for

cis-$[Rh(CO)_2I_2]^-$, suggesting a more electron-rich metal center in the triethylphosphine complexes. Indeed, *trans*-$[Rh(PEt_3)_2(CO)Cl]$ turned out to be a very active catalyst precursor for AcOH production [9].

Complexes containing *P*,*P*-linked bis[phosphine] ligands have also been studied as catalysts for the carbonylation of MeOH [10][11], they are in general more stable than their complexes containing unlinked bis(monophosphine) analogues. However, since complexes containing *P*,*P*-linked bis[phosphines] are usually *cis*-configured, they are less active than the *trans*-configured bis(monophosphine) complexes [11]. The stability of such Rh-complexes employed as catalysts under the harsh carbonylation conditions is a crucial point. Therefore, we decided to develop *trans*-spanning *P*,*P*-linked bis[phosphine] (diphos) ligands that, in combination with Rh^I complexes, might combine the activity of complexes such as *trans*-$[Rh(PEt_3)_2(CO)Cl]$ [9] with the stability of complexes such as *cis*-$[Rh(Ph_2PCH_2CH_2PAr_2)(CO)Cl]$ [11].

The diphos ligand 2-{[2-(diphenylphosphino)benzoyl]phenylamino}ethyl 2-(diphenylphosphino)benzoate (pbpbz) reacts with $[Rh(CO)_2Cl]_2$ to give *trans*-[Rh(pbpbz)(CO)Cl] (**1**), imposing *trans* coordination at the Rh-center [12] (*Scheme 2*). Indeed, this complex turned out to be very robust and highly active for MeOH carbonylation: it converts MeOH into AcOH at 170° and a CO pressure of 22 bar within 15 min with a turnover number (TON) of 800 mol product per mol catalyst (as compared to 380 for *cis*-$[Rh(CO)_2I_2]^-$). Moreover, **1** can be reused after a catalytic run showing almost the same activity [12].

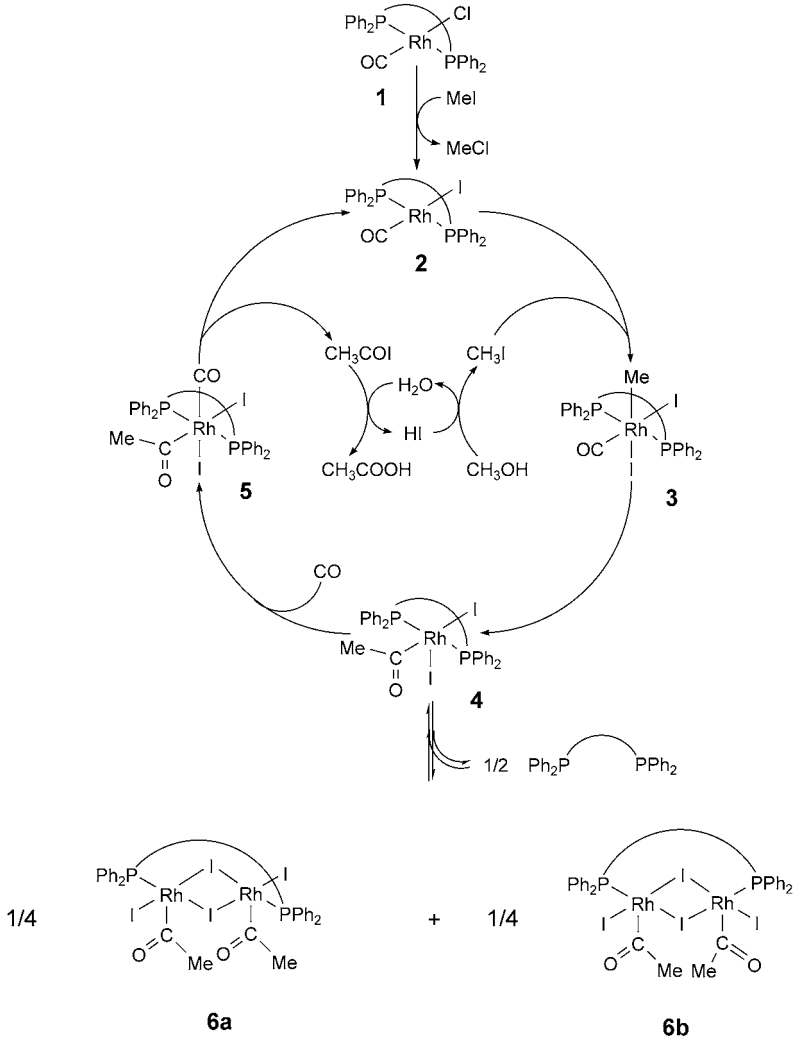
Scheme 2. trans-*Coordination of the diphos Ligand pbpbz Generating Square-Planar Rhodium(I) Centers*



pbpbz *trans*-[Rh(pbpbz)(CO)Cl] **1**

Based on the fundamental mechanistic work of *Forster* [3][13] and *Maitlis* and coworkers [14][15] on the catalytic cycle involving *cis*-$[Rh(CO)_2I_2]^-$, we have proposed the mechanism shown in *Scheme 3* when *trans*-[Rh(pbpbz)(CO)Cl] (**1**) is used as a catalyst precursor [12]: after generation of the catalytically active iodo derivative **2**, the oxidative addition of MeI generates complex **3**, which rearranges to give complex **4**. Uptake of CO converts **4** into **5**, which reductively eliminates AcI to regenerate **2**. From the catalytic mixture, we have isolated the dinuclear complexes **6a** and **6b**, which arise from the mononuclear complex **4** by loss of a bis[phosphine] ligand; **6a** and **6b** may be considered a resting state of the key species **4** [12].

Scheme 3. *Proposed Mechanism of the Carbonylation of Methanol to Acetic Acid Catalyzed by* **1** *as the Catalyst Precursor* [12]



As shown by their single-crystal X-ray structure analyses, the isomeric **6a** and **6b** differ in the orientation of the two acetyl ligands and the coordination sites of the bridging diphos ligand [12]. The formation of these two isomers is presumably due to the rotational freedom of the C–O (acyl) bond with respect to the more restricted rotation of the C–N (amide) bond of pbpbz in **1**, which can be explained by an increased steric angle of the N-atom carrying an additional substituent.

For this reason, we decided to develop more-rigid diphos ligands imposing *trans* geometry by using linkers containing two amide functions. We, therefore, synthesized the diphos ligands *N*,*N*′-(1,2-phenylene)bis[2-(diphenylphosphino)benzamide] (pbpb)

[16] and *N*,*N*′-naphthalene-1,8-diylbis[2-(diphenylphosphino)benzamide] (nbpb) [17] as well as the well known *trans*-configurated racemic ligand *N*,*N*′-[(*1RS*,*2RS*)-cyclohexane-1,2-diyl]bis[2-(diphenylphosphino)benzamide] (cbpb), which was first synthesized by *Trost* and co-workers [18] (see *Fig. 1*).

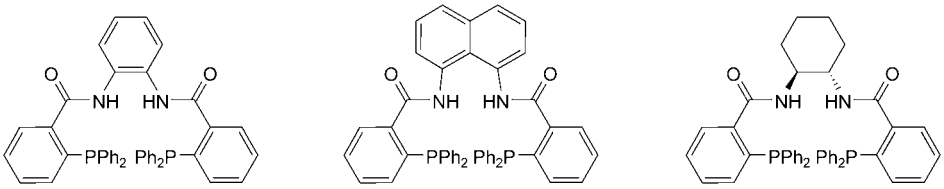


Fig. 1. *The rigid diphos ligands* N,N′*-(1,2-phenylene)(*pbpb), N,N′*-naphthalene-1,8-diyl(*nbpb*), and* N,N′*-[(1*RS,2RS*)-cyclohexane-1,2-diyl]bis[2-(diphenylphosphino)benzamide](*cbpd*)*

In this paper, we report the coordination of these diphos ligands to Rh^I to give the *trans*-configured square-planar complexes *trans*-[Rh(pbpb)(CO)Cl] (**7**), *trans*-[Rh(nbpb)(CO)Cl] (**8**), and *trans*-[Rh(cbpb)(CO)Cl] (**9**), the molecular structure of **7**, and the catalytic potential of these complexes for the carbonylation of MeOH.

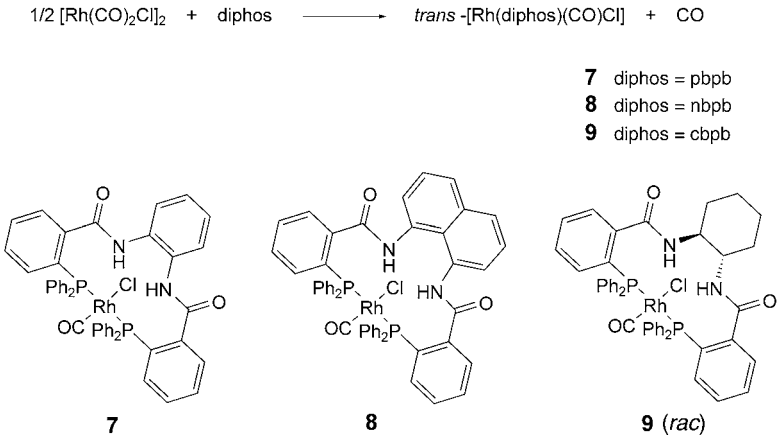
Results and Discussion. – The 2-(diphenylphosphino)benzoic acid, easily available by *Wurtz* coupling from sodium 2-chlorobenzoate and sodium diphenylphosphide [19], is an attractive building block for the synthesis of *P*,*P*-linked bis[phosphine] ligands by condensation of the acid function with diols, diamines, or amino alcohols [20]. Peptidic coupling between benzene 1,2-diamine, naphthalene-1,8-diamine, or racemic *trans*-cyclohexane-1,2-diamine and 2-(diphenylphosphino)benzoic acid afforded the diphos ligands pbpb [16], nbpb [17], and cbpb [18] in good yields (see *Fig. 1*). These diphos ligands are expected to form *trans*-coordinated square-planar complexes comprising a 13- or 14- membered metallacycle due to their rigid C-framework. Accordingly, the Pd^{II} complex *trans*-[Pd(pbpb)Cl_2] has been synthesized and structurally characterized [16].

Di-μ-chlorotetracarbonyldirhodium, [Rh(CO)$_2$Cl]$_2$, reacted with 2 equiv. of pbpb, nbpb, and cbpb to give the Rh^I complexes **7**, **8**, and **9**, respectively (*Scheme 4*). These compounds were isolated after chromatographic purification as air-stable yellow solids.

The symmetrical complexes **7** and **8** showed only one resonance in the ^{31}P-NMR spectrum, while **9** gave rise to two signals. All complexes displayed a characteristic *s* in the ^{1}H-NMR spectrum ($CDCl_3$) at δ *ca.* 8.5 for the amide protons and a strong $\tilde{\nu}$(CO) absorption around 1950 cm^{-1} in the IR spectrum, comparable with the $\tilde{\nu}$(CO) reported for other *trans*-[Rh(PR_3)$_2$(CO)X] complexes [7][23] but significantly lower than that of *cis*-[Rh(dppe)(CO)I] (dppe = ethane-1,2-diylbis[diphenylphosphine] [11]. A medium-to-strong absorption at *ca.* 3370 cm^{-1} is indicative of the amide function in each complex. The *trans*-coordination of the diphos ligands in complexes **7**–**9**, deduced from IR and NMR data, was unequivocally confirmed by the single-crystal X-ray structure analysis of **7** (*Fig. 2*).

In the crystal structure of **7**, the Rh-atom is in a square-planar geometry, surrounded by a Cl-, a C-, and two P-atoms. The chelating diphos ligand pbpb adopts a

Scheme 4. *Synthesis of* trans-*[Rh(diphos)(CO)Cl] Complexes* **7**–**9** *from [Rh(CO)$_2$Cl]$_2$ and the diphos Ligands pbpb, nbpb, and cbpb*



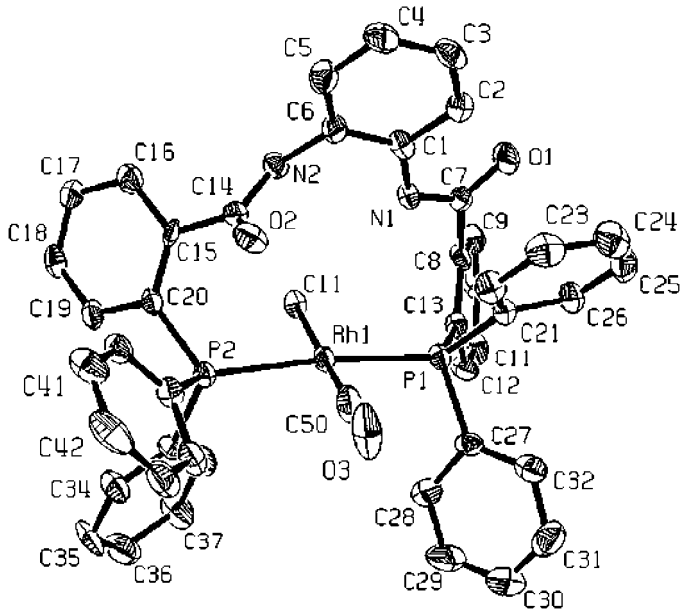


Fig. 2. *ORTEP* [24] *View of complex* **7**. Displacement ellipsoids are drawn at the 50% probability level, H-atoms and $CHCl_3$ molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)–Rh(1) 2.318(2), P(2)–Rh(1) 2.343(2), Cl(1)–Rh(1) 2.373(2), C(50)–Rh(1) 1.818(10), C(50)–O(3) 1.147(11); C(50)–Rh(1)-Cl(1) 179.2(3), Cl(1)–Rh(1)–P(1) 91.47(8), Cl(1)–Rh(1)–P(2) 89.13(8), C(50)–Rh(1)–P(2) 91.2(3), C(50)–Rh(1)-P(1) 88.3(3), P(1)–Rh(1)–P(2) 173.44(9), O(3)–C(50)–Rh(1) 177.9(9).

trans coordination geometry. The C–Rh–Cl and the P–Rh–P axes are almost linear, the corresponding angles being 179.2(3) and 173.44(9)°, respectively. The Rh–CO distance is comparable to those observed in other *trans*-[Rh(PR$_3$)$_2$(CO)Cl] complexes

[24–30]. In the crystal structure of **7**, an intramolecular H-bond is observed between the NH of an amine function and the Rh–Cl moiety (N–Cl 3.355(7) Å, N–H ··· Cl 161.7°). The N ··· Cl distance is slightly longer than the one observed in the analogous complex [Rh(Ph_2P–CH(*o*-ClC_6H_4)–NHPh)$_2$(CO)Cl] (3.116(3) Å) [31]. Intermolecular interactions also take place: the five $CHCl_3$ molecules present in the crystal interact weakly with complex **7**.

The bis[phosphine] ligands pbpb, nbpb, and cbpb were studied in combination with [$Rh(CO)_2Cl_2$] for the catalytic carbonylation of MeOH to give AcOH in the presence of MeI and H_2O. The reaction was carried out at 170° under a CO pressure of 22 bar, the catalyst/substrate ratio being 1:2000. After 15 min of stirring at 170°, the reaction was stopped and the mixture analyzed by ^{1}H-NMR and GC to determine the quantities of products formed. In all cases, ^{1}H-NMR and GC gave substantially the same results. As a control experiment, the catalytic reaction was also carried out with the *Monsanto* catalyst [$Rh(CO)_2I_2]^-$, which was formed *in situ* from [$Rh(CO)_2Cl]_2$ under the reaction conditions (*Table*, *Entry 1*) and also with the asymmetric bis[phosphine] ligand $Ph_2PC_6H_4C(O)N(Ph)(CH_2)_2OC(O)C_6H_4PPh_2$ (pbpbz), which we reported previously (*Table*, *Entry 3*) [12]. After each experiment, all volatiles were removed under reduced pressure, and the residue was used for a second catalytic run. The same quantities of MeOH, MeI, and H_2O were used for each test. The results of the catalytic runs are summarized in the *Table*.

Table. *Methanol Carbonylation Data*[a])

Entry	Catalyst precursor	TON[b])
1	[$Rh(CO)_2Cl]_2$	380 ± 10
2	Residue of *Entry 1*	200 ± 10
3	[$Rh(CO)_2Cl]_2$/pbpbz[c])	800 ± 10
4	Residue of *Entry 3*	800 ± 10
5	[$Rh(CO)_2Cl]_2$/pbpb	950 ± 10
6	Residue of *Entry 5*	750 ± 10
7	*trans*-[Rh(pbpb)(CO)Cl] (**7**)	970 ± 10
8	Residue of *Entry 7*	740 ± 10
9	[$Rh(CO)_2Cl]_2$/nbpb	600 ± 10
10	Residue of *Entry 9*	500 ± 10
11	*trans*-[Rh(nbpb)(CO)Cl] (**8**)	630 ± 10
12	Residue of *Entry 11*	520 ± 10
13	[$Rh(CO)_2Cl]_2$/cbpb	800 ± 10
14	Residue of *Entry 13*	600 ± 10
15	*trans*-[Rh(cbpb)(CO)Cl] (**9**)	820 ± 10
16	Residue of *Entry 15*	590 ± 10

[a]) Catalytic conditions: [$Rh(CO)_2Cl]_2$ (57 μmol), ligand (0.12 mmol, 2 equiv.), MeOH (110.2 mmol), MeI (11.4 mmol), H_2O (81.9 mmol), 170°, 22 bar, 900 rpm, reaction time 15 min. [b]) Turnover number = mol MeOH converted into AcOH per mol catalyst precursor. [c]) For pbpbz, see *Scheme 2*.

The MeOH carbonylation data (*Table*) clearly showed an increase in the catalytic activity in the presence rigid bis[phosphine] ligands imposing *trans* geometry at the Rh-center: with respect to the classical *Monsanto* catalyst, which gave a turnover number of 380 within 15 min under standard conditions (*Entry 1*), higher turnover numbers (600–950) were observed in the presence of these diphos ligands (*Entries 3*, *5*, *9*, and

13), the highest activity being observed for the combination $[Rh(CO)_2Cl]_2$/pbpb (TON 950, *Entry 5*). The lower activity of the system $[Rh(CO)_2Cl]_2$/nbpb (TON 600, *Entry 9*) is presumably due to the lower solubility of nbpb in the reaction medium. The isolated complexes *trans*-[Rh(pbpb)(CO)Cl] (**7**), *trans*-[Rh(nbpb)(CO)Cl] (**8**), and *trans*-[Rh(cbpb)(CO)Cl] (**9**) exhibited the same catalytic activities (*Entries 7*, *11*, and *15*) as the mixtures of $[Rh(CO)_2Cl]_2$ and the corresponding diphos ligand (*Entries 5*, *9* and *13*). Also, the stability of the catalytic system was increased with these diphos ligands: Whereas the catalytic activity of the classical *Monsanto* catalyst $[Rh(CO)_2Cl]_2$ decreased from TON 380 to 200 for the second catalytic run (*Entries 1* and *2*), the activity loss was considerably lower with the diphos ligands (TON 950 *vs.* 750 for pbpb, TON 600 *vs.* 500 for nbpb, and TON 800 *vs.* 600 for cbpb), however without reaching the stability of the $[Rh(CO)_2Cl]_2$/pbpbz system (*Entries 3* and *4*) [12].

Conclusions. – The bis[phosphine] ligands pbpb, nbpb, and cbpb containing rigid spacers reacted with $[Rh(CO)_2Cl]_2$ to give the *trans*-configured Rh-complexes *trans*-[Rh(pbpb)(CO)Cl] (**7**), *trans*-[Rh(nbpb)(CO)Cl] (**8**), and *trans*-[Rh(cbpb)(CO)Cl] (**9**). The catalytic activities of these complexes in the carbonylation of MeOH to give AcOH was studied. Complexes **7**–**9** turned out to be more active and more stable than the classical *Monsanto* catalyst. The same catalytic activity as for **7**–**9** was also obtained by *in situ* formation of these complexes from the precursor mixtures $[Rh(CO)_2Cl]_2$/diphos (diphos = pbpb, nbpb, or cbpb).

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Experimental Part

General. The ligands pbpb, nbpb, and cbpb were synthesized according to [16–18]. Solvents were dried and distilled under N_2 prior to use. All reactions were carried out under N_2 by using standard *Schlenk* techniques. All other reagents were purchased (*Fluka*) and used as received. CC = Column chromatography. IR Spectra: *Perkin-Elmer 1720X* FTIR spectrometer; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Varian Gemini-200-BB* instrument; δ in ppm referenced to the signals of the residual protons of the deuterated solvents, *J* in Hz. MS: in *m*/*z*. Microanalyses were carried out in the Laboratory of Pharmaceutical Chemistry, University of Geneva, Switzerland.

Catalytic Runs. In a typical experiment, $[Rh(CO)_2Cl]_2$ (24 mg, 0.06 mmol) and the ligand (0.12 mmol) (or directly the complex) were dissolved in MeOH (4.46 ml). The soln. was placed in a 100-ml stainless-steel autoclave, and MeI (11 mmol) and H_2O (200 mmol) were added. After purging with CO (3×), the autoclave was pressurized with CO (22 bar) and placed into an oil bath preheated to 170°. The mixture was magnetically stirred at 900 rpm. After 35 min, the autoclave was cooled to r.t., and the pressure was released. The soln. was filtered and analyzed by NMR and GLC (*Dani-86.10* gas chromatograph, split-mode capillary injection system, flame-ionization detector, *Cp-wax-52-CB* capillary column (25 m × 0.32 mm).

*[1](SP-4-1)-Carbonylchloro[*N,N′*-(1,2-phenylene)bis[2-(diphenylphosphino-*κP*)benzamide]]rhodium* (**7**). A soln. of $[Rh(CO)_2Cl]_2$ (50 mg, 0.13 mmol) and pbpb (95 mg, 0.14 mmol) in CH_2Cl_2 (20 ml) was stirred at r.t. for 2 h. The solvent was evaporated, the residue dissolved in acetone (10 ml), the soln. filtered and then evaporated, and the resulting yellow solid washed with hexane (3 × 10 ml), dried *in vacuo*, and subjected to CC (silica gel, CH_2Cl_2/EtOH (9 : 1): 67 mg (56%) of **7**. IR (KBr): 3390*m*, 3029*w*, 2975*m*, 2854*m*, 1976v*s*, 1650*m*, 1586*m*, 1493*m*, 1450*s*, 1269*m*, 1100*m*, 760*m*, 701*s*. [1] H-NMR ($CDCl_3$): 8.63 (*s*, 2 NH); 7.60–6.80 (*m*, 32 arom. H); $^{13}C\{^1H\}$-NMR ($CDCl_3$). 168.75 (C=O), 141.75, 136.34, 135.06, 135.00, 131.43, 131.05, 130.91, 130.48, 129.55, 129.18, 128.92, 128.88, 125.91, 125.15 (arom. C). ^{31}P-NMR ($CDCl_3$): 37.12 (*J*(P,Rh) = 130). ESI-MS: 816 ($[M-Cl]^+$). Anal. calc. for $C_{45}H_{34}ClN_2O_3P_2Rh$ (851.07): C 63.5, H 4.0, N 3.3; found: C 63.2, H 4.1, N 3.1.

*(*SP-*4-1)-Carbonylchloro[*N,N′*-naphthalene-1,8-diylbis[2-(diphenylphsophino-*κA*benzamide]]rhodium* (**8**). As described for **7**, with $[Rh(CO)_2Cl]_2$ (50 mg, 0.13 mmol), pbpb (95 mg, 0.14 mmol), and CH_2Cl_2 (20 ml).

CC (silical gel, CH_2Cl_2/EtOH 20:1) gave 50 mg (40%) of **8**. IR (KBr): 3378*m*, 3019*w*, 2956*m*, 2875*m*, 1964v*s*, 1648*m*, 1599*m*, 1490*m*, 1478*m*, 1438*s*, 1266*m*, 1098*m*, 747*m*, 698*s*. ^{1}H-NMR ($CDCl_3$): 8.63 (*s*, 2 NH); 7.70–6.80 (*m*, 34 arom. H). $^{13}C\{^1H\}$-NMR ($CDCl_3$). 168.42 (C=O); 141.65, 136.40, 136.29, 135.67, 135.21, 135.01, 132.02, 131.43, 131.09, 130.78, 129.99, 129.54, 128.91, 128.84, 126.76, 125.33 (arom. C). ^{31}P-NMR ($CDCl_3$): 35.47 (J(P,Rh) = 135). ESI-MS: 865 ($[M-Cl]^+$). Anal. calc. for $C_{49}H_{36}ClN_2O_3P_2Rh$ (901.13): C 65.3, H 4.0, N 3.1; found: C 65.1, H 4.3, N 3.2.

*(*SP*-4-1)-Carbonylchloro[*N,N′*-[(1*RS*,2*RS*)-cyclohexane-1,2-diyl]bis[2-(diphenylphosphino-*KP*)benzamide]}-rhodium* (**9**). As described for **7**, with $[Rh(CO)_2Cl]_2$ (50 mg, 0.13 mmol), cbpb (95 mg, 0.14 mmol), and CH_2Cl_2 (20 ml). CC (silica gel, acetone/hexane 1:2) yielded 73 mg (61%) of **9**. IR (KBr): 3364*m*, 3026*w*, 2955*m*, 2933*m*, 2869*m*, 1965*s*, 1650*s*, 1602*m*, 1583*m*, 1478*m*, 1316*m*, 1300*m*, 1255*s*, 1219*m*, 1190*s*, 1156*m*, 1095*m*, 1044*m*, 977*m*, 865*w*, 738*m*, 673*w*, 624*w*, 599*w*. ^{1}H-NMR ($CDCl_3$): 8.66 (*s*, 2 NH): 7.70–6.80 (*m*, 28 arom. H); 3.48 (*m*, 2 NHC*H*); 1.0–2.0 (*m*, 8 H (chx). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 179.63, 179.30 (C=O); 141.62, 138.11, 137.21, 136.39, 136.03, 135.79, 135.48, 135.17, 134.86, 134.35, 133.98, 133.59, 133.24, 132.69, 131.96, 131.54, 131.13, 130.55, 130.36, 130.22, 129.40, 129.13, 129.01, 128.58, 128.14, 127.76 (arom. C); 49.38 (NHCH); ^{31}P-NMR ($CDCl_3$): 35.68 (*d*, J(P,Rh) = 130); 35.54 (*d*, J(P,Rh) = 130). ESI-MS: 821 ($[M-Cl]^+$). Anal. calc. for $C_{45}H_{40}ClN_2O_3P_2Rh$ (857.12): C 63.6, H 4.7, N 3.3; found: C 63.9, H 4.4, N 3.2.

X-Ray Crystallographic Study. Crystal data for **7** · $(CHCl_3)_5$: $C_{50}H_{39}Cl_{16}N_2O_3P_2Rh$, M 1447.88; triclinic, space group P-1; cell parameters $a = 12.700(1)$, $b = 14.785(1)$, $c = 17.058(2)$ Å, $\alpha = 70.49(1)$, $\beta = 80.42(1)$, $\gamma = 89.36(1)^\circ$, $V = 2973.4(5)$ Å^3, T 153(2) K, $Z = 2$, $D_c = 1.617$ g cm^{-3}, $\mu = 1.103$ mm^{-1}; 23385 reflections measured, 10742 unique ($R_{int} = 0.1514$), which were used in all calculations. Crystals of **7** were obtained by slow evaporation of a $CHCl_3$ soln. A crystal (yellow plate, 0.48 × 0.38 × 0.07 mm) was mounted on a *Stoe Image-Plate-Diffraction* system equipped with a ϕ circle goniometer; Mo-*Ka* graphite monochromated radiation (λ 0.71073 Å); ϕ range 0–200^0, increment of 1.4°; exposure time 10 min per frame, 2θ range from 2.0–26^0; D_{max}–D_{min} = 12.45–0.81 Å. The structure was solved by direct methods by using the program SHELXS-97 [33]. The refinement and all further calculations were carried out with SHELXL-97 [34]. The H-atoms were included in calculated positions and treated as riding atoms with the SHELXL default parameters. The non-H-atoms were refined anisotropically by using weighted full-matrix least-square on F^2 with 667 parameters. $R_1 = 0.0855$ ($I > 2\sigma(I)$) and $wR_2 = 0.2029$; g.o.f. = 0.882; max./min. residual density 1.759/ – 1.194 eÅ^{-3}.

CCDC-249715 (**7** · $(CHCl_3)_5$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the *Cambridge Crystallographic Data Centre*, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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